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Organic Chemistry

ENTIRELY NEW EDITION

(November 1911)

PART I

BY

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PREFACE.

THE thorough revision of this widely used text-book having again become necessary owing to the continued progress of Organic Chemistry, the whole of the subject-matter has been brought up-to-date, and various alterations in arrangement, &c., have been made, where improvements suggested themselves in the light of further experience.

The subject-matter which previously formed a separate appendix has now been incorporated in Parts I. and II., and several new chapters or sections (e.g. those dealing with the Grignard reagents, the configurations of some of the carbohydrates, the cycloparaffins, &c.) have been added; the scope of the work has thus been enlarged to some extent, chiefly by the addition of matter which meets the requirements of medical students and of those preparing for an Honours degree examination.

At the same time, the interests of less advanced readers have been kept prominently in mind; and it is hoped that the arrangement of the text in different sizes of type, together with instructions printed in notes, will help to direct the reading of those commencing the study of Organic Chemistry.

The original aims and general plan of the book remain unaltered, and may be indicated by the following extracts from the Preface to the first edition:

'Part I., which deals with the fatty compounds, contains, in the first place, a general account of the methods most frequently employed in the separation, purification, and analysis

of organic compounds, and in the determination of molecular weight. The preparation and properties of typical compounds are then described, attention being directed to those changes which come under the heading of general reactions, rather than to isolated facts regarding particular substances. Questions of constitution are also discussed at some length, and in the case of most of the typical compounds, the facts on which the given constitutional formula is based are specifically mentioned. This course was adopted because, in our opinion, a constant use of constitutional formulæ, accompanied by a clear conception of their meaning, is one of the greatest helps, even to a beginner, in committing the facts to memory.

'The opening chapter of Part II. contains an account of coal-tar and its treatment. This leads naturally to a description of the preparation and properties of benzene, and to a discussion of its constitution in the light of facts previously dealt with; the student is thus made acquainted with the principal characteristics of aromatic, as distinct from fatty, compounds, and is then in a position to understand the classification of organic substances into these two main divisions.

'The more important classes of aromatic compounds are then described, but in a somewhat different manner from that adopted in Part I., inasmuch as a general account of the properties of each class of substances is given before, instead of after, the more detailed description of typical compounds; this course is to a great extent free from the disadvantages which are found to attend its adoption at earlier stages, as the student has by this time acquired some experience of the more systematic method from a study of the summaries given in Part I.

'Particular attention is given, as in Part I., to questions of constitution, one of the objects being to train the student to think out such matters, and to try to deduce a constitutional formula for a given substance, by comparing its properties with those of others of known constitution; with this end in view, the most important evidence in favour of the accepted constitutional formula is often withheld until the subject has been discussed at some length.

'One of the principal objects throughout has been to treat the subject from a practical point of view (as far as this could be done in a text-book on theoretical chemistry), because, unless a thorough course of practical work accompanies the theoretical, no really satisfactory progress can be made.'

W. H. PERKIN.
F. STANLEY KIPPING.

November 1911.

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INORGANIC CHEMISTRY.

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ORGANIC CHEMISTRY.

PART I.

CHAPTER I.

Composition, Purification, and Analysis of Organic Compounds.

Origin and Present Meaning of the Word 'Organic.'—Although spirit of wine, sugar, fats, and many other substances, obtained directly or indirectly from animals or plants, have been known from the earliest times, their investigation made but little progress until towards the close of the eighteenth century, when the compositions of many of these natural products were established by Lavoisier (1743–94). He it was who first showed that, in spite of their great number, nearly all vegetable substances are composed of carbon, hydrogen, and oxygen, whereas animal substances, although also consisting for the most part of the same three elements, frequently contain nitrogen, and sometimes phosphorus and sulphur.

This peculiarity in composition, and probably also the fact that these natural products behaved differently from mineral compounds in being *combustible*, led to the belief that all animal and vegetable substances were produced under the influence of a peculiar *vital force*, and that their formation was regulated by laws quite different from those which governed the formation of mineral substances; consequently,

it was thought impossible to prepare any animal or vegetable product artificially or synthetically in the laboratory.

For these reasons, compounds obtained from animals and plants—that is to say, directly or indirectly from living *organisms*—were called **organic** compounds, and were classed separately from **inorganic** or mineral substances.

This distinction between organic and inorganic compounds appears to have been generally accepted until 1828, when Wöhler succeeded in obtaining urea (an excretion of certain animal organisms) from ammonium cyanate, a substance which might be considered to be inorganic or mineral, because it could be produced in the laboratory; this synthesis showed that the influence of a living organism was not necessary for the production of the 'organic' substance urea.

In the course of time it was found that many other so-called 'organic' substances could be prepared in the laboratory from 'inorganic' materials, and ultimately it came to be generally acknowledged that although many processes which occur in animals and plants cannot yet be carried out in a laboratory, simply from lack of knowledge, the formation of an organic compound is no more dependent on the help of a vital force than is that of an inorganic compound.

The supposed difference between the two classes of compounds having thus been recognised as purely an imaginary one, the terms 'organic' and 'inorganic' lost, of course, their original meanings; they are, nevertheless, still made use of in the classification of chemical compounds for the following reasons:—

(1) The compounds of carbon, which are already known, are far more numerous than the known compounds of any other element. (2) These carbon compounds are related to one another, and differ widely in general behaviour from those of other elements; they form, in fact, a distinct group. It is convenient, therefore, to class them separately, and to distinguish them by the term *organic*, which recalls the fact that carbon compounds are the most important components

of all animals and plants; *organic chemistry*, therefore, is *the chemistry of the carbon compounds.*

Some of the simpler compounds of carbon, such as carbon dioxide and carbon monoxide, which are of general importance, are always described in works on inorganic chemistry for the sake of convenience; they are, nevertheless, organic compounds, because they contain carbon.

The reasons why so many carbon compounds are known are not far to seek. All the chief components of animals and plants are derivatives of carbon, and many of them occur in extraordinary abundance; each of these naturally occurring compounds has formed a starting-point from which many others have been obtained artificially in the laboratory; these new substances, in their turn, have served as materials for further investigation.

Composition of Organic Compounds.—In spite of their great number, most organic compounds are made up of only from two to four or five elements; many of them consist of carbon and hydrogen only, and are called *hydrocarbons.*

The most striking difference between carbon and all other elements is, in fact, that the atoms of carbon seem to be able to combine with one another and with hydrogen to an almost unlimited extent, forming hydrocarbons, such as CH_4, C_6H_6, $C_{10}H_8$, &c., the molecules of which are often composed of a very large number of atoms; other elements rarely combine with hydrogen to form more than a few compounds, and their atoms seem to possess only to a very limited extent the power of combining with one another.

Those organic compounds—such as sugar, starch, and tartaric acid—which occur in the vegetable kingdom, generally consist of *carbon*, *hydrogen*, and *oxygen*, although a few—morphine and strychnine, for example—contain *nitrogen* as well. Those occurring in the animal kingdom, generally contain nitrogen, as well as carbon, hydrogen, and oxygen: urea and uric acid, for instance, are composed of these four

elements; some vegetable and animal substances also contain *sulphur* and *phosphorus*.

In addition to two or more of the elements mentioned above, organic compounds prepared in the laboratory often contain a halogen or a metal; organic derivatives of most of the non-metals are known, and doubtless it would be possible to prepare a carbon compound containing any known element, except those of the argon family.

Separation and Purification of Organic Compounds.—It need hardly be pointed out that every organic substance must be submitted to a quantitative analysis in order that a formula may be assigned to it, and that the preparation of the compound in a state of purity is a step which must precede its analysis. Now, the purification of an organic compound, its separation from a mixture of any kind, is often a matter of considerable difficulty, and it is usually necessary to employ different processes in different cases. Although, therefore, it is impossible to give directions which would be applicable in every instance, the more important processes may be briefly indicated.*

To commence with, a small portion of the substance is first ignited on platinum foil; if it leaves a non-combustible residue, it is probably a salt of some organic acid, or it contains inorganic compounds as impurity.

The separation of an organic, from an inorganic, substance can usually be accomplished by shaking or warming the mixture with some solvent, such as alcohol, ether, benzene, chloroform, petroleum, &c. Most organic compounds are soluble in one or other of these liquids, whereas inorganic compounds, as a rule, are insoluble, or nearly so. Water or dilute acids may often be employed for the same purpose, since many inorganic substances are soluble, many organic substances insoluble, in these liquids.

* It is important that the student should have some knowledge of these processes, otherwise he will not understand the descriptions of the methods of preparation of various compounds.

The separation of two or more organic substances may sometimes be effected in a similar manner. In the case of a mixture of cane-sugar, tartaric acid, and benzoic acid, for example, the last-named compound (only) can be dissolved out with ether; the tartaric acid may then be separated from the sugar by treatment with alcohol, in which it is much more readily soluble than is sugar.

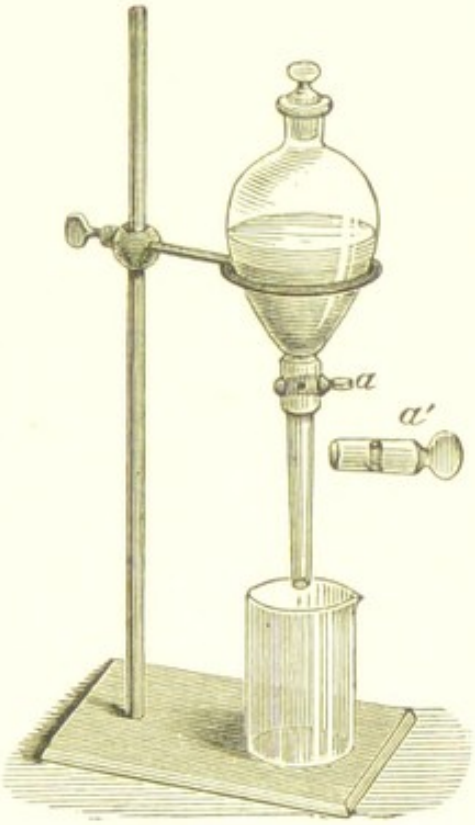


Fig. 1.

Solid or liquid organic substances, suspended or dissolved in water, may often be isolated by shaking the mixture or solution with some solvent, such as ether, benzene, chloroform, &c., which does not mix with water. This is done in a **separating funnel** (fig. 1), and after the operation the two solutions are separated by turning the tap (a, a') and running off that which is underneath; the extraction is then repeated, if necessary, with a fresh quantity of the organic solvent. The combined extracts are dried (p. 10), and the solvent is distilled off, or the solution is allowed to evaporate.

* In extractions with ether, petroleum, or benzene, the organic solvent forms the upper layer; but chloroform is heavier than water. When ether is employed it is usually advisable to first saturate the aqueous solution with sodium chloride, calcium chloride, or some other readily soluble salt, in order to lessen the solubility of the ether in the water, and also that of the organic compound which is to be extracted; this process is called 'salting out.'

* *When this book is being studied for the first time, all the subject-matter in small type may be omitted, except the examples and the detailed descriptions of the preparation of ethylene, methyl alcohol, acetaldehyde, ether, and formic acid.*

The process of **crystallisation** is a very efficient method of separating and purifying solid organic substances, provided that a suitable solvent is employed.

About a centigram of the substance is heated in a test-tube with 1–2 c.c. of some solvent (such as water, ether, alcohol, carbon disulphide, benzene, light petroleum, &c.*), and the hot liquid is allowed to cool; if then the substance is deposited in crystals, the solvent may be regarded as suitable, and the rest of the material is treated in the same way, the insoluble portion, if any, being examined separately. Should no separation of crystals take place, the solution is concentrated by evaporation, and then allowed to cool; if, again, crystals are not deposited, some other solvent is tried.

The crystals ultimately obtained are collected on a suction-filter, washed with a small quantity of the solvent, and further purified by recrystallisation if necessary.

The separation of a crystalline product from small quantities of mother-liquor, or of oily impurities, is best accomplished by pressing the substance on a piece of an unglazed tile or plate, by which the liquids are absorbed.

If only one component of a mixture is dissolved by the liquid employed, this particular substance is obtained in a state of purity without difficulty, because the others are easily got rid of by filtration; when, however, two or more of the components are soluble, their further separation can usually be effected by **fractional crystallisation**. In this process, advantage is taken of the difference in solubility of the substances. On a hot solution of two (or more) substances being cooled slowly, one of them is often deposited in crystals before the other, and can then be separated by filtration; the substance remaining in the *mother-liquor* may then be obtained in crystals by concentrating the solution; the two crops of crystals are afterwards separately redissolved, and the fractionation repeated until each substance is obtained in a pure state, as shown by a determination of its melting-point (p. 12).

* In working with highly inflammable liquids great caution is necessary to avoid serious accidents.

Animal charcoal, prepared by strongly heating bones or blood out of contact with air, is often used in purifying organic compounds, as it has the property of absorbing coloured or resinous impurities from solutions. For this purpose the impure substance is dissolved in some suitable solvent, a small quantity of animal charcoal is added, and the mixture is heated for some time (with reflux condenser, p. 75); when the liquid is afterwards filtered, a colourless or much lighter-coloured solution is usually obtained, and the dissolved substance generally crystallises more readily. Before use, the charcoal should be repeatedly extracted with boiling hydrochloric acid to remove calcium salts and other impurities, washed well, dried, and heated strongly in a crucible closed with a lid.

Another method frequently used in the separation and purification of organic substances, both solid and liquid, is

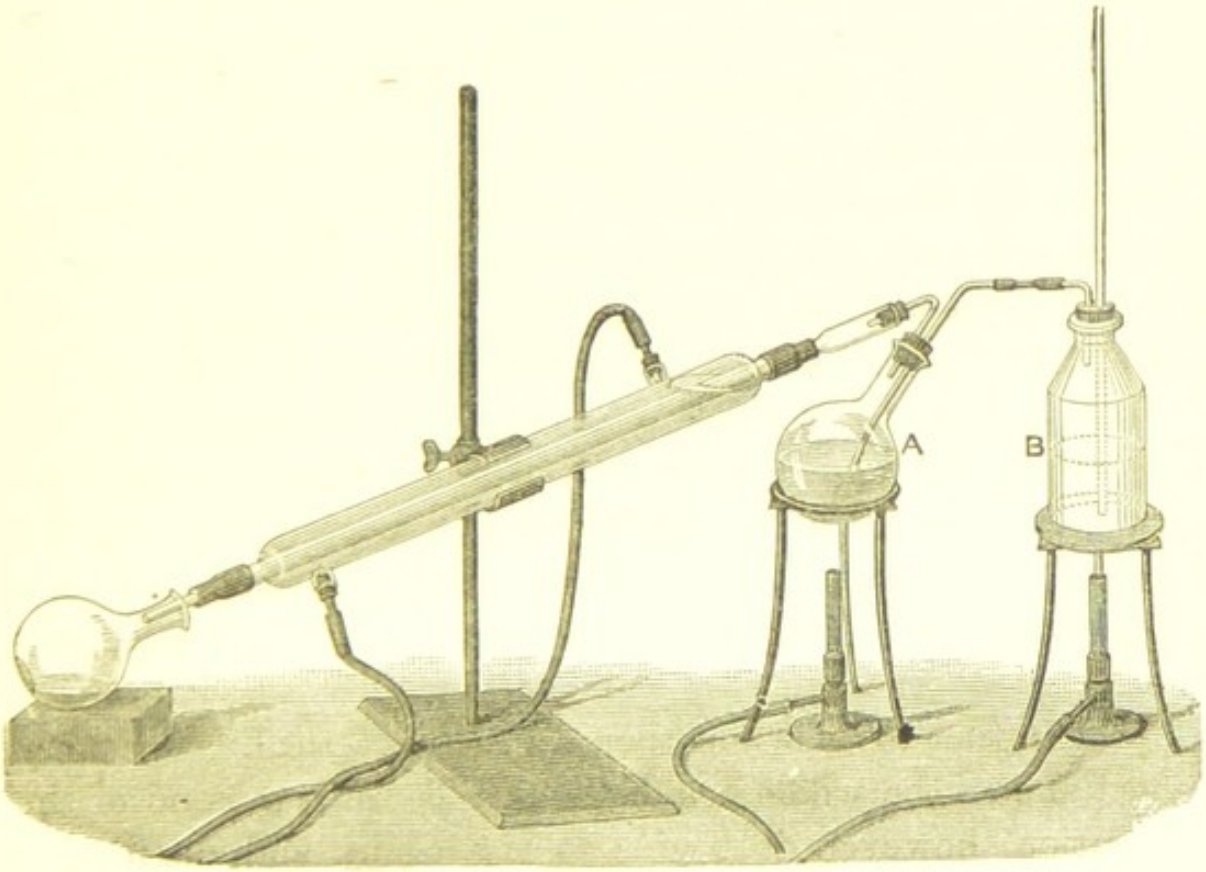


Fig. 2.

distillation in a current of steam. The substance and a little water are placed in a flask (A, fig. 2) which is connected with a condenser, and heated on a water- or sand-bath; a rapid current of steam, generated in a separate vessel (B), is then

passed through the mixture. The distillate, which contains the volatile organic substance in solution, or in suspension, is afterwards extracted with ether, or filtered, or treated in some other way, according to circumstances. In this simple manner it is often possible to isolate a compound when all other methods fail; it is, however, only applicable in the case of the comparatively few organic substances which are **volatile in steam.** Some compounds which cannot be distilled in the ordinary way, because they undergo decomposition, are volatile in steam, and pass over unchanged, even when their boiling-points are much higher than that of water.

When a substance volatilises very slowly, *superheated* steam is often employed; in such cases the steam from B is passed through a strongly heated coil of copper tubing before being led into A.

Organic substances which boil without decomposing can be purified by **distillation.** The substance is placed in a distillation flask (A, fig. 3), which is connected with a condenser, the neck of the flask being closed with a cork, through which a thermometer passes; the bulb of the thermometer is placed just below the opening of the side-tube (B), and a few scraps of unglazed porcelain, or platinum, are put in the distillation flask, to prevent 'bumping' or sudden ebullition.* In the case of liquids which boil at temperatures above 130° or so, a long glass tube (C) without a water-jacket is used instead of a Liebig's condenser, which is apt to crack. When the compound to be purified contains only *non-volatile* impurities, the thermometer rises very rapidly as soon as the liquid begins to boil, but then remains practically stationary until almost the whole has distilled. Towards the end of the operation, however, it begins to rise again, and distillation is then stopped. If the distillate is now transferred to a clean flask, and redistilled, it will boil at a constant temperature, which is the **boiling-point** † of the substance.

* This must always be done *before* the liquid is heated; the addition of a solid when the liquid is superheated causes a violent ebullition.

† See footnote, p. 14.

All pure substances, which boil without decomposing, have a definite boiling-point (b.p.), which is dependent on the pressure. As the pressure diminishes, the boiling-point is lowered, so that, by carrying out the process under *reduced*

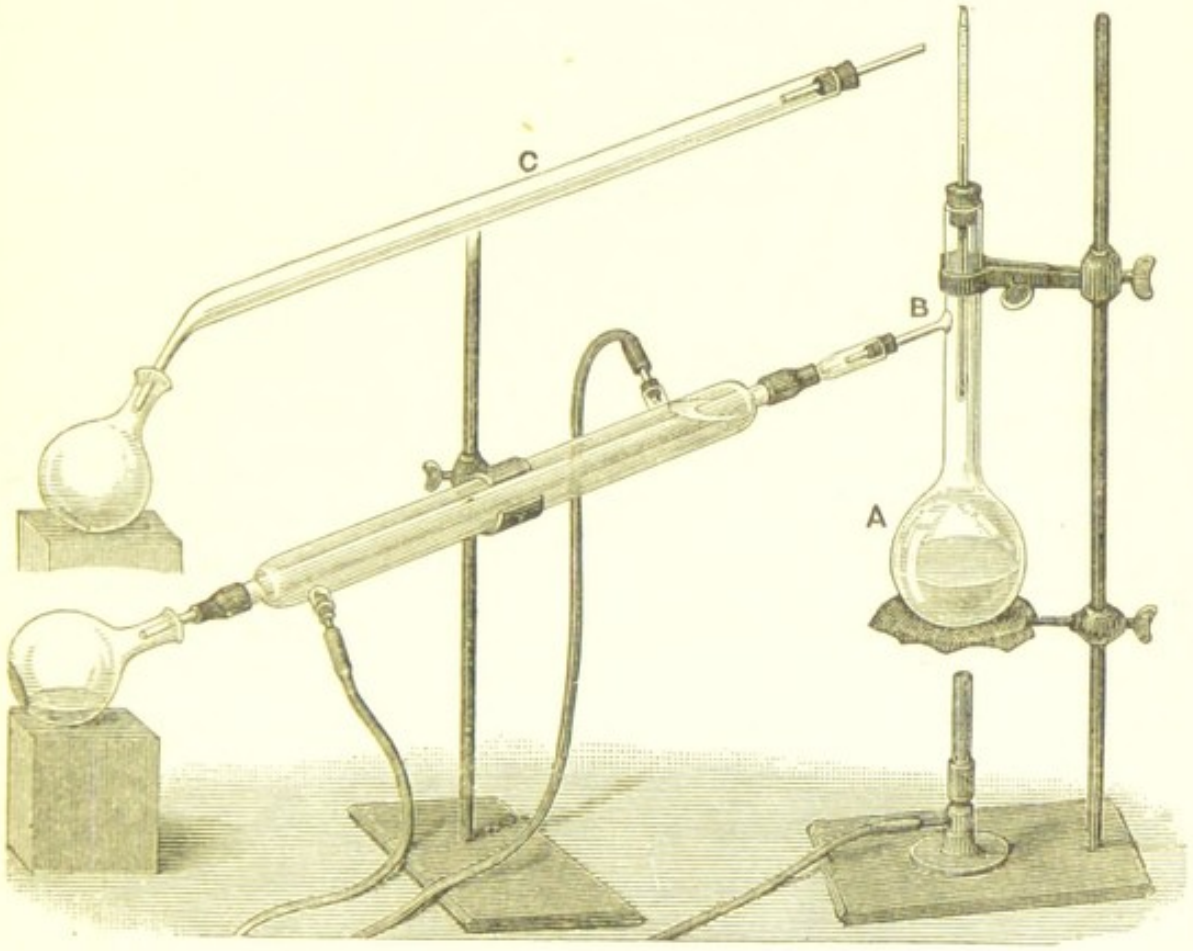


Fig. 3.

pressure, it is often possible to distil a substance which would undergo decomposition under ordinary atmospheric pressure, because in the latter case it would have to be heated more strongly.

The boiling-point is one of the more important physical constants of a substance, and affords a valuable means of *identifying* it. An observation of the boiling-point should always be made with an apparatus similar to that shown (fig. 3), and a sample of the liquid should be distilled completely, in order to make sure that it has a constant boiling-point; if not, it is impure, or it is decomposing.

Before a substance is distilled, it should be carefully freed from any water it may contain; for this purpose liquids are shaken with a few *small* pieces of fused calcium chloride, potassium carbonate, potash, or other dehydrating agent, according to the nature of the liquid, and are then decanted or filtered.

When a mixture of two (or more) *volatile* substances is distilled in the manner described above, the liquid begins to boil at some temperature lying between the boiling-points of its components. As distillation proceeds the boiling-point rises, and towards the end of the operation usually becomes nearly the same as that of the liquid which boils at the higher temperature. In the case of a mixture of alcohol (b.p. 78·3°) and water (b.p. 100°), for example, the thermometer at first registers some temperature between 78·3° and 100°, according to the proportion of the two substances, and the first portions of the distillate contain a larger proportion of alcohol than does the original mixture. During distillation the thermometer slowly but continuously rises, and at last registers 99–100°, the portions passing over at this temperature consisting of practically pure water. The change in boiling-point is due to a change in the composition of the mixture; the alcohol, being the more volatile, passes off more quickly than the water. It is possible, therefore, to separate the liquids to some extent by collecting the distillate in portions or **fractions** at intervals of 5° or 10°; this operation is termed **fractional distillation.** By redistilling each fraction separately a further separation is effected, and, after a sufficient number of operations, the components of the mixture may be obtained in a practically pure condition, boiling at constant temperatures. Such a separation, however, can only be easily accomplished provided that there is a difference of at least 20–30° between the boiling-points of the liquids; in many cases, even when there is a greater difference than this, a *complete* separation cannot be effected.

As an illustration of the process of fractional distillation, the

case of a mixture of 50 c.c. of benzene (b.p. 81°) and 50 c.c. of xylene (b.p. 140°) may be taken. The mixture begins to boil at about 87°, and the thermometer rises gradually to 140°; if the receiver is changed every 10°, the following fractions are obtained:

87–100°	100–110°	110–120°	120–130°	130–140°
33 c.c.	16 c.c.	8·5 c.c.	8 c.c.	33 c.c.
(1)	(2)	(3)	(4)	(5)

The first and last are larger than the others, because the temperatures at which they are collected are near the boiling-points of the components. If, now, the fractions 1 and 5 are separately redistilled, the former yields a large fraction boiling at 81–85°, while the latter gives one boiling at 135–140°; other fractions, which are collected separately and added to 2, 3, or 4, are also obtained. These operations being repeated with the fractions 2, 3, and 4, a large proportion of the mixture is ultimately separated into two principal fractions, from which benzene and xylene respectively can be obtained, in an almost pure condition, by a final distillation.

The process of fractional distillation is greatly facilitated when a flask with a long neck is used, or when the mixed vapours are passed through a long vertical tube (*fractionating column*) before they enter the condenser. By these means the vapour of the liquid of higher boiling-point is partially condensed, and the liquid runs back into the distillation flask instead of passing over with the more volatile component.

Fractional distillation is frequently carried out under reduced pressure for the reasons already stated in the case of ordinary distillation. A simple apparatus for this purpose is easily made by inserting the side-tube of one distillation flask (A, fig. 4) into the neck of a second flask (B), and connecting the side-tube (of B) with a water-pump and pressure-gauge.* The liquid to be distilled is placed in A; the pump is then started, and, as soon as the pressure is sufficiently low, distillation is carried out in the usual manner, the process being interrupted when the receiver is being changed.

Tests of Purity.—For many purposes it is very important

* Various forms of apparatus are made for distillation under reduced pressure.

to know whether or not a given compound is *pure.* If the substance is a solid, its purity or otherwise may often be ascertained by an examination under the microscope. A pure substance looks homogeneous, and if crystalline, the crystals are all of the same form. Much more trustworthy evidence, however, is obtained by an observation of the melting-point.

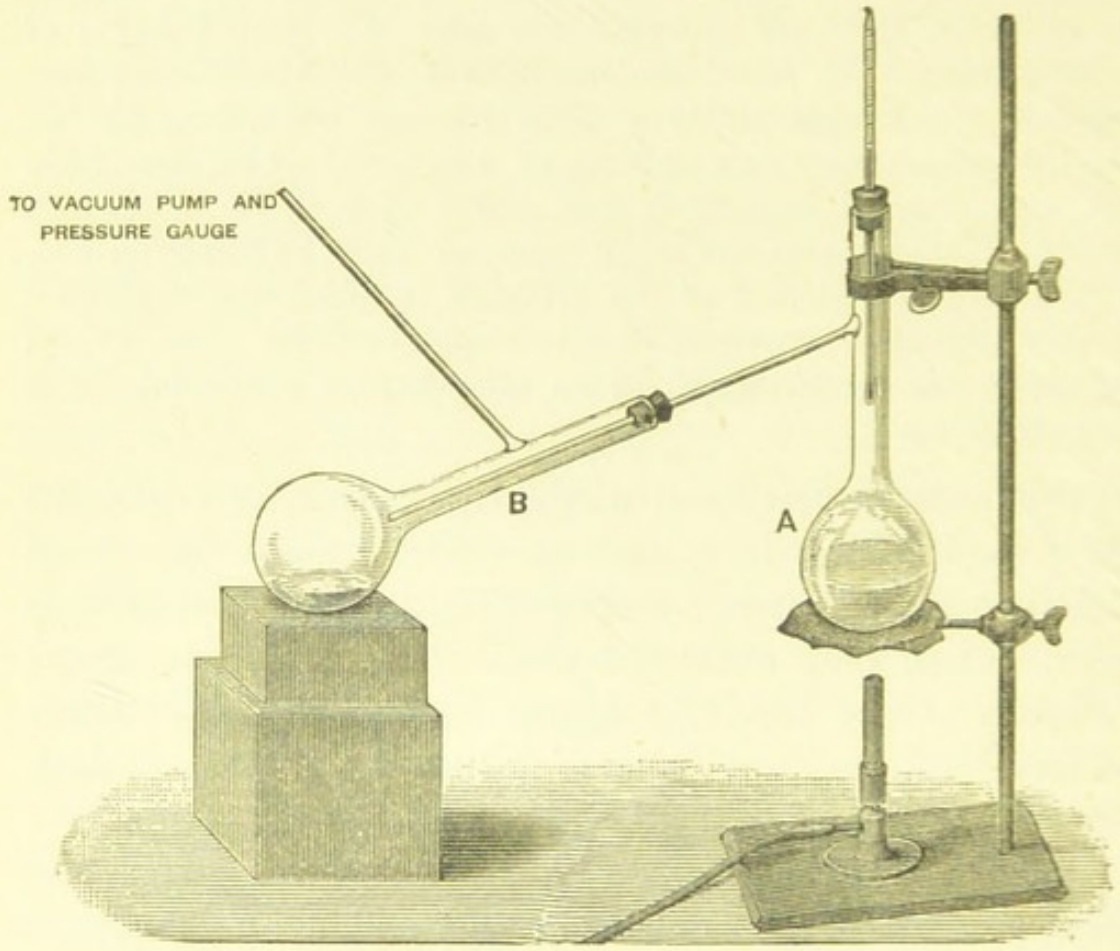


Fig. 4.

Pure substances which melt or liquefy without decomposing have a definite **melting-point**; when, however, a substance is impure, its melting-point is usually not only lowered, but is also rendered indefinite. An impure substance becomes soft and pasty (sinters) at a certain temperature, and does not melt completely until heated considerably above this point. The determination of the melting-point, therefore, affords a valuable test of purity, and also serves as a means of identifying a compound.

The apparatus generally employed for determining the melting-point consists of a small beaker (*a*, fig. 5) of about 50 c.c. capacity, containing concentrated sulphuric acid, and fitted with a glass stirrer (*b*). A minute quantity of the substance is placed in a capillary tube (*c*), closed below, which is attached to a thermometer (*d*) by means of a small india-rubber ring, or simply caused to adhere to it by capillary attraction. The acid is slowly heated, being constantly stirred, and the temperature at which the substance liquefies—that is to say, its melting-point (m.p.)—is noted.

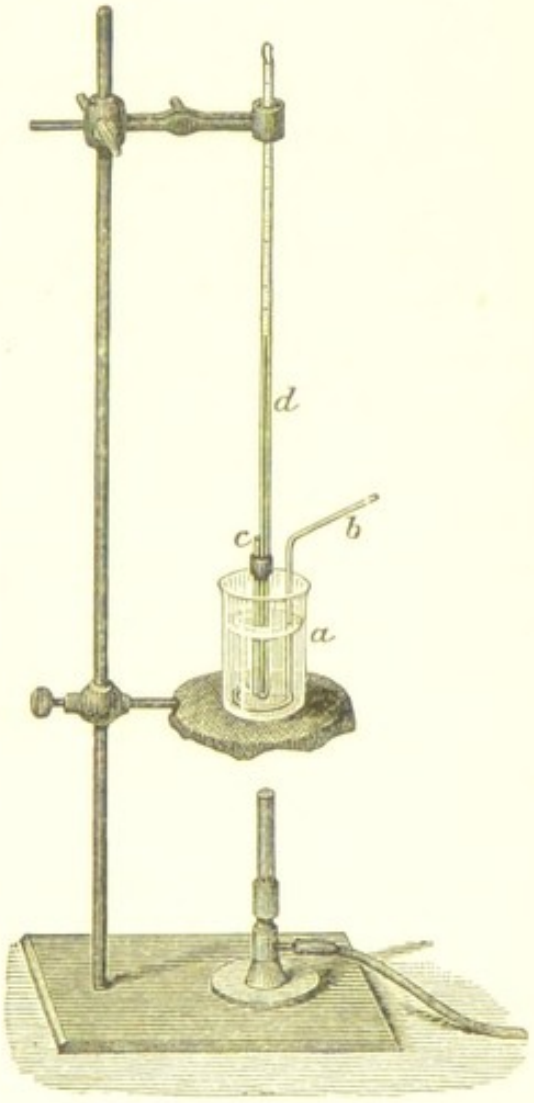


Fig. 5.

In the case of a compound which distils without undergoing decomposition, a determination of its **boiling-point**, or rather an examination of its behaviour on distillation, will show whether it is pure or not.

QUALITATIVE ELEMENTARY ANALYSIS.

The methods used in the qualitative analysis of organic compounds are relatively simple and differ entirely from those employed in the case of inorganic substances. Not only are most organic compounds insoluble in water and in acids, but even those which are soluble do not, except in rare cases, show a behaviour sufficiently characteristic to allow of their recognition by the ordinary 'wet methods' of analysis. Moreover, whereas a mixture of inorganic compounds may be

directly submitted first to qualitative and then to quantitative examination, a mixture of organic compounds must almost invariably be separated into its components before the further qualitative and quantitative examination of these components can be undertaken. The term qualitative analysis, therefore, as used in reference to organic compounds, usually means the detection of the *elements* of which a *pure* compound is composed; for this reason the process is often known as *qualitative elementary analysis.* This process is a necessary step in the determination of the formula of every organic compound.

When the object of the examination of an organic compound is to identify the substance—that is to say, to prove that it is identical with some substance of known composition—the process is generally called *identification.** A compound may often be identified by noting its appearance, smell, crystalline form, solubility, and other properties, and by determining its melting- or boiling-point;† when, however, such methods are insufficient, or when the nature of the compound is quite unknown, a qualitative elementary analysis, and often even a quantitative analysis, must also be made.

When the substance under examination is known to be an organic compound it is of course unnecessary to test it for **carbon**; but when the nature of the substance is entirely unknown, this element may be detected by the following methods:—

The substance is heated on platinum foil. If it inflames and burns away, or swells up, giving a black mass, which on

* The identity of two solids is best tested by mixing a small quantity of the substance under examination with an approximately equal quantity of the compound with which it is supposed to be identical, and then determining the melting-point of the mixture; if it is the same as that of the separate components, the identity of the latter may be taken to be established.

† The *observed* melting- or boiling-point of a substance is usually 1–3° lower than the true value, because, as a rule, a portion of the column of mercury is not immersed in the heating liquid or vapour.

being strongly heated entirely disappears, the substance is in all probability organic. The metallic salts of organic acids usually char when treated in this way, and when further heated, the carbonaceous matter burns away, leaving a *residue* which may be dissolved in water or acids and examined by the usual methods of inorganic analysis. Sodium acetate, for example, leaves sodium carbonate, but copper acetate gives the oxide of the metal, and silver acetate gives the metal. If a halogen, sulphur, or phosphorus is present in the salt, it is generally found in the residue in combination with the metal.

The behaviour of a substance when it is heated with concentrated sulphuric acid often affords an indication of the presence of carbon, as many organic substances blacken under these conditions, owing to the separation of carbonaceous matter.

If neither of these tests gives a decisive result, the compound (0·1–0·5 g.) is mixed with 10–20 times its weight of pure copper oxide, and the mixture is heated to redness in a tube of hard glass sealed at one end, the escaping gases being led into lime-water; under these conditions all organic substances * are decomposed, yielding carbon dioxide, the formation of which is proved by the lime-water becoming turbid.

It is rarely necessary to test for **hydrogen** in organic compounds, and the only reliable method is to mix the *dry* substance (0·1–0·5 g.) with *dry* copper oxide and heat the mixture in a stream of *dry* air or oxygen; if hydrogen is present, it will be oxidised to water, which collects in the calcium chloride tube and may generally be seen there; but if the percentage of hydrogen is very small, the calcium chloride tube must be weighed before and after the experiment in order to prove that water has been formed.

The presence of **nitrogen** in an organic substance may often be detected when a little (0·1–0·5 g.) of the substance is strongly heated with soda-lime † in a hard glass tube; if

* Except the stable carbonates and cyanides of the alkalis and alkaline earths.

† An intimate mixture of slaked lime and caustic soda, which has been strongly heated until it is quite dry.

ammonia is evolved, the presence of nitrogen is proved. As, however, certain organic compounds containing nitrogen do not yield ammonia when they are heated with soda-lime, the following test must be applied before the absence of nitrogen may be considered to be proved.

A small quantity (0·1–0·2 g.) of the substance is placed in a test-tube, together with a bright piece of sodium (or potassium) about the size of a pea, and gently heated, care being taken, especially in the case of volatile compounds, that the metal is brought into contact with the substance and thoroughly chars it. The mixture is then heated more and more strongly until all action ceases, and when the tube has cooled a little, the hot end is plunged into about 5 c.c. of water contained in an evaporating basin, whereby the tube is broken and the soluble product is dissolved.*

The alkaline solution is filtered from carbonaceous matter, and a few drops of ferrous sulphate are added to the filtrate; the mixture is then warmed for a moment, acidified with pure hydrochloric acid, and tested with a drop of ferric chloride, when, if nitrogen was present in the original substance, a deep bluish-green colouration, or a precipitate of Prussian blue, is produced.

This test depends on the fact that the nitrogen and some of the carbon in the organic compound combine with the sodium to form sodium cyanide; when the alkaline solution of sodium cyanide is warmed with ferrous sulphate, ferrous hydrate is precipitated and sodium ferrocyanide is formed,

$$6NaCN + Fe(OH)_2 = Na_4Fe(CN)_6 + 2NaOH,$$

so that on the addition of a ferric salt† to the acidified solution, Prussian blue is produced.

The presence of **chlorine, bromine,** or **iodine** in organic

* This should be done in such a way that the eyes are not endangered.

† During the experiment some of the ferrous hydrate generally becomes oxidised to ferric hydrate, which, with hydrochloric acid, gives ferric chloride; a precipitate of Prussian blue is then produced without the addition of a ferric salt.

compounds cannot be detected, as a rule, by the methods employed in the examination of inorganic substances, as, for example, by means of silver nitrate, or manganese dioxide and sulphuric acid; chloroform, for instance, contains a very large proportion of chlorine, but when pure it does not give a precipitate with silver nitrate, and simply boils away when it is heated with manganese dioxide and sulphuric acid.

A simple test for the halogens is the following:—A piece of copper wire is heated in the oxidising zone of the Bunsen flame until that portion within about three inches from the end ceases to colour the flame green.* A small quantity of the substance is then heated on the end of the wire in the flame, when, if a halogen is present, a green colouration is usually observed, due to the formation of a volatile halogen compound of copper. As, however, this test sometimes fails, and as, moreover, it does not give any information as to which of the halogens is present, the following method is generally adopted:—

The substance is carefully heated with a bright piece of sodium or potassium exactly as described in the test for nitrogen. The alkaline solution is filtered from carbonaceous matter, and a portion of the filtrate, acidified with nitric acid, is tested with silver nitrate; if a precipitate is formed, the presence of halogen (or of *nitrogen*, see below) in the original substance is proved, and its nature may be determined by examining the rest of the solution, or the precipitate, by the usual methods. This test depends on the fact that when any organic substance containing chlorine, bromine, or iodine is heated with sodium, the halogen combines with the metal to form chloride, bromide, or iodide of sodium.

When nitrogen is present the above test for halogens is not conclusive, as the precipitate may be silver *cyanide*; under these circumstances, and if the presence of a halogen cannot be established by the copper test, the precipitate is

* The colouration, if any, is caused by *volatile* compounds, such as copper chloride.

collected, dried, and ignited on a porcelain crucible-lid, when the cyanide is decomposed, leaving silver, whereas the halogen silver salt is merely fused. The residue is then warmed with dilute nitric acid; if it does not dissolve completely the presence of halogen is established.

Sulphur and **phosphorus** may be detected by gradually adding the substance, *in very small quantities*, to a fused mixture of potassium carbonate and nitre, or sodium peroxide, heated on a piece of platinum foil; under these conditions the sulphur is oxidised to sulphuric acid, the phosphorus to phosphoric acid. The residue is dissolved in water, and the solution of alkali salts is tested for the above-mentioned acids in the usual way. Another method, similar in principle, consists in oxidising the substance with nitric acid in a sealed tube, as described later (p. 29).

Sulphur may also be detected by heating the substance with sodium or potassium in the manner described above, and bringing a portion of the alkaline solution into contact with a bright silver coin; if the original substance contained sulphur, an alkaline sulphide will have been formed, and the solution produces a black stain on the silver coin.

Metals contained in organic salts may usually be detected by the ordinary methods of analysis, but as a rule it is better to ignite the compound and then test for the metal in the residue (compare p. 15).

QUANTITATIVE ELEMENTARY ANALYSIS.*

Just as the qualitative analysis generally consists of a series of tests for the elements present in the substance, so the quantitative analysis of an organic compound usually comprises one or more processes by means of which these elements are estimated. For this reason, and because the presence of certain elements necessitates slight changes in the

* The following account of the methods commonly adopted in the quantitative analysis of organic compounds is only intended to indicate the nature of the processes; the details of manipulation, upon which success depends, can only be learned by practice in the laboratory.

methods to be employed, the qualitative examination must be completed before the quantitative analysis is commenced.

Estimation of Carbon and Hydrogen.—All organic compounds* are decomposed when they are brought into contact with red-hot copper oxide, the carbon being converted into *carbon dioxide*, the hydrogen into *water;* by employing a known weight of substance, and collecting and weighing these products of combustion, the percentage of carbon and hydrogen may be readily determined. The apparatus generally used for this purpose is shown in the accompanying figures.

The **calcium chloride** or **water tube** (fig. 6) is filled with granulated anhydrous calcium chloride, or with fragments of

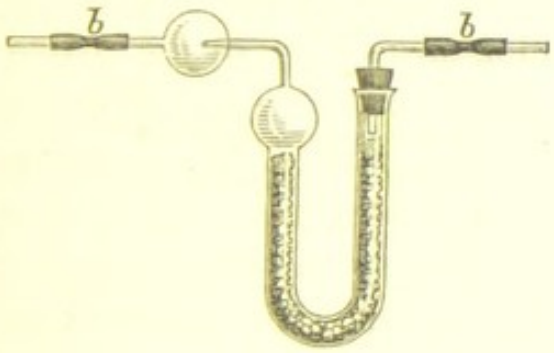


Fig. 6.

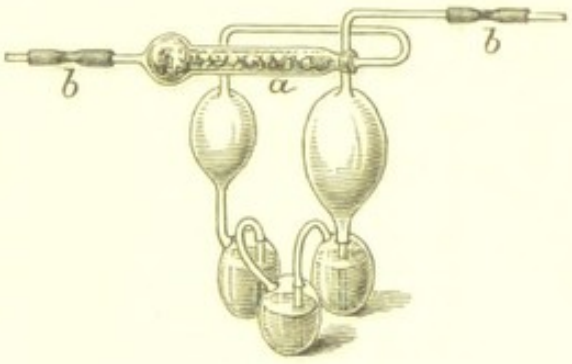


Fig. 7.

pumice moistened with concentrated sulphuric acid, and serves to absorb the water; the **potash bulbs** (fig. 7) are partly filled, as shown, with strong potash (sp. gr. about 1·28),† the small tube (*a*), which contains anhydrous calcium chloride, serving to retain the aqueous vapour, which is taken up by the gases in their passage through the potash. The calcium chloride tube and the potash bulbs are carefully weighed before and after the combustion, the caps (*b*, *b*) with which they are closed being removed on both occasions; the gain in weight of the former corresponds with the amount of water produced, and that of the latter with the amount of carbon dioxide formed.

* With the exceptions already mentioned (footnote, p. 15).

† The word potash is used, for the sake of brevity, to denote an aqueous solution of potassium hydroxide.

The combustion is carried out in a piece of hard glass combustion tubing (*a*, *b*, fig. 8), which is usually about 90 cm. long, and open at both ends; part of the tube (*f* to *f*) is filled with a layer of granulated copper oxide, kept in its place by loose asbestos plugs (*e*, *e*). Before the analysis is started the tube is heated in a combustion furnace (*k*) at a dull-red heat, and a current of air, carefully freed from carbon dioxide and moisture—by being passed first through potash contained in the wash-bottle (*g*), and then through the two towers (*h*, *j*)* containing pumice moistened with concentrated sulphuric acid—is led through it, in order that any moisture or traces of organic matter in the tube may be removed; the *empty* section *only* of the tube is then allowed to cool.

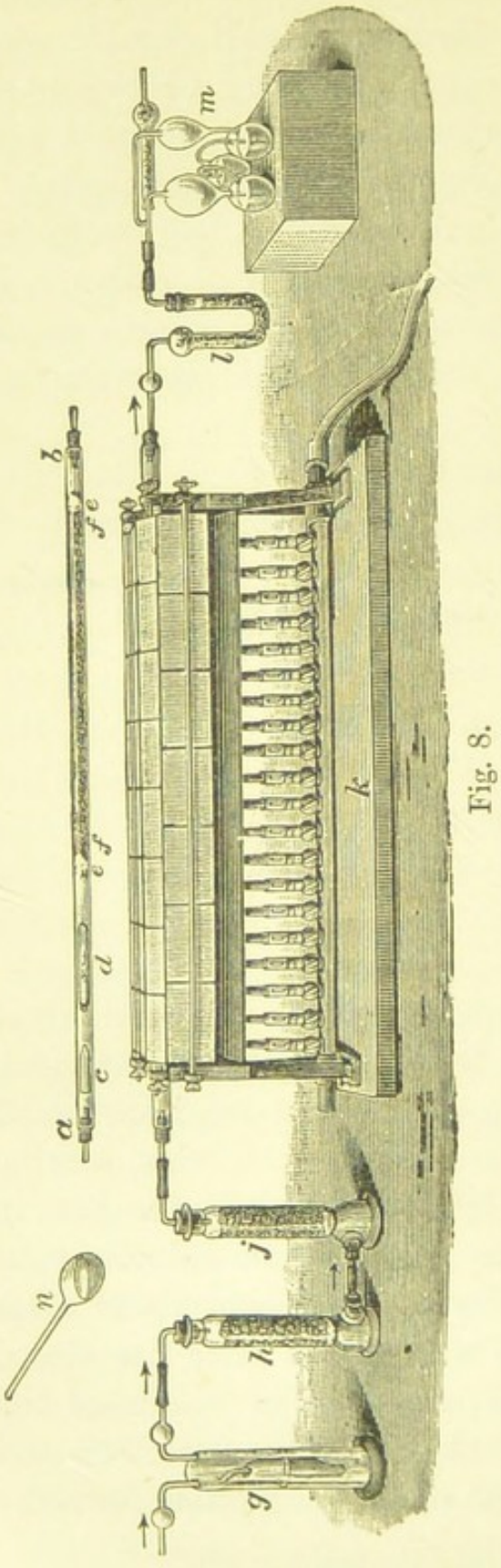


Fig. 8.

The water tube (*l*) having been fitted into the end (*b*) through a rubber stopper, and the potash bulbs (*m*) attached by means of a short piece of rubber tubing, 0·15 to 0·2 gram of the substance, accurately weighed out in a narrow

* In practice, two such sets of drying apparatus are usually employed, one for the air, the other for the oxygen.

porcelain or platinum *boat* (*d*), is introduced into the tube; a freshly ignited roll of copper gauze (*c*) is then placed behind the boat in order to prevent as far as possible any backward diffusion of the products of combustion. When a very volatile liquid is to be analysed, it is weighed out in a thin glass bulb (shown on a larger scale at *n*), which is afterwards placed in the boat (at *d*).

A slow stream of air, carefully freed from moisture and carbon dioxide, as before, is now passed through the tube, and the combustion of the substance is started and regulated by lighting the gas burners (beginning at *c*). As soon as the whole of the tube has been gradually raised to a dull-red heat, the current of air is turned off, and a stream of pure oxygen is passed, in order to burn any remaining organic matter and to oxidise the copper which has been formed by the reduction of some of the copper oxide; finally, air is again passed until the oxygen is expelled from the apparatus. The whole operation occupies from $1\frac{1}{2}$ to 3 hours, according to the nature of the substance. The water tube and the potash bulbs are then disconnected, and their ends are closed with the rubber caps; after they have been left for about two hours to cool thoroughly, they are again weighed.

Now, since the gain in weight of the potash bulbs is due to the absorption of carbon dioxide, which has been formed during the combustion, $\frac{12}{44}$ths or $\frac{3}{11}$ths (C/CO_2) of this gain in weight represents the quantity of carbon in the amount of substance taken; as also the gain in weight of the water tube corresponds with the amount of water formed, $\frac{2}{18}$ths or $\frac{1}{9}$th (H_2/H_2O) of this increase represents the amount of hydrogen.* The percentage of carbon and hydrogen may therefore be calculated.

Example.—0·1582 g. of substance gave on combustion 0·0614 g. of H_2O and 0·3620 g. of CO_2; therefore, 0·1582 g. of substance contains $0·0614 \times 1/9 = 0·0068$ g. of hydrogen, and $0·3620 \times 3/11 = 0·0987$ g.

* The rounded atomic weights H=1, C=12, O=16, N=14 are used here and in other calculations.

of carbon, so that 100 parts of the substance contain $\frac{0{\cdot}0068 \times 100}{0{\cdot}1582}$ $= 4{\cdot}3$ parts of hydrogen, and $\frac{0{\cdot}0987 \times 100}{0{\cdot}1582} = 62{\cdot}4$ parts of carbon.

If the substance consisted of carbon, hydrogen, and oxygen *only*, the difference between the sum of the above numbers and 100 must represent the percentage of oxygen; the composition of the substance, therefore, is,

C.....62·4 per cent.
H..... 4·3 "
O.....33·3 " (by difference).

The percentage of oxygen is always obtained by difference, there being no satisfactory method by which this element may be directly estimated.

The following points remain to be noticed in connection with the determination of carbon and hydrogen:—When the substance contains *nitrogen*, it is necessary to insert a roll of bright copper gauze, about four inches long, into the front part (*b*) of the tube, in the place of some of the copper oxide; this roll is kept red-hot during the combustion, and serves to decompose any oxides of nitrogen which may be produced during the operation, and which would otherwise be absorbed by the water in the calcium chloride tube and by the potash.* When the substance contains a *halogen*, a roll of silver gauze must be used in order to prevent any halogen, or halogen compound of copper, from passing into the absorption apparatus.

Usually, in analysing a substance containing *halogens*, *sulphur*, or *phosphorus*, the space *f* to *f* (fig. 8) is filled with lumps of fused lead chromate, instead of copper oxide. Lead chromate, like copper oxide, is a powerful oxidising agent at high temperatures,

$$2PbCrO_4 = 2Pb + Cr_2O_3 + 5O;$$

* In order to render the roll of gauze as efficient as possible, it is heated in a blowpipe flame until thoroughly oxidised, and, while red-hot, dropped into a little (1 c.c.) pure methyl alcohol contained in a test-tube; the methyl alcohol reduces the copper oxide, giving a very bright surface of copper. The roll is then completely freed from methyl alcohol by being heated at 160–180° for a few minutes, just before the combustion is started.

any sulphur dioxide, halogen, or phosphorus pentoxide, produced during the combustion is completely retained by the lead, as lead sulphate, lead chloride, &c., and thus its passage into the absorption apparatus is prevented.

Estimation of Nitrogen.—Nitrogen may be estimated in three ways: as nitrogen by Dumas' method, or as ammonia by Will and Varrentrap's, or by Kjeldahl's, method.

1. **Dumas' Method.**—This process is based on the fact that, when ignited with copper oxide, nitrogenous organic substances are entirely decomposed into carbon dioxide, water, and nitrogen (or its oxides). If the gaseous products of combustion are passed over heated copper, to decompose the oxides of nitrogen, and then collected over potash, the carbon dioxide is absorbed, and the residual gas consists of nitrogen; by measuring the volume of the gas obtained from a known weight of substance, the percentage of nitrogen can be determined.

The analysis is carried out in a combustion tube similar to that used in the estimation of carbon and hydrogen (fig. 8), but containing in the front end (*b*) a roll of copper gauze (see footnote, p. 22). Instead, however, of the substance being placed in a boat, the weighed quantity is intimately mixed with finely powdered copper oxide, and this mixture occupies the space *c* to *e*. Before the substance is heated, a stream of carbon dioxide * is passed through the tube until the air has been expelled, which is the case when the bubbles are almost entirely absorbed by the potash; † at the same time the roll of copper gauze and the front part of the tube are raised to dull redness. The stream of gas is now stopped and the combustion is started by gradually heating the mixture of substance and copper oxide; the escaping gases are either collected over mercury in a eudiometer containing potash, or more conveniently in the apparatus shown in fig. 9.

* The gas is generated in a Kipp's apparatus or by heating native magnesite.

† The bubbles are never completely absorbed, as it is impossible to drive out the last traces of air.

As soon as the whole of the tube has been raised to a dull or cherry-red heat, and gases cease to be evolved, a current of carbon dioxide is again led through the combustion tube until the rest of the nitrogen has been expelled. The eudiometer is then closed with the thumb, inverted in a cylinder of water, and the thumb removed so that the mercury may fall out and the strong potash mix with the water. After about half-an-hour's time, the tube is held vertically in such a position that the levels of the water inside and outside are the same, and the volume (v) of the nitrogen is observed; the temperature ($t°$) of the gas —that is, of the water surrounding the tube—and the height (B) of the barometer are also noted.

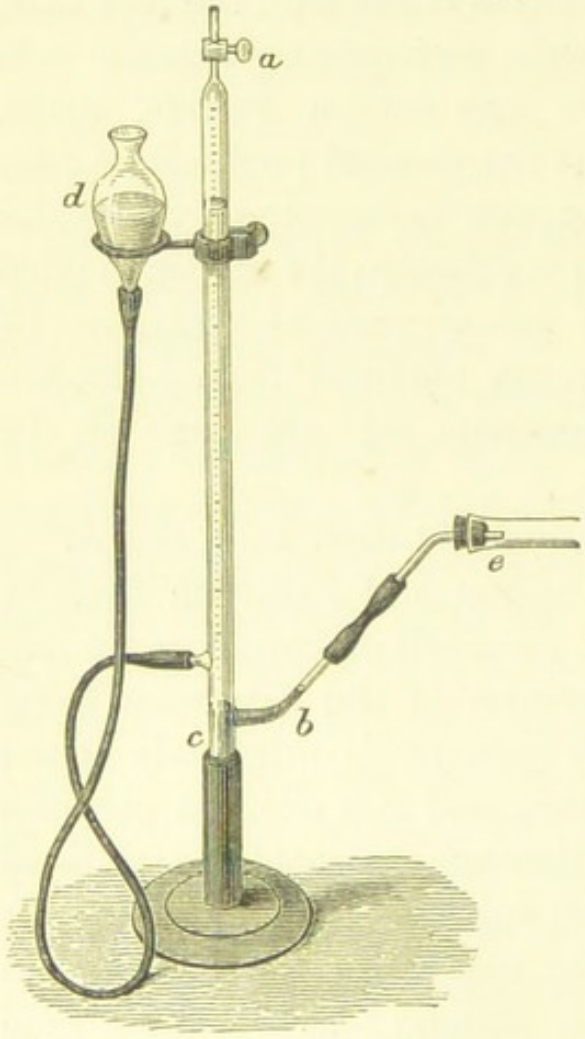


Fig. 9.

The apparatus (Schiff's nitrometer) shown in fig. 9, which is generally used in nitrogen determinations, consists of a graduated tube (a, c), provided with a stop-cock (a) and a reservoir (d), by means of which the tube may be filled with potash (sp. gr. 1·3), and which also serves for regulating the pressure in the apparatus; the lower part of the tube (c, b) is filled with mercury, which forms a seal and prevents the passage of the potash into the combustion tube (e). After carbon dioxide has been passed through the combustion tube for a considerable time, the tube (b) is connected, and the reservoir (d) is lowered. If the bubbles are almost completely

absorbed as they ascend through the potash, the combustion is proceeded with, and the nitrogen which remains in the tube at the end of the operation is swept into the apparatus by means of carbon dioxide, as described above. The apparatus is now placed aside for about an hour to cool; the reservoir (*d*) is then raised until the potash is at the same level in it and in the tube (*a*, *c*), and the volume of nitrogen (*v*), the temperature ($t°$), and the barometric pressure (B) are noted.

The weight of nitrogen in the quantity of substance taken is readily ascertained when its volume (in cubic centimetres) has been determined by either of the methods described. Since the volume v is measured at $t°$ under a pressure B – T, where T = the tension of aqueous vapour in mm. of mercury,* at the temperature $t°$, the volume V at 0° and 760 mm. would be $v \times \frac{B-T}{760} \times \frac{273}{273+t°}$. As, 1 c.c. of nitrogen weighs 0·001251 g. at N.T.P., the weight of V c.c. is V × 0·001251 g.

Example.—0·2248 g. of substance gave 7·1 c.c. of nitrogen measured at 16°; B = 753·5 mm., T = 13·5 mm.

The weight of the gas is $7{\cdot}1 \times \frac{740}{760} \times \frac{273}{289} \times 0{\cdot}001251 = 0{\cdot}00817$ g., and the percentage of nitrogen $\frac{0{\cdot}00808 \times 100}{0{\cdot}2248} = 3{\cdot}6$.

2. **Will and Varrentrap's Method** depends on the fact already stated, that many nitrogenous organic substances, when heated with caustic alkalis, are decomposed in such a way that the whole of their nitrogen is converted into ammonia; by estimating the ammonia produced by the decomposition of a known weight of the substance, the percentage of nitrogen is determined.

* Some of the values of T which are often required are the following:—

$t°$ =	10°	12°	14°	16°	18°	20°
T =	9·14	10·43	11·88	13·51	15·33	17·36 mm.

When the apparatus shown in fig. 9 is employed, the vapour tension of the strong potash is much less than that of pure water; if the potash has a sp. gr. = 1·3, it is usual, in practice, to deduct from B half the tension of aqueous vapour at the temperature $t°$.

The apparatus (fig. 10) employed for this purpose consists of a piece of hard glass tube (*a*, *d*) about 45 cm. long, drawn out and sealed at one end (*a*); an asbestos wad is loosely fitted into the end (*a*), and the space *a* to *b* is filled with coarsely powdered, *freshly ignited* soda-lime; the part *b* to *c* contains an intimate mixture of the weighed substance and finely powdered soda-lime, and the remainder of the tube (*c* to *d*) is filled with coarsely powdered soda-lime only, the whole being kept in position by an asbestos wad (at *d*).

The absorption apparatus (*e*) contains dilute hydrochloric acid, and serves to absorb the ammonia; it is fitted into the

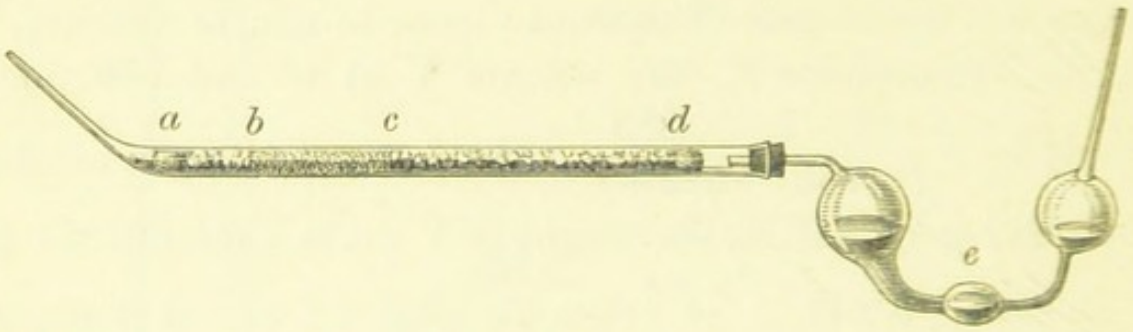


Fig. 10.

open end of the tube by means of a rubber stopper. The tube is tapped gently so as to ensure a clear channel for the escape of the gaseous products,* and is then gradually heated in a combustion furnace (commencing at *d*), just as in the determination of nitrogen volumetrically; when the whole has been raised to a red heat, the ammonia remaining in the tube is drawn into the absorption bulb by breaking off the sealed end (*a*) and aspirating air through the apparatus.

The weight of ammonia which has been produced may be determined gravimetrically by precipitation with platinic chloride, or a known volume of standard hydrochloric acid is introduced into the bulbs to start with, and the quantity which has been neutralised by the ammonia is estimated volumetrically by titration with standard alkali.

* Should this precaution be neglected the tube may get choked up and a serious explosion ensue.

The soda-lime method is not altogether satisfactory, because, owing to the decomposition of some of the ammonia formed during the operation, the results are usually too low; this decomposition may be prevented to some extent by adding a little sugar to the mixture of the substance and soda-lime. Furthermore, the method is not of universal application, as many nitrogenous organic substances do not yield the whole of their nitrogen in the form of ammonia when they are heated with soda-lime.

3. **Kjeldahl's Method,** which is used more particularly in agricultural laboratories for the analysis of foods, fertilisers, &c., depends on the fact that when nitrogenous organic compounds are completely decomposed with hot, concentrated sulphuric acid, their nitrogen is obtained in the form of *ammonium* sulphate.

The substance (0·5–5 grams) is placed in a round-bottomed flask of hard glass, and covered with about 20 c.c. of concentrated sulphuric acid. The flask is then heated directly over an Argand burner, very gently at first, afterwards sufficiently to boil the acid; the process is continued until the liquid (which is usually very dark in colour owing to the separation of carbonaceous matter) has become almost colourless. As a rule, this operation is hastened by adding potassium sulphate (5–10 grams) after the first 15–30 minutes' heating, in order to raise the boiling-point. The ammonia which has been produced is separated by distillation with excess of caustic soda in a current of steam,* collected in standard sulphuric acid, and estimated by titration.

Estimation of Chlorine, Bromine, and Iodine.—The halogens in an organic compound are generally estimated by the method devised by **Carius,** which consists in oxidising the substance with nitric acid at a high temperature in presence of silver nitrate. Under these conditions the carbon is completely oxidised to carbon dioxide, and the hydrogen to water, while the halogen combines with the silver; the chloride, bromide, or iodide of silver thus produced is collected and weighed in the ordinary way. The decomposition is carried out in a strong glass tube (*a*, *b*, fig. 11), about 40 cm. long and 25 mm. wide, sealed at one

* Special distillation apparatus is employed where this method is in frequent use.

end (*a*); the substance is weighed out in a small glass tube, which is placed in the larger tube, together with a few crystals of silver nitrate. Pure concentrated nitric acid (about 10 c.c.) having been added, the open end is drawn out and sealed, as shown at *b*. The tube is then placed in an iron case, and heated in a furnace (fig. 11) at a tempera-

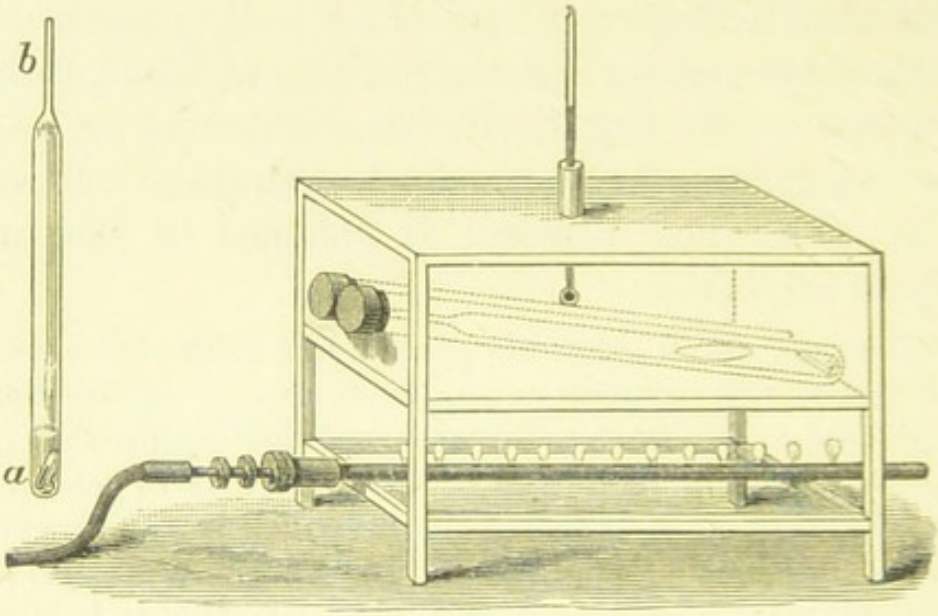


Fig. 11.

ture necessary to ensure complete decomposition, usually at about 180°, for four hours; in the case of very stable substances, a much higher temperature and prolonged heating are required, and fuming nitric acid must be used. When *quite cold* the tube is opened,* the contents are transferred to a beaker with the aid of distilled water, and boiled gently for about fifteen minutes; the halogen silver salt is further treated in the usual way.

* Very great care must always be taken in working with sealed tubes, as they frequently explode, and very serious accidents may occur. The tube should *not be removed from its iron case*, but should be cautiously pulled or tipped forwards until the capillary just projects, using a cloth to protect the hand; a Bunsen flame is then played cautiously on the tip of the capillary until the glass softens and blows out; after the pressure has been released the tube is cut with a file in the usual way, but before doing so, the capillary should be examined in order to make sure that it has not been choked up by any solid particles.

Another method of estimating the halogens, especially useful in the case of substances which are difficult to decompose, consists in heating the compound with pure, *freshly ignited* quicklime (prepared by calcining marble) in a narrow piece of combustion tube, about 50 cm. long, and closed at one end. In charging the tube, a little lime is first introduced, and then the mixture of the substance with about ten times its weight of quicklime, the remainder of the tube being nearly filled with quicklime. The tube is tapped gently to form a clear channel for the passage of the gases (compare footnote, p. 26), and is then heated in a combustion furnace, the front part being raised to a bright-red heat before the decomposition of the substance is proceeded with. When quite cold, the contents of the tube are cautiously shaken into excess of dilute nitric acid, the acid solution is filtered from carbonaceous matter, and the halogen is precipitated with silver nitrate.

Sulphur and **phosphorus** may be estimated by heating the substance in a sealed tube with nitric acid, as described above, but without the addition of silver nitrate. The whole of the sulphur is oxidised to sulphuric acid, the phosphorus to phosphoric acid, which may then be estimated by the ordinary methods of analysis.

Another method for determining sulphur and phosphorus, and also halogens (applicable only in the case of organic acids and some non-volatile neutral compounds), consists in heating the substance with a mixture of potassium carbonate and nitre, or sodium peroxide, until the product is colourless.* Here, again, the substance is completely oxidised, and the sulphate or phosphate produced may be estimated in the residue.

* A sufficiently large proportion of potassium carbonate must be used, otherwise the mixture may be an *explosive* one.

CHAPTER II.

Deduction of a Formula from the Results of Analyses and Determination of Molecular Weight.

The quantitative analysis of a pure organic compound is usually made with one of two objects: (*a*) to prove that a particular compound is what it is supposed to be; (*b*) to ascertain the percentage composition of some substance in order to determine its formula.

In the first case, the results of the analysis are compared with the calculated percentage composition, and if the two series of values agree within the limits of experimental error, this fact is taken as evidence that the substance in question is what it was believed to be.

Example.—A substance obtained by oxidising a fat with nitric acid is suspected to be succinic acid, $C_4H_6O_4$, and, on analysis, it gave the following results :—C = 40·56, H = 5·12, O = 54·32 (by difference) per cent. Since the percentage composition of succinic acid, calculated from its formula, is C = 40·68, H = 5·08, O = 54·24 per cent., the results of the analysis afford strong confirmatory evidence as to the nature of the substance under examination.

In the second case, where the object of the analysis is to deduce a formula for the substance, the process is just the same as that applied to the results of the analysis of inorganic compounds—that is to say, the percentage of each element is divided by the atomic weight of that element, and the ratio is then expressed in whole numbers by dividing each term by the lowest value or by some simple fraction of this value.

Example.—The percentage composition of a substance is found to be C = 84·0, H = 16·0; deduce its formula. Since an atom of carbon weighs twelve times as much as an atom of hydrogen, the ratio between the number of *atoms* of carbon and the number of

atoms of hydrogen is 84/12 : 16/1 or 7 : 16; the formula, therefore, is C_7H_{16}.

Example.—The percentage composition of a substance is C = 39·95, H = 6·69, O = 53·36; deduce its formula.

Here the ratio between the number of atoms is found to be 3·33 : 6·69 : 3·33,

$$C=\frac{39\cdot95}{12}=3\cdot33,\ H=\frac{6\cdot69}{1}=6\cdot69,\ O=\frac{53\cdot36}{16}=3\cdot33;$$

and when each term is divided by 3·33, and experimental errors are allowed for, the ratio of the atoms C : H : O = 1 : 2 : 1; the formula of the substance, therefore, is CH_2O.

Example.—The percentage composition of a substance as determined by analysis is C = 19·88, H = 6·88, N = 46·86, O = 26·38; deduce its formula.

Here the ratio is found to be:

$$C=1\cdot657,\ H=6\cdot880,\ N=3\cdot347,\ O=1\cdot649;$$

and when these values are all divided by 1·649, the formula CH_4N_2O is obtained.

The ratio of the atoms determined experimentally is hardly ever expressed *exactly* by whole numbers, owing to unavoidable errors, and for this reason, *when a formula has been deduced from the results of analysis it should always be checked by calculating the percentage composition from the formula so obtained and comparing the values with those found experimentally;* the two values for each element should agree within about 0·1–0·3, the calculated value for carbon being usually a little higher, that for hydrogen a little lower, than the experimental value.*

The formula calculated from the results of analysis is merely the *simplest* expression of the *ratio* of the atoms in the molecule, and is termed the **empirical formula**; such a formula may, or may not, show how many atoms of each element the molecule of the substance contains: formaldehyde, CH_2O, acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, for example, have the same percentage composition, and consequently, on analysis, they would all be found to have the same empirical formula, CH_2O.

* The results of combustions and of nitrogen determinations are usually given to one decimal place only, as the second place has no significance.

In order to determine the **molecular formula**, by which is meant a formula expressing not only the ratio, but also the actual numbers of the atoms in the molecule, the **molecular weight** of the compound must be determined. If, for example, it can be proved that a compound of the empirical formula, CH_2O, has a molecular weight = 60, its molecular formula must be $C_2H_4O_2$, and not CH_2O or $C_3H_6O_3$.

The determination of the molecular weight of a substance, therefore, is of great importance, and for this purpose certain physical methods, described later, are adopted whenever possible; no purely *chemical* methods are known by which molecular weight can be established, but such methods may often afford valuable indications of the *minimum* value of the molecular weight, as will be seen from the following examples.

Analysis of Organic Salts for the Determination of Equivalent Weights.

In the case of organic acids, the analysis of a salt of the acid is often of value; the silver salt is generally employed for this purpose, and a weighed quantity of the pure substance is ignited in a porcelain crucible, when complete decomposition ensues, and a residue of pure silver is obtained.

Example.—The percentage composition of an organic acid is C = 39·95, H = 6·69, O = 53·36; its empirical formula is, therefore, CH_2O. Its silver salt was prepared; 0·2955 g. of the pure salt gave on ignition 0·1620 g. of silver, so that the percentage of silver in the salt is $\frac{0{\cdot}1620 \times 100}{0{\cdot}2955} = 54{\cdot}82$.

Now, since 54·82 parts of silver are contained in 100 parts of the salt, 1 gram-atom or 107·9 parts of silver are contained in $\frac{100 \times 107{\cdot}9}{54{\cdot}82} = 196{\cdot}83$ parts of salt. The minimum molecular weight of the salt (its equivalent weight), therefore, is 196·83; and, as in the formation of the salt from the acid 1 part of hydrogen is displaced by 107·9 parts of silver, the equivalent weight of the acid is $196{\cdot}83 - 107{\cdot}9 + 1 = 89{\cdot}93$.

Since, however, the acid is composed of carbon, hydrogen, and oxygen, the atomic weights of which are all taken as whole numbers, and as the analytical results are not free from experimental errors, the minimum molecular weight of the acid may also be taken to be a whole number—that is to say, 90. The minimum molecular weight of the acid being 90, its *molecular formula* is not CH_2O (=30) or $C_2H_4O_2$ (=60), but may be $C_3H_6O_3$ (=90), in which case that of the silver salt would be $C_3H_5O_3Ag$ (=196·9).

It is clear, however, that the analysis of the silver salt does not establish the molecular formula of the acid. If the acid had the molecular formula, $C_6H_{12}O_6$, and contained two atoms of displaceable hydrogen—that is to say, were dibasic—the silver salt, $C_6H_{10}O_6Ag_2$, would contain, as before, 54·82 per cent. of silver, and the minimum molecular weight, calculated as above, would again be 90. But if the acid were dibasic, it might be possible to displace only one atom of hydrogen, and obtain a hydrogen salt, $C_6H_{11}O_6M'$, the analysis of which would give the minimum molecular formula, $C_6H_{12}O_6$. Should the preparation of such a hydrogen salt be found impossible, the fact might be taken as evidence against the molecular formula, $C_6H_{12}O_6$, but the matter would not be definitely settled.

Instead of an analysis of a salt, a titration of the acid with standard alkali is often carried out in order to obtain the equivalent weight or the minimum molecular weight of an acid.

Most organic bases combine with hydrochloric acid to form salts which, like ammonium chloride, unite with platinic chloride and with auric chloride, giving complex salts. These complex salts usually have the compositions, B'_2,H_2PtCl_6 and $B',HAuCl_4$ respectively where B′ represents one molecule of a monacid base, such as methylamine, CH_5N, ethylamine, C_2H_7N, &c. When these salts are ignited in a porcelain crucible, pure finely divided platinum, or gold, remains, so that the percentage of metal in the salt is very

easily determined. The minimum molecular weight of the base can then be calculated.

Example.—The complex platinum salt (*platinichloride*) of an organic base gave on ignition 36·9 per cent. of platinum; what is its minimum molecular weight? Since 36·9 parts of platinum are contained in 100 parts of the salt, 195 parts of the metal are contained in $\frac{100 \times 195}{36{\cdot}9} = 528$ parts of salt; as 195 is the atomic weight of platinum, the minimum molecular weight of the salt is 528. The equivalent weight or the minimum molecular weight of the base (C_3H_9N), therefore, is $\frac{B'_2,H_2PtCl_6 - H_2PtCl_6}{2}$ or

$$\frac{528-(2+195+213)}{2} = \frac{528-410}{2} = 59{\cdot}0.$$

As in the case of acids, so in that of bases, the minimum value calculated from the analytical results may not be the real molecular weight of the compound. Some bases are diacid, and form platinichlorides of the composition, B'',H_2PtCl_6, so that a diacid base of the molecular weight 118 would yield a platinichloride containing the same percentage of platinum as the salt of a monacid base of the molecular weight 59.

Other Methods of Examination.—It will be seen from the above examples that, if there are any grounds for assuming that there is only *one atom* of any particular element in the molecule of the compound, the probable molecular weight of that compound may be calculated from the results of any analysis which gives the percentage of that particular element.

This being the case, the probable molecular formula of a compound, other than an acid or a base, may often be determined by preparing and analysing some simple derivative of it.

Example.—A liquid hydrocarbon has the percentage composition C = 92·31, H = 7·69; its empirical formula, therefore, is CH. On being treated with bromine this hydrocarbon yields hydrogen bromide and a bromo-derivative consisting of C = 45·86, H = 3·18, Br = 50·96 per cent. The ratio of these elements being

$$C = 3{\cdot}82,\ H = 3{\cdot}18,\ Br = 0{\cdot}637,$$

the empirical formula of this derivative is found to be C_6H_5Br. Now, since it is known from experience that, as a rule, the number of atoms of carbon in a molecule is not changed when a hydro-

carbon is treated with bromine, the probable molecular formula of the hydrocarbon is C_6H_6; it cannot be less than this, but it may be greater. A hydrocarbon, $C_{12}H_{12}$, for example, might give a bromo-derivative, $C_{12}H_{10}Br_2$, and these compounds would have the same percentage compositions as C_6H_6 and C_6H_5Br respectively.

The probable molecular weight may often be suggested with confidence if the boiling-point and the percentage composition of the compound are known. When, for example, acetone (p. 134) is distilled with concentrated sulphuric acid, it is converted into a hydrocarbon which, on analysis, is found to have the empirical formula, C_3H_4. The fact that this hydrocarbon boils at 163° affords very strong evidence that the molecular formula is not C_3H_4 or C_6H_8, but probably C_9H_{12}, because it is known that other hydrocarbons, which contain only three or six atoms of carbon in the molecule, boil at temperatures much below 163°, and in the case of analogous compounds an increase in molecular weight is generally accompanied by a rise in boiling-point.

The Determination of Molecular Weight.—The principles on which the determination of molecular weight are based are of course the same for organic as for inorganic substances, and are described in text-books of inorganic chemistry.* The methods used are also the same; but whereas the molecular weights of many inorganic compounds are unknown, there are relatively few instances in which the molecular weight of an organic compound cannot be determined by one or other of the ordinary processes. For this reason, and also because a knowledge of the *molecular* formula is, generally speaking, more important in the case of organic than in that of inorganic substances, the chief methods for the determination of molecular weight, although described elsewhere (loc. cit.), are given again here.

One of the more important physical methods by which the molecular weight can be ascertained is by a determination of the vapour density. Since the vapour density is a number expressing how many times a given volume of the gas or vapour is as heavy as the same volume of hydrogen, it also expresses how many times one molecule of the substance is

* Kipping and Perkin, *Inorganic Chemistry*, Part I. pp. 193–197; Part II. pp. 375 and 379.

as heavy as one *molecule* of hydrogen (= 2), because the equal volumes contain an equal number of molecules. The molecular weight, on the other hand, is a number expressing how many times one molecule of the substance is as heavy as one *atom* of hydrogen (= 1); therefore the molecular weight is double the vapour density, because the standard with which it is compared is half as great: M.W. = V.D. × 2.

Sometimes the density of air is taken as unity in stating the vapour density; since air is 14·43 times as heavy as hydrogen, the vapour density compared with air is 1/14·43 of the value when compared with hydrogen.

Determination of Vapour Density.

The vapour density of a substance is ascertained experimentally, (*a*) by measuring the *volume* occupied by the vapour of a known *weight* of the substance at known temperature and pressure, or (*b*) by ascertaining the *weight* of a known *volume* of the vapour of the substance at known temperature and pressure. The observed volume of the vapour is then reduced to 0° and 760 mm., and the weight of a volume of hydrogen at 0° and 760 mm., equal to the corrected volume of the vapour, is calculated; the weight of the vapour divided by that of the hydrogen gives the vapour density, from which the molecular weight is then deduced.

The molecular weight determined experimentally frequently differs from the theoretical value by *several units*, owing to experimental errors; this, however, is of little importance, since all that is required in most cases is to decide between multiples of the empirical formula.

Example.—An organic liquid has the empirical formula, $C_4H_{10}O$; 0·062 g. of the liquid gave 23·2 c.c. of vapour at 50° and 720 mm.; what is its molecular formula?

$$\text{The volume at } 0° \text{ and } 760 = 23{\cdot}2 \times \frac{720}{760} \times \frac{273}{273+50} = 18{\cdot}57 \text{ c.c.};$$

and as 1 c.c. of hydrogen at N.T.P. weighs 0·0000899 g., 18·57 c.c. weigh 0·00167 g.

$$\frac{\text{The weight of the vapour}}{\text{The weight of the hydrogen}} = \frac{0{\cdot}062}{0{\cdot}00167} = 37{\cdot}1 = \text{V.D.}$$

Hence the molecular weight is V.D. $\times 2$ or $37{\cdot}1 \times 2 = 74{\cdot}2$, and the molecular formula, $C_4H_{10}O$, so that in this case the empirical is identical with the molecular formula.

The determination of the vapour density is only possible, of course, when a substance can be converted into vapour without its decomposing under the conditions of the experiment. In many cases, however, a non-volatile compound can be converted into some simple derivative which is volatile, so that, by determining the vapour density of the latter, the molecular weight of the parent substance can be ascertained.

The following are some of the methods employed in determining vapour density :—

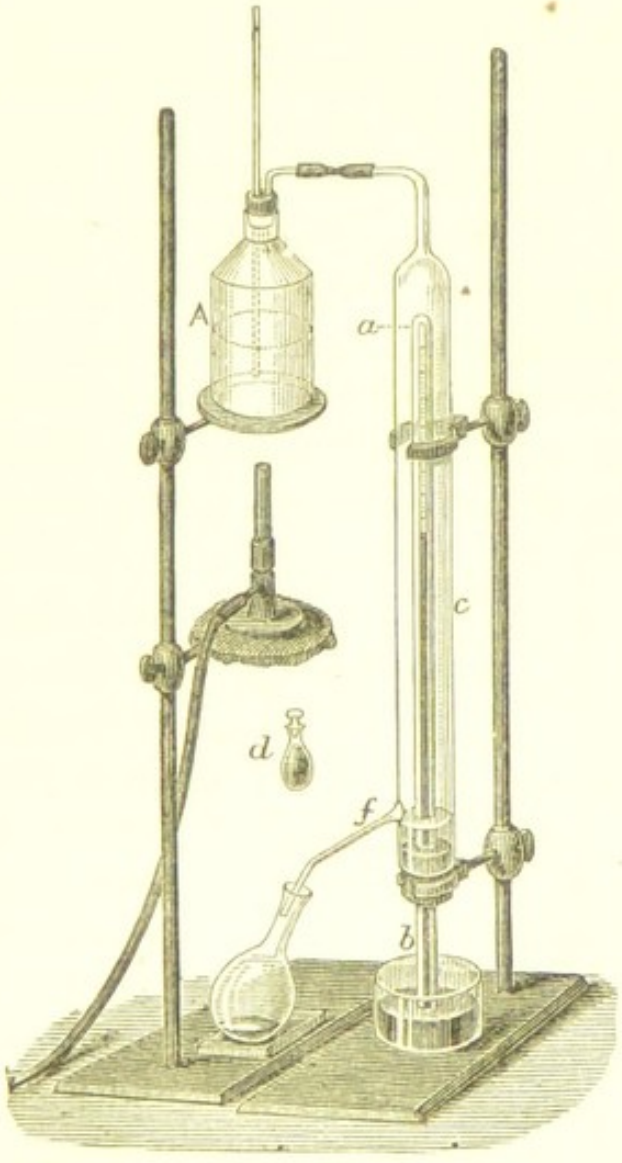


Fig. 12.

Gay-Lussac's or Hofmann's Method. — A graduated barometer tube (*a*, *b*, fig. 12), about 85 cm. long and 35 mm. wide, filled with and then inverted in mercury, is surrounded by a wider tube (*c*), through which is passed the vapour of some liquid boiling at a known and constant temperature.* For this pur-

* The liquids most commonly employed are water (b.p. 100°), xylene (b.p. 140°), aniline (b.p. 183°), and ethyl benzoate (b.p. 213°).

pose the upper end of the outer tube (*c*) is connected with a vessel (A), usually made of copper, in which the heating liquid is kept in rapid ebullition. The condensed liquid escapes through the side-tube (*f*), and is collected for subsequent use.

As soon as the barometer tube is at a constant temperature, a weighed quantity (about 0·05 g.) of the substance, contained in a small stoppered vessel (*d*), which it fills completely, is placed under the open end (*b*). The vessel immediately rises to the surface of the mercury in the tube, the substance vaporises into the Torricellian vacuum, and the mercury is forced downwards; as soon as the level remains stationary, the *volume* of the vapour is noted. The *temperature* of the vapour is the boiling-point of the liquid employed to heat the barometer tube. The *pressure* is determined by subtracting the height of the column of mercury in the inner tube (*a*, *b*), above the level in the trough, from the height of the barometer, both readings having been first reduced to 0°.* The *weight* of the vapour is that of the substance taken.

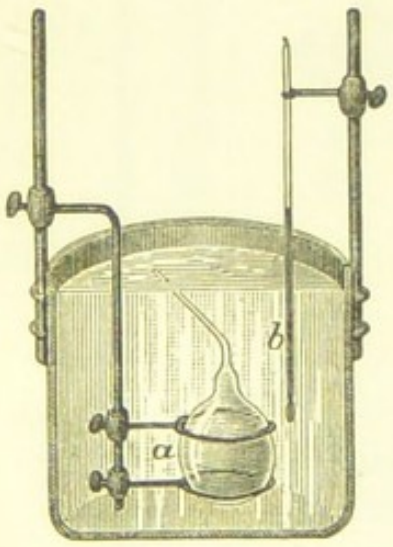


Fig. 13.

The great advantage of this method lies in the fact that it affords a means of determining the vapour densities of substances under greatly reduced pressures, and therefore at temperatures very much below their ordinary boiling-points, so that it can often be employed with success in the case of substances which would decompose if they were heated under atmospheric pressure.

Dumas' Method. — A globe-shaped vessel of about 200 c.c. capacity (*a*, fig. 13), the neck of which is drawn out to a fine tube, is carefully weighed, the temperature (t'°) and barometric pressure (B′) being noted. A fairly large quantity of the substance (about 8–10 grams) is now introduced by gently

* By correcting for the expansion of the mercury.

heating the globe and quickly dipping the tube into the liquid. The vessel is then immersed in an oil-bath (shown in section in fig. 13) which contains a thermometer (b), and is heated at a constant temperature, at least 20° above the boiling-point of the compound. The air in the apparatus is quickly expelled by the rapid vaporisation of the substance, and the vessel is filled with the vapour of the liquid. As soon as the whole of the liquid has been vaporised, which is known by the fact that vapour ceases to issue from the fine tube, the point of the latter is sealed before the blowpipe, the *temperature* of the oil-bath ($t°$) and the *height of the barometer* (B) being noted. The globe is allowed to cool, and is then cleaned, dried, and weighed.

The point of the tube is now broken under water (or mercury), which rushes in and fills the globe completely, except for the minute quantity of liquid produced by the condensation of the vapour in the globe; the globe is again weighed, and its capacity or *volume* (v) obtained from the weight of the water contained in it. The volume may also be measured directly by transferring the liquid from the globe to a graduated vessel.

When the globe is weighed the first time it is full of air, but at the second weighing it is full of vapour; when, therefore, the first weight is subtracted from the second, the difference, W, is the weight of the volume, v, of vapour *less* the weight of the volume, v, of air.* The weight of the air is calculated by reducing the volume, v, at $t'°$ and B′ to N.T.P., and multiplying by 0·001293 the weight of 1 c.c. of air at N.T.P.; this weight added to W gives the weight of the volume, v, of vapour at $t°$ and B. The volume, v, of vapour at $t°$ and B is then reduced to N.T.P., the weight of an equal volume of hydrogen at N.T.P. is calculated, and this weight is divided into that of the vapour.

* Changes in the temperature of the air, height of the barometer, and volume of the globe, occurring during the experiment, may be neglected.

Victor Meyer's Method.—Owing to its simplicity, and the rapidity with which the determination may be made, this method is now used whenever possible; the apparatus is represented in fig. 14. The bulb tube (*a*, *b*) is closed (at *a*) by means of a rubber stopper, and is heated by the vapour of some liquid of constant boiling-point* contained in the outer vessel (*c*); as the air expands, it escapes through the narrow tube (*d*), which dips under the water in the vessel (*e*). As soon as the temperature of the bulb tube (*a*, *b*) becomes constant—that is to say, when bubbles of air cease to escape (from *d*)—the graduated tube (*g*) is filled with water and inverted over the end of *d*; the stopper (*a*) is now removed, and a small bottle or bulb (*d*, fig. 12) completely filled with a weighed quantity (about 0·05 g.) of the liquid is dropped into the apparatus,†

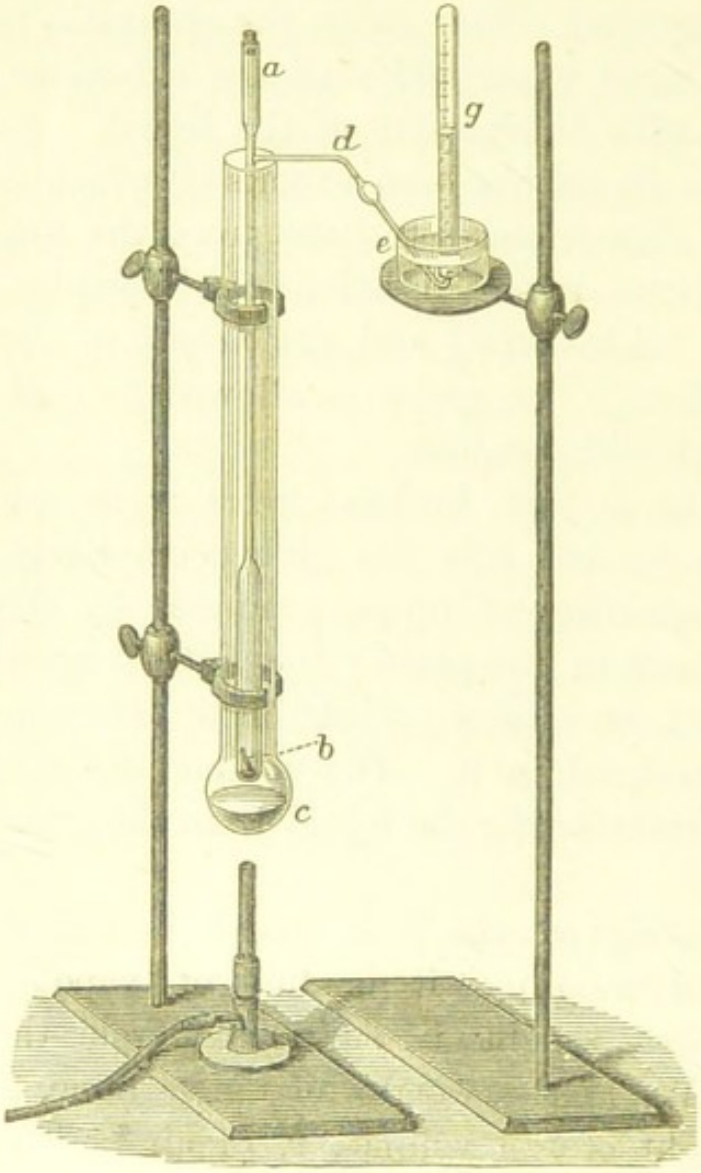


Fig. 14.

* Footnote, p. 37; in determining the vapour density of a substance of high boiling-point, diphenylamine (b.p. 310°) or sulphur (b.p. 448°) may be used, or the bulb tube (*a*, *b*) may be heated at a constant temperature in a metal bath.

† In order to prevent fracture, a little dry asbestos, glass-wool, or sand is placed in *b*.

the stopper being replaced as quickly as possible. The substance immediately vaporises, and the vapour forces some of the air out of the apparatus into the graduated vessel (g). When air ceases to issue (from d), the stopper (a) is at once taken out to prevent the water (in e) from being sucked back into the apparatus.

The *volume* of the vapour is ascertained by measuring the volume (v) of the air in the graduated tube,* its *temperature* ($t°$) and the barometric *pressure* (B) being noted. The volume of the air (in g) is not the same as that actually occupied by the hot vapour (in a, b), because the displaced air has been cooled, and is measured under a different pressure. Its volume now is *equal to that which the given weight of vapour would occupy under the same conditions of temperature and pressure.*

The temperature of the volume, v, of air being $t°$, and the height of the barometer B, the volume at N.T.P. would be $v \times \frac{273}{273+t} \times \frac{B-T}{760}$, T being the tension of aqueous vapour at $t°$ (see footnote, p. 25). The weight of an equal volume of hydrogen at N.T.P. is then calculated and divided into the weight of the substance taken; the vapour density is thus obtained.

The liquid in (c) should have a boiling-point at least 25° higher than that of the substance of which the vapour density is required in order that the latter may be *rapidly* vaporised—otherwise its vapour may condense again higher up the tube. If, as is generally the case, the temperature of the air in the tube (a, b) is lower at the top than at the bottom, this is of no consequence; nor does it matter if the displaced air is colder than the vapour, or if the vapour is cooled a *little* while it is displacing the air. This is because any diminution in the volume of the air displaced from the tube (a, b) arising from these causes is exactly compensated for during the subsequent cooling to $t°$; the lower the original temperature, the smaller the subsequent contraction. If, for example, the hot vapour measured 25 c.c. at 250°, but only displaced 24·04 c.c. of air owing to the latter being of the average temperature of 230°,

* Compare p. 24.

the 24·04 c.c. of air at 230° would occupy the same volume as 25 c.c. at 250° if both were cooled to $t°$.

Determination of Molecular Weight by the Cryoscopic Method.—When sugar is dissolved in water, the solution has a lower freezing-point than that of pure water, and the extent to which the freezing-point is lowered or depressed is, within certain limits of concentration, directly proportional to the weight of sugar in solution; 1 part of sugar, for example, dissolved in 100 parts of water, depresses the freezing-point about 0·058°—that is to say, the solution freezes at −0·058° instead of at 0°, the freezing-point of pure water; 2 parts of sugar, dissolved in 100 parts of water, lower the freezing-point 0·116°; 3 parts, 0·174°, and so on.

Solutions of other compounds in other solvents, such as acetic acid, benzene, &c., behave in a similar manner, and, in sufficiently dilute solutions, the depression of the freezing-point is (approximately) proportional to the number of molecules of the dissolved substance in a given weight of the solvent, and independent of the nature of the substance. If, then, molecular proportions of various substances are dissolved separately in a given (and sufficiently large) quantity of the same solvent, the depression of the freezing-point is *the same* (approximately) in all the solutions, but different with different solvents. From actual experiments with dilute solutions, the depression of the freezing-point, which should be produced by dissolving the molecular weight in grams of any substance in 100 grams of a given solvent, can be calculated; the constant quantity, K, which is thus found, is termed the *molecular depression* of that solvent.

If, for example, 1 g. of sugar dissolved in 100 g. of water depresses the freezing-point by 0·058°, 342 g. (i.e. the molecular weight in grams) would theoretically cause a depression of 19·8° = K.

This constant having been determined for any solvent, the molecular weight, M, of a substance can then be ascertained by observing the depression of the freezing-point of a sufficiently dilute solution, containing a known quantity of that

substance. If 1 gram of the substance were dissolved in 100 grams of the solvent, the observed depression, D, would be $K \times \frac{1}{M}$, because K is the depression produced by the molecular weight in grams—that is to say, by M grams—and the depression varies directly with the weight of dissolved substance. If, again, P grams of the substance were dissolved in 100 grams of the solvent, the depression, $D = K \times \frac{P}{M}$, hence the molecular weight $M = \frac{K \times P}{D}$; K and P being known, if the depression, D, is ascertained experimentally, the molecular weight, M, can be calculated.

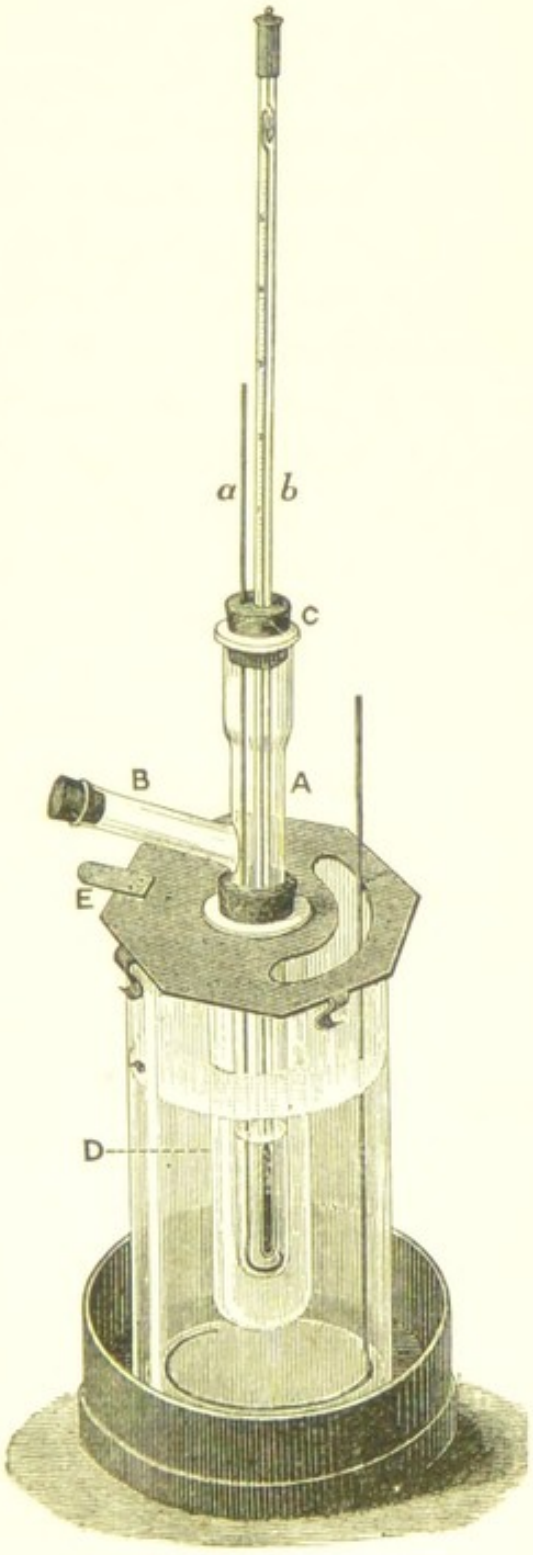


Fig. 15.

This method of determining the molecular weight of organic compounds was first applied by **Raoult**, and is usually known as Raoult's or the *cryoscopic method*. The observation is made with the aid of the apparatus devised by Beckmann (fig. 15), in the following manner:—A large tube (A), about 3 cm. in diameter, and provided with a side-tube (B), is closed with a cork (C), through which pass a stirrer (*a*) and a thermometer (*b*) graduated to $\frac{1}{100}^{\circ}$. A weighed quantity

(about 15 g.) of the solvent is placed in the tube, which is then fitted into a wider tube (D); the latter serves as an air-jacket and protects the solvent from a too rapid change in temperature. The apparatus is now introduced through a hole in the metal plate (E) into a vessel which is partly filled with a liquid, the temperature of which is about 5° lower than the freezing-point of the solvent. The solvent (in A) is now constantly stirred, whereupon the thermometer rapidly falls, and sinks below the freezing-point of the solvent, until the latter begins to freeze; the thermometer now rises again, but soon becomes stationary at a temperature which is the *freezing-point of the solvent.* A weighed quantity of the substance is now introduced through the side-tube (B), and after the solvent has been allowed to melt completely, the *freezing-point of the solution* is ascertained as before. The difference between the two freezing-points is the depression (D); the molecular weight of the substance is then calculated with the aid of the above formula.

Example.—4·98 g. of cane-sugar, ($C_{12}H_{22}O_{11}$), dissolved in 96·9 g. of water, caused a depression in the freezing-point of 0·295° (D). Since 96·9 g. of the solvent contain 4·98 g. of substance, P, the quantity in 100 g. is 5·14 g. The constant, K, for water is 19; hence the molecular weight, M, of cane-sugar is found to be $\frac{19 \times 5{\cdot}14}{0{\cdot}295} = 331$, the true value being 342.

As in the determination of molecular weight from the vapour density, the experimental and theoretical values frequently differ by several units; but this is of little importance, for the reasons already stated.

The constants, K, for the solvents most frequently used are:—acetic acid, 39; benzene, 49; phenol, 76; water, 19.

The *thermometer* used in such experiments has a very large bulb, and the total range shown on the scale is only about 6°, the smallest divisions corresponding with hundredths of a degree. The capillary tube connected with the bulb terminates above in a reservoir, as shown in fig. 16, and by warming the bulb very cautiously some of the mercury may be driven into this reservoir, and detached from

the main quantity by gently tapping the thermometer. It is thus possible to diminish the quantity of mercury in the bulb (and to increase it again when required), so that the top of the column in the capillary thread stands at some suitable point on the scale, when the thermometer is at the temperature which is to be registered in the experiment. All that is required is that the thermometer shall show *differences* in temperature with a high degree of accuracy.

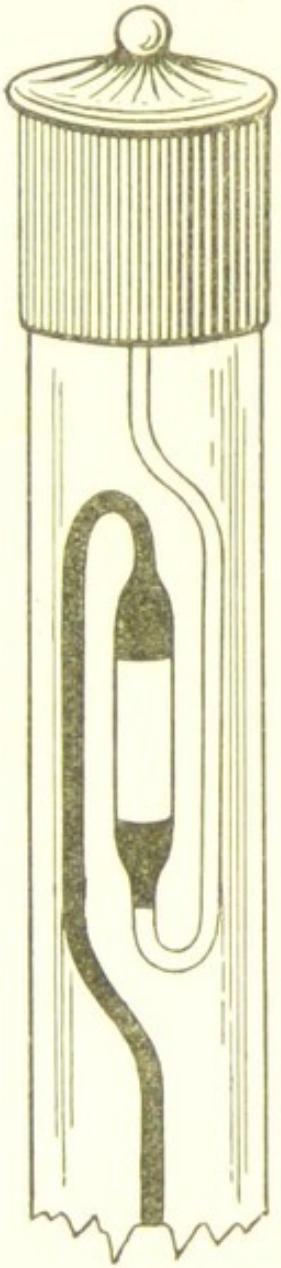


Fig. 16.

Determination of Molecular Weight by the Ebullioscopic Method.—When molecular proportions of different substances are dissolved in a fixed and sufficiently large quantity of a given solvent, the boiling-point of the solution is *raised* by the *same* amount in each case; experiments with dilute solutions give the actual rise in boiling-point, and then by calculation, the *molecular elevation*—that is, the rise which should be produced by the molecular weight in grams of the substance in 100 grams of the solvent—may be deduced.

The value thus determined is (approximately) a constant, K, but is different for different solvents; if now the value of K is known, the molecular weight of a substance soluble in that solvent can be determined experimentally by finding the elevation of the boiling-point, E, produced by dissolving a known weight of the substance in a known weight of the solvent, the formula $M = \frac{K \times P}{E}$ being employed. (Compare p. 43).

A form of apparatus devised by Beckmann is shown in fig. 17. A known weight of the solvent is put into the tube (*a*), the thermometer is placed in position, and some glass beads are poured through the side-tube (*b*) until the

bulb of the thermometer is nearly covered; the object of these beads is to ensure a regular boiling of the liquid. The tube (*a*) is surrounded by the outer jacket (*c*), which also contains some of the solvent; the object of this jacket is to prevent superheating. The apparatus is then placed, as shown, on an asbestos frame (*d*), and the condensers (*e*, *e'*) are fitted on. The asbestos frame, which is provided with chimneys (*f*, *f*), is then very gradually heated below, and when the solvent has been boiling *constantly* for some time (at least five minutes) the position of the mercury thread is noted. The condenser (*e*) is now removed, and a weighed quantity of the substance (compressed into a tablet) is introduced through the side-tube, the condenser being immediately replaced. The temperature falls at first, but rapidly rises again, and in two or three minutes the position of the mercury thread becomes constant. The difference between the readings with the solvent and the solution respectively give the elevation, E.

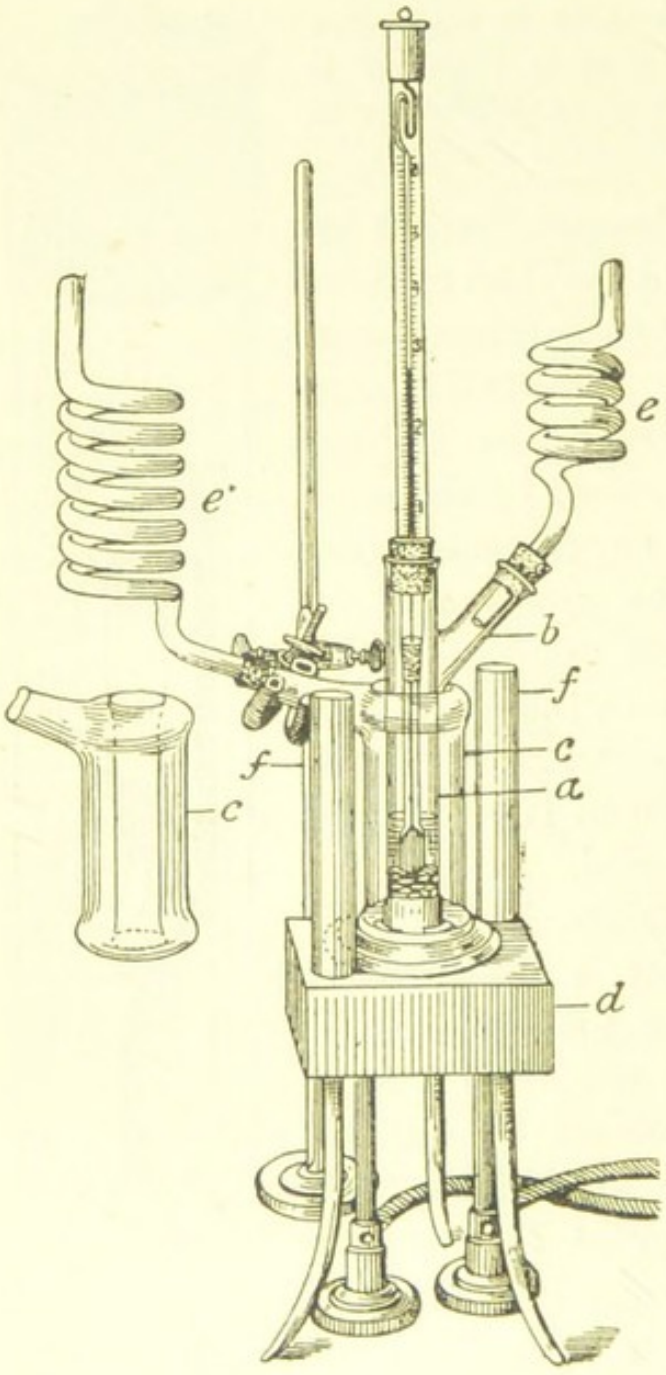


Fig. 17.

A simpler form of apparatus is that devised by Landsberger (fig. 18). A suitable quantity of the solvent is placed in the tube (*a*), which is about 16 cm. in height and 3 cm. in diameter, and which has a small opening (*b*) for the escape of the vapour; this tube (*a*)

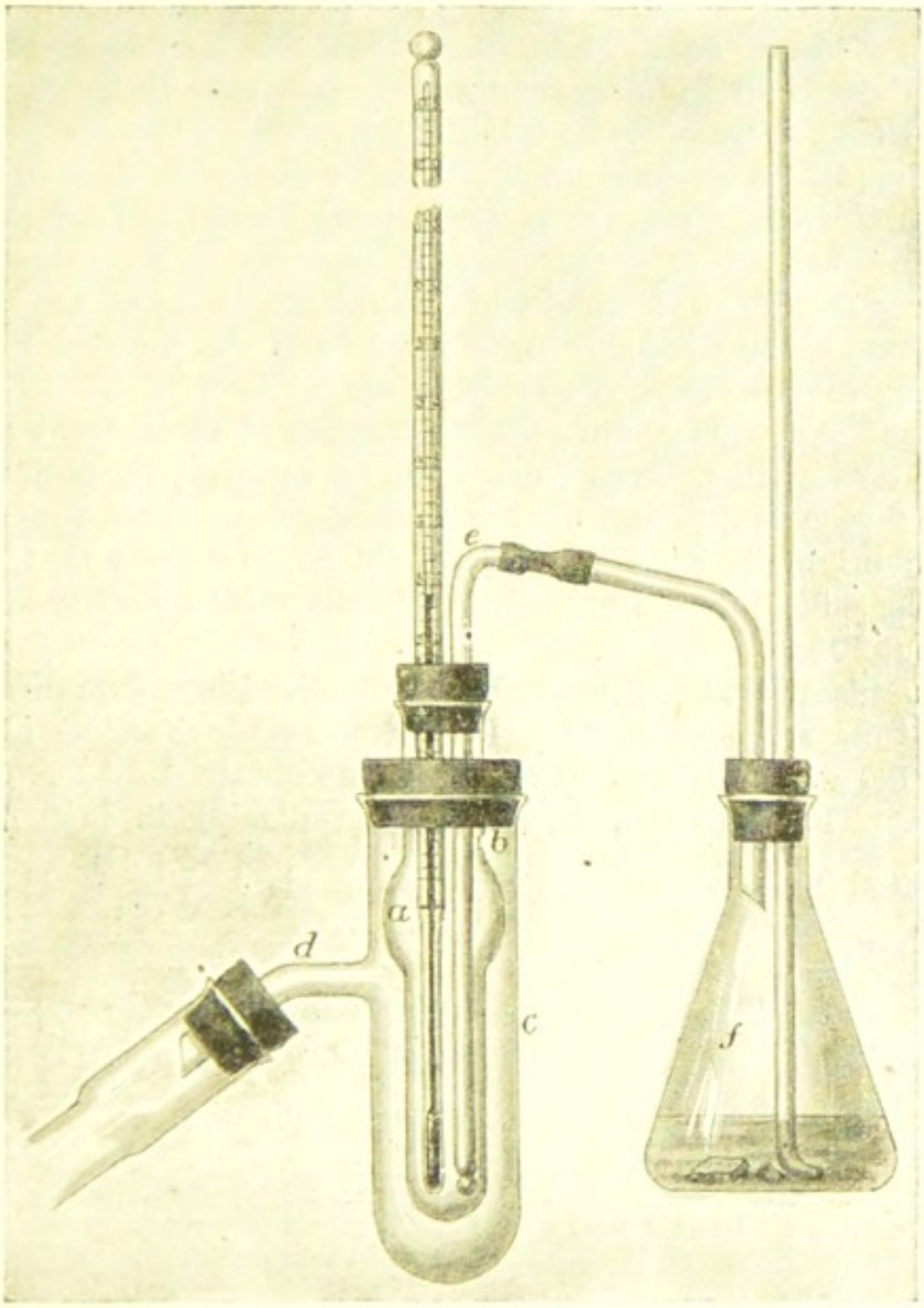


Fig. 18.

is fitted by means of a cork into a larger one (*c*) which serves as an air-jacket, and the outlet (*d*) of which is connected with an ordinary Liebig's condenser. The inner tube (*a*) is closed with a cork through which pass a thermometer, graduated to $\frac{1}{20}°$, and a tube (*e*) the end of which has been cut off in a slanting direction,

or perforated with a number of holes. The solvent in the tube (*a*) is not heated directly, but only by the vapour of the *same* solvent, which is generated in the flask (*f*); in this way superheating is avoided.

The boiling-point of the solvent alone is first determined by heating the solvent in the flask (*f*) and passing its vapour through the solvent in (*a*) until the thermometer shows a constant temperature; the solvent in (*a*) is then *mixed* with that in the flask (*f*), about the same quantity as originally used being poured back into the tube (*a*). A weighed quantity of the substance is now placed in (*a*), and vapour from (*f*) is again passed until the temperature is again constant. The *difference* between the two readings gives the *elevation*, E. The weight of the solvent in (*a*) at the time of the second reading has now to be found, and the molecular weight of the substance can then be calculated.

If the tube (*a*) is graduated, the weight of the solvent may be ascertained with sufficient accuracy by multiplying the volume by the specific gravity at the boiling-point. The quantity of solvent originally placed in (*a*) should be so chosen that by the time the solvent is boiling constantly the total quantity amounts to about 10 g.

Example.—0·562 g. of naphthalene dissolved in carbon disulphide raised the boiling-point by 0·784°; the solvent alone weighed 12·7 g., hence 100 g. of the solvent would have contained 4·42 g. of substance. The constant, K, for carbon disulphide is 23·7; the calculated molecular weight, therefore, is $\frac{23{\cdot}7 \times 4{\cdot}42}{0{\cdot}784} = 134$, the true value being 128.

The constants for the solvents generally used are:—acetic acid, 25·3; benzene, 26·7; water, 5·2; ether, 21·1; ethyl alcohol, 11·5; acetone, 16·7; chloroform, 36·6.

The cryoscopic and ebullioscopic methods are not applicable to *all* substances; in the case of electrolytes the results obtained with certain solvents, such as water, acetic acid, and alcohol, accord with the view that the molecules of the dissolved substances are *dissociated* into simpler portions (ions); in the case of *some* non-electrolytes the results obtained with solvents, such as ether, benzene, and carbon disulphide, indicate that the chemical molecules of the dissolved substance are *associated* and form more or less complex aggregates.

CHAPTER III.

Constitution or Structure of Organic Compounds.

Even when the molecular formula of an organic compound has been established by the methods described in the foregoing pages, the most difficult and important steps in the investigation of the substance have still to be taken.

A great many cases are known of the existence of two or more compounds which have the *same molecular formula*, and yet differ in chemical and physical properties, not only in the solid, but also in the liquid and gaseous states; there are, for example, two compounds of the molecular formula, C_4H_{10}, three of the molecular formula, C_5H_{12}, at least six of the molecular formula, $C_3H_6O_2$, and so on.

Now, if the properties of a compound depended simply on the nature and number of the atoms of which its molecule was composed, facts such as these could not be explained. It must be concluded, therefore, (*a*) that the atoms of which molecules are composed are arranged in a definite manner; and (*b*) that when two or more compounds of the same molecular formula are known, the molecules of the one differ in arrangement, structure, or constitution from those of the other or others.

Although the actual arrangement of the atoms in a molecule cannot be directly observed, it is possible to obtain a clear idea of the structure or constitution of a compound from a consideration of (*a*) the valencies of the elements of which the compound consists, and (*b*) the chemical and physical properties of the compound.

The *valency* or atom-fixing power of an element is deduced from the molecular formulæ of those compounds which contain *one* atom of the element in question united with other elements of known valency. Thus, in the case of carbon,

the molecular formulæ of compounds such as (*a*) CH_4 and $CHCl_3$; (*b*) CO_2 and COS; (*c*) $COCl_2$; and (*d*) HCN, which contain only one atom of carbon in the molecule are considered. In all these compounds the atom of carbon is combined with (*a*) 4 univalent atoms, (*b*) 2 bivalent atoms, (*c*) 1 bivalent and 2 univalent atoms, or (*d*) 1 tervalent and 1 univalent atom—that is to say, with four univalent atoms or their valency equivalent. With the doubtful exception of carbon monoxide, CO,* no compound containing only *one* carbon atom is known, in which the carbon atom is combined with *more* or *less* than four univalent elements or their valency equivalent; carbon, therefore, is *quadrivalent*, and this deduction may be expressed by writing its symbol,

$$C\equiv \quad \text{or} \quad =C= \quad \text{or} \quad \begin{array}{c} | \\ -C- \\ | \end{array}$$

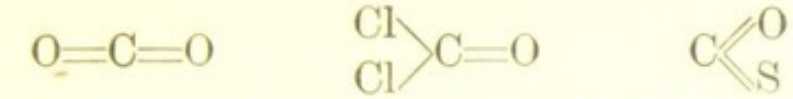
In a similar manner the univalent hydrogen atom may be represented by H—, bivalent oxygen by O= or —O—, tervalent nitrogen by $N\equiv$ or $\begin{array}{c} | \\ -N- \end{array}$, and so on; the number of lines drawn from the symbol then shows the valency of the atom.

If, now, in the case of substances such as CH_4, CH_3Cl, $CHCl_3$, in which the carbon atom is united with four univalent atoms, the symbol of each of the latter is placed at the extremity of one of the four lines which represents a carbon valency, formulæ such as the following are obtained:—

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array} \qquad \begin{array}{c} H \\ | \\ H-C-H \\ | \\ Cl \end{array} \qquad \begin{array}{c} H \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

If in the case of substances such as CO_2, $COCl_2$, COS, the symbol of each of the bivalent atoms is given two lines, formulæ such as,

* Oxygen may be assumed to be quadrivalent in CO.



are obtained. Similarly, HCN may be represented by the formula H—C≡N.

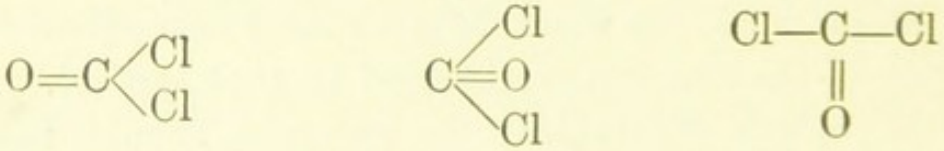
Formulæ of this kind are termed *graphic formulæ*, and the elements whose symbols are joined by one or more lines are said to be *directly united*. Thus in the case of the compound, $COCl_2$, the oxygen atom is directly united to the carbon atom; so also are the two chlorine atoms; but the oxygen and chlorine atoms are *not* directly united. The idea is that the carbon atom is holding or fixing the oxygen atom *and* the two atoms of chlorine, the whole forming a molecule of definite structure. A graphic formula, therefore, expresses the structure or constitution of the compound—that is to say, it shows not only the valency of each of the atoms in the molecule, but also indicates the *disposition* of the atoms. In all such formulæ, obviously, the number of lines running to or from any given symbol must correspond with the valency of the element represented by that symbol. The formula of carbon disulphide, for example, should not be written  , or that of carbon dioxide O—C—O, because the valencies of the elements are not correctly indicated by the lines drawn from their symbols.

These lines, which represent units of valency, are sometimes called **bonds** or **linkings**; in the compound H—C≡N, the hydrogen atom is said to be combined with carbon by one bond or linking, the nitrogen atom by three. The hydrogen and nitrogen atoms are not directly combined, but are both united with carbon.

It is obvious that such lines or bonds may be shortened or lengthened at will without their significance being altered: as a rule, they are shortened, as in the formulæ H·C:N O:C:S, and when this is done the formulæ are generally called **structural** or **constitutional** formulæ, instead of graphic formulæ, but there is no essential difference between these terms.

It may next be pointed out that although in a structural, constitutional, or graphic formula, all the atoms in the molecule are necessarily represented as lying in one plane (the plane of the paper), there is every reason for concluding that the atoms in a molecule are arranged in space of *three* dimensions. In spite of this difficulty, the use of structural formulæ, instead of mere molecular formulæ, is a prime necessity in the case of organic compounds, for reasons which will be obvious later. Consequently it is essential that the meaning of a structural formula, and its *limitations*, should be clearly understood. Since the formula is not intended to show how the atoms are arranged *in space*, but merely which atoms are directly united to one another, it makes no difference how the formula is written, provided that it fulfils this condition and represents correctly the valencies of the elements in the molecule.

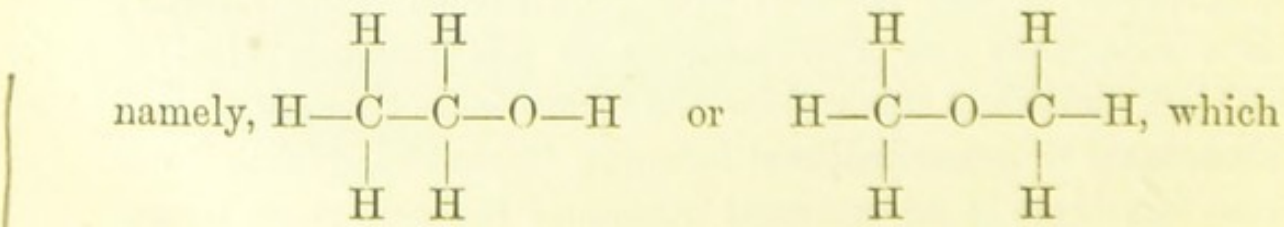
Thus, the formulæ,



are all equally good as expressions of the constitution of carbonyl chloride.

In all the cases considered above, the structural formula was based on considerations of valency alone. An example may now be given in which the chemical behaviour of the compound must also be studied, before the structure of the molecule can be represented by a formula.

The compound ethyl alcohol has the molecular formula, C_2H_6O. On the assumption that hydrogen is univalent, oxygen bivalent, and carbon quadrivalent, the molecule of ethyl alcohol might be represented by one of two graphic formulæ—



correspond with the structural formulæ, $CH_3—CH_2—OH$ (I.) and $CH_3—O—CH_3$ (II.) respectively.* Now, ethyl alcohol is readily acted on by sodium, yielding a compound of the composition, C_2H_5NaO, which is formed by the displacement of one hydrogen atom (*a*) by one atom of the metal; the other five hydrogen atoms in the molecule of ethyl alcohol cannot be displaced, no matter how large a quantity of sodium is employed. Again, when ethyl alcohol is treated with hydrogen chloride under certain conditions, one atom of hydrogen *and* one atom of oxygen are displaced by one atom of chlorine, a compound of the composition, C_2H_5Cl being formed,

$$C_2H_6O + HCl = C_2H_5Cl + H_2O.$$

When this compound is heated with water it is transformed into ethyl alcohol, one atom of chlorine being displaced by one atom of oxygen *and* one atom of hydrogen; the change, in fact, is the reverse of that represented above.

From these and other experiments it is concluded that ethyl alcohol contains one atom of hydrogen (*a*) combined differently from the other five. Also, that one atom of hydrogen is closely associated with the oxygen atom, forming a univalent group $-OH$; if this were not the case, it would be difficult to understand how one atom of univalent chlorine could displace, or be displaced by, one atom of univalent hydrogen *and* one atom of bivalent oxygen.

* In these and in other structural formulæ of a similar kind, each of the *univalent* atoms is to be considered as directly united to that atom, the symbol of which it immediately follows or precedes without the interposition of a line (or dot, or bracket). Thus in the formula, $CH_3—CH_2—OH$, $CH_3{\cdot}CH_2{\cdot}OH$, or $CH_3{\cdot}CH_2(OH)$, the three hydrogen atoms of the CH_3 group are directly combined to the carbon atom of this group; the two hydrogen atoms which follow are directly united to the second carbon atom, and not to the oxygen atom. This slight difficulty which arises in regard to structural formulæ may cause misapprehension, and is best avoided by a careful comparison of the graphic and structural formulæ used in the above and in other cases.

Hence a study of the chemical behaviour of ethyl alcohol shows that the structure of its molecule is expressed by formula I. given above; a compound of the structure represented by formula II. would show a totally different behaviour, as is proved later (p. 115). Further, since the compound, C_2H_5Cl, does not contain a hydrogen atom which can be displaced by sodium, it is concluded that the particular hydrogen atom (*a*) in ethyl alcohol, which is displaceable by sodium, is the same as that which is closely associated with the oxygen atom; hence the structure of the sodium derivative is written $CH_3 \cdot CH_2 \cdot ONa$.

Now, any compound, such as propyl alcohol, C_3H_8O (p. 110), which behaves in the above-mentioned respects like ethyl alcohol, under the same conditions, may be supposed to contain one atom of hydrogen and one atom of oxygen in the same state of combination as in ethyl alcohol, and may be represented by a formula such as $C_3H_7(OH)$, which expresses this conclusion. The constitution of a compound, therefore, may be ascertained by carefully studying its chemical behaviour under various conditions, and also, if possible, by comparing its behaviour with that of other compounds of known constitution. Compounds which are found to show a similar behaviour are considered to contain atoms or groups of atoms in a similar state of combination.

It is thus possible, with the help of valency considerations, to determine the state of combination of all the atoms of which the molecule is composed, and to express the results in a structural formula; this formula then not only shows the constitution or structure of the compound, but also summarises in a concise and simple manner the more important chemical properties of the compound.

CHAPTER IV.

Saturated Hydrocarbons.

The Paraffins, or Hydrocarbons of the Methane Series.

It has already been noted that carbon differs from all other elements in forming an extraordinarily large number of compounds with hydrogen; these compounds, composed of hydrogen and carbon only, are called **hydrocarbons.**

Methane or **Marsh-gas**, CH_4, is the simplest hydrocarbon. It is met with, as its name implies, in marshes and other places in which the decomposition or decay of vegetable matter is taking place under water.* It is one of the principal components of the gas which streams out of the earth in the petroleum districts of America and Russia; it also occurs in coal-mines, the gas (fire-damp), which issues from the fissures in the coal, sometimes containing as much as 80–90 per cent. of methane, to the presence of which, mixed with air, explosions in coal-mines are due. Ordinary coal-gas usually contains about 40 per cent. of methane.

Methane is formed† by the direct union of carbon and hydrogen at a temperature of about 1200°. It is also obtained when hydrogen sulphide or steam, together with the vapour of carbon disulphide, is passed over heated copper (Berthelot),

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S,$$
$$CS_2 + 2H_2O + 6Cu = CH_4 + 2Cu_2S + 2CuO;$$

and when chloroform (p. 181) or carbon tetrachloride (p. 183)‡ is reduced with sodium amalgam and water (footnote, p. 57),

* When a marshy pond or swamp is stirred, bubbles consisting of methane, carbon dioxide, and other gases frequently rise.

† The words *formed*, *obtained*, and *produced* are used when the method is of theoretical importance, but is not a convenient one for the actual *preparation* of the compound.

‡ Many compounds are often unavoidably mentioned long before their properties are described; in such cases references are given.

$$CHCl_3 + 6H = CH_4 + 3HCl,$$
$$CCl_4 + 8H = CH_4 + 4HCl.$$

Methane is formed when magnesium methyl iodide (p. 227) is decomposed by water or by an amine,

$$Mg\begin{matrix}<^{CH_3}\\ _{I}\end{matrix} + H_2O = CH_4 + MgI{\cdot}OH,$$

$$Mg\begin{matrix}<^{CH_3}\\ _{I}\end{matrix} + C_2H_5{\cdot}NH_2 = CH_4 + C_2H_5{\cdot}NH{\cdot}MgI;$$

also when a mixture of carbon monoxide and hydrogen is passed over finely divided nickel which is heated at 220°.

Methane is prepared by heating anhydrous sodium or potassium acetate (1 part) with soda-lime (4 parts) in a hard glass tube or retort,

$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3.$$

The gas obtained in this way and collected over water contains a small proportion of hydrogen, ethylene (p. 73), and other impurities; if, however, barium oxide is used instead of soda-lime, the methane is nearly pure.

Pure methane is prepared by dropping a solution of methyl iodide * in about an equal volume of 95 per cent. alcohol, from a stoppered funnel, into a flask containing a large quantity of a zinc-copper couple.† The methyl iodide is reduced by the nascent hydrogen, formed by the action of the aqueous alcohol on the zinc-copper couple, and a slow but continuous evolution of methane takes place without the application of heat,

$$CH_3I + 2H = CH_4 + HI;$$

the gas is passed through a tube containing some zinc-copper couple, in order to free it from methyl iodide, and collected over water.

* The groups of atoms, CH_3–, C_2H_5–, C_3H_7–, and C_4H_9–, are termed *methyl*, *ethyl*, *propyl*, and *butyl* respectively (p. 107).

† The zinc-copper couple is prepared by heating copper powder (obtained by reducing the oxide in hydrogen) with small pieces of clean zinc foil, or with zinc filings, in an atmosphere of coal-gas, until the mixture begins to cake together. It may also be prepared by immersing clean zinc filings in a 2 per cent. solution of copper sulphate, and then washing them with alcohol and ether successively; that prepared by the first method gives the better results.

In a similar manner, all halogen derivatives of methane (p. 180) are converted into methane on treatment with nascent hydrogen, generated in some suitable manner.*

* The substances most frequently used in reducing organic compounds are :—*Sodium* and *alcohol ; sodium amalgam* and *water ; zinc*, *iron*, or *tin*, and *an acid ; stannous chloride* and *hydrochloric acid ; hydrogen iodide ; hydrogen sulphide ; sulphurous acid ; hydrogen*, in presence of a catalyst.

Sodium, acting on an alcoholic or *moist* ethereal solution of the substance, is one of the more active reducing agents,

$$Na+C_2H_5\cdot OH=C_2H_5\cdot ONa+H,$$
$$Na+H_2O=NaOH+H.$$

In cases where a high temperature is required, boiling amyl alcohol (p. 111) is used instead of ethyl alcohol.

Sodium amalgam, an alloy of sodium and mercury, acts on aqueous or aqueous alcoholic solutions in the same way as metallic sodium, but the action of the latter is greatly moderated by the presence of the mercury.

Zinc and *iron* are generally used with hydrochloric, dilute sulphuric, or acetic acid. Zinc dust is sometimes employed in alkaline solution, as, for instance, in the presence of caustic alkalis,

$$Zn+2KOH=Zn(OK)_2+2H.$$

Substances which are reduced only with great difficulty are frequently mixed with zinc dust and heated at a high temperature.

Tin is employed with hydrochloric acid,

$$Sn+2HCl=SnCl_2+2H.$$

Stannous chloride is not acted on by hydrochloric acid alone, but, in presence of reducible substances, the mixture is a very active reducing agent, stannic chloride being formed,

$$SnCl_2+2HCl=SnCl_4+2H.$$

Hydrogen iodide, in concentrated aqueous solution, is a very active reducing agent at high temperatures, as it decomposes giving (nascent) hydrogen and iodine ; it is usual to add a small quantity of red phosphorus to the mixture, in order that the iodine may be reconverted into hydrogen iodide ($3I+P+3H_2O=H_3PO_3+3HI$).

Hydrogen sulphide, being readily decomposed into sulphur and hydrogen, is frequently used, generally in the form of ammonium sulphide, as a mild reducing agent.

Sulphurous acid has only a limited use ; in presence of reducible substances it is converted into sulphuric acid,

$$H_2SO_3+H_2O=H_2SO_4+2H.$$

Hydrogen (molecular), in presence of finely divided nickel, combines directly with many substances at temperatures of about 250° (Sabatier and Senderens) ; in presence of other catalysts, such as platinum black, or colloidal palladium, it unites with many compounds at ordinary temperatures (Part II. p. 623).

Methane is a colourless, tasteless gas; it condenses to a liquid at $-11°$ under a pressure of 180 atmospheres. It burns with a pale-blue, non-luminous flame, and forms a highly explosive mixture with certain proportions of air or oxygen,

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$1 \text{ vol.} + 2 \text{ vols.} = 1 \text{ vol.} + 2 \text{ vols.}$$

It is almost insoluble in water, but rather more soluble in alcohol. It is very stable; when passed through bromine, potash, nitric acid, sulphuric acid, or a solution of potassium permanganate or chromic acid, it is not absorbed or changed in any way. When mixed with chlorine in the dark it is not attacked; but if a mixture of 1 vol. of methane and 2 vols. of chlorine is exposed to direct sunlight an explosion ensues, and carbon is deposited,

$$CH_4 + 2Cl_2 = C + 4HCl.$$

In diffused sunlight there is no explosion, but after some time a mixture of hydrogen chloride and four other compounds is produced, the proportion of each depending on the quantity of chlorine present, and on the other conditions of the experiment,

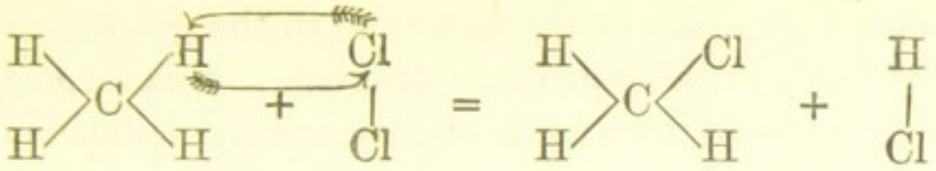
$CH_4 + Cl_2 = CH_3Cl + HCl.$ Methyl Chloride.

$CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl.$ Methylene Dichloride.

$CH_4 + 3Cl_2 = CHCl_3 + 3HCl.$ Chloroform.

$CH_4 + 4Cl_2 = CCl_4 + 4HCl.$ Carbon Tetrachloride.

All these compounds are formed by the displacement of one or more hydrogen atoms by an equivalent quantity of chlorine. The carbon atom cannot combine with more than four univalent atoms, so that hydrogen must be displaced if any action at all takes place. Now, it may be supposed that in the formation of methyl chloride—CH_3Cl, for example—one of the hydrogen atoms is displaced by one atom of chlorine without the other atoms in the molecule being disturbed or their state of combination altered; this view may be represented diagrammatically as follows:—



In the formation of methylene dichloride, CH_2Cl_2, it may be supposed that a repetition of this process occurs, and so also in the case of the other products; in other words, it may be assumed that, in all the above examples, the action of the chlorine is not such that the molecule of methane is completely broken up into atoms, which then, by combination with chlorine, form totally new molecules, but that certain atoms simply change places. To such changes as these, in which certain atoms are merely displaced by an equivalent quantity of other atoms, without the state of combination of the rest of the atoms being altered, the term **substitution** is applied, and the compounds formed, as the result of the change, are called **substitution products.**

The four compounds mentioned above are substitution products of methane and of one another. Methyl chloride, CH_3Cl, is a *mono*-substitution product, methylene *di*chloride, CH_2Cl_2, a *di*-substitution product of methane, and so on; chloroform, $CHCl_3$, is a *tri*-substitution product of methane, a *di*-substitution product of methyl chloride.

Similarly, when by treatment with nascent hydrogen in the manner described above, any of these substitution products is converted into methane, the change is a process of substitution.

The only way in which it is possible for a chemical change to occur in the case of methane and its chloro-substitution products is by a process of substitution. The atom of carbon already holds in combination its maximum number of atoms, some of which must be displaced if any other atom enters the molecule. Compounds such as these, in which the maximum combining capacity of all the carbon atoms is exerted, and which can only yield derivatives by substitution, are termed **saturated compounds.**

Ethane, C_2H_6, like methane, occurs in the gas which issues from the earth in the petroleum districts. It is formed when methyl chloride or, more conveniently, methyl iodide is treated with sodium* in *dry* ethereal solution,

$$2CH_3I + 2Na = C_2H_6 + 2NaI;$$

this reaction affords a possible means of preparing ethane from its elements, because methane can be formed from its elements, as already stated, and then converted into methyl chloride by treatment with chlorine.

Ethane is also formed when ethylene (p. 73) is treated with hydrogen in presence of platinum black, even at ordinary temperatures,

$$C_2H_4 + H_2 = C_2H_6.$$

Magnesium ethyl bromide (p. 226) is readily decomposed by water and by amines (such as aniline) with formation of ethane; these reactions are analogous to those which occur in the case of magnesium methyl iodide (p. 56).

Ethane is prepared by reducing ethyl iodide with the zinc-copper couple and water, exactly as described in the preparation of pure methane,

$$C_2H_5I + 2H = C_2H_6 + HI.$$

Also, by the electrolysis of dilute acetic acid, or of a concentrated aqueous solution of potassium acetate (Kolbe); when acetic acid is used, ethane and carbon dioxide are evolved at the positive, hydrogen at the negative, pole,

$$\left.\begin{matrix}CH_3\cdot CO_2H\\CH_3\cdot CO_2H\end{matrix}\right\} = \overbrace{C_2H_6 + 2CO_2} + H_2;$$

when potassium acetate is employed the following changes occur:—

$$\left.\begin{matrix}CH_3\cdot CO_2K\\CH_3\cdot CO_2K\end{matrix}\right\} = \overbrace{C_2H_6 + 2CO_2} + 2K,$$

and

$$2K + 2H_2O = 2KOH + H_2,$$

so that the same gases are evolved as before.

* The sodium is best used in the form of wire, which is obtained with the aid of a sodium press.

Ethane is a colourless, tasteless gas, which liquefies at 4° under a pressure of 46 atmospheres; it is practically insoluble in water, slightly soluble in alcohol. It is inflammable, burns with a feebly luminous flame, and can be exploded with air or oxygen,

$$2\,C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$
$$2 \text{ vols.} + 7 \text{ vols.} = 4 \text{ vols.} + 6 \text{ vols.}$$

It is very stable, and is not acted on by alkalis, nitric acid, sulphuric acid, bromine, or oxidising agents, at ordinary temperatures. When mixed with chlorine and exposed to diffused sunlight it gives various *substitution products*, 1, 2, 3, 4, 5, or 6 atoms of hydrogen being displaced by an equivalent quantity of chlorine,

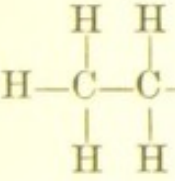
$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$ (Ethyl Chloride.) $\quad C_2H_6 + 2Cl_2 = C_2H_4Cl_2 + 2HCl.$ (Ethylene Dichloride.)

The *final* product is hexachlorethane,

$$C_2H_6 + 6Cl_2 = C_2Cl_6 + 6HCl.$$

Ethane, like methane, cannot combine directly with chlorine or with any element; it is a *saturated* compound.

The *constitution* of ethane is expressed by the formula,



or $CH_3 \cdot CH_3$ which is based principally on considerations of valency. The two atoms of carbon must be directly united, because a univalent hydrogen atom could not link the two carbon atoms together; as, moreover, carbon is quadrivalent, each of the carbon atoms must also be directly united with three atoms of hydrogen.

Propane, C_3H_8, occurs in petroleum, and can be obtained by reducing propyl iodide or isopropyl iodide (p. 187) with zinc and an acid, or with the zinc-copper couple and water,

$$C_3H_7I + 2H = C_3H_8 + HI.$$

It is also obtained (together with methane and butane) by heating a mixture of ethyl and methyl iodides with sodium,

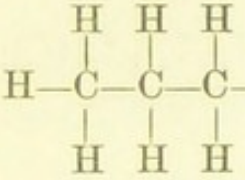
$$C_2H_5I + CH_3I + 2Na = C_3H_8 + 2NaI,$$

and by decomposing magnesium propyl bromide with water or with an amine (p. 56).

Propane is a gas, and closely resembles methane and ethane in chemical properties, but it burns with a more luminous flame than ethane. When treated with chlorine in diffused sunlight it yields propyl chloride and other substitution products, one or more hydrogen atoms being displaced by an equivalent quantity of chlorine,

$$C_3H_8 + Cl_2 = C_3H_7Cl + HCl.$$

The *constitution* of propane is represented by the formula



$H—C(H)(H)—C(H)(H)—C(H)(H)—H$, or $CH_3 \cdot CH_2 \cdot CH_3$, which is based principally on considerations of valency, but which is fully confirmed by a study of the derivatives of the hydrocarbon (p. 110). Propane may be regarded as derived from ethane, just as ethane may be considered as derived from methane, by the substitution of the univalent group of atoms CH_3- for one atom of hydrogen.

Butanes, C_4H_{10}.—Two hydrocarbons of the molecular formula, C_4H_{10}, are known. One of them, **normal butane**, occurs in petroleum, and can be obtained by heating ethyl iodide with sodium,

$$2CH_3 \cdot CH_2I + 2Na = CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 + 2NaI.$$

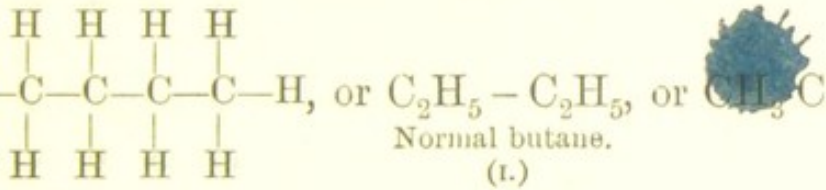
The other, **isobutane**, or trimethylmethane, is formed when tertiary butyl iodide (compare p. 187) is reduced with nascent hydrogen,

$$(CH_3)_3CI + 2H = (CH_3)_3CH + HI.$$

These two hydrocarbons, which have been proved to have the same molecular formula, are very different in properties. Although they are both gases under ordinary conditions,

normal butane liquefies at about 0°, isobutane not until about −17°, under atmospheric pressure. In chemical properties they closely resemble propane and one another. They give substitution products with chlorine, but every compound obtained from normal butane is different from the substance of the same molecular formula, which is produced from isobutane.

Constitutions of the two Butanes.—The production of normal butane from ethyl iodide in the above-mentioned manner indicates that this hydrocarbon is formed by the union of two CH_3–CH_2– groups. It is, therefore, represented by the formula,

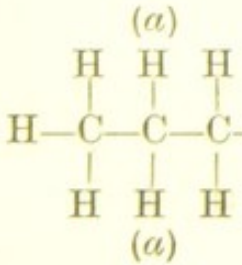


$C_2H_5 - C_2H_5$, or $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

Normal butane.
(I.)

Normal butane, in fact, may be regarded as propane in which one atom of hydrogen has been displaced by the univalent CH_3– group.

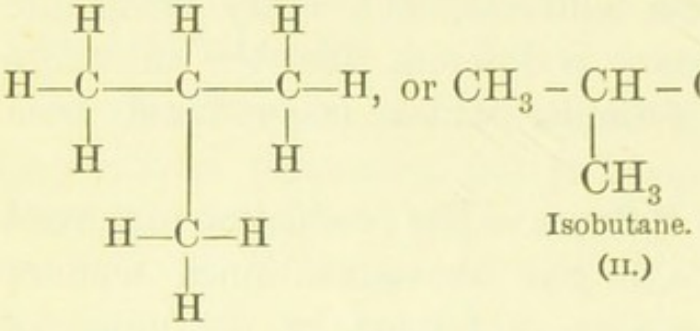
When, however, the graphic formula of propane is carefully considered, it will be seen that the eight atoms of hydrogen are not all in the same state of combination relatively to the rest of the molecule, but that two of them (*a*),



$CH_3 - CH_2 - CH_3$, or $CH_2(CH_3)_2$,
(*a*) (*a*)

are united with a carbon atom which is itself combined with *two* carbon atoms, whereas each of the other six atoms of hydrogen is combined with a carbon atom which is united with only *one* other. In order to derive from propane a hydrocarbon having the structure of normal butane, one of the *six* similarly situated hydrogen atoms must be displaced

by a CH_3- group. If, on the other hand, one of the (*a*) hydrogen atoms were displaced by a CH_3- group, the constitution of the product would be represented by the formula,

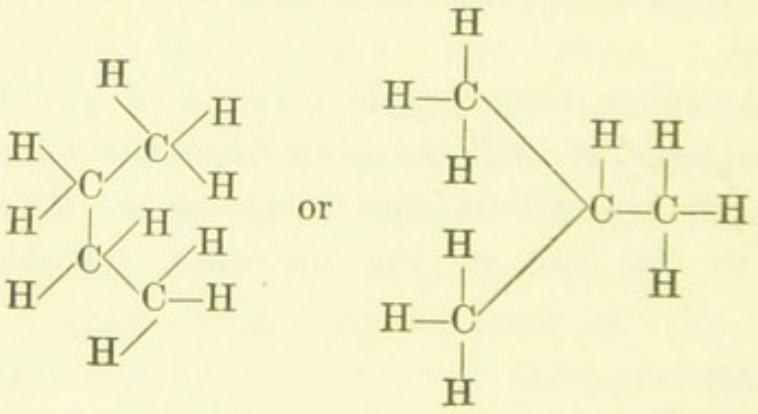


or $CH_3-CH(CH_3)-CH_3$, or $CH(CH_3)_3$.

Isobutane.
(II.)

It is thus possible to account for the existence of two hydrocarbons of the molecular formula, C_4H_{10}; the molecules of the two compounds differ in structure and consequently also in properties.

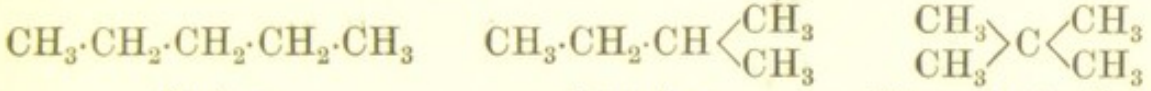
It is next important to note that the above two are the only formulæ which can be constructed with four atoms of carbon and ten atoms of hydrogen, on the assumption that carbon is quadrivalent and hydrogen univalent. Formulæ such as



which at first sight might seem to express arrangements different from either of those given above, will, on examination, be found to be identical with one of the latter. For these reasons it may be concluded that formula I. represents the constitution of normal butane, and formula II. that of isobutane (or trimethylmethane). These conclusions are confirmed by a study of other methods of formation and of the chemical behaviour of the two hydrocarbons.

Pentanes.—Three hydrocarbons of the molecular formula, C_5H_{12}, are known; two of them—namely, **normal pentane**

(b.p. 37°)* and **isopentane** (b.p. 30°)—occur in petroleum, and are colourless mobile liquids; the third, **tetramethylmethane** (b.p. 9·5°), can be obtained synthetically. The constitutions of the three pentanes are respectively represented by the following formulæ,



Pentane. Isopentane. Tetramethylmethane.

which are based on considerations of valency, combined with a careful study of the properties and methods of formation of the compounds. All three hydrocarbons may be regarded as derived from the butanes (pentane and isopentane from *normal* butane, tetramethylmethane from *iso*butane) by the substitution of a CH_3– group for one atom of hydrogen.

Isomerism.—Compounds, such as the two hydrocarbons, C_4H_{10}, or the three hydrocarbons, C_5H_{12}, which have the *same molecular formula, but different constitutions or structures*, are said to be **isomeric**. The phenomenon is spoken of as **isomerism**, and the compounds themselves are called **isomers** or **isomerides**. Isomerism, as already explained, is due to a difference in the state of combination or disposition of the atoms in the molecules, and isomeric substances always differ more or less both in physical and in chemical properties.

Isomeric hydrocarbons of the class described above are usually distinguished by the terms *normal* or *primary*, *iso-* or *secondary*, and *tertiary*. A normal or primary hydrocarbon is one in which no carbon atom is directly combined with more than two others, as, for example,



Normal Butane. Normal Hexane.

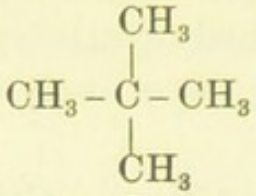
A secondary or iso-hydrocarbon contains at least one carbon atom directly united with three others,



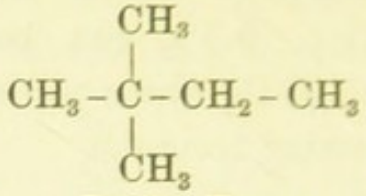
Isobutane (or Trimethylmethane). Di-isopropyl.

* Except when otherwise stated, all the boiling-points given in this book refer to ordinary atmospheric pressure.

A tertiary hydrocarbon contains at least one carbon atom directly combined with four others,



Tertiary Pentane
(or Tetramethylmethane).



Tertiary Hexane
(or Trimethylethylmethane).

In the case of iso- and tertiary hydrocarbons, it is also convenient, if possible, to use a name which readily expresses the constitution of the compound; examples of such names are given above in brackets.

If one hydrogen atom in each of the three pentanes were displaced by a CH_3-group, a number of isomeric hydrocarbons, C_6H_{14}, would be obtained, from each of which, by a repetition of the same process, at least one hydrocarbon, C_7H_{16}, might be formed, and so on. It is evident, then, that theoretically a great number of hydrocarbons may exist, and as a matter of fact very many have actually been obtained, either from petroleum (p. 71) or in other ways.

As the number of carbon atoms in the molecule increases, the number of possible isomerides rapidly becomes larger; 7 isomerides of the molecular formula, C_7H_{16}, 18 of the formula, C_8H_{18}, and no less than 802 of the formula, $C_{13}H_{28}$ could, theoretically, be formed.

The hydrocarbons, methane, ethane, propane, &c. are not only all produced by similar reactions, but they also show very great similarity in chemical properties because they are similar in *structure;* for these reasons they are classed together and are known collectively as the **paraffins**, or hydrocarbons of the **methane series.** The class name 'paraffin' was assigned to this group because paraffin-wax consists principally of the higher members of the methane *series* (see below). Paraffin-wax is a remarkably inert and stable substance, and is not acted on by strong acids, alkalis, &c.; the name paraffin, from the Latin *parum affinis* (small or slight affinity), was given to it for this reason. All the paraffins are **saturated hydrocarbons.**

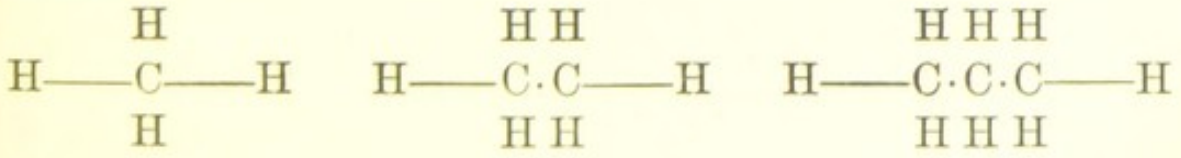
Homologous Series.—When the paraffins are arranged in the order of their (increasing) molecular weights they form a series, the molecular formula of each member of which contains one atom of carbon and two atoms of hydrogen more than the molecular formula of the preceding member.

Methane,	CH_4	
Ethane,	C_2H_6	difference CH_2
Propane,	C_3H_8	" CH_2
Butane,	C_4H_{10}	" CH_2
Pentane,	C_5H_{12}	" CH_2

Such a series, the members of which are *similar in constitution, and therefore, also, in chemical properties*, is termed a **homologous series**, and the several members are spoken of as **homologues** of one another; there are a great many homologous series of organic compounds.

Although the members of a homologous series are always more or less alike in chemical behaviour, *because* they are similar in structure, both the chemical and the physical properties undergo a gradual and regular *variation* as the molecular weight increases.

General Formulæ.—The molecular composition of all the members of a homologous series can be expressed by a **general formula.** In the case of the paraffin series the general formula is C_nH_{2n+2}, which means that in any member containing n atoms of carbon in the molecule there are $2n + 2$ atoms of hydrogen; in propane, C_3H_8, for example, $n = 3$; $2n + 2 = 8$. That this is so can be readily seen by writing the graphic formulæ of some of the paraffins in the following manner:—



when it is at once obvious that for every atom of carbon there are two atoms of hydrogen, the molecule containing, in

addition, two extra hydrogen atoms. It is perhaps not superfluous to add that the molecular formulæ of all these paraffins have been established by the usual methods—namely, by quantitative elementary analysis followed by a vapour density determination.

Owing to their inertness the paraffins are not easily distinguished from one another, or identified. The gaseous paraffins may be distinguished and identified by exploding a known volume of the gas with excess of oxygen in a eudiometer; from the *contraction* which occurs and a measurement of the volume of the carbon dioxide which is formed, the molecular formula of the paraffin may be ascertained. In the case of the higher members, the boiling-point, melting-point, and specific gravity, may serve for the identification of the compound.

Paraffins are easily distinguished from olefines, acetylenes, and aromatic hydrocarbons, because they are not attacked by bromine or by sulphuric acid in the cold.

Since the members of a homologous series, as a rule, can be obtained by similar or *general methods*, if these are given it is usually unnecessary to describe the preparation of each member separately. In view, also, of their great similarity in chemical properties, a detailed account of each compound may be omitted, if the *general properties* of the members of the series are described; the physical properties may also be dealt with in a general manner, since they undergo a regular and gradual variation as the molecular weights of the members increase.

The following is a summary of the principal facts relating to the paraffins treated in this way; *it will be found advantageous to omit this and other summaries during the first year given to the study of organic chemistry.*

SUMMARY AND EXTENSION.

The Paraffin or Methane Series. *Saturated* hydrocarbons of the general formula, C_nH_{2n+2}.—The more important members of the series are the following:—The number of possible isomerides is indicated by the figures in brackets, and the boiling-points of the *normal* hydrocarbons are given.

Methane (1),	CH_4	b.p. $-11°$	180 atmos.
Ethane (1),	C_2H_6	" $+4°$	46 "
Propane (1),	C_3H_8	" $-45°$	1 "
Butane (2),	C_4H_{10}	" $0°$	1 "
Pentane (3),	C_5H_{12}	" $+37°$	1 "
Hexane (5),	C_6H_{14}	" $69°$	1 "
Heptane (9),	C_7H_{16}	" $98°$	1 "
Octane (18),	C_8H_{18}	" $125{\cdot}5°$	1 "
Nonane (35),	C_9H_{20}	" $149{\cdot}5°$	1 "
Decane (75),	$C_{10}H_{22}$	" $173°$	1 "

Nomenclature.—The names of all the hydrocarbons of this series have the distinctive termination **ane**; those of the higher members have a prefix which denotes the number of carbon atoms in the molecule.

Occurrence.—The paraffins are found in nature in enormous quantities as petroleum or mineral naphtha, in smaller quantities as natural gas, and as earth-wax, or ozokerite (p. 70).

Methods of Formation or Preparation.—(1) The alkali salt of a fatty acid (p. 149) is heated with potash, soda, or soda-lime,

$$CH_3{\cdot}COONa + NaOH = CH_4 + Na_2CO_3$$
$$C_3H_7{\cdot}COOK + KOH = C_3H_8 + K_2CO_3.$$

(2) The halogen substitution products of the paraffins are reduced with nascent hydrogen,

$$CH_3Cl + 2H = CH_4 + HCl$$
$$C_2H_5I + 2H = C_2H_6 + HI.$$

(3) The alkyl* halogen compounds are heated with sodium or zinc (Würtz),

$$2C_2H_5I + 2Na = C_2H_5{\cdot}C_2H_5 + 2NaI$$
$$2CH_3I + 2Na = CH_3{\cdot}CH_3 + 2NaI.$$

(4) The zinc alkyl compounds (p. 229) are decomposed with water (Frankland), or the magnesium alkyl halides (p. 226) are decomposed with water, or with a primary or secondary base (p. 227),

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2$$
$$Mg\begin{matrix}Pr\\I\end{matrix} + H_2O = C_3H_8 + Mg\begin{matrix}OH\\I\end{matrix}.$$

(5) The alkyl halogen compounds are treated with the zinc alkyl derivatives, or with the magnesium alkyl halides,

$$2CH_3I + Zn(C_2H_5)_2 = 2CH_3{\cdot}C_2H_5 + ZnI_2$$
$$Mg\begin{matrix}Et\\I\end{matrix} + EtI = C_4H_{10} + MgI_2.$$

* The meaning of the word *alkyl* is given on p. 107.

Tertiary hydrocarbons, such as tetramethylmethane, may be prepared from certain dihalogen derivatives of the paraffins (p. 146),

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CCl_2 + Zn(CH_3)_2 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} + ZnCl_2.$$

(6) Aqueous solutions of the sodium or potassium salts of the fatty acids are submitted to electrolysis (Kolbe),

$$2CH_3\cdot COOK + 2H_2O = CH_3\cdot CH_3 + 2CO_2 + 2KOH + H_2.$$

Physical Properties.—The first four members of the series are colourless gases, while those containing from 5 to about 16 atoms of carbon are colourless liquids under ordinary conditions; the boiling-point rises regularly as the series is ascended, but the difference between the boiling-points of consecutive *normal* hydrocarbons gradually diminishes (see table). The higher members of the series, from about $C_{16}H_{34}$ (m.p. 18°), are colourless solids.

The specific gravity of the hydrocarbons gradually increases from butane (sp. gr. 0·6) until the higher members are reached, when it becomes almost constant at 0·775–0·780, this value being determined at the melting-point of the compound in the case of solids.

The paraffins are insoluble, or nearly so, in water, but they are miscible with alcohol, ether, and many other organic liquids.

Chemical Properties.—The paraffins are all characterised by great stability. At ordinary temperatures, they are not acted on by nitric acid, fuming sulphuric acid, sodium, alkalis, or such powerful oxidising agents as chromic acid and potassium permanganate, and even at higher temperatures they are only very slowly attacked. They react, however, with chlorine and, less readily, with bromine in sunlight with formation of substitution products. Iodine has no action on the paraffins.

PARAFFINS AND OTHER SATURATED HYDROCARBONS OF COMMERCIAL IMPORTANCE.

In Pennsylvania, North America, in Baku, South-east Russia, and in other parts of the world, a gas escapes from the earth under considerable pressure, either spontaneously or as the result of boring. This *natural gas* is variable in composition, but usually contains a large proportion of methane and hydrogen, small quantities of other gaseous paraffins, and other hydrocarbons. It is employed as a fuel in many places for a variety of industrial purposes.

In the localities already mentioned enormous quantities of

petroleum or *mineral naphtha* are also obtained, either from natural springs or from artificial borings.

The origin of natural gas and petroleum is unknown, but it is possible that these mixtures of hydrocarbons have been produced by the destructive distillation in the lower layers of the earth's crust of the fatty remains of (sea) animals, or by the action of water on carbides.*

Crude petroleum is specifically lighter than water, and varies greatly in consistency and colour, being generally a thick, yellow or brown liquid, with a greenish colour when viewed by reflected light. It consists almost entirely of a mixture of hydrocarbons, that obtained from Pennsylvania being composed chiefly of paraffins, that from Baku of hydrocarbons belonging to a different (naphthene or cycloparaffin) series.

Petroleum is not only, next to coal-gas, one of the more important illuminating agents of the present day, but is also the source of a number of substances of commercial value. The crude oil is not directly employed, owing to the fact that it contains very volatile hydrocarbons which render it too inflammable, and also hydrocarbons of high molecular weight, which volatilise only at very high temperatures. In order to obtain products of a nature suitable for the purposes for which they are required, the crude oil is distilled from large iron vessels and the distillate is collected in fractions. American petroleum, treated in this way, yields :—*Petroleum ether* or *petrol* (b.p. 40–70°), *gasoline* (b.p. 70–90°), and *ligroin* or *light petroleum* (b.p. 80–120°), colourless mobile liquids used in petrol-engines and as solvents for resins, oils, caoutchouc, &c. ; *cleaning oil* (b.p. 120–150°), employed for cleaning purposes, and as a substitute for oil of turpentine in the preparation of varnishes ; *refined petroleum*, *kerosene*, or burning oil (b.p. 150–300°), used for illuminating purposes ; † the portions collected above 300° are employed as

* Certain carbides, such as aluminium carbide, are decomposed by water, giving paraffins,

$$Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3.$$

† All petroleum products of low boiling-point are highly inflammable and form explosive mixtures with air (use in petrol-engines) ; they should

lubricating oils, *vaseline*, &c., and the residual carbonaceous mass is used for electrical purposes.

Russian petroleum also yields a variety of products, such as *benzine*, *kerosene*, *solar oil*, *vaseline*, and *paraffin*, which, though slightly different in composition, are similar in ordinary properties and uses to those obtained from American oil.

Ordinary paraffin-wax is also obtained from the tar which is produced by the destructive distillation of cannel-coal or shale.

When this tar is fractionally distilled, it yields several liquid products similar to those obtained from petroleum—such as *photogene* and *solar oil*, which are used as solvents and for illuminating purposes—and solid paraffins, or paraffin-wax, which is purified by treatment with concentrated sulphuric acid and redistillation.

Paraffin-wax is a colourless, semi-crystalline, waxy substance, soluble in ether, &c., but insoluble in water; its melting-point ranges from about 45–65°, according to its composition; its principal use is for the preparation of candles (p. 178).

Ozokerite is a naturally occurring solid paraffin or *earth-wax* which is found in Galicia and Roumania; it is purified by treatment with concentrated sulphuric acid and distillation.

CHAPTER V.

Unsaturated Hydrocarbons. The Olefines, or Hydrocarbons of the Ethylene Series.

When the halogen mono-substitution products of the paraffins, such as ethyl bromide, propyl chloride, &c. (p. 180), are heated with an alcoholic solution of potash, they are converted into hydrocarbons,

be handled with extreme caution. Petroleum for use in lamps should be free from the more volatile paraffins, as shown by a determination of its 'flash-point,' otherwise it may give rise to dangerous explosions.

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O,$$
$$C_3H_7Cl + KOH = C_3H_6 + KCl + H_2O.$$

The molecules of the compounds obtained in this way, and by other methods to be described later, contain two atoms of hydrogen less than those of the corresponding paraffins; as, moreover, the new hydrocarbons are formed by similar processes from compounds which resemble one another in structure, they themselves are similar in constitution, and form a homologous series of the general formula, C_nH_{2n}; their names are derived from those of the corresponding paraffins by changing the termination *ane* into *ylene*,

Methane, CH_4; Ethane, C_2H_6; Propane, C_3H_8; Butane, C_4H_{10}.
—— Ethylene, C_2H_4; Propylene, C_3H_6; Butylene, C_4H_8.

The simplest member of this series is *ethylene;* a hydrocarbon CH_2, which would correspond with methane, is *unknown*, and all attempts to prepare it from a halogen mono-substitution product of methane, or in other ways, have been unsuccessful; this seems to show that a compound in which carbon would be *bivalent* is incapable of existence.

The word '**olefine**' is derived from '*olefiant*' or '*oil-making*' gas, a name originally given to ethylene on account of its property of forming an oily liquid (ethylene dichloride or Dutch liquid) with chlorine; the term 'olefine' is now applied as a class name to all the hydrocarbons of this series.

Ethylene, C_2H_4, is formed during the destructive distillation of many organic substances, and occurs in coal-gas, of which it forms about 6 per cent. by volume; the luminosity of a coal-gas flame is to a great extent due to ethylene.

Ethylene is formed when acetylene (p. 83), in the form of copper acetylide, is reduced with zinc dust and ammonia,

$$C_2H_2 + 2H = C_2H_4.$$

Ethylene is also obtained when a solution of potassium succinate (p. 249) is submitted to electrolysis (Kekulé),

$$C_2H_4(COOK)_2 + 2H_2O = C_2H_4 + 2CO_2 + 2KOH + H_2;$$

a mixture of ethylene and carbon dioxide rises from the positive

pole, while the alkali metal which separates at the negative pole acts on the water and liberates hydrogen. This method of formation of ethylene recalls the production of ethane by the electrolysis of potassium acetate (p. 60).

Ethylene is prepared by heating ethyl alcohol with concentrated sulphuric acid or with phosphoric acid; the *final results* may be expressed by the equation,

$$C_2H_5 \cdot OH = C_2H_4 + H_2O;$$

but the reaction really takes place in two stages (p. 192).

A mixture of 95 per cent. ethyl alcohol (25 g.) and concentrated sulphuric acid (150 g.) is placed in a capacious flask (fig. 19), and

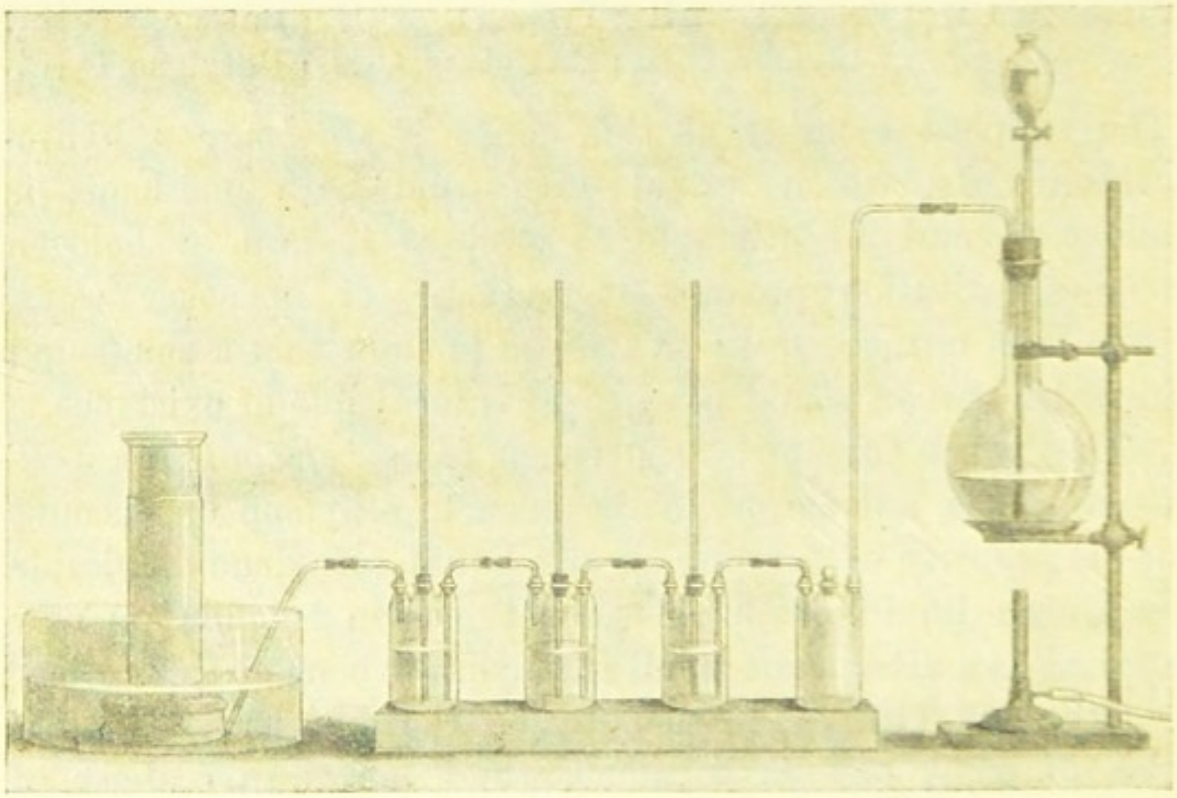


Fig. 19.

heated to about 165° (the bulb of the thermometer is immersed in the *liquid*); the gas thus produced is passed first through water and then through dilute potash, in order to free it from sulphur dioxide and carbon dioxide, and is finally collected over water.* When the evolution of gas slackens, a further supply may be

* In presence of about 5 per cent. of anhydrous aluminium sulphate the reaction takes place more rapidly, and the mixture need not be heated so strongly.

obtained by dropping a mixture of 1 part of alcohol and 2 parts by weight of sulphuric acid through the funnel, the temperature being kept constant. The liquid in the flask generally darkens considerably, owing to the oxidising action of the acid, and unless good alcohol is used a large quantity of carbonaceous matter is often formed. For this reason phosphoric acid may be advantageously employed, in which case the alcohol is dropped into syrupy phosphoric acid heated at about 220°; the yield by this method is good, and for most purposes the gas does not require purification.

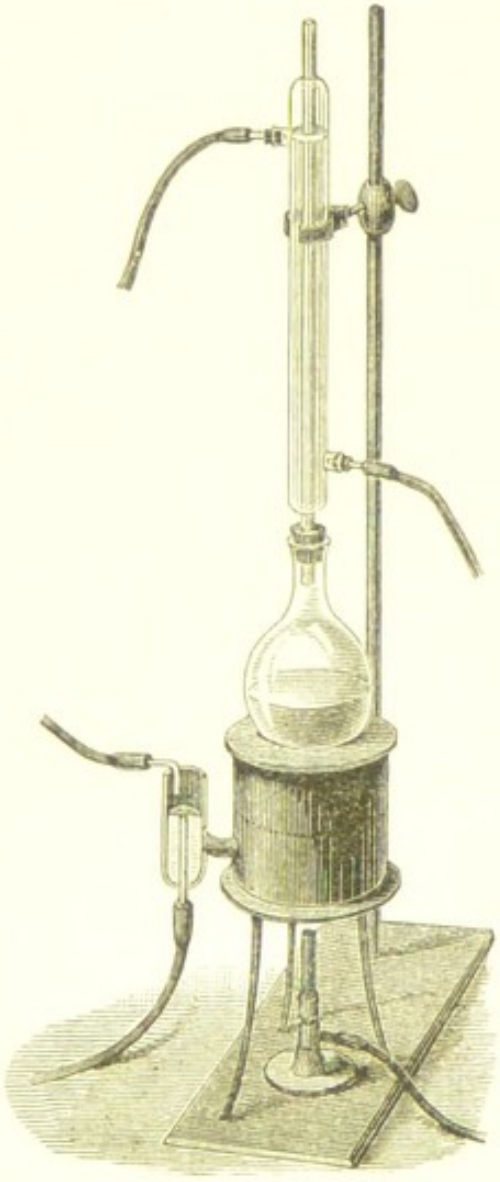


Fig. 20.

Another method for the preparation of ethylene is to drop ethyl bromide from a stoppered funnel into a flask containing excess of boiling alcoholic potash,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O.*$$

The flask is heated on a water-bath, and is provided with a *reflux condenser* (fig. 20), the end of which is connected to a delivery tube passing to the pneumatic trough; during the reaction potassium bromide separates from the solution.

A reflux condenser is always used when it is necessary to prevent the loss of a volatile solvent or of a substance present in solution; the vapours, which would otherwise pass away, are condensed, and the liquid runs back into the flask. The flask may

* Alcoholic potash (a solution of potassium hydroxide in methyl or ethyl alcohol) often has an action on organic compounds different from that of an aqueous solution of potassium hydroxide. The latter attacks ethyl bromide relatively slowly, and converts it principally into ethyl alcohol (p. 96).

be heated over a piece of wire-gauze or on a sand-bath; but when alcohol, ether, or other substances of low boiling-point are being used, a water-bath is always employed. In a form of apparatus similar to that shown, a liquid may be kept boiling during several days.

Ethylene is a colourless gas, has a peculiar sweet but not unpleasant smell, and liquefies at 10° under a pressure of 60 atmospheres; it is only sparingly soluble in water, more readily in alcohol and ether. It burns with a luminous flame, and forms a highly explosive mixture with air or oxygen,

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$
$$1 \text{ vol.} + 3 \text{ vols.} = 2 \text{ vols.} + 2 \text{ vols.}$$

Its chemical behaviour is totally different from that of the paraffins. It combines *directly* with hydrogen at high temperatures (in presence of platinum black at ordinary temperatures) forming ethane,

$$C_2H_4 + H_2 = C_2H_6.$$

Although it is not acted on by hydrochloric acid, it combines *directly* with concentrated hydrobromic and hydriodic acids at 100°, forming ethyl bromide and ethyl iodide respectively,

$$C_2H_4 + HBr = C_2H_5Br \qquad C_2H_4 + HI = C_2H_5I.$$

It combines *directly* with chlorine and bromine (p. 79), and also with iodine (which is dissolved in alcohol),

$$C_2H_4 + X_2 = C_2H_4X_2 \qquad (X = Cl, Br, I).$$

It is absorbed by, and combines *directly* with, anhydro-sulphuric acid, and, more slowly, with ordinary sulphuric acid, yielding ethyl hydrogen sulphate (p. 191),

$$C_2H_4 + H_2SO_4 = C_2H_5 \cdot HSO_4.*$$

Constitution of Ethylene.—It can be proved by analysis and by vapour density determinations that the molecular formula of ethylene is C_2H_4. The two carbon atoms in this molecule are known to be directly united, because hydrogen is a univalent element; further, a study of all the methods of formation

* The absorption of ethylene by fuming sulphuric acid is easily shown with the aid of Hempel's gas-analysis apparatus.

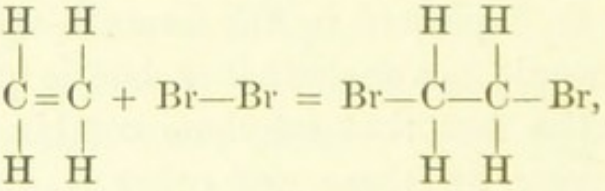
of ethylene leads to this conclusion, because the carbon atoms in the molecules of ethyl bromide and of ethyl alcohol are known to be directly united, and there is no reason to suppose that they become separated when these two compounds are converted into ethylene. The four hydrogen atoms in the ethylene molecule must all be directly united to the carbon atoms, and therefore may be distributed in one of two possible ways, represented respectively by the expressions, CH_2-CH_2 and CH_3-CH.

Now, two isomeric compounds of the molecular formula, $C_2H_4Br_2$, are known. One of these, *ethylene dibromide*, is formed by the direct combination of ethylene and bromine (p. 79); the isomeride, *ethylidene dibromide*, is obtained from acetaldehyde, and is known to have the structure, CH_3-CHBr_2 (p. 146). As these are the only two compounds of the molecular formula, $C_2H_4Br_2$, which, theoretically, are possible, and as the isomeride of ethylidene dibromide must have the structure, CH_2Br-CH_2Br, it is concluded that this formula must represent the constitution of ethylene dibromide. Further, since ethylene dibromide is formed by the direct union of ethylene and bromine, each of the carbon atoms in the ethylene molecule must be combined with two atoms of hydrogen. This being the case, the constitution of ethylene might be expressed by the formula, CH_2-CH_2. But such a formula would not show that carbon is quadrivalent, nor would it recall the fact that ethylene combines directly with Cl_2, Br_2, HBr, &c.; for these and other reasons the constitution of ethylene is represented by the formula, $\begin{matrix}H\\H\end{matrix}\!>\!C=C\!<\!\begin{matrix}H\\H\end{matrix}$ or $CH_2=CH_2$ or $CH_2:CH_2$, and the two carbon atoms are said to be united by a **double bond**, or double linking.

The above view of the constitution of ethylene receives support from the formation of the gas by the electrolysis of succinic acid, as is clearly seen if the decomposition is represented thus:—

$$\begin{matrix}CH_2\cdot COOH\\|\\CH_2\cdot COOH\end{matrix} = \begin{matrix}CH_2-\\|\\CH_2-\end{matrix} + \begin{matrix}CO_2\ H-\\+\\CO_2\ H-\end{matrix} = \begin{matrix}CH_2\\\|\\CH_2\end{matrix} + 2CO_2 + \begin{matrix}H\\|\\H\end{matrix}.$$

It must not be supposed that a double bond has any mechanical significance, or that it implies that the two carbon atoms attract one another more strongly than when they are singly bound. A double bond in the structural formula of any compound is merely a convenient expression of certain facts which have been established experimentally—namely, that *the compound is capable of combining directly with two univalent atoms or groups of particular elements, and that these atoms or groups unite with those carbon atoms which are represented as being doubly bound.* All organic compounds, which, like ethylene, contain carbon atoms having the power of combining directly with certain other atoms or groups, are said to be **unsaturated.** In the graphic or structural formulæ of all such substances, these particular carbon atoms are represented as being joined by a **double bond**; the structural formula thus summarises the more important chemical properties of the compound. When an unsaturated compound enters into direct combination, the double bond is said to be 'broken,' and in the structural formula of the product the two carbon atoms, previously represented as being doubly bound, are now shown as being united together in the same way as those in the formula of ethane (p. 61); the combination of ethylene with bromine, for example, is expressed graphically,



and the formula of ethylene dibromide shows that, like the paraffins, this substance is saturated, and cannot give derivatives except by substitution.

The substances formed by the direct union of unsaturated compounds with atoms or groups of atoms are called **additive products,** in contradistinction to substitution products.*

* In the case of a halogen additive product the hydrocarbon is named first, but in the case of a halogen substitution product the hydrocarbon is named last; *ethylene* dibromide, for example, is also called dibrom-*ethane*.

Unsaturated compounds may contain two or more unsaturated carbon atoms, but they always combine with an *even* number of univalent atoms or groups. A single unsaturated carbon atom never occurs in the molecule of an unsaturated hydrocarbon. This last fact is the principal reason why the formula—$CH_2 \cdot CH_2$—is not used to represent the structure of ethylene; such a formula would not give any indication of the dependence of one unsaturated carbon atom on the presence of another.

Derivatives of Ethylene.—**Ethylene dichloride**, $C_2H_4Cl_2$, or $CH_2Cl \cdot CH_2Cl$, was originally called Dutch liquid, or oil of Dutch chemists, by whom it was discovered. It is obtained by the direct combination of ethylene and chlorine, and is a colourless liquid of sp. gr. 1·28 at 0°, boiling at 85°. It is isomeric with ethylidene dichloride, $CH_3 \cdot CHCl_2$ (p. 130). **Ethylene dibromide**, $C_2H_4Br_2$, or $CH_2Br \cdot CH_2Br$, is prepared by passing ethylene into bromine until the colour of the latter disappears; the product is purified by distillation.* It is a colourless crystalline substance, melts at 9·5°, and boils at 131°; its sp. gr. is 2·21 at 0°. It is isomeric with ethylidene dibromide, $CH_3 \cdot CHBr_2$ (p. 146).

Substitution products of ethylene, such as *chlorethylene* or *vinyl chloride*, $CH_2{:}CHCl$, *bromethylene* or *vinyl bromide*, $CH_2{:}CHBr$, cannot be obtained by treating ethylene with a halogen, because additive products are produced in this way. They are the first products of the action of alcoholic potash on the halogen additive products of ethylene (p. 84),

$$CH_2Br \cdot CH_2Br + KOH = CH_2{:}CHBr + KBr + H_2O.$$

Vinyl chloride is a gas, vinyl bromide a colourless liquid, boiling at 16°; they are unsaturated compounds, and combine directly with bromine, hydrogen bromide, &c.

Propylene, C_3H_6, or $CH_3 \cdot CH{:}CH_2$, is formed when either propyl or isopropyl bromide is boiled with alcoholic potash,

$$\begin{matrix} \text{Propyl bromide, } CH_3 \cdot CH_2 \cdot CH_2Br \\ \text{Isopropyl bromide, } CH_3 \cdot CHBr \cdot CH_3 \end{matrix} \Big\rangle CH_3 \cdot CH{:}CH_2 + HBr.$$

* The ethylene (free from sulphur dioxide, p. 74) is passed through a wash-bottle which contains bromine, covered with water to diminish loss by evaporation. When the wash-bottle no longer contains free bromine, the heavy oily product is separated with the aid of a separating funnel, dried with calcium chloride (p. 10), and distilled.

It is prepared by heating propyl alcohol (4 vols.) with sulphuric acid (3 vols.) and 5 per cent. of anhydrous aluminium sulphate at about 105°,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH = CH_3{\cdot}CH{:}CH_2 + H_2O.$$

It is a gas very similar to ethylene in properties, and being an unsaturated compound, it combines readily with bromine, forming *propylene dibromide*, $CH_3{\cdot}CHBr{\cdot}CH_2Br$, an oily liquid boiling at 141°.

The higher members of the olefine series are obtained by methods similar to those employed in the case of propylene.

Three isomeric **butylenes** of the molecular formula, C_4H_8, are known—namely,

$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$	$CH_3{\cdot}CH{:}CH{\cdot}CH_3$	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CH_2$.
Normal or α-butylene.	β-Butylene.	Iso- or γ-butylene.

The first two compounds are derived from normal butane, the third from isobutane, and it should be noted that the number of possible isomerides in the case of any olefine which exhibits isomerism is greater than in that of the corresponding paraffin. The three butylenes are all colourless gases, and combine directly with chlorine, bromine, hydrogen bromide, &c.

Five isomeric **amylenes** or **pentylenes**, C_5H_{10}, are known, the most important being *trimethylethylene* or *β-iso-amylene*, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CH{\cdot}CH_3$, which is obtained (mixed with isomerides) by heating fusel oil (pp. 102, 111) with zinc chloride; it is a colourless liquid, and boils at 32°.

The great difference in chemical properties between the saturated hydrocarbons of the paraffin series and the unsaturated compounds of the olefine series is conveniently demonstrated by contrasting the behaviour of 'light petroleum' with that of (commercial) amylene. When a few drops of bromine are added to, say, 50 cc. of light petroleum, the solution retains the colour of the halogen for a long time, and if any action occurs hydrogen bromide is evolved because substitution takes place. When, on the other hand, bromine is cautiously dropped into amylene, the colour of the halogen immediately

disappears and a vigorous reaction occurs; but hydrogen bromide is not evolved. After sufficient bromine has been added, the liquid product (amylene dibromide) is found to sink when placed in water, whereas amylene floats.

Concentrated sulphuric acid does not mix with, and has no appreciable action on, light petroleum; but an energetic reaction occurs when the acid is cautiously added to amylene, and some of the unsaturated hydrocarbon passes into solution in the form of amylsulphuric acid (p. 111).

Light petroleum does not decolourise a dilute solution of potassium permanganate, when the two liquids are shaken together, but amylene is readily oxidised.

The gaseous olefines may be distinguished or identified by methods such as those given in the case of the paraffins; a more convenient process is to convert the olefine into the liquid dibromide, which may then be identified by its boiling-point.

SUMMARY AND EXTENSION.

The Olefine or **Ethylene Series.** *Unsaturated* hydrocarbons of the general formula, C_nH_{2n}.—The following are the more important members of this series, the number of possible isomerides being given in brackets :—

Ethylene (1),	C_2H_4	Amylene (5),	C_5H_{10}
Propylene (1),	C_3H_6	Hexylene (13),	C_6H_{12}
Butylene (3),	C_4H_8		

Methods of Preparation.—(1) The alcohols are heated with sulphuric or phosphoric acid (p. 193),

$$CH_3{\cdot}CH_2{\cdot}OH = CH_2{:}CH_2 + H_2O.$$

(2) The alkyl halogen compounds (p. 187), are heated with alcoholic potash,

$$CH_3{\cdot}CH_2Br + KOH = CH_2{:}CH_2 + KBr + H_2O$$
$$CH_3{\cdot}CHBr{\cdot}CH_3 + KOH = CH_3{\cdot}CH{:}CH_2 + KBr + H_2O.$$

(3) Aqueous solutions of the alkali salts of certain dibasic acids are submitted to electrolysis,

$$\begin{matrix} CH_2{\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{matrix} = \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2 + H_2.$$

Physical Properties.—The first four members of the series are

gases, but the following fourteen or so are liquids and the higher members are solids at ordinary temperatures: the boiling-point rises as the molecular weight increases, just as in the case of the paraffins. They are insoluble, or nearly so, in water, but readily soluble in alcohol.

Chemical Properties.—The olefines burn with a luminous smoky flame, and can be exploded with oxygen or air. They are unsaturated hydrocarbons, and differ very considerably in chemical properties from the saturated hydrocarbons of the paraffin series. Whereas at ordinary temperatures the latter are only acted on by chlorine and give substitution products, the olefines, as a rule, combine readily with Cl_2, Br_2, HCl, HBr, HClO, H_2SO_4, &c., and form saturated additive products.

The olefines are converted into paraffins on treatment with nascent hydrogen,

$$C_nH_{2n}+2H=C_nH_{2n+2}.$$

They combine with chlorine and bromine, sometimes with iodine, forming saturated compounds, which may be regarded as di-substitution products of the paraffins,

$$CH_3\cdot CH:CH_2+Cl_2=CH_3\cdot CHCl\cdot CH_2Cl.$$

They combine with hydrogen bromide and hydrogen iodide, but not, as a rule, with hydrogen chloride, yielding alkyl halogen compounds,

$CH_2:CH_2+HBr=C_2H_5Br$, $CH_3\cdot CH:CH_2+HI=CH_3\cdot CHI\cdot CH_3$;

combination generally taking place in such a manner that the halogen atom unites with that carbon atom which is combined with the smallest number of hydrogen atoms; propylene, for example, yields with hydrobromic acid, isopropyl bromide, $CH_3\cdot CHBr\cdot CH_3$, and not propyl bromide, $CH_3\cdot CH_2\cdot CH_2Br$; normal butylene, $CH_3\cdot CH_2\cdot CH:CH_2$, with hydriodic acid, gives secondary butyl iodide,* $CH_3\cdot CH_2\cdot CHI\cdot CH_3$, and so on.

Fuming sulphuric acid, in some cases ordinary sulphuric acid, readily absorbs the olefines, forming alkyl hydrogen sulphates,

$$CH_2:CH_2+H_2SO_4=CH_3\cdot CH_2\cdot SO_4H.$$

Hypochlorous acid, in aqueous solution, converts the olefines into *chlorohydrins* (p. 236),

$$CH_2:CH_2+HOCl=CH_2Cl\cdot CH_2\cdot OH.$$

Unlike the paraffins, the olefines are readily oxidised by chromic acid and by potassium permanganate. When oxidation is carried out carefully, under suitable conditions, a product containing the

* Compare footnote p. 293.

same number of carbon atoms as the original olefine is obtained; ethylene, for example, gives ethylene glycol (p. 233), butylene, the corresponding butylene glycol,

$$CH_2{:}CH_2 + O + H_2O = CH_2(OH)\cdot CH_2\cdot OH$$
$$CH_3\cdot CH_2\cdot CH{:}CH_2 + O + H_2O = CH_3\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH.$$

Generally speaking, when a substance contains the group —CH=CH—, this group, on oxidation, is in the first place converted into —CH(OH)·CH(OH)—. The compounds thus formed readily undergo further oxidation in such a way that the originally unsaturated carbon atoms become separated. Propylene, on vigorous oxidation, yields ultimately acetic and formic acids; α-butylene gives propionic and formic acids,

$$CH_3\cdot CH{:}CH_2 + 4O = CH_3\cdot COOH + H\cdot COOH$$
$$CH_3\cdot CH_2\cdot CH{:}CH_2 + 4O = CH_3\cdot CH_2\cdot COOH + H\cdot COOH.$$

HYDROCARBONS OF THE ACETYLENE SERIES.

The homologous hydrocarbons of the acetylene series are related to those of the olefine series just as the latter are related to the paraffins; in other words, the molecules of the members of the acetylene series contain two atoms of hydrogen less than those of the corresponding olefines, and the general formula of the series is C_nH_{2n-2}.

Paraffins, C_nH_{2n+2}	*Olefines*, C_nH_{2n}	*Acetylenes*, C_nH_{2n-2}
Methane, CH_4	——	——
Ethane, C_2H_6	Ethylene, C_2H_4	Acetylene, C_2H_2
Propane, C_3H_8	Propylene, C_3H_6	Allylene, C_3H_4
Butane, C_4H_{10}	Butylene, C_4H_8	Crotonylene, C_4H_6

Acetylene, C_2H_2, the simplest member of the series, occurs in small quantities (about 0·06 per cent. by vol.) in coal-gas. It is formed when hydrogen is led through a globe in which the electric arc is passing between carbon poles (Berthelot),

$$C_2 + H_2 = C_2H_2.$$

This synthesis of acetylene from its elements is of great interest, because acetylene can be reduced to ethylene, and ethylene is readily converted into ethyl alcohol (p. 97). As, moreover, a large number of organic substances can be produced from ethyl alcohol, it is possible to prepare all these compounds, starting with carbon and hydrogen.

Acetylene is produced during the incomplete combustion of methane, ethyl alcohol, coal-gas, and other substances; also when such substances are passed through a red-hot tube.

An ordinary Bunsen burner is lighted below, and an inverted glass funnel, connected by tubing with a Woulfe's bottle, is placed over it; with the aid of a water-pump, or aspirator, the products are drawn through an ammoniacal solution of cuprous chloride, contained in the Woulfe's bottle, when the red copper derivative of acetylene is precipitated. This product is collected, washed with water, and warmed with hydrochloric acid, the liberated acetylene being collected over water.

Acetylene is also formed when ethylene dibromide is dropped into boiling alcoholic potash (compare p. 75),

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

The reaction takes place in two stages, and the first product is vinyl bromide (p. 79),

$$C_2H_4Br_2 + KOH = C_2H_3Br + KBr + H_2O,$$

which is then converted into acetylene,

$$C_2H_3Br + KOH = C_2H_2 + KBr + H_2O.$$

The same apparatus is used as in the preparation of ethylene from ethyl bromide (p. 75), and the formation of acetylene is shown by passing the gas into an ammoniacal solution of cuprous chloride.

Acetylene is now prepared in the laboratory, and is also manufactured, from *calcium carbide*, a very hard, gray, crystalline substance, prepared by heating a mixture of coke and calcium carbonate, or oxide, at a very high temperature in an electric furnace,

$$CaO + 3C = CaC_2 + CO.$$

When calcium carbide is placed in cold water it is rapidly decomposed with development of heat, and acetylene is evolved,

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

This reaction is made use of in the commercial preparation of the gas.

For laboratory and lecture experiments a small lump of the carbide is placed under a gas-cylinder filled with, and inverted in, a vessel of water; but when a stream of gas is required the carbide is placed in a *small* flask, which contains a layer of sand and is provided with a dropping funnel and delivery tube; cold water is then dropped slowly on the carbide, when a steady stream of gas is obtained.*

Acetylene is a colourless gas, which liquefies at 1° under a pressure of 48 atmospheres; it has a characteristic smell, resembling that of garlic. It is slightly soluble in water, much more readily in alcohol. Acetylene is a strongly endothermic compound, and can be detonated (with fulminate) under atmospheric pressure; a mixture of acetylene and air or oxygen, in suitable proportions, *explodes with great violence* when it is ignited.† When burnt in an open gas-jar or from an ordinary flat-flame burner, acetylene gives a very smoky flame, a behaviour which is shown, but to a less extent, by all hydrocarbons which contain a very large percentage of carbon; when, however, suitably constructed burners are employed, smoking is prevented and the flame is almost dazzling in its brilliancy, and very rich also in actinic rays (use in photography).‡

Owing to the very high illuminating power of the acetylene flame, on the discovery of a cheap method of manufacturing calcium carbide, great expectations were formed that acetylene would be the illuminating agent of the future; hitherto, although acetylene is used alone in small quantities for such a purpose (bicycle lamps), in larger quantities for enriching oil-gas (for use principally in railway carriages), and also in the production of the oxy-acetylene blow-pipe flame, these high expectations have not been realised. This is partly due to the fact that acetylene is liable to explode when it is under a pressure of more than 30 lbs. per square inch,

* Commercial calcium carbide may contain calcium phosphide, and the acetylene obtained in this way may contain hydrogen phosphide (phosphine) as well as other impurities.

† It is not safe to explode a mixture of acetylene and air or oxygen in a soda-water bottle, or even in an open gas-jar.

‡ The illuminating power of acetylene is about 15 times as great as that of ordinary coal-gas.

and, therefore, cannot be safely stored in bottles or cylinders; it should not be stored in metallic holders even under atmospheric pressure, as explosive metallic derivatives may be formed. As acetylene is readily soluble in acetone (24 vols. dissolve in 1 vol. of acetone under atmospheric pressure), solutions of the gas in this solvent are often used instead of the compressed gas itself.

Copper acetylide, C_2Cu_2, is a brownish-red, amorphous compound which is precipitated when acetylene is passed into an ammoniacal solution of cuprous chloride; its formation serves as a delicate test for acetylene, and with the aid of this compound acetylene is easily separated from other gases. The dry substance explodes when struck on an anvil, or when heated at about 120°. It is decomposed by hydrochloric acid, with formation of acetylene.* *Silver acetylide*, C_2Ag_2, is obtained as a colourless, amorphous compound, when acetylene is passed into an ammoniacal solution of silver nitrate. It is far more readily explosive than the copper compound, and detonates when it is gently rubbed with a glass rod, or heated.†

When acetylene is passed over heated sodium or potassium, hydrogen is liberated, and metallic substitution products, such as C_2HNa and C_2Na_2, are formed.

Potassium acetylide was first obtained by Davy, in the preparation of potassium by heating together charcoal and calcined tartar (carbonised hydrogen potassium tartrate) in an iron bottle; he showed that this compound was decomposed by water, giving a gas 'bicarburet of hydrogen' (acetylene), which burnt with a brilliant flame.

Acetylene combines *directly* with nascent hydrogen, and is converted first into ethylene (p. 73), then into ethane (p. 60),

$$C_2H_2 + 2H = C_2H_4 \qquad C_2H_2 + 4H = C_2H_6;$$

in presence of finely divided nickel, it unites with *molecular* hydrogen, giving the same two products.

* Traces of vinyl chloride (p. 79) are also formed, but when cuprous acetylide is warmed with a solution of potassium cyanide, it yields pure acetylene.

† About 0·1 gram of *air-dried* silver acetylide is wrapped in a filter-paper, which is suspended by a wire to a retort-stand and then ignited.

It combines *directly* with chlorine, forming dichlorethylene and tetrachlorethane,

$$C_2H_2 + Cl_2 = C_2H_2Cl_2 \qquad C_2H_2 + 2Cl_2 = C_2H_2Cl_4;$$*

and with bromine, forming dibromethylene and tetrabromethane.

Acetylene combines with chlorine with explosive violence. When a small piece of calcium carbide is placed under a gas-jar, which is half-filled with chlorine (free from air) and is standing mouth downwards in a trough of water, the bubbles of acetylene 'puff' when they rise into the chlorine, and a deposit of carbon is formed. The reaction which occurs under these conditions is probably expressed by the equation,

$$C_2H_2 + Cl_2 = 2C + 2HCl.$$

Acetylene combines with the halogen acids under certain conditions, giving in the first place substitution products of ethylene. Thus, when cuprous acetylide is decomposed with hydrochloric acid, small quantities of chlorethylene, C_2H_3Cl, are produced.

Sulphuric acid absorbs acetylene.† When the solution is diluted with water, and then distilled, acetaldehyde (p. 127) passes over, so that the final result may be expressed by the equation,

$$C_2H_2 + H_2O = C_2H_4O.$$

This change takes place in two stages, and corresponds with the conversion of ethylene into ethyl alcohol,

$$C_2H_2 + 2H_2SO_4 = CH_3{\cdot}CH(SO_4H)_2,$$
$$CH_3{\cdot}CH(SO_4H)_2 + H_2O = CH_3{\cdot}CHO + 2H_2SO_4.$$

Acetaldehyde is also formed when acetylene is shaken with a warm aqueous solution of mercuric bromide, and the precipitate is then boiled with dilute sulphuric acid.

When acetylene is heated at a dull-red heat it is converted into benzene (Part II. p. 341),

$$3C_2H_2 = C_6H_6.$$

* These compounds are prepared on the large scale; they are non-inflammable, and may be used in the extraction of fats and oils from wool, &c., and in the preparation of varnishes and paints.

† This can be shown with the aid of Hempel's gas-analysis apparatus, as in the case of ethylene.

Constitution of Acetylene.—As the two carbon atoms in the molecule of acetylene must be directly united, the first matter to consider is whether the two hydrogen atoms are united to the same or to different carbon atoms—that is to say, whether the expression, CH_2-C or $CH-CH$, represents the arrangement of the atoms in the molecule. Now, in the formation of ethylene, $CH_2{:}CH_2$, from ethyl bromide, CH_3-CH_2Br, an atom of hydrogen and an atom of bromine are removed from *different* carbon atoms. As the formation of acetylene from ethylene dibromide, CH_2Br-CH_2Br, apparently, is a change of the same kind, but one which involves the loss of two molecules of hydrogen bromide, it may be inferred that this loss takes place in two stages, each of which is similar to that which occurs in the production of ethylene. This argument, which is based on analogy, clearly points to the arrangement $CH-CH$.

But since carbon is quadrivalent, and acetylene combines directly with four univalent atoms of certain elements, the structure of the hydrocarbon is represented by the formula, $H-C\equiv C-H$, or $CH\equiv CH$, or $CH{:}CH$, which is intended to show that the two carbon atoms in the molecule are unsaturated to a greater extent than are those in the molecule of ethylene. This view of the constitution of acetylene accords well with all that is known of the hydrocarbon.

Thus, its formation by the electrolysis of a salt of fumaric acid (Kekulé) is a reaction which lends support to the above structural formula (compare pp. 60, 73),

$$\begin{matrix} CH{-}COOH \\ \| \\ CH{-}COOH \end{matrix} = \begin{matrix} CH{-} \\ \| \\ CH{-} \end{matrix} + CO_2 + CO_2 + \begin{matrix} H{-} \\ \\ H{-} \end{matrix} = \begin{matrix} CH \\ \| \\ CH \end{matrix} + 2CO_2 + H_2.$$

Fumaric Acid.

The two carbon atoms in the molecule of acetylene are said to be united by a **treble bond** or treble linking; this treble bond, like the double bond, is merely a convenient expression of certain facts—namely, that the carbon atoms which are represented as being trebly bound are capable of uniting with four univalent atoms of certain elements.

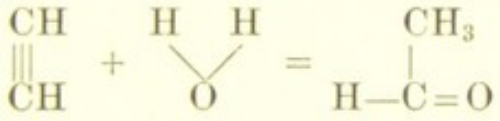
When acetylene combines with two univalent atoms it becomes less unsaturated, and the two carbon atoms, which before were represented as being trebly bound, are now represented as being united by a double linking, as in the olefines,

$$CH:CH + 2H = CH_2:CH_2 \qquad CH:CH + Br_2 = CHBr:CHBr.$$

When these *additive* compounds, which are still unsaturated, again combine with two univalent atoms, they are converted into saturated compounds,

$$CH_2:CH_2 + 2H = CH_3\cdot CH_3,$$
$$CHBr:CHBr + Br_2 = CHBr_2\cdot CHBr_2.$$

Acetylene can also combine with the equivalent of four univalent atoms—as, for example, with one atom of oxygen and two atoms of hydrogen (p. 87),



Two hydrocarbons of the molecular formula, C_3H_4, are known; they may be respectively represented by the formulæ,

$$CH_3\cdot C:CH \qquad \text{and} \qquad CH_2:C:CH_2.$$

Allylene or Methylacetylene. Allene.

Allylene, like acetylene, contains two trebly bound carbon atoms, whereas allene resembles rather ethylene in constitution, and contains what may be regarded as two pairs of doubly bound carbon atoms, $\overbrace{CH_2:\underbrace{C:CH_2}}$; allene, therefore, is *not* a homologue of acetylene, but belongs to the di-olefine series (see below). This example shows that the number of possible isomerides in the case of a member of the C_nH_{2n-2} series is greater than in that of the corresponding member of the olefine series.

Allylene, or methylacetylene, $CH_3\cdot C:CH$, is prepared by heating propylene dibromide (dibromopropane) with alcoholic potash,

$$CH_3\cdot CHBr\cdot CH_2Br + 2KOH = CH_3\cdot C:CH + 2KBr + 2H_2O.$$

It is a gas, very similar to acetylene in properties, and it gives copper and silver compounds.

Crotonylene, or dimethylacetylene, $CH_3\cdot C:C\cdot CH_3$, prepared by warming the dibromide of β-butylene (p. 80) with alcoholic potash,

$$CH_3\cdot CHBr\cdot CHBr\cdot CH_3 + 2KOH = CH_3\cdot C:C\cdot CH_3 + 2KBr + 2H_2O,$$

is a liquid boiling at 27–28°; it does *not* form copper or silver derivatives with ammoniacal solutions of cuprous chloride or silver nitrate, as this property is shown only by those hydrocarbons which contain the group, –C:CH.

Isoprene, $CH_2=C(CH_3)-CH=CH_2$, is a hydrocarbon of the *di-olefine* series, of which *allene* (see above) is the first member. It is obtained by the destructive distillation of india-rubber, and it boils at 37°. When it is treated with concentrated hydrochloric acid it undergoes polymerisation, giving a product which is very like rubber.

Diallyl, $CH_2:CH\cdot CH_2\cdot CH_2\cdot CH:CH_2$, is also a hydrocarbon of the *di-olefine* series. It is a liquid (b.p. 59°) prepared by warming allyl iodide (p. 289) with sodium,

$$2CH_2:CH\cdot CHI + 2Na = CH_2:CH\cdot CH_2\cdot CH_2\cdot CH:CH_2 + 2NaI.$$

It combines directly with *two* molecules of bromine, yielding *diallyl tetrabromide*, which, when dropped into hot alcoholic potash, is converted into *dipropargyl*,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot CH_2\cdot CHBr\cdot CH_2Br + 4KOH = CH:C\cdot CH_2\cdot CH_2\cdot C:CH + 4KBr + 4H_2O.$$

Dipropargyl is an important member of the *di-acetylene* series; it is a liquid boiling at 85°, and resembles acetylene in forming copper and silver derivatives.

SUMMARY AND EXTENSION.

The hydrocarbons, C_nH_{2n-2}, may be classed in two groups:—(1) The true acetylene series, consisting of those compounds which, like *acetylene*, contain the group, —C:C—; and (2) the *di-olefines*, or hydrocarbons, such as *allene*, $CH_2:C:CH_2$, and *diallyl*, $CH_2:CH\cdot CH_2\cdot CH_2\cdot CH:CH_2$, which resemble the olefines in constitution. The former behave on the whole like acetylene, whereas the latter are similar to the olefines.

The Acetylene Series. *Unsaturated* hydrocarbons of the general formula, C_nH_{2n-2}.—The more important members of this series are *acetylene*, CH:CH; *allylene*, $CH_3\cdot C:CH$; and *crotonylene*, $CH_3\cdot C:C\cdot CH_3$.

Methods of Preparation.—(1) The monohalogen substitution products of the olefines, or the dihalogen substitution products of the paraffins, are heated with alcoholic potash,

$$CH_2:CHBr + KOH = CH:CH + KBr + H_2O$$
$$CH_3\cdot CHBr\cdot CH_2Br + 2KOH = CH_3\cdot C:CH + 2KBr + 2H_2O.$$

(2) Aqueous solutions of the alkali salts of unsaturated dibasic acids are submitted to electrolysis,

$$\begin{matrix}CH\cdot COOH\\ \|\\ CH\cdot COOH\end{matrix} = \begin{matrix}CH\\ \|\|\\ CH\end{matrix} + 2CO_2 + H_2.$$

Physical and Chemical Properties.—The members of the acetylene series up to $C_{12}H_{22}$ are gases or volatile liquids, having a peculiar odour. They are sparingly soluble in water, more readily in alcohol, and burn with a luminous, very smoky flame.

Those hydrocarbons of the true acetylene series which contain the group, $\equiv CH$ form metallic compounds such as copper acetylide, C_2Cu_2, and silver acetylide, C_2Ag_2, when treated with ammoniacal solutions of cuprous chloride or of silver nitrate. The copper compounds are red, the silver compounds white, and both classes are explosive, the latter more so than the former. These compounds are decomposed by hydrochloric acid and also by warm potassium cyanide solution, the acetylenes being regenerated. The diolefines, and those members of the true acetylene series, such as $CH_3\cdot C{:}C\cdot CH_3$, which do not contain the group, $\equiv CH$, do not form these metallic derivatives.

The hydrocarbons of the true acetylene series may be caused to combine with the elements of water by dissolving them in strong sulphuric acid, and then adding water and warming; or by shaking them with a concentrated aqueous solution of mercuric chloride or bromide, and then decomposing the precipitate, which is formed, with a dilute mineral acid; or by merely heating them with water at about 325°,

$$CH{:}CH + H_2O = CH_3\cdot CHO \qquad CH_3\cdot C{:}CH + H_2O = CH_3\cdot CO\cdot CH_3.$$

In the case of all the higher members, combination takes place in such a way that the oxygen atom becomes united with the carbon atom which is not combined with hydrogen; allylene, for example, yields acetone, as shown above, and not propaldehyde, $CH_3\cdot CH_2\cdot CHO$.

All the hydrocarbons of the C_nH_{2n-2} series combine directly with two molecules of chlorine, bromine, halogen acids, &c., and with nascent hydrogen, the action taking place in two stages,

$$C_2H_2 + 2H = C_2H_4 \qquad C_2H_2 + 4H = C_2H_6$$
$$CH_3\cdot C{:}CH + Br_2 = CH_3\cdot CBr{:}CHBr$$
$$CH_3\cdot CBr{:}CHBr + Br_2 = CH_3\cdot CBr_2\cdot CHBr_2.$$

Like the olefines, they are readily oxidised and finally converted into products which contain a smaller number of carbon atoms in their molecules than the original compounds.

CHAPTER VI.

The Monohydric Alcohols.

The monohydric alcohols form a homologous series of the general formula, $C_nH_{2n+1}\cdot OH$, or R·OH.* They may be regarded as derived from the paraffins by the substitution of the univalent hydroxyl-group for one atom of hydrogen.

Methyl alcohol,	$CH_3\cdot OH$,	derived from methane,	$CH_3\cdot H$
Ethyl	"	$C_2H_5\cdot OH$,	"	ethane, $C_2H_5\cdot H$
Propyl	"	$C_3H_7\cdot OH$,	"	propane, $C_3H_7\cdot H$, &c.

Methyl alcohol, or *wood-spirit*, $CH_3\cdot OH$, occurs in nature in a combined form in certain essential oils—as, for example, in oil of winter-green (*Gaultheria procumbens*), which contains methyl salicylate. It may be obtained from methane by first converting the hydrocarbon into methyl chloride (p. 58), and then heating the latter with a dilute aqueous solution of potassium hydroxide in closed vessels,

$$CH_3Cl + KOH = CH_3\cdot OH + KCl.$$

These operations are difficult to carry out and are only of theoretical interest; since methane can be obtained synthetically, it is clear that methyl alcohol can also be produced from its elements.

Methyl alcohol is prepared on the large scale from the products of the destructive distillation of wood. When wood is heated in iron retorts out of contact with air, gases are evolved; water, *methyl alcohol*, *acetic acid*, tar, and other products collect in the receiver, and wood-charcoal remains.

After the distillate has settled, the brown aqueous layer, which contains methyl alcohol, acetic acid, acetone, and other substances, is drawn off from the wood-tar and distilled from a copper vessel; the vapours are passed through hot milk of lime, to free them from acetic acid, and are then condensed

* R represents an alkyl radicle (compare p. 107).

in a receiver. This distillate is diluted with water, when hydrocarbons and other oily impurities, which are insoluble in the dilute alcohol, are thrown out of solution and collect at the surface. The aqueous solution is filtered through charcoal and submitted to fractional distillation; in this way the methyl alcohol is separated from most of the water, but some remains, and quicklime is added in order to remove it. The liquid, which is then distilled from the quicklime and calcium hydroxide may contain 98–99 per cent. of methyl alcohol.

This product still contains acetone and other impurities; it is mixed with powdered anhydrous calcium chloride, with which the methyl alcohol combines to form a crystalline compound of the composition $CaCl_2,4CH_4O$. This substance is gently heated, or pressed between cloths (to remove acetone), and is then decomposed by distillation with water; the aqueous methyl alcohol is finally dehydrated by repeated distillation with quicklime, but it still contains traces of acetone and other substances.

Pure methyl alcohol can be prepared in the laboratory by warming this impure liquid with anhydrous oxalic acid, when methyl oxalate is produced (p. 247),

$$2CH_3\cdot OH + C_2O_4H_2 = C_2O_4(CH_3)_2 + 2H_2O;$$

this crystalline substance is well drained on a filter-pump, washed with a little water, and then hydrolysed with potash. The methyl alcohol, which is regenerated, is distilled from the alkaline solution, and is then freed from water by distillation first with quicklime and then with calcium.

Methyl alcohol is a colourless, mobile liquid of sp. gr. 0·796 at 20°; it boils at 66°, and has an agreeable vinous or wine-like odour and a burning taste. It mixes with water in all proportions, a slight contraction in volume taking place, and heat being developed; it burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air or oxygen,

$$2CH_3\cdot OH + 3O_2 = 2CO_2 + 4H_2O.$$

It is largely used as a solvent in the manufacture of organic dyes and varnishes, and for the preparation of methylated spirit (p. 104).

Methyl alcohol is rapidly acted on by sodium and potassium, with evolution of hydrogen and formation of metallic compounds called *methoxides* or *methylates*,

$$2CH_3\cdot OH + 2Na = 2CH_3\cdot ONa + H_2,$$

a reaction which is similar to the decomposition of water by sodium. Sodium methoxide is readily soluble in methyl alcohol, but can be obtained in a solid condition by evaporating the solution in a stream of hydrogen; it is a colourless, crystalline, very deliquescent compound, which rapidly absorbs carbon dioxide from the air, and is immediately decomposed by water with regeneration of methyl alcohol,

$$CH_3\cdot ONa + H_2O = CH_3\cdot OH + NaOH.$$

Potassium methoxide has similar properties.

Although neutral to test-paper, methyl alcohol acts like a weak basic hydroxide, and with acids it gives *esters* (or ethereal salts) and water; when saturated with hydrogen chloride, it yields methyl chloride,

$$CH_3\cdot OH + HCl = CH_3Cl + H_2O,$$

and, when warmed with sulphuric acid, it gives methyl hydrogen sulphate, and very small quantities of dimethyl sulphate,

$$CH_3\cdot OH + H_2SO_4 = CH_3\cdot HSO_4 + H_2O,$$
$$2CH_3\cdot OH + H_2SO_4 = (CH_3)_2SO_4 + 2H_2O.$$

These reactions may be compared with those which occur when a metallic hydroxide is treated with an acid, but they take place incompletely even in presence of a large excess of the acid (p. 195). When phosphorus pentachloride, trichloride, or oxychloride is added to methyl alcohol, a considerable development of heat occurs, and methyl chloride is formed,

$$CH_3\cdot OH + PCl_5 = CH_3Cl + HCl + POCl_3,$$
$$3CH_3\cdot OH + PCl_3 = 3CH_3Cl + H_3PO_3,*$$
$$3CH_3\cdot OH + POCl_3 = 3CH_3Cl + H_3PO_4.*$$

* These reactions only take place to a small extent; the principal products are esters of phosphorous or phosphoric acid,

$$3CH_3\cdot OH + PCl_3 = P(OCH_3)_3 + 3HCl$$
$$3CH_3\cdot OH + POCl_3 = PO(OCH_3)_3 + 3HCl.$$

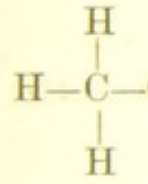
The corresponding bromides of phosphorus act in a similar manner.

Methyl alcohol is readily oxidised,* and is converted first into formaldehyde and then into formic acid,

$$CH_3{\cdot}OH + O = \underset{\text{Formaldehyde.}}{CH_2O} + H_2O \qquad CH_2O + O = \underset{\text{Formic Acid.}}{CH_2O_2}.$$

The presence of water in methyl alcohol may be detected by a sp. gr. determination; acetone is detected by means of the iodoform reaction (p. 99).

Constitution of Methyl Alcohol.—If the atoms in the molecule, CH_4O, have their usual valencies, the only structural formula which can be given to methyl alcohol is $CH_3{\cdot}OH$ or



A study of the method of formation and

* The substances frequently used for the oxidation of organic compounds in the wet way are:—*Nitric acid, chromic acid, potassium permanganate, manganese dioxide and sulphuric acid, chlorine water*, and *bromine water*. Nitric acid gives up some of its oxygen and is reduced to an oxide of nitrogen, the nature of which depends on that of the substance undergoing oxidation and on the conditions of the experiment,

$$2HNO_3 = H_2O + N_2O_3 + 2O \qquad 2HNO_3 = H_2O + 2NO_2 + O, \text{ \&c.}$$

Chromic acid, in the presence of sulphuric or acetic acid, gives oxygen and a chromic salt,

$$2CrO_3 = Cr_2O_3 + 3O, \text{ or } 2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O.$$

A mixture of potassium dichromate and sulphuric acid, which is very often used instead of chromic acid, yields oxygen and a solution of chromic sulphate and potassium sulphate, which may subsequently deposit purple octahedra of chrome-alum, K_2SO_4, $Cr_2(SO_4)_3$,$24H_2O$,

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

Potassium permanganate, in *alkaline* solution, is decomposed, yielding a precipitate of hydrated manganese dioxide,

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O;$$

but in *acid* solution the same quantity of permanganate gives five, instead of three, atoms of oxygen,

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O,$$

because manganese dioxide and sulphuric acid yield oxygen,

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

Chlorine and bromine, in presence of water, supply oxygen,

$$Cl_2 + H_2O = 2HCl + O.$$

of the chemical properties of methyl alcohol would lead equally conclusively to the adoption of this formula. Since only one of the four hydrogen atoms in methyl alcohol, CH_4O, is displaceable by potassium or sodium, it must be concluded that this particular hydrogen atom is in a different state of combination from the other three; but methyl alcohol is formed by the action of dilute alkalis on methyl chloride,

$$CH_3Cl + KOH = CH_3 \cdot OH + KCl,$$

and the three hydrogen atoms in methyl chloride, which are known to be combined with carbon, are not displaceable by metals. It is evident, therefore, that the displaceable hydrogen atom in methyl alcohol is not combined with carbon; the only other possibility is that it is combined with oxygen. The above formula also accounts for the fact that the oxygen atom cannot be displaced without one of the hydrogen atoms accompanying it; when the alcohol is treated with HCl, PCl_5, PBr_5, &c., the univalent hydroxyl-group is displaced by *one* atom of the univalent halogen. The relationship between methyl alcohol and the metallic hydroxides is also accounted for; the alcohol may be regarded as derived from water, H–O–H, by the substitution of the univalent CH_3– group for one atom of hydrogen, just as sodium hydroxide, Na–OH, is obtained by the substitution of one atom of sodium. Methyl alcohol, in fact, is *methyl hydroxide*, and, like other basic hydroxides, it forms salts and water when it is treated with acids (p. 179). Like water and certain metallic hydroxides, it contains displaceable hydrogen,

$$2CH_3 \cdot OH + 2Na = 2CH_3 \cdot ONa + H_2,$$
$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

It may also be considered as a hydroxy-substitution product of the paraffin, methane; it is termed a *monohydric* alcohol because it contains one hydroxyl-group.

Ethyl alcohol, alcohol, or *spirit of wine*, $C_2H_5 \cdot OH$, has been known from very early times, as it is contained in all

fermented liquors; it occurs in many plants in combination with organic acids.

It may be obtained from ethane by converting the hydrocarbon into ethyl chloride (p. 61) and heating the latter with dilute alkalis under pressure,

$$C_2H_5Cl + KOH = C_2H_5 \cdot OH + KCl;$$

also by passing ethylene into fuming sulphuric acid, and then boiling the solution of ethyl hydrogen sulphate with water,

$$C_2H_4 + H_2SO_4 = C_2H_5 \cdot HSO_4,$$
$$C_2H_5 \cdot HSO_4 + H_2O = C_2H_5 \cdot OH + H_2SO_4.$$

These reactions are of considerable theoretical importance, because both ethane and ethylene can be produced synthetically. Ethyl alcohol is also formed when acetaldehyde (p. 127) is reduced with sodium amalgam and water,

$$C_2H_4O + 2H = C_2H_6O.$$

Alcohol is prepared by placing a weak (5–10 per cent.) aqueous solution of cane- or grape-sugar in a capacious flask, adding a small quantity of brewer's yeast, and keeping the mixture in a warm place (at about 20°). The liquid soon begins to froth and ferment (p. 100), and if the flask is fitted with a cork and delivery tube it can be proved that carbon dioxide is being evolved. After about twenty-four hours' time the yeast is filtered off, and the solution is distilled from a flask (heated on a sand-bath) until about one-third has passed over. In this way the more volatile alcohol is partially separated from the water (fractional distillation). The distillate has a peculiar vinous smell, and consists of an aqueous solution of slightly impure alcohol. A considerable quantity of quicklime in the form of small lumps is slowly added to it, and after some hours the alcohol is distilled from a water-bath. By repeating this process several times, employing fresh caustic lime in sufficient quantity, alcohol containing only about 0·2 per cent. of water is obtained, but it is impossible to free it completely from water by distillation over lime. When the alcohol contains less than about 0·5

per cent. of water it is known commercially as *absolute* alcohol.

Any water contained in absolute alcohol may be removed with the aid of *calcium;* small pieces of the metal are left in contact with the liquid for several hours, and the alcohol is then distilled, the absorption of atmospheric moisture being prevented.

Wines, beers, and spirits contain alcohol, and its preparation from these liquids is a comparatively simple task. The liquid is distilled, and the alcohol, thus freed from colouring matter and other solid substances, is then dehydrated by distillation with quicklime; it still contains traces of volatile impurities.

Alcohol is a colourless, mobile liquid of sp. gr. 0·8062 at 0°; it has a pleasant vinous odour and a burning taste; it boils at 78°, but does not solidify until about −130° (hence its use in alcohol thermometers). It burns with a pale, non-luminous flame, and its vapour forms an explosive mixture with air or oxygen,

$$C_2H_5{\cdot}OH + 3O_2 = 2CO_2 + 3H_2O.$$

It mixes with water in all proportions with development of heat and diminution of volume; 52 vols. of alcohol and 48 vols. of water give a mixture occupying only 96·3 vols.

Ethyl alcohol closely resembles methyl alcohol in chemical properties. It is rapidly acted on by sodium and potassium, with evolution of hydrogen and formation of *ethoxides* or *ethylates*,

$$2C_2H_5{\cdot}OH + 2Na = 2C_2H_5{\cdot}ONa + H_2.$$

These compounds are readily soluble in alcohol, but may be obtained in a solid condition by evaporating the solution in a stream of hydrogen. They are colourless,* hygroscopic substances, which rapidly absorb carbon dioxide from the air, and are immediately decomposed by water, with regeneration of alcohol,

$$C_2H_5{\cdot}OK + H_2O = C_2H_5{\cdot}OH + KOH.$$

* Impure alcohol gives a yellow or brown solution of the ethoxide, because the impurities are decomposed and charred by the metal.

Although it has a neutral reaction, alcohol acts like a weak basic hydroxide, and when treated with acids it is converted into esters (or ethereal salts), with formation of water,

$$C_2H_5{\cdot}OH + HI = C_2H_5I + H_2O.$$

When treated with the chlorides or bromides of phosphorus, it gives ethyl chloride or ethyl bromide, an energetic action taking place (compare footnote, p. 94),

$$C_2H_5{\cdot}OH + PBr_5 = C_2H_5Br + HBr + POBr_3.$$

Alcohol is readily oxidised by chromic acid, yielding acetaldehyde, which on further oxidation is converted into acetic acid,

$$C_2H_5{\cdot}OH + O = \underset{\text{Acetaldehyde.}}{C_2H_4O} + H_2O \qquad C_2H_4O + O = \underset{\text{Acetic Acid.}}{C_2H_4O_2}.$$

In the presence of the ferment, *mycoderma aceti*, under certain conditions (p. 155), it is oxidised to acetic acid at ordinary temperatures by atmospheric oxygen.

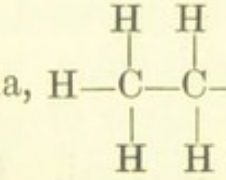
The presence of alcohol in dilute aqueous solution is very easily detected. (1) The solution is gently warmed with a little potassium dichromate and dilute sulphuric acid; if alcohol is present the highly characteristic odour of *acetaldehyde* is observed, and the dichromate is reduced. (2) The solution is gently warmed with a crystal of iodine, and a solution of potassium hydroxide is then added drop by drop until the colour of the iodine disappears. If alcohol is present, a yellow precipitate of *iodoform* is produced either immediately or after some time;* iodoform may be recognised by its odour and by the characteristic appearance under the microscope of its six-sided crystals. By means of the latter reaction (Lieben's iodoform reaction) it is possible to detect 1 part of alcohol in 2000 parts of water. The iodoform reaction is especially valuable as affording a means of distinguishing ethyl from methyl alcohol (or of testing for ethyl alcohol in a sample of methyl alcohol), as the latter does *not* give the iodoform reaction; but as many other substances,

* Iodoform is soluble in alcohol; if the solution is very rich in alcohol a precipitate may not be produced until after the addition of water.

such as acetone and aldehyde, give the reaction, the formation of iodoform is not a proof of the presence of ethyl alcohol.

The presence of water in alcohol may be detected, but not very easily if the proportion is small, by the following tests :— (1) A little anhydrous copper sulphate is added to the sample ; if water is present the colourless powder slowly turns blue, owing to the formation of the hydrated salt. (2) A large volume of light petroleum is added to the sample ; if water is present the mixture is turbid, owing to the separation of the water in very small drops.

The presence of water may also be detected, and its quantity may be estimated, by determining the sp. gr. of the sample (p. 105).

The *constitution* of ethyl alcohol has already been discussed (p. 52), and it has been shown that the methods of formation and the chemical behaviour of this compound can be accounted for very satisfactorily with the aid of the structural formula,  or $C_2H_5 \cdot OH$. Ethyl alcohol, like methyl alcohol, is a monohydroxy-substitution product of a paraffin ; the two compounds are similar in properties *because* they are similar in structure.

Production of Wine and Beer ; Alcoholic Fermentation.

When the juice of grapes is kept during a few days at ordinary temperatures, it changes into wine ; the sugars (p. 294), glucose and fructose, contained in the juice are decomposed into alcohol and carbon dioxide. This change is brought about by a small living vegetable organism (yeast), which is present on the grapes and their stalks and also in the air ; the process is called *fermentation*, and the living agent which causes the change is termed a *ferment*. All wines, beers, and spirits, and the whole of the alcohol of commerce, are prepared by a process of fermentation.

Yeast (*saccharomyces*) consists of rounded, almost transparent, living cells about 0·01 mm. in diameter, which are usually grouped together in chain-like clusters; when magnified (350 diameters), yeast cells have the appearance shown in figs. 21 and 22.* When placed in solutions of certain sugars containing small quantities of mineral and nitrogenous substances, which the organism requires for food, the cells soon begin to bud and multiply, provided also that the temperature is kept between about 5° and 30°; if it greatly

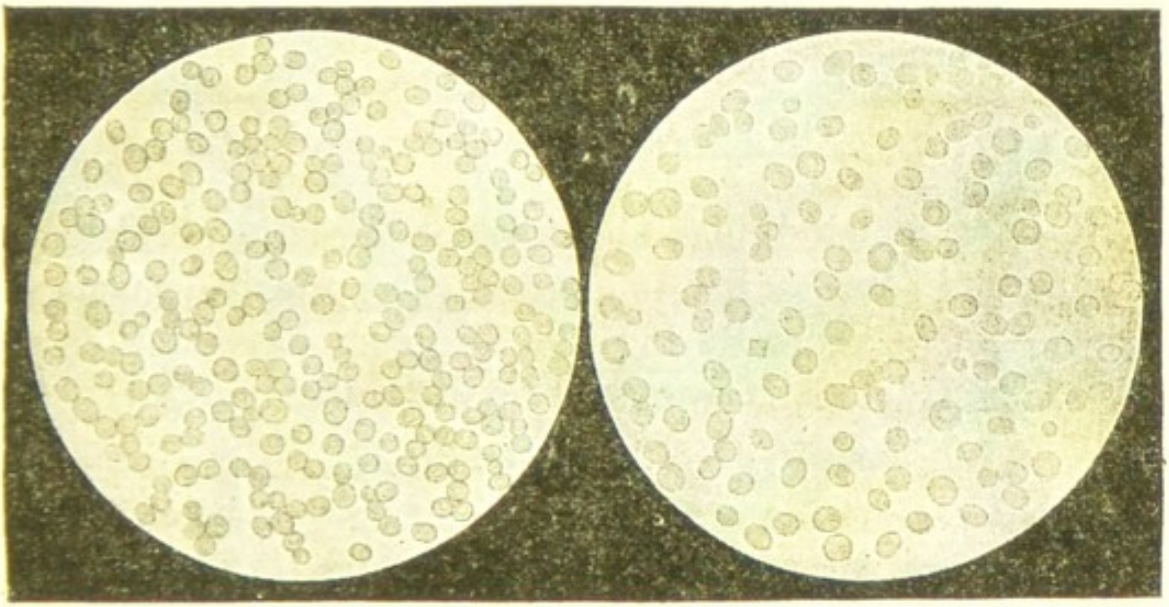


Fig. 21. Burton Yeast. Fig. 22. London Yeast.

exceeds these limits the plant stops growing, and may ultimately be killed. The action of yeast is due to certain *enzymes* which are contained in the cells, and fermentation can be brought about by the juice of the cells, in absence of the living organism. An enzyme is a lifeless, unorganised, amorphous, nitrogenous material of complex composition, which seems to act catalytically in bringing about a chemical change; as a rule, the action of a given enzyme is limited to one, or to a few, substances, and different enzymes produce different results. Enzymes are changed in some way at higher temperatures, and lose their activity.

* From *The Microscope in the Brewery.*

Enzymes, unlike inorganic catalysts, are gradually used up and disappear during the processes which they bring about. It would seem that some enzymes, previously believed to be distinct substances, are really mixtures of two components (named the enzyme and the co-enzyme respectively) which may differ very greatly in properties, and each of which plays a distinct part during the chemical change.

Yeast cells contain several enzymes. (1) *Zymase*, which brings about the alcoholic fermentation of glucose (grape-sugar) and fructose (fruit-sugar). (2) *Invertase*, which brings about the hydrolysis of sucrose (cane-sugar), and converts it into a mixture of glucose and fructose,

$$\underset{\text{Sucrose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

(3) *Maltase*, which brings about the hydrolysis of maltose (p. 305), and converts it into glucose. The principal chemical change, which occurs during the alcoholic fermentation of glucose and fructose, is expressed by the equation,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2;$$

but in the preparation of beer from malt, and of alcohol from grain, potatoes, &c. (see below), small quantities of fusel oil, glycerol, succinic acid, lactic acid, and other substances are also formed. *Fusel oil* is a variable mixture of the higher homologues of ethyl alcohol (pp. 110, 111).

The fusel oil, produced in the preparation of alcohol, is formed by the action of yeast on certain amino-acids, which are themselves decomposition products of the proteins of the malt or other vegetable matter (Part II. p. 558).

Beer is prepared from malt and hops. Malt is the grain of barley, which has been caused to sprout or germinate by being soaked in water and then kept in a moist atmosphere at a suitable temperature. During the process of germination an enzyme, *diastase*, is formed in the grain. The malt is now heated at 50–100° in order to stop germination and to cause the production of various substances which impart to it both colour and flavour, the character of the beer depending

largely on the temperature and the duration of heating. The malt is then stirred up with water and kept at 60–65°, when *diastatic fermentation* sets in, and the diastase converts the *starch* in the malt into *dextrin* and a sugar, *maltose*,

$$\underset{\text{Starch.}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}.*$$

The solution (*'wort'*) is now boiled in order to stop the diastatic fermentation, and hops, the flower of the hop-plant, are added in order to impart a slight bitter taste, and also on account of the preservative properties of the hops. The liquid is then cooled to from 5° to 20°, and *yeast* is added to it; the *maltase* in the yeast hydrolyses the maltose, and the *zymase* then sets up alcoholic fermentation. The beer is afterwards run off and kept until ready for consumption.

Beer usually contains 3–6 per cent. of alcohol, small quantities of dextrin, sugars, colouring matters, and other substances. It contains, moreover, carbon dioxide, to which it owes its refreshing taste, and small quantities of *fusel oil*, which help to give it a flavour.

Manufacture of Alcohol and Spirits.—Alcohol is prepared on the large scale from potatoes, grain, and various other substances rich in starch. The raw material is reduced to a pulp or paste with water, mixed with a little malt, and the mixture kept at about 55° for 30–60 minutes, when diastatic fermentation takes place, and the starch is converted into dextrin and maltose. The solution is cooled to about 15°, yeast is added, and the mixture is kept until alcoholic fermentation is at an end. Alcohol is also prepared from beetroot, molasses (treacle), and other substances rich in sugar, by direct fermentation with yeast.

It is possible to obtain alcohol from starch without the use of malt, since starch is converted into glucose when it is heated with dilute sulphuric acid, and the solution, having been neutralised with lime, can be fermented with yeast.

* Starch and dextrin have the same empirical formula, and their molecular formulæ are unknown (p. 309).

The weak solution of alcohol, obtained by any of these methods, is submitted to fractional distillation in various forms of 'stills.' The distillate is known as 'raw spirit,' and contains from 80–95 per cent. of alcohol, and a small quantity of fusel oil, which passes over in spite of the fact that its components boil at a higher temperature than does alcohol or water. If a stronger alcohol is required, the 'raw spirit' is again fractionated, or distilled over quicklime.

For the preparation of spirits, liqueurs, and other articles of consumption, the raw spirit must be freed as much as possible from fusel oil, which is very injurious to health. For this purpose it is diluted with water and filtered through charcoal, which absorbs some of the fusel oil. Finally, the spirit is again fractionally distilled, and the portions which pass over first ('first runnings') and last ('last runnings') are collected separately; the intermediate portions consist of 'refined' or 'rectified spirit,' most of the fusel oil, which has not been removed, being present in the last runnings.

Alcohol is used in large quantities for the manufacture of ether, chloroform, &c., and in the purification of the alkaloids. It is employed as a solvent for gums, resins, and other substances, in the preparation of tinctures, varnishes, perfumes, &c., and is also used in spirit-lamps. In this country a heavy excise duty has long been levied on spirit of wine, a fact which acted as a serious impediment to its extended use; but since 1856 the Government has permitted the manufacture and sale of methylated spirit free of duty, and more recently it has allowed the use of duty-free alcohol for scientific purposes.

Methylated spirit contains about 90 per cent. of raw spirit (aqueous ethyl alcohol), about 10 per cent. of partially purified wood-spirit or methyl alcohol, and a small quantity of paraffin-oil, the addition of which renders the alcohol unfit for drinking purposes, without greatly affecting its value as a solvent; methylated spirit, therefore, is often used instead of alcohol, as it is so much cheaper.

Methylated spirit cannot be completely separated into its com-

ponents by any commercial process, but the water and tarry impurities can be got rid of almost completely by distilling it with strong potash, and then dehydrating it over lime; the purified spirit may be employed in some chemical experiments in the place of pure ethyl alcohol, but the purification is troublesome and wasteful.

Alcoholometry.—In order to ascertain the strength of a sample of alcohol—that is, the percentage of alcohol in pure aqueous spirit—it is only necessary to determine the specific gravity of the sample at some particular temperature, and then to refer to published tables, in which the sp. gr. of any mixture of alcohol and water is given. If, for example, the sp. gr. is found to be 0·8605 at 15·5°, reference to the tables would show that the sample contained 75 per cent. of alcohol by weight.

For excise and general purposes, the sp. gr. is determined with the aid of hydrometers, graduated in such a manner that the percentage of alcohol can be read off directly on the scale. The standard referred to in this country is *proof-spirit*, which contains 49·3 per cent. by weight, or 57·1 per cent. by volume of alcohol; it is defined by Act of Parliament as being 'such a spirit as shall at a temperature of 51° F. weigh exactly $\frac{12}{13}$ths of an equal measure of distilled water.' Spirits are termed *under* or *over* proof according as they are weaker or stronger than proof-spirit: thus 20° over proof means that 100 vols. of this spirit, diluted with water, would yield 120 vols. of proof-spirit, whilst 20° under proof means that 100 vols. of the sample contain as much alcohol as 80 vols. of proof-spirit.

The name *proof-spirit* owes its origin to the ancient practice of testing the strengths of samples of alcohol by pouring them on to gunpowder and then igniting them. If the sample contained much water, the alcohol burnt away, and the water made the powder so damp that it did not ignite; but if the spirit was strong enough, the gunpowder took fire. A sample which ignited the powder was called proof-spirit.

For the *determination of alcohol* in beers, wines, and spirits,

a measured quantity of the sample is distilled from a flask connected with a condenser, until about one-third has passed over. The distillate, which contains the whole of the alcohol, is then diluted with water to the volume of the sample taken, and its sp. gr. is determined at the standard temperature; the percentage of alcohol is found by referring to the tables already mentioned. Distillation is necessary because the sugary and other extractive matters, contained in the sample, influence the sp. gr. to such an extent that a direct observation would be of no value.

The percentage of alcohol by weight in some of the better known fermented liquors varies greatly, but is roughly as follows:—

Brandy.....50%	Port.....20%	Claret.....7%
Whisky.....50%	Sherry.....16%	Burton Ale...5·5%
Gin.....40%	Hock..... 8%	Lager-beer.....3%

Radicles.—A study of the constitutions or structures of organic compounds clearly shows that certain groups of atoms often remain unchanged during a whole series of operations. Ethane, for example, may be converted into ethyl chloride, the latter may be transformed into ethyl alcohol, and this compound may be reconverted into ethyl chloride; but during all these interactions the group, C_2H_5–, remains unchanged, and behaves, in fact, as if it were a single atom,

$$C_2H_5\cdot H + Cl_2 = C_2H_5Cl + HCl,$$
$$C_2H_5\cdot Cl + H\cdot OH = C_2H_5\cdot OH + HCl,$$
$$C_2H_5\cdot OH + PCl_5 = C_2H_5\cdot Cl + HCl + POCl_3.$$

Numerous examples of a similar kind might be quoted; amongst others, the changes by which the compounds, $CH_3\cdot H$, $CH_3\cdot Cl$, $CH_3\cdot OH$, may be transformed one into the other.

Groups of atoms, such as CH_3– and C_2H_5–, which act like *single atoms*, and which *enter unchanged* into a number of compounds, are termed **radicles**, or sometimes, compound radicles.

Radicles may be univalent, bivalent, &c., according as

they act like univalent, bivalent, &c., atoms; the radicles C_2H_5- and CH_3-, for example, are univalent because they combine with one atom of hydrogen or its valency equivalent, as shown in the above equations.

The name, **alkyl** (or alcohol radicle), is given to all the *univalent* groups of atoms which, *theoretically*, are obtained when one atom of hydrogen is removed from the molecules of the paraffins, methane, ethane, propane, butane, &c.; the distinctive names of these radicles are derived from those of the hydrocarbons by changing the termination *ane* into *yl*, thus:—*methyl*, CH_3-; *ethyl*, C_2H_5- or $CH_3{\cdot}CH_2-$; *propyl*, C_3H_7- or $CH_3{\cdot}CH_2{\cdot}CH_2-$; *isopropyl*, C_3H_7- or $(CH_3)_2CH-$; *butyl*, C_4H_9- or $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2-$; *isobutyl*, C_4H_9- or $(CH_3)_2CH{\cdot}CH_2-$, &c.

The paraffins, the compounds formed by the combination of these *hypothetical* alkyl radicles with hydrogen—as, for example, $CH_3{\cdot}H$, $C_2H_5{\cdot}H$, $C_3H_7{\cdot}H$—are occasionally called the *alkyl hydrides;* the corresponding chlorine compounds, such as $CH_3{\cdot}Cl$, $C_2H_5{\cdot}Cl$, $C_3H_7{\cdot}Cl$, are termed the *alkyl chlorides*, and so on. The letter R is frequently employed to represent any alkyl radicle—as, for example, in the formula $R{\cdot}OH$, which is that of a monohydric alcohol. The symbols Me, Et, Pr, Bu, &c. are also often used instead of CH_3-, C_2H_5-, C_3H_7-, C_4H_9-, &c., and when the radicle may assume two isomeric forms—as, for example, in the case of C_3H_7-, which may be either $CH_3{\cdot}CH_2{\cdot}CH_2-$ or $(CH_3)_2CH-$, the former is represented by Pr^{α}, the latter by Pr^{β}.

The name, **alkylene**, is given to the hypothetical *bivalent* radicle *methylene*, $>CH_2$, which may be regarded as derived from methane; similarly, the olefines, although they are capable of existing alone, are often classed as alkylenes, and the compounds which they form, with chlorine for example, such as $CH_2{:}Cl_2$, $C_2H_4{:}Cl_2$, are termed collectively the *alkylene dichlorides*, &c.

Other radicles of great importance are:—hydroxyl $-OH$; carbonyl, $=CO$; carboxyl, $-CO{\cdot}OH$; cyanogen, $-CN$;

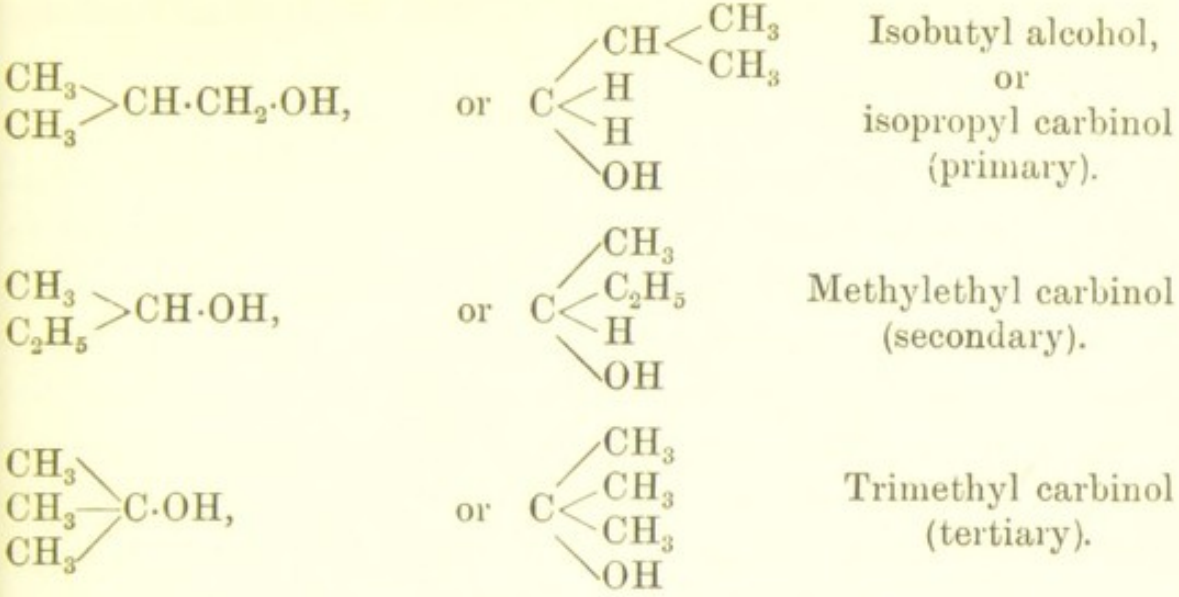
acetyl, $-CO\cdot CH_3$, and the aldehyde, $-CHO$, amino-, $-NH_2$, and nitro-, $-NO_2$, groups.

One of the principal objects which the student should keep in view is, to obtain a clear idea of the behaviour of these and of other groups, and to learn how they determine the properties of the molecules of which they form a part.

Homologues of Ethyl Alcohol.—All the members of the series of monohydric alcohols may be considered as derived from the paraffins by the substitution of the univalent HO– radicle for one atom of hydrogen. Except the first two members, they all show isomerism, and as two or more isomeric alcohols may be derived from one hydrocarbon, the number of isomeric alcohols is greater than that of the corresponding paraffins. There is, for example, only one hydrocarbon, C_3H_8 (propane); but two isomeric alcohols may be derived from it —namely, propyl alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot OH$, and isopropyl alcohol, $CH_3\cdot CH(OH)\cdot CH_3$.

In order to distinguish the various isomerides by names expressive of their structures, the alcohols may be considered as derivatives of methyl alcohol, $CH_3\cdot OH$, which for this particular purpose is called *carbinol*. Thus, propyl alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot OH$, may be termed ethyl carbinol, because it may be considered as derived from carbinol by the displacement of one atom of hydrogen by the ethyl group, C_2H_5-. Isopropyl alcohol, $(CH_3)_2CH\cdot OH$, may be called dimethyl carbinol, and regarded as derived from carbinol, by the substitution of two methyl or CH_3- groups for two atoms of hydrogen. Such names as these serve to express the *constitutions* of the substances, as will be seen by considering the case of the four isomeric butyl alcohols, $C_4H_9\cdot OH$,

$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, or $C\begin{cases} CH_2\cdot CH_2\cdot CH_3 \\ H \\ H \\ OH \end{cases}$ Normal butyl alcohol, or propyl carbinol (primary).



Three classes of monohydric alcohols are distinguished —namely, primary, secondary, and tertiary alcohols.

Primary alcohols—as, for example, normal * propyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$—contain the group, $-CH_2{\cdot}OH$, and may be considered as mono-substitution products of carbinol. On oxidation with chromic acid, &c., they are converted first into aldehydes (p. 123) and then into fatty acids (p. 149), the group, $-CH_2{\cdot}OH$ being transformed first into $-C\begin{matrix}H\\ \diagdown\!\!\diagup O\end{matrix}$ and then into $-C\begin{matrix}O-H\\ \diagdown\!\!\diagup O\end{matrix}$

$$CH_3{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CHO + H_2O,$$
$$CH_3{\cdot}CHO + O = CH_3{\cdot}CO{\cdot}OH.$$

These oxidation products contain the *same* number of carbon atoms in the molecule as the alcohols from which they are obtained.

Secondary alcohols—as, for example, isopropyl alcohol,† $CH_3{\cdot}CH(OH){\cdot}CH_3$—contain the group, $>CH{\cdot}OH$, and may be regarded as di-substitution products of carbinol. On oxidation they are converted into ketones (p. 134) which contain the *same* number of carbon atoms in the molecule as the alcohols

* The term '*normal*' is applied to those primary alcohols which are derived from normal paraffins (p. 65).

† The term '*iso*' is often applied to those *primary* (*or secondary*) alcohols the molecules of which contain the group $(CH_3)_2CH-$.

from which they are derived, the group, $>CH\cdot OH$, becoming $>CO$,

$$CH_3\cdot CH(OH)\cdot CH_3 + O = CH_3\cdot CO\cdot CH_3 + H_2O.$$

Tertiary alcohols, such as tertiary butyl alcohol, $(CH_3)_3C(OH)$, contain the group, $R_3C\cdot OH$, and may be regarded as tri-substitution products of carbinol. On oxidation they yield both ketones and fatty acids, which contain a *smaller* number of carbon atoms in their molecules than the alcohol from which they are derived, because the molecule of the latter is broken up. Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3C(OH)$, for example, yields acetone, $CH_3\cdot CO\cdot CH_3$, acetic acid, $CH_3\cdot CO\cdot OH$, carbon dioxide, and other products. It could not be converted by simple loss of hydrogen into a compound, $(CH_3)_3CO$, containing the same number of carbon atoms—a change which would be analogous to that undergone by primary and secondary alcohols—because carbon is quadrivalent and not quinquevalent, as represented in this formula.

Propyl alcohol (normal), $CH_3\cdot CH_2\cdot CH_2\cdot OH$, is one of the important components of fusel oil, from which it is prepared by fractional distillation. It is formed when propyl iodide is heated with freshly precipitated silver hydroxide and water,

$$C_3H_7I + Ag\cdot OH = C_3H_7\cdot OH + AgI.$$

It is a colourless liquid of sp. gr. 0·804 at 20°, boils at 97°, and is miscible with water in all proportions. On oxidation with chromic acid, it is converted first into propaldehyde and then into propionic acid,

$$CH_3\cdot CH_2\cdot CH_2\cdot OH + O = \underset{\text{Propaldehyde.}}{CH_3\cdot CH_2\cdot CHO} + H_2O,$$

$$CH_3\cdot CH_2\cdot CH_2\cdot OH + 2O = \underset{\text{Propionic acid.}}{CH_3\cdot CH_2\cdot CO\cdot OH} + H_2O.$$

Isopropyl alcohol, $(CH_3)_2CH\cdot OH$, may be prepared by the reduction of acetone with sodium amalgam and water,

$$CH_3\cdot CO\cdot CH_3 + 2H = CH_3\cdot CH(OH)\cdot CH_3.$$

It may also be produced by treating acetaldehyde with magnesium

methyl iodide, and decomposing the product with a dilute acid (p. 228).

It is a colourless liquid of sp. gr. 0·789 at 20°, and boils at 82°, or about 15° lower than normal propyl alcohol. On oxidation it yields acetone,

$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O,$$

and when heated with zinc chloride it gives propylene,

$$CH_3{\cdot}CH(OH){\cdot}CH_3 = CH_3{\cdot}CH{:}CH_2 + H_2O.$$

There are four isomeric **butyl alcohols**, $C_4H_9{\cdot}OH$. *Normal butyl alcohol*, or propyl carbinol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, may be prepared by the reduction of butaldehyde, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, and is produced during the fermentation of glycerol by certain bacteria. It boils at 117°.

Isobutyl alcohol, or isopropyl carbinol, $(CH_3)_2CH{\cdot}CH_2{\cdot}OH$, is contained in fusel oil. It boils at 107°.

Methylethyl carbinol, $CH_3{\cdot}CH(OH){\cdot}C_2H_5$, may be obtained by reducing methyl ethyl ketone, $CH_3{\cdot}CO{\cdot}C_2H_5$ (p. 134), with sodium amalgam and water, or by treating acetaldehyde with magnesium ethyl bromide, and then decomposing the product with an acid (p. 228). It boils at 101°.

Trimethyl carbinol, $(CH_3)_3C{\cdot}OH$, may be prepared from acetone with the aid of magnesium methyl iodide, a reaction which is described later (p. 228). It may also be obtained from isobutyl alcohol (p. 114). Trimethyl carbinol is one of the few alcohols of low molecular weight which are solid at ordinary temperatures. It melts at 25°, and boils at 83–84°.

Amyl alcohols, $C_5H_{11}{\cdot}OH$.—Of the eight structural isomerides theoretically capable of existing, the following two occur in fusel oil :—

Isobutyl carbinol, (Isoamyl alcohol.) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. B.p. 131°.

Active amyl alcohol, $\begin{matrix}CH_3\\CH_3{\cdot}CH_2\end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}OH$. B.p. 129°.

These alcohols form ordinary commercial amyl alcohol, and their boiling-points lie so close together that they cannot be separated by fractional distillation. A separation, however, may be accomplished by treating the mixture with sulphuric acid, and thus converting both alcohols into alkyl hydrogen sulphates,

$$C_5H_{11}{\cdot}OH + H_2SO_4 = C_5H_{11}{\cdot}HSO_4 + H_2O.$$

By neutralising these compounds with barium hydroxide, the barium salts, $(C_5H_{11}\cdot SO_4)_2Ba$, are obtained, and, as the barium salt of the isobutyl compound is more sparingly soluble than that of the isomeride, the two may be separated by fractional crystallisation. From the pure salts the respective alcohols are then obtained in a pure condition by distillation with dilute mineral acids,

$$C_5H_{11}\cdot HSO_4 + H_2O = C_5H_{11}\cdot OH + H_2SO_4.$$

Commercial amyl alcohol is prepared from fusel oil by fractionation, and is a mixture of about 87 per cent. of isobutyl carbinol and about 13 per cent. of active amyl alcohol. It has a pungent, unpleasant smell, boils at about 130°, and is used as a solvent and in the preparation of essences and perfumes (p. 197).

SUMMARY AND EXTENSION.

The Monohydric Alcohols. Hydroxy-derivatives of the paraffins of the general formula, $C_nH_{2n+1}\cdot OH$ or R·OH.—The more important members of the series are the following. The letters p., s., t., in brackets, denote primary, secondary, and tertiary respectively.

Name and Composition.		B.p.	Sp. gr.
Methyl alcohol (p.).....	$CH_3\cdot OH$,	66°	0·812 at 0°
Ethyl alcohol (p.).....	$C_2H_5\cdot OH$,	78°	0·806 "
Propyl alcohol (p.).....	$C_3H_7\cdot OH$,	97°	0·817 "
Isopropyl alcohol (s.).....		82°	0·816 "
Butyl alcohol (p.).....	$C_4H_9\cdot OH$,	117°	0·823 "
Isobutyl alcohol (p.).....		107°	0·816 "
Methylethyl carbinol (s.)..		101°	0·827 at 20°
Trimethyl carbinol (t.).....		83°	0·786 "
Active amyl alcohol (p.) .	$C_5H_{11}\cdot OH$,	129°	— "
Isoamyl alcohol (p.).....		131°	0·825 "
Six other isomerides of little importance.....			

Special Methods of Preparation.—Methyl alcohol is prepared from the products of the dry distillation of wood. Ethyl alcohol is obtained by the alcoholic fermentation of sugars by means of yeast; the fusel oil produced at the same time contains propyl, isobutyl, isoamyl, and active amyl alcohols.

General Methods of Preparation.—(1) The alkyl halogen compounds are heated with water, dilute aqueous alkalis, or moist, freshly precipitated silver hydroxide,

$$CH_3Br + KOH = CH_3\cdot OH + KBr \qquad C_3H_7I + Ag\cdot OH = C_3H_7\cdot OH + AgI.$$

(2) The alkyl halogen compounds are heated with silver, or potassium, acetate, and the products are hydrolysed,

$$C_2H_5I + C_2H_3O_2Ag = C_2H_5 \cdot C_2H_3O_2 + AgI$$

Silver Acetate. Ethyl Acetate.

$$C_2H_5 \cdot C_2H_3O_2 + KOH = C_2H_5 \cdot OH + C_2H_3O_2K.$$

This method gives very good results, and is much used in the preparation of the higher alcohols, because the halogen derivatives of the higher paraffins (such as hexyl chloride, $C_6H_{13}Cl$), when treated directly with alkalis, are mainly converted into olefines,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl + KOH =$$
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH : CH_2 + KCl + H_2O,$$

and the yield of alcohol is small.

(3) The hydrocarbons of the olefine series are dissolved in sulphuric acid, and the solutions are boiled with water,

$$C_3H_6 + H_2SO_4 = C_3H_7 \cdot HSO_4$$
$$C_3H_7 \cdot HSO_4 + H_2O = C_3H_7 \cdot OH + H_2SO_4.$$

(4) Aldehydes and ketones are reduced with nascent hydrogen, aldehydes giving primary, ketones secondary, alcohols,

$$CH_3 \cdot CH_2 \cdot CHO + 2H = CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$$
$$CH_3 \cdot CO \cdot CH_3 + 2H = CH_3 \cdot CH(OH) \cdot CH_3.$$

(5) Aldehydes, ketones, and esters are treated with a Grignard reagent (p. 226), and the products are decomposed with a mineral acid; in this way secondary alcohols are obtained from aldehydes, tertiary alcohols from ketones and esters. These reactions are more fully considered later (p. 228).

Conversion of Primary into Secondary and Tertiary Alcohols.— A secondary alcohol may be prepared from the corresponding primary compound by first converting the latter into an olefine (p. 72),

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH = CH_3 \cdot CH : CH_2 + H_2O.$$

The olefine is then dissolved in fuming sulphuric acid, when an alkyl hydrogen sulphate is formed, the SO_4H– group uniting with that carbon atom which is combined with the least number of hydrogen atoms,

$$CH_3 \cdot CH : CH_2 + H_2SO_4 = \begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot SO_4H.$$

The alkyl hydrogen sulphate is finally converted into a secondary alcohol by boiling it with water,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot SO_4H + H_2O = \begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot OH + H_2SO_4.$$

In a similar manner, a primary alcohol, such as isobutyl alcohol, may be converted into the tertiary alcohol, trimethyl carbinol,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\cdot CH_2\cdot OH \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CH_2$$

$$\rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_3\\SO_4H\end{matrix} \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_3\\OH\end{matrix}$$

Physical Properties.—Most of the members up to $C_{12}H_{25}O$ are colourless liquids at ordinary temperatures; all the higher alcohols, such as cetyl alcohol, $C_{16}H_{33}\cdot OH$, which occurs in spermaceti in combination with palmitic acid, and melissyl alcohol, $C_{30}H_{61}\cdot OH$, which is found in beeswax, also in combination with palmitic acid, are solids. Trimethyl carbinol is also a solid. Methyl, ethyl, and the propyl alcohols are miscible with water, but as the series is ascended the solubility in water rapidly decreases; the amyl alcohols, for example, are only sparingly soluble. The alcohols are miscible in all proportions with most organic liquids.

The sp. gr. increases and the boiling-point rises as the molecular weight increases; *but* as a primary alcohol boils at a higher temperature than the corresponding secondary alcohol, and the latter at a higher temperature than the tertiary isomeride (as shown in the table, p. 112), the regular variation in this, and in other physical properties, is obvious only when alcohols of *similar constitution* are compared. It may also be pointed out that, as a rule, the first member of a homologous series shows a somewhat abnormal behaviour; methyl alcohol, for example, has a *higher* sp. gr. than ethyl alcohol, and its boiling-point is only 12° lower than that of ethyl alcohol; in the case of the higher homologues, the difference between the boiling-points of two consecutive *normal* alcohols is about 20°.

A comparison of the properties of an alcohol with those of the paraffin from which it is derived shows that the substitution of the hydroxyl-group for an atom of hydrogen in the molecule not only raises the boiling-point very considerably, but also greatly increases the solubility in water; as, however, the hydrocarbon radicle, R, in the alcohol, R·OH, increases in molecular weight, the influence of the hydroxyl-group on the physical properties diminishes.

Chemical Properties.—The fact that the alcohols react with other compounds so much more readily than the paraffins is due to the presence of the hydroxyl-group in their molecules; it is this group only which is changed in many of their general reactions.

The alcohols are acted on by sodium and potassium, with evolution of hydrogen,

$$2C_3H_7\cdot OH + 2Na = 2C_3H_7\cdot ONa + H_2.$$

They react with acids, forming esters, such as CH_3Cl, C_2H_5Br, $C_3H_7{\cdot}HSO_4$, $CH_3{\cdot}COOC_2H_5$.

They are converted into halogen-derivatives of the paraffins when they were treated with PCl_5, PCl_3, $POCl_3$ (compare footnote p. 94), or with the corresponding bromo-derivatives, or with red phosphorus and iodine,

$$PCl_5 + C_3H_7{\cdot}OH = C_3H_7Cl + POCl_3 + HCl.$$

They are converted into olefines by sulphuric and by phosphoric acid,

$$CH_3{\cdot}CH_2{\cdot}OH = CH_2{:}CH_2 + H_2O.$$

The action of oxidising agents varies with the nature of the alcohol. Primary alcohols are converted into aldehydes, and then into fatty acids, secondary alcohols into ketones, and in both cases the oxidation product contains the same number of carbon atoms in the molecule as the alcohol from which it is formed,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH + O = CH_3{\cdot}CH_2{\cdot}CHO + H_2O$$
$$CH_3{\cdot}CH(OH){\cdot}CH_3 + O = CH_3{\cdot}CO{\cdot}CH_3 + H_2O.$$

Tertiary alcohols undergo a more profound change and are decomposed, giving a mixture of simpler acids, or of acid and ketone. The three classes of alcohols, therefore, can be *distinguished* by their different behaviour on oxidation.

CHAPTER VII.

The Ethers.

The ethers, such as dimethyl ether, $CH_3{\cdot}O{\cdot}CH_3$, methyl ethyl ether, $CH_3{\cdot}O{\cdot}C_2H_5$, &c., are substances of the type, R–O–R, and they contain two identical, or different, alkyl groups (p. 107), such as CH_3–, C_2H_5–, and C_3H_7–, united to an oxygen atom. They may be regarded as the oxides of the hydrocarbon radicles.

Methyl ether (dimethyl ether), $CH_3{\cdot}O{\cdot}CH_3$, may be prepared by the action of sulphuric acid on methyl alcohol; the reaction takes place in two stages as described below.

It is a gas which liquefies at $-23°$ (760 mm.), and dissolves readily in water (1 vol. of water dissolves 37 vols. of the ether at 18°).

Ethyl ether, diethyl ether, ether, or sulphuric ether,

$C_2H_5{\cdot}O{\cdot}C_2H_5$, is formed, together with sodium iodide, when sodium ethoxide is warmed with ethyl iodide (Williamson),

$$C_2H_5{\cdot}ONa + C_2H_5I = C_2H_5{\cdot}O{\cdot}C_2H_5 + NaI.$$

It is prepared by heating ethyl alcohol with sulphuric acid under suitable conditions.

Ethyl alcohol (5 parts by weight)* and concentrated sulphuric acid (9 parts) are *cautiously* mixed, and the mixture is heated in a

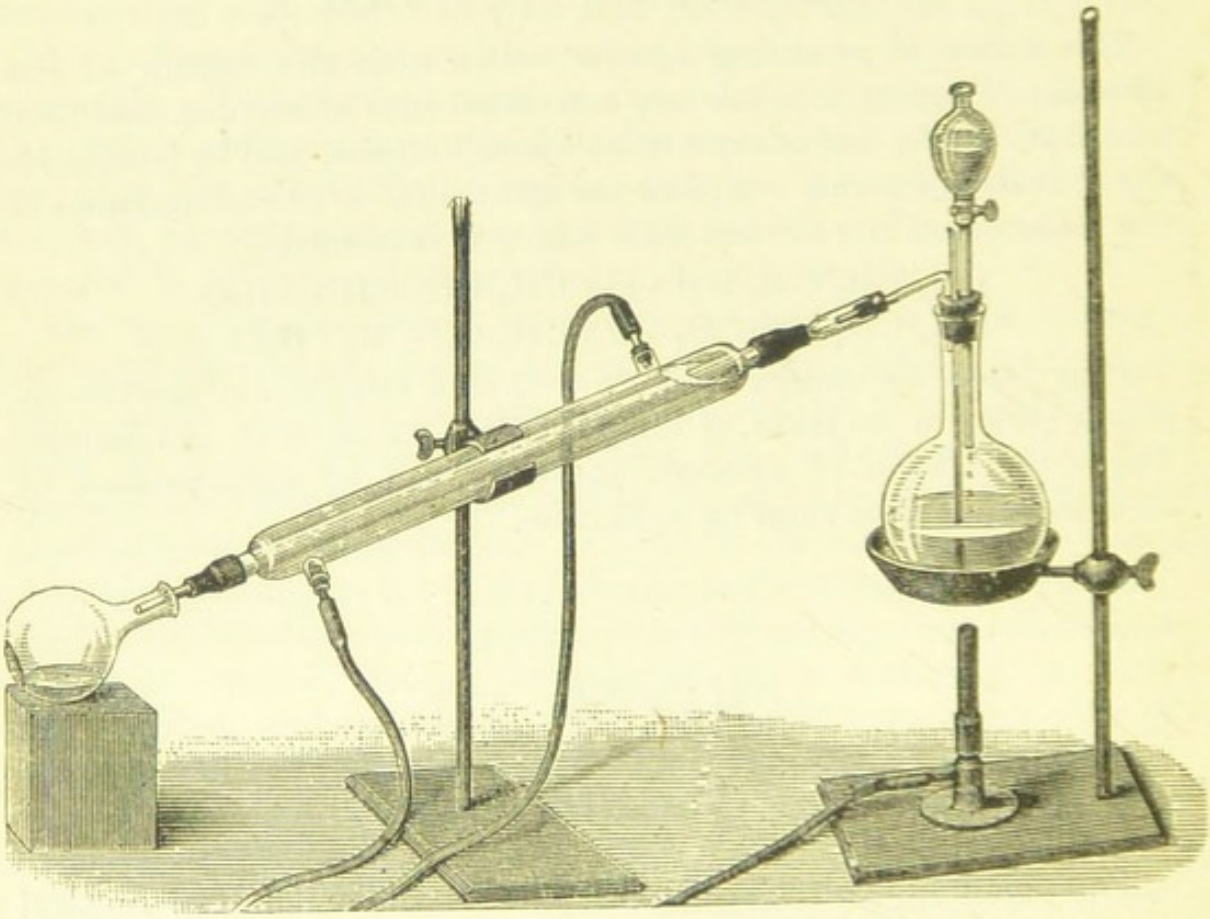


Fig. 23.

flask fitted with a tap-funnel and thermometer, and connected with a condenser (fig. 23). As soon as the temperature of the liquid rises to 140°, ether begins to distil over.† Alcohol is now dropped from the tap-funnel at about the same rate as that at which the ether distils over, and the temperature is kept at 140-145°; the

* The alcohol should not contain more than about 10 per cent. of water.

† The bulb of the thermometer is immersed in the *liquid*. It is advisable to cool the receiver with ice in warm weather, and great care should be taken to condense the vapour efficiently, otherwise it may catch fire (compare p. 118).

process is continued until a sufficient quantity of ether has collected. The crude product in the receiver is a mixture of ether, alcohol, and water, and may also contain sulphur dioxide. It is shaken with dilute soda in a separating-funnel, and the aqueous solution is run off; the ether is then dried over calcium chloride or quicklime, and purified by redistillation from a water-bath. The ether still contains traces of water and alcohol, to remove which bright pieces of sodium are added, and the ether is left in contact with the metal (in a flask closed with a calcium chloride tube) until the evolution of hydrogen ceases. The ether is finally distilled from the sodium ethoxide and sodium hydroxide, which have been produced.

The formation of ether from alcohol takes place in two stages. When alcohol is heated with sulphuric acid, it is converted into ethyl hydrogen sulphate (p. 191),

$$C_2H_5{\cdot}OH + H_2SO_4 = C_2H_5{\cdot}HSO_4 + H_2O;$$

this compound then reacts with alcohol, yielding ether and sulphuric acid,

$$C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2SO_4.$$

This explanation of the formation of ether was first given by Williamson; that it is the true one is shown by the fact that ether is formed when pure ethyl hydrogen sulphate is heated with alcohol.

Now, since the sulphuric acid necessary for the conversion of the alcohol into ethyl hydrogen sulphate is regenerated when the latter is heated with alcohol, a given quantity of the acid might, theoretically, convert an unlimited quantity of alcohol into ether. As a matter of fact, a small quantity of sulphuric acid can transform a very large quantity of alcohol into ether; but the process has a limit, because the acid becomes *diluted* by the water formed in the first stage of the reaction, and part of it is *reduced* by the alcohol, with formation of sulphur dioxide. Nevertheless, as this method of preparing ether by the *continuous* addition of alcohol to a solution of alcohol in sulphuric acid is practicable within limits, it is termed the *continuous process.**

* In presence of anhydrous aluminium sulphate the reactions take place rapidly at about 135°. If, instead of sulphuric acid, benzenesulphonic acid

Ether is a colourless, mobile, neutral, pleasant-smelling liquid of sp. gr. 0·736 at 0°. It boils at 35°, and does not solidify at −80°. It is very volatile, and *highly inflammable*, and as its vapour forms an explosive mixture with air or oxygen,

$$C_4H_{10}O + 6O_2 = 4CO_2 + 5H_2O,$$

all experiments in which ether is used should be conducted at least ten feet away from all flames or hot objects. Ether is soluble in about ten times its own volume of water, and is miscible with alcohol and other organic liquids in all proportions.

Compared with alcohol, ether is a very inactive substance. It is not acted on by sodium or potassium, by alkalis or weak acids, or by phosphorus pentachloride in the cold. Concentrated acids, however, decompose ether, with formation of esters (p. 179),

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5\cdot HSO_4 + H_2O,$$
$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Ether is used in considerable quantities in surgery as an anæsthetic, since, like chloroform, it causes insensibility when inhaled; it is also very largely employed as a solvent for resins, fats, oils, alkaloids, &c.

Constitution of Ether.—Since ether is produced by the action of ethyl iodide, C_2H_5I, on sodium ethoxide, $C_2H_5\cdot ONa$, it may be concluded that it is formed by the substitution of the univalent C_2H_5- group for the sodium atom, and its constitution may be expressed by the formula, $C_2H_5\cdot O\cdot C_2H_5$. This view is confirmed by a study of the chemical properties

(Part II. p. 430) is used (Krafft), the process is really continuous, as this acid is not reduced by the alcohol, and the water which is produced is not retained by the acid, but distils over with the ether,

$$C_6H_5\cdot SO_2\cdot OH + C_2H_5\cdot OH = C_6H_5\cdot SO_2\cdot OC_2H_5 + H_2O$$
$$C_6H_5\cdot SO_2\cdot OC_2H_5 + C_2H_5\cdot OH = C_2H_5\cdot O\cdot C_2H_5 + C_6H_5\cdot SO_2\cdot OH.$$

Ether may also be prepared by passing the vapour of ethyl alcohol through copper tubes containing alumina (precipitated), which is heated at about 260°; the alumina acts catalytically and the alcohol is converted into ether and water, but at higher temperatures ethylene is also formed.

of ether; its molecule, unlike that of alcohol, does not contain a hydroxyl-group, and therefore it is not acted on by sodium or potassium, or by phosphorus pentachloride.

Ether was formerly regarded as an *anhydride* of alcohol and as being formed from alcohol (2 mols.) by the removal of the elements of water, just as nitric anhydride is formed from nitric acid,

$2C_2H_5{\cdot}OH = (C_2H_5)_2O + H_2O$ $\quad$ $2NO_2{\cdot}OH = (NO_2)_2O + H_2O.$

It is better compared with the metallic oxides, and regarded as *ethyl oxide*, since its relationship to alcohol or ethyl hydroxide is similar to that of the metallic oxides to the metallic hydroxides,

$C_2H_5{\cdot}OH$	$C_2H_5{\cdot}O{\cdot}C_2H_5$	or	$(C_2H_5)_2O$
$Na{\cdot}OH$	$Na{\cdot}O{\cdot}Na$	or	$Na_2O.$

Finally, it may be regarded as a di-substitution product of water, the mono-substitution product being the corresponding alcohol,

$H{\cdot}O{\cdot}H$ $\quad$ $C_2H_5{\cdot}O{\cdot}H$ $\quad$ $C_2H_5{\cdot}O{\cdot}C_2H_5.$

The *homologues* of ether are very similar to diethyl ether in properties.

MERCAPTANS AND SULPHIDES.

There are two classes of organic compounds derived from hydrogen sulphide—namely, the hydrosulphides and the sulphides, and the relation between them is similar to that between the alcohols and the ethers (or the metallic hydrosulphides and the sulphides),

Ethyl hydrosulphide,	$C_2H_5{\cdot}SH$	Ethyl sulphide,	$(C_2H_5)_2S$
Ethyl hydroxide,	$C_2H_5{\cdot}OH$	Ethyl oxide,	$(C_2H_5)_2O.$

The organic hydrosulphides are usually called **mercaptans** (*mercurium captans*) on account of their property of combining readily with mercuric oxide to form crystalline compounds; they may be regarded as *sulphur-* or *thio-alcohols*, and the organic sulphides, as *thio-ethers*.

Ethyl mercaptan, $C_2H_5 \cdot SH$, may be obtained by treating alcohol with phosphorus pentasulphide,

$$5C_2H_5 \cdot OH + P_2S_5 = 5C_2H_5 \cdot SH + P_2O_5;$$

it is prepared by distilling a concentrated solution of ethyl potassium sulphate with potassium hydrosulphide,

$$C_2H_5 \cdot KSO_4 + KSH = C_2H_5 \cdot SH + K_2SO_4,$$

or by the interaction of ethyl chloride and potassium hydrosulphide. It is a colourless liquid, has a most offensive smell, and boils at 36°. The hydrogen atom in the HS– group is displaceable by metals more readily than that in the HO– group of the alcohols; when ethyl mercaptan is treated with sodium or potassium, it yields *sodium* or *potassium mercaptide*, $C_2H_5 \cdot SNa$, or $C_2H_5 \cdot SK$, with evolution of hydrogen; when shaken with mercuric oxide it yields *mercuric mercaptide*,

$$2C_2H_5 \cdot SH + HgO = (C_2H_5 \cdot S)_2Hg + H_2O,$$

a crystalline compound, which is decomposed by hydrogen sulphide, giving ethyl mercaptan,

$$(C_2H_5 \cdot S)_2Hg + SH_2 = 2C_2H_5 \cdot SH + HgS.$$

Other mercaptans can be obtained by similar reactions; they are characterised by having a highly unpleasant, garlic-like smell, and in chemical properties they resemble ethyl mercaptan; on oxidation with nitric acid they are converted into *sulphonic acids*,

$$C_2H_5 \cdot SH + 3O = C_2H_5 \cdot SO_2 \cdot OH.$$

Ethylsulphonic Acid.

Sulphonic acids contain the group $-SO_2 \cdot OH$, the alkyl-group being attached to the sulphur atom; they are powerful acids, forming salts, such as potassium ethylsulphonate, $C_2H_5 \cdot SO_2 \cdot OK$.

Ethyl sulphide, $(C_2H_5)_2S$, may be obtained by heating ether with phosphorus pentasulphide,

$$5(C_2H_5)_2O + P_2S_5 = 5(C_2H_5)_2S + P_2O_5,$$

and by distilling a concentrated aqueous solution of ethyl potassium sulphate with potassium sulphide,

$$2C_2H_5 \cdot KSO_4 + K_2S = (C_2H_5)_2S + 2K_2SO_4.$$

It is a colourless, neutral, unpleasant-smelling liquid, and

boils at 91°; like the ethers, it does not contain hydrogen displaceable by metals, and is a comparatively inert substance.

Other sulphides can be obtained by similar methods, and have similar properties; on oxidation with nitric acid, they are finally converted into very stable crystalline compounds termed *sulphones*, of which *ethyl sulphone*, $(C_2H_5)_2SO_2$, is an example.

Sulphonal, $(CH_3)_2C(SO_2 \cdot C_2H_5)_2$, is an important and interesting compound, first prepared by Baumann, and largely used as a soporific. Although acetone and other ketones do not react readily with alcohols, giving acetals, as do aldehydes (p. 148), they *condense* with mercaptans in presence of hydrogen chloride; acetone and ethyl mercaptan, for example, give *acetone mercaptole* (b.p. 190–191°),

$$(CH_3)_2CO + 2C_2H_5 \cdot SH = (CH_3)_2C(S \cdot C_2H_5)_2 + H_2O.$$

When this mercaptole is oxidised with potassium permanganate, it unites directly with four atoms of oxygen (the bivalent sulphur atom becoming quadri- or sexvalent), giving sulphonal, a crystalline compound melting at 126°.

SUMMARY AND EXTENSION.

Some of the more important higher ethers are the following :—

Dipropyl ether $(CH_3 \cdot CH_2 \cdot CH_2)_2O$ ..... B.p. 90·7°

Di-isopropyl ether $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\right)_2O$ ..... " 69°

Di-isobutyl ether $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH \cdot CH_2\right)_2O$ ..... " 122°

Di-isoamyl ether $(C_5H_{11})_2O$ ..... " 173°

General Methods of Formation.—(1) The sodium compounds of the alcohols are heated with the alkyl halogen compounds,

$$CH_3 \cdot ONa + CH_3I = CH_3 \cdot O \cdot CH_3 + NaI.$$

(2) The alkyl halogen compounds are heated with silver oxide,

$$2C_3H_7I + Ag_2O = (C_3H_7)_2O + 2AgI.$$

(3) The alcohols are heated with sulphuric acid; this method is applicable only in the case of the lower alcohols, and, as a rule, it is further restricted to primary alcohols; secondary alcohols generally, and tertiary alcohols always, give olefines.

When a mixture of two alcohols is treated with sulphuric acid, *three* ethers are formed. A mixture of methyl and ethyl alcohols, for example, yields *methyl ether*, *ethyl ether*, and *methyl ethyl ether*, $CH_3 \cdot O \cdot C_2H_5$. The formation of the first two compounds will be

understood from the equations given above in the case of ethyl ether. Methyl ethyl ether is produced by the interaction (*a*) of methyl hydrogen sulphate and ethyl alcohol, (*b*) of ethyl hydrogen sulphate and methyl alcohol,

$$CH_3 \cdot HSO_4 + C_2H_5 \cdot OH = CH_3 \cdot O \cdot C_2H_5 + H_2SO_4$$
$$C_2H_5 \cdot HSO_4 + CH_3 \cdot OH = C_2H_5 \cdot O \cdot CH_3 + H_2SO_4.$$

All ethers, such as methyl ethyl ether, $CH_3 \cdot O \cdot C_2H_5$, which contain two *different* hydrocarbon groups are termed *mixed ethers*, to distinguish them from *simple ethers*, such as ethyl ether, $C_2H_5 \cdot O \cdot C_2H_5$, and those given in the above table, which contain two identical radicles. Mixed ethers can also be obtained by treating the sodium compounds of the alcohols with alkyl halogen compounds,

$$CH_3 \cdot ONa + C_3H_7I = CH_3 \cdot O \cdot C_3H_7 + NaI.$$

General Properties.—With the exception of methyl ether, which is a gas, the ethers are mobile, volatile, inflammable liquids, specifically lighter than water; they boil at much lower temperatures than the corresponding alcohols. In chemical properties they closely resemble ethyl ether. They are not acted on by alkalis or alkali metals, and do not react with dilute acids, but they are decomposed when heated with strong acids, yielding esters,

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5 \cdot HSO_4 + H_2O$$
$$CH_3 \cdot O \cdot C_2H_5 + 2HBr = CH_3Br + C_2H_5Br + H_2O.$$

Chlorine and bromine act on ethers, forming substitution products, such as

$$CH_2Cl \cdot O \cdot CH_3,\ CH_2Br \cdot O \cdot CH_2Br,\ C_2H_5 \cdot O \cdot C_2H_4Cl,\ \&c.$$

The ethers exist in isomeric forms. There are, for example, three ethers of the formula, $C_4H_{10}O$,

$CH_3 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH_3$	$CH_3 \cdot O \cdot CH\begin{matrix}<^{CH_3}_{CH_3}\end{matrix}$	$CH_3 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_3$.
Methyl Propyl Ether.	Methyl Isopropyl Ether.	Ethyl Ether.

These three ethers are also isomeric with the four butyl alcohols $C_4H_9 \cdot OH$ (p. 111).

CHAPTER VIII.

Aldehydes and Ketones.

The *aldehydes* form a homologous series of the general formula, $C_nH_{2n}O$, or R·CHO; they are derived from the primary alcohols, R·CH_2·OH, by the loss of two atoms of hydrogen from the –CH_2·OH group,

Paraffins.	Alcohols.	Aldehydes.
H·CH_3	H·CH_2·OH	H·CHO
CH_3·CH_3	CH_3·CH_2·OH	CH_3·CHO
C_2H_5·CH_3	C_2H_5·CH_2·OH	C_2H_5·CHO

The word aldehyde is a contraction of *al*cohol *dehyd*rogenatum, a name originally given to acetaldehyde, because it is formed when hydrogen is taken from alcohol by a process of oxidation.

Formaldehyde, H·CHO (methaldehyde), is said to occur in those plant cells which contain the green colouring matter chlorophyll, and is possibly an intermediate product in that wonderful process—the formation of starch and sugars from the carbon dioxide which the plant absorbs from the air.

Formaldehyde is produced when carbon dioxide is reduced, in aqueous solution, with palladium hydride,* and it is also formed in small quantities when calcium formate is subjected to dry distillation,

$$(H\cdot COO)_2Ca = H\cdot CHO + CaCO_3.$$

It is prepared by passing a stream of air, saturated with the vapour of methyl alcohol, through a tube containing a copper spiral, or platinised asbestos, heated to dull redness;† the change is a process of oxidation,

$$2CH_3\cdot OH + O_2 = 2H\cdot CHO + 2H_2O.$$

The pungent-smelling aqueous solution which collects in the

* The substance obtained when hydrogen is passed over warm palladium.

† Unless special precautions are taken, explosions frequently occur.

receiver may contain, under favourable conditions, as much as 30–40 per cent. of formaldehyde, together with methyl alcohol; when the solution is evaporated, even at ordinary temperatures, the formaldehyde gradually undergoes change, and is converted into *paraformaldehyde* (p. 125), which remains as a white solid.

The formation of formaldehyde may be readily demonstrated by heating a spiral of platinum wire to dull redness and quickly suspending it over methyl alcohol contained in a beaker; the spiral begins to glow, irritating vapours are rapidly evolved, and a slight but harmless explosion often takes place.

Formaldehyde is a gas at ordinary temperatures, but it may be condensed to a liquid, boiling at $-21°$. Even at this low temperature it slowly changes into *trioxymethylene* (p. 125), and at ordinary temperatures it does so with great rapidity, and with a considerable development of heat. Aqueous solutions of formaldehyde have a very penetrating, suffocating odour, and a neutral reaction; they have also a powerful reducing action, since formaldehyde readily undergoes oxidation, yielding formic acid,

$$H{\cdot}CHO + O = H{\cdot}CO{\cdot}OH.$$

Thus an aqueous solution of formaldehyde reduces an ammoniacal solution of silver oxide, and silver is deposited,

$$H{\cdot}CHO + Ag_2O = H{\cdot}CO{\cdot}OH + 2Ag;$$

mercuric chloride is also reduced, first to mercurous chloride, then to mercury.

Formaldehyde is a strong antiseptic, and is fatal to bacteria of various kinds; an aqueous solution containing about 40 per cent. of formaldehyde (or of its hydrates) is sold under the name of *formalin*, and is an important article of commerce. Formalin is used as a reducing agent and as an antiseptic and disinfectant; also as a preservative for biological and anatomical specimens, which it hardens without increasing their opacity. Gelatin, a substance

readily soluble in water, becomes insoluble when it is treated with formalin.

When a concentrated aqueous solution of formaldehyde is mixed with a saturated solution of sodium hydrogen sulphite, direct combination takes place, and a compound of the constitution, $OH \cdot CH_2 \cdot SO_3Na$ is formed. Formaldehyde interacts with hydroxylamine in aqueous solution, yielding *formaldoxime*,

$$H \cdot CHO + NH_2 \cdot OH = H \cdot CH : NOH + H_2O,$$

a substance which is only known in solution, since it very readily undergoes polymerisation.

Constitution.—Since carbon is quadrivalent, there is only one way of expressing the constitution of formaldehyde, CH_2O—namely, by the formula, $H-C\begin{matrix}H\\ \diagdown\!\!\diagup\\ O\end{matrix}$.

In the formation of formaldehyde by the oxidation of methyl alcohol, CH_3-O-H, one of the hydrogen atoms of the CH_3- group is probably oxidised to $-OH$, thus giving an unstable compound, $CH_2(OH)_2$, which, unless kept in solution, decomposes into CH_2O and H_2O. It will be seen that the oxygen atom in the molecule of formaldehyde is represented as being in a state of combination different from that in which it exists in the molecule of methyl alcohol. Formaldehyde, in fact, is an unsaturated compound, and is capable of forming additive products under certain conditions; it must be carefully noted, however, that the atoms or groups with which formaldehyde unites directly are not, generally speaking, those which combine readily with two unsaturated carbon atoms; a double binding between carbon and oxygen must be distinguished from a double binding between two carbon atoms, although in both cases it indicates the power of forming additive products.

Paraformaldehyde is formed, as stated above, when an *aqueous solution* of formaldehyde is evaporated; it is a colourless, amorphous substance, soluble in warm water, and has probably the molecular formula, $(CH_2O)_2$.

Trioxymethylene, or *metaformaldehyde*, $(CH_2O)_3$, is formed

by the polymerisation of *anhydrous* liquid formaldehyde (p. 124), and also when paraformaldehyde is carefully heated; it is an indefinitely crystalline compound which sublimes readily, and melts at 171°. When strongly heated it is completely decomposed into pure, *gaseous formaldehyde*, CH_2O, as is proved by vapour density determinations; but as the gas cools, trioxymethylene is again produced. When heated with a large quantity of water at about 140°, it is also converted into formaldehyde.

Polymerisation.—It will be seen from what has already been stated, that formaldehyde readily changes, either spontaneously or when heated, giving new compounds, which can be reconverted into formaldehyde, CH_2O, by simple means. As the new compounds have the *same* percentage composition as the parent substance, their molecules may be regarded as having been produced by the aggregation of *several* molecules of the latter. This view led to the introduction of the word **polymerisation**, which means the change of some (simple) substance into another of the same percentage composition, but having a molecular weight equal to several multiples of that of the parent substance; the more complex compounds, thus formed, were then termed *polymers*, *polymerides*, or *polymeric modifications* of the original substance, and they received names, such as paraformaldehyde and metaformaldehyde, which expressed their origin or derivation. The relation between formaldehyde and its polymeric modifications was thus regarded as being somewhat similar to that existing between the several allotropic forms of an element. At the present time it is recognised that a polymeric modification may show no relation whatsoever to the parent substance; that its molecules are not merely *aggregates* or *collections* of simpler molecules, but are produced by the chemical union of two or more molecules of the latter to form a new and distinct compound, which in many cases cannot be reconverted into the original substance.

Polymerisation, then, is merely a chemical change, result-

ing in the formation of a new compound, whose molecular weight is a multiple of that of the original substance because the polymeride is produced by the direct union of two or more molecules of the latter; other examples of this change are given later (pp. 131, 314).

Formaldehyde gives several polymeric modifications, and the readiness with which it undergoes polymerisation is one of its more characteristic properties. When its aqueous solution is treated with lime-water or other weak alkali, formaldehyde undergoes polymerisation into *formose*, a mixture of substances, some of which have the composition, $(CH_2O)_6$, or $C_6H_{12}O_6$, and belong to the sugar-group. This reaction is of great interest, since it shows that complex vegetable substances, such as the sugars, may be formed by very simple means (p. 300).

Methylal, $CH_2(OCH_3)_2$, is an important derivative of formaldehyde. It may be obtained by boiling aqueous formaldehyde with methyl alcohol and a small quantity of sulphuric acid, but is usually prepared by oxidising methyl alcohol with manganese dioxide and sulphuric acid, when the formaldehyde which is first produced combines with some of the unchanged methyl alcohol,

$$H\cdot CHO + 2CH_3\cdot OH = H\cdot CH(OCH_3)_2 + H_2O.$$

Methylal, a pleasant-smelling liquid, which boils at 42° and is readily soluble in water, is used in medicine as a soporific. When distilled with dilute sulphuric acid, it gives an aqueous solution of methyl alcohol and formaldehyde, a reaction which may be conveniently employed for preparing the latter.

Acetaldehyde, $CH_3\cdot CHO$ (ethaldehyde), is formed in small quantities by atmospheric oxidation when alcohol is filtered through charcoal, or exposed to the air in presence of platinum black, or heated platinum (compare p. 124); it is also formed when a mixture of calcium acetate and calcium formate is submitted to dry distillation,

$$(CH_3\cdot COO)_2Ca + (H\cdot COO)_2Ca = 2CH_3\cdot CHO + 2CaCO_3.$$

Acetaldehyde is prepared by oxidising alcohol with potassium dichromate and sulphuric acid,

$$CH_3\cdot CH_2\cdot OH + O = CH_3\cdot CHO + H_2O.$$

Coarsely powdered potassium dichromate (3 parts) and water (12 parts) are placed in a capacious flask fitted with a tap-funnel and attached to a condenser, and the flask is gently heated on a water-bath; a mixture of alcohol (3 parts) and concentrated sulphuric acid (4 parts) is then added drop by drop, and the flask is shaken almost continuously during the operation. A vigorous action sets in, and a liquid, which consists of aldehyde, alcohol, water, and small quantities of acetal (see below), collects in the receiver. This product is now fractionally distilled from a water-bath, and the portion which passes over below 25° is collected, and again fractionated, preferably with the aid of a *column*; the liquid which passes over between 20° and 22° consists of acetaldehyde, and is sufficiently free from impurities for most purposes.* The receiver should be well-cooled with ice in all these operations.

Acetaldehyde, or aldehyde, as it is usually called, is a colourless, mobile, inflammable liquid of sp. gr. 0·801 at 0°; it boils at 20·8°. It has a characteristic, penetrating, and suffocating odour, by means of which it is easily identified; it mixes with water, alcohol, and ether in all proportions. Aldehyde is slowly oxidised to acetic acid on exposure to the air, and, like formaldehyde, it has powerful reducing properties; it precipitates silver from ammoniacal solutions of silver oxide, and is itself oxidised to acetic acid,

$$CH_3{\cdot}CHO + Ag_2O = CH_3{\cdot}CO{\cdot}OH + 2Ag.$$

When reduced with sodium amalgam and water, it is converted into alcohol,

$$CH_3{\cdot}CHO + 2H = CH_3{\cdot}CH_2{\cdot}OH.$$

When aldehyde is shaken with a concentrated solution of sodium hydrogen sulphite (sodium bisulphite), direct combination occurs, and a colourless substance, $CH_3{\cdot}CH(OH){\cdot}SO_3Na$,

* Pure acetaldehyde is best prepared from paraldehyde (p. 131), into which crude acetaldehyde is easily converted. It may also be prepared from the liquid (b.p. 20–22°), described above, in the following manner:—The liquid is mixed with *dry* ether, and the solution, cooled in ice, is saturated with *dry* ammonia, when a crystalline precipitate of *aldehyde ammonia* (p. 129) is obtained. This substance is transferred to a filter, washed with ether, and then decomposed by distillation with dilute sulphuric acid at as low a temperature as possible; the aldehyde is finally dehydrated by distillation with coarsely powdered, anhydrous calcium chloride.

separates in crystals. This compound is readily decomposed by acids, alkalis, and alkali carbonates, aldehyde being liberated. Aldehyde also combines directly with dry ammonia, to form a colourless, crystalline substance, *aldehyde ammonia*, $CH_3 \cdot CH(OH) \cdot NH_2$, which is decomposed by acids, aldehyde being regenerated.

Aldehyde very readily undergoes polymerisation on treatment with acids and other substances (see below). Its behaviour with alkalis is also characteristic; when it is very gently warmed with concentrated potash a violent action sets in, and the aldehyde is converted into a brown substance called *aldehyde resin*.

Aldehyde is most easily detected by its highly characteristic smell; its reducing action on silver oxide may be used as a confirmatory test.

The magenta or rosaniline test (Schiff's reaction) may also be employed :—Sulphurous acid is added to a very dilute solution of rosaniline hydrochloride until the pink colour is just discharged; the solution to be tested is now added, when, if it contains aldehyde, a violet or pink colour immediately appears. This behaviour is not characteristic of acetaldehyde, as, with very few exceptions, all aldehydes give this reaction.

Constitution.—Aldehyde is formed by the oxidation of ethyl alcohol, just as formaldehyde is produced by the oxidation of methyl alcohol, and the final result in both cases is that two atoms of hydrogen are removed from the molecule of the primary alcohol. Now, it is known that, in the formation of formaldehyde, this change involves a hydroxyl-group and a hydrogen atom, which are united to one and the same carbon atom, because $\begin{matrix}H\\H\end{matrix}\!>\!C\!<\!\begin{matrix}H\\OH\end{matrix}$ becomes $\begin{matrix}H\\H\end{matrix}\!>\!C=O$. If, then, acetaldehyde is produced from ethyl alcohol in a similar manner—namely, by a reaction which may be supposed to occur in two stages (compare p. 125),

$$CH_3 \cdot CH_2 \cdot OH + O = CH_3 \cdot CH\!<\!\begin{matrix}OH\\OH\end{matrix} = CH_3 \cdot C\!<\!\begin{matrix}H\\O\end{matrix} + H_2O,$$

—the constitution of acetaldehyde would be expressed by the formula, $CH_3-C\begin{matrix}H\\ \diagdown\!\!\diagup O\end{matrix}$ and *not* by the formula, $\begin{matrix}O\\ \diagup\quad\diagdown\\ CH_2-CH_2\end{matrix}$, which is the only theoretically possible alternative if the elements retain their normal valencies.

Judging from analogy, then, the constitution of aldehyde is expressed by the formula, $CH_3\cdot C\begin{matrix}H\\ \diagdown\!\!\diagup O\end{matrix}$; this view accords very well with the whole chemical behaviour of the compound. Aldehyde, unlike alcohol, does not contain a hydrogen atom displaceable by sodium or potassium, and does not form esters with acids; these facts are expressed by the above formula, which shows that aldehyde does not contain the HO– group. When aldehyde is treated with phosphorus pentachloride, one atom of oxygen is displaced by *two* atoms of chlorine (giving *ethylidene dichloride*), a change which is very different from that which occurs in the case of alcohol, and which affords further evidence that aldehyde is not a hydroxy-compound. This point is rendered very clear if the reactions are represented side by side,

$$\begin{aligned} CH_3\cdot CHO + PCl_5 &= CH_3\cdot CHCl_2 + POCl_3,\\ CH_3\cdot CH_2\cdot OH + PCl_5 &= CH_3\cdot CH_2Cl + POCl_3 + HCl. \end{aligned}$$

The fact that aldehyde has the power of combining directly with nascent hydrogen, ammonia, sodium hydrogen sulphite, &c., is also indicated by the above constitutional formula; acetaldehyde, like formaldehyde, is an unsaturated compound, and combines directly with two univalent atoms or groups.

It must be concluded, therefore, that both formaldehyde and acetaldehyde contain in their molecules the univalent group, $-C\begin{matrix}H\\ \diagdown\!\!\diagup O\end{matrix}$, which is usually written –CHO (not COH, which might be confused with C–OH); it is to the presence of this *aldehyde-group* that the compounds owe their characteristic properties, because nearly all the changes which they undergo are limited to the group, –CHO, which they both contain; all aldehydes contain a group of this kind.

Polymerisation of Acetaldehyde. — Three well-defined polymerides of aldehyde are known — namely, aldol, paraldehyde, and metaldehyde.

Aldol, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO$, is produced by the action of dilute hydrochloric acid, or of zinc chloride, on aldehyde at ordinary temperatures. It is a colourless, inodorous liquid, miscible with water, and shows all the ordinary properties of an aldehyde. It can be distilled under reduced pressure without its decomposing; but when distilled under ordinary pressure, or when heated with dehydrating agents, it is converted into *crotonaldehyde* (p. 290) and water,

$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO = CH_3 \cdot CH : CH \cdot CHO + H_2O.$$

Paraldehyde, $(C_2H_4O)_3$, is readily produced by adding a drop of concentrated sulphuric acid to aldehyde at ordinary temperatures, an almost explosive action taking place. It is a colourless, pleasant-smelling liquid, which boils at 124°. It is only sparingly soluble in water, and its cold saturated solution becomes turbid when it is warmed, as the compound is less soluble in hot than in cold water; when *distilled* with a few drops of concentrated sulphuric acid, paraldehyde is converted into aldehyde, which distils over.* Paraldehyde is used in medicine as a soporific.

Metaldehyde, $(C_2H_4O)_3$, is produced by the action of acids on aldehyde at *low temperatures*. It crystallises in colourless needles, and is insoluble in water; it can be sublimed, but it is converted into acetaldehyde when it is heated for a long time, or distilled with dilute sulphuric acid.

Paraldehyde and metaldehyde show none of the ordinary properties of aldehydes, and do not contain the aldehyde or –CHO group; in other words, they are not aldehydes (p. 148). Metaldehyde is isomeric with paraldehyde, but its relation to the latter is not known exactly.

Acetal, $CH_3 \cdot CH(OC_2H_5)_2$, is produced when a mixture of aldehyde and alcohol is heated at 100°, or when alcohol is oxidised with manganese dioxide and sulphuric acid (compare methylal, p. 127),

$$CH_3 \cdot CHO + 2C_2H_5 \cdot OH = CH_3 \cdot CH(OC_2H_5)_2 + H_2O.$$

* The conversion of acetaldehyde into paraldehyde by sulphuric acid is a reversible reaction, so that as the (more volatile) acetaldehyde is removed by distillation, the paraldehyde is slowly reconverted into acetaldehyde.

It is a colourless, pleasant-smelling liquid, and boils at 104°; when distilled with dilute acids it is decomposed into alcohol and aldehyde,

$$CH_3{\cdot}CH(OC_2H_5)_2 + H_2O = CH_3{\cdot}CHO + 2C_2H_5{\cdot}OH.$$

Chloral, or trichloracetaldehyde, $CCl_3{\cdot}CHO$, was discovered by Liebig during an investigation of the action of chlorine on alcohol. It can be obtained by the direct action of chlorine on acetaldehyde, but it is prepared on the large scale from alcohol.

Alcohol is saturated with chlorine, first at ordinary temperatures, and then at the boiling-point, an operation which occupies some days. The crystalline product, which consists for the greater part of *chloral alcoholate*, $CCl_3{\cdot}CH<\begin{matrix}OC_2H_5\\OH\end{matrix}$, is distilled with concentrated sulphuric acid, and the oily distillate of crude chloral is converted into chloral hydrate (see below). After the hydrate has been purified by recrystallisation from water, it is distilled with sulphuric acid, when pure chloral passes over.

The formation of chloral alcoholate, by the action of chlorine on alcohol, involves a series of reactions, which it is unnecessary to describe in detail because they are not sufficiently typical; it may be noted, however, that the chlorine acts here both as an oxidising and as a chlorinating agent.

Chloral is an oily liquid of sp. gr. 1·512 at 20°, and boils at 97°. It has a penetrating and irritating smell, and in chemical properties closely resembles aldehyde, a fact which was only to be expected, since it is a simple substitution product of aldehyde, and contains the characteristic aldehyde-group. It has reducing properties, combines directly with ammonia, sodium hydrogen sulphite, &c., and on oxidation it is converted into trichloracetic acid (p. 170), just as aldehyde is converted into acetic acid,

$$CCl_3{\cdot}CHO + O = CCl_3{\cdot}CO{\cdot}OH.$$

On the addition of small quantities of acids, chloral very readily undergoes polymerisation, and is transformed into a white amorphous modification called *metachloral;* the same change takes

place when chloral is kept for a considerable time. One of the more interesting reactions of chloral is its behaviour with boiling potash, by which it is quickly decomposed, giving chloroform (p. 181) and potassium formate,

$$CCl_3{\cdot}CHO + KOH = CHCl_3 + H{\cdot}COOK.$$

Pure chloroform is often prepared in this way.

Chloral hydrate, $CCl_3{\cdot}CH(OH)_2$, is produced, with development of heat, when chloral is treated with one molecular proportion of water. It forms colourless crystals, melts at 57°, and is readily soluble in water; it is decomposed on distillation with sulphuric acid, and chloral passes over. In some respects it is a very stable substance; it does not polymerise, and does not show some of the reactions of aldehydes. These facts point to the conclusion that chloral hydrate does not contain the aldehyde-group, but is a substance of the constitution, $CCl_3{\cdot}CH<\begin{matrix}OH\\OH\end{matrix}$.*

Chloral hydrate is extensively used in medicine as a soporific.

Butyl-chloral, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO$, is formed when chlorine is passed into aldehyde, first in the cold and then at 100°; it boils at 164–165°, and combines readily with water, forming *butyl-chloral hydrate*, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH)_2$, a crystalline substance melting at 78°, which is used in medicine.

The formation of butyl-chloral may be explained by assuming that chloracetaldehyde, produced by substitution, reacts with unchanged aldehyde, giving chlorocrotonaldehyde (compare aldol, p. 131),

$$CH_3{\cdot}CHO + CH_2Cl{\cdot}CHO = CH_3{\cdot}CH{:}CCl{\cdot}CHO + H_2O,$$

which then unites directly with chlorine.

Homologues of Acetaldehyde.—The higher members of the homologous series of aldehydes, such as *propaldehyde*, $C_2H_5{\cdot}CHO$, and *butaldehyde*, $C_3H_7{\cdot}CHO$, may be produced by the oxidation of the corresponding primary alcohols, or by the dry distillation of the calcium salts of the corresponding fatty acids with calcium formate; they resemble acetaldehyde in chemical properties.

* Very few compounds containing two hydroxyl-groups united to the *same* carbon atom are known; as a rule, such compounds are very unstable and readily lose the elements of water, the group, $>C(OH)_2$, giving $>CO + H_2O$ (pp. 125, 129).

Heptaldehyde, or **Œnanthol**, $C_6H_{13}\cdot CHO$, is one of the products of the dry distillation of castor-oil. It is a colourless oil, boils at 154°, and has a penetrating, disagreeable odour; on oxidation it yields normal heptylic acid, $C_6H_{13}\cdot COOH$ (p. 164), and on reduction, normal heptyl alcohol, $C_6H_{13}\cdot CH_2\cdot OH$.

KETONES.

The ketones, of which the simplest, acetone, $CH_3\cdot CO\cdot CH_3$, may be taken as an example, are derived from the secondary alcohols, such as isopropyl alcohol, $CH_3\cdot CH(OH)\cdot CH_3$, by the removal of two atoms of hydrogen from the $>CH(OH)$ group; this process is analogous to that which occurs in the formation of aldehydes from primary alcohols. Ketones are substances of the type, $R-CO-R$, and their molecules contain the bivalent group, $>C=O$, united with two identical or different alkyl radicles, as in $C_2H_5\cdot CO\cdot C_2H_5$, $CH_3\cdot CO\cdot C_2H_5$, &c. Their compositions may be expressed by the general formula, $C_nH_{2n}O$, and a ketone is isomeric with the aldehyde which contains the same number of carbon atoms.

Propaldehyde,	$CH_3\cdot CH_2\cdot CHO$	C_3H_6O
Dimethyl ketone,	$CH_3\cdot CO\cdot CH_3$	
Butaldehyde,	$CH_3\cdot CH_2\cdot CH_2\cdot CHO$	C_4H_8O.
Methylethyl ketone,	$CH_3\cdot CH_2\cdot CO\cdot CH_3$	

Acetone, or dimethyl ketone, $CH_3\cdot CO\cdot CH_3$, occurs in small quantities in normal urine, and in cases of *diabetes mellitus* and *acetonuria* the quantity increases considerably. It also occurs in small quantities in the blood.

Acetone is formed when isopropyl alcohol is oxidised with potassium dichromate and sulphuric acid,

$$CH_3\cdot CH(OH)\cdot CH_3 + O = CH_3\cdot CO\cdot CH_3 + H_2O,$$

and is produced in considerable quantities during the dry distillation of wood and many other organic compounds, such as sugar, gum, &c.

Crude wood-spirit, which has been freed from acetic acid (p. 92), consists in the main of water, methyl alcohol, and acetone. The

last two substances are separated from the water by fractional distillation and the mixture is treated with anhydrous calcium chloride, which combines with the methyl alcohol (p. 93); the crude acetone may then be purified by distillation and by conversion into the bisulphite compound (see below).

Acetone is prepared in the laboratory and on the large scale by the dry distillation of calcium (or barium) acetate,

$$(CH_3{\cdot}COO)_2Ca = CH_3{\cdot}CO{\cdot}CH_3 + CaCO_3.$$

The distillate is fractionated, and the portion which passes over between 50° and 60° is mixed with a strong solution of 'sodium bisulphite.' The crystalline 'acetone sodium bisulphite,' which separates after a short time, is well pressed, to free it from impurities, and is decomposed by distillation with a solution of sodium carbonate; the product is then freed from water by distillation over calcium chloride.

Acetone is a colourless, mobile liquid of sp. gr. 0·792 at 20°; it boils at 56·5°, has a peculiar and highly characteristic odour, and is miscible with water, alcohol, and ether in all proportions.

In chemical properties acetone *resembles* aldehyde in several important particulars. When it is shaken with a concentrated aqueous solution of sodium hydrogen sulphite, a considerable development of heat occurs, and a colourless, crystalline substance, *acetone sodium bisulphite*,

$$CH_3{\cdot}CO{\cdot}CH_3,\ NaHSO_3,\ \text{or}\ (CH_3)_2C{<}\begin{matrix}OH\\SO_3Na,\end{matrix}$$

separates. This compound is readily soluble in water, and is quickly decomposed by dilute acids and alkalis, acetone being regenerated.

When acetone is treated with phosphorus pentachloride, the oxygen atom in its molecule is displaced by two atoms of chlorine, and $\beta\beta$-dichloropropane is formed,

$$(CH_3)_2CO + PCl_5 = (CH_3)_2CCl_2 + POCl_3;$$

on reduction, acetone is converted into isopropyl alcohol,

$$(CH_3)_2CO + 2H = (CH_3)_2CH{\cdot}OH.$$

Acetone, like aldehyde, reacts with hydroxylamine in aqueous solution, forming *acetoxime*,

$$(CH_3)_2CO + NH_2 \cdot OH = (CH_3)_2C{:}N \cdot OH + H_2O,$$

a crystalline substance, melting at 59°.

At the same time acetone *differs from* aldehyde very widely in one or two important respects. It does *not* undergo polymerisation, and does *not* reduce ammoniacal solutions of silver oxide; it is oxidised only by moderately powerful agents, by which its molecule is broken up, with formation of acetic acid and carbon dioxide,

$$CH_3 \cdot CO \cdot CH_3 + 4O = CH_3 \cdot COOH + CO_2 + H_2O.$$

Acetone gives the iodoform reaction (p. 99), and is employed for the preparation of iodoform, chloroform, and sulphonal; it is also used as a solvent and in gelatinising gun-cotton in the manufacture of cordite (p. 312).

Constitution.—Acetone is formed when two atoms of hydrogen are removed from a molecule of isopropyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH \cdot OH$ (p. 110), by oxidation. If, therefore, this process involves reactions analogous to those which occur in the oxidation of ethyl alcohol (p. 129) and methyl alcohol (p. 125), the group $>C<\begin{matrix}H\\OH\end{matrix}$ is oxidised to $>CO$, and the change may be represented as follows:—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C<\begin{matrix}H\\OH\end{matrix} + O = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C<\begin{matrix}OH\\OH\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}O + H_2O.$$

This view of its constitution accords well with the whole chemical behaviour of acetone. That its molecule does not contain a hydroxyl-group is shown by the fact that acetone, unlike the alcohols, is not directly attacked by sodium, and also by the fact that its behaviour with phosphorus pentachloride is similar to that of aldehyde (p. 130), but quite different from that of alcohol. These and many other considerations show that acetone has the constitution, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O$

or $(CH_3)_2CO$; its characteristic properties are determined by the presence of the bivalent **carbonyl** or **ketonic** group, $>C=O$, which is contained in the molecules of all ketones.

The similarity in chemical behaviour between acetone and aldehyde is expressed by their structural formulæ; both molecules contain the carbonyl-group,

$$\text{Acetone, } \begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O \qquad \text{Aldehyde, } \begin{matrix}H\\CH_3\end{matrix}\!>C=O;$$

and therefore those changes, in which only this group takes part, are common to both substances. Thus, they behave in a similar manner towards phosphorus pentachloride, and they both combine directly with hydrogen, and with sodium hydrogen sulphite; in the last two, and in many other reactions, acetone, like aldehyde, behaves as an unsaturated compound. The difference between the two compounds as regards oxidation is also expressed by the above formulæ; acetone does not contain the readily oxidisable hydrogen atom of the aldehyde-group, and, therefore, it is less readily acted on than aldehyde, and does not reduce silver oxide.

Acetone and many other ketones give Schiff's reaction (p. 129), but the colour usually reappears more slowly than with aldehydes; by far the best means of distinguishing between an aldehyde and a ketone is to study the behaviour of the compound on oxidation (p. 147).

Condensation of Acetone.—When acetone is treated with certain dehydrating agents, it undergoes changes in which two or more molecules combine together with elimination of one or more molecules of water,

$$2(CH_3)_2CO = \underset{\text{Mesityl Oxide.}}{C_6H_{10}O} + H_2O \qquad 3(CH_3)_2CO = \underset{\text{Phorone.}}{C_9H_{14}O} + 2H_2O.$$

These and similar changes, in which two or more molecules of the same or of different substances combine, with separation of water, are termed **condensations**, and the substances which are formed, **condensation products**; the process differs from polymerisation in this, that water is eliminated.

Acetone yields three interesting condensation products. When it is saturated with dry hydrogen chloride, and the solution is kept for some time, a mixture of *mesityl oxide* and *phorone* is formed, in accordance with the above equations; but when it is distilled with concentrated sulphuric acid, acetone yields a hydrocarbon, *mesitylene* (Part II. p. 377), a derivative of benzene,

$$3(CH_3)_2CO = C_9H_{12} + 3H_2O.$$

Mesityl oxide, $C_6H_{10}O$, is a colourless oil, boiling at 130°, and having a strong peppermint-like smell; when boiled with dilute sulphuric acid it is decomposed, with regeneration of acetone. Its constitution may be represented by the formula, $CH_3{\cdot}CO{\cdot}CH{:}C<^{CH_3}_{CH_3}$.

Phorone, $C_9H_{14}O$, crystallises in pale-yellow prisms, melting at 28°; it boils at 196°, has a pleasant aromatic odour, and is decomposed by boiling dilute sulphuric acid, with formation of acetone.

Substitution Products of Acetone.—Acetone is readily attacked by chlorine with formation of *monochloracetone*, $CH_3{\cdot}CO{\cdot}CH_2Cl$ (b.p. 119°), and *asymmetrical dichloracetone*, $CH_3{\cdot}CO{\cdot}CHCl_2$ (b.p. 120°). *Symmetrical dichloracetone*, $CH_2Cl{\cdot}CO{\cdot}CH_2Cl$ is produced by the oxidation of dichlorisopropyl alcohol (glyceryl dichlorohydrin, p. 285), $CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$; it is a colourless, crystalline solid (m.p. 45°; b.p. 172·5°). Higher substitution products of acetone have been obtained by indirect methods. The final product, *hexachloracetone*, or *perchloracetone*, $CCl_3{\cdot}CO{\cdot}CCl_3$, is a colourless liquid, boiling at 204°. Corresponding bromo-substitution products of acetone have also been prepared.

These halogen substitution products have an exceedingly irritating action on the eyes, and mere traces of them in the air of a laboratory are sufficient to cause a copious flow of tears; when dropped on the skin they produce very painful blisters.

Homologues of Acetone may be obtained by the oxidation of the corresponding secondary alcohols and by the dry distillation of the calcium salts of the higher fatty acids; they resemble acetone very closely in chemical properties.

Oximes (or *hydroximes*).—Aldehydes and ketones react readily with hydroxylamine, $NH_2{\cdot}OH$ (p. 188), and give compounds which are called *oximes*; those formed from

aldehydes are called *aldoximes*, those obtained from ketones, *ketoximes*. Acetaldehyde, for example, yields acetaldoxime,

$$CH_3{\cdot}CHO + NH_2{\cdot}OH = CH_3{\cdot}CH{:}N{\cdot}OH + H_2O,$$

and acetone gives acetoxime (or dimethyl ketoxime),

$$(CH_3)_2CO + NH_2{\cdot}OH = (CH_3)_2C{:}N{\cdot}OH + H_2O.$$

These two important *general reactions* were discovered by Victor Meyer, and in both cases the change may be expressed by the equation,

$$>C{:}O + H_2{:}N{\cdot}OH = >C{:}N{\cdot}OH + H_2O.$$

The oximes are usually prepared by adding to an alcoholic solution of the aldehyde or ketone (2 mols.) a very concentrated aqueous solution of hydroxylamine hydrochloride, $NH_2{\cdot}OH,HCl$ (2 mols.), and then a concentrated solution of sodium carbonate (1 mol.), which decomposes the hydrochloride and sets free the base (and generally gives a precipitate of sodium chloride),

$$2NH_2{\cdot}OH,HCl + Na_2CO_3 = 2NH_2{\cdot}OH + 2NaCl + CO_2 + H_2O.$$

The mixture is kept at the ordinary temperature, or heated gently, for some hours, and most of the alcohol is then evaporated on the water-bath. At this stage, or on the addition of water, the oxime is usually deposited in crystals; if not, it is extracted with ether.

The formation of the oxime is often greatly accelerated by making the solution strongly alkaline with alcoholic potash (Auwers); in such cases, after the alcohol has been evaporated, it is often necessary to neutralise the solution with dilute sulphuric acid in order to precipitate the oxime.

The lower aldoximes are mostly colourless, volatile, solid compounds, which distil without decomposing under reduced pressure, and mix with water in all proportions; the higher members are only sparingly soluble in water. The ketoximes have similar properties. Many oximes are decomposed when they are heated with moderately strong hydrochloric acid, with formation of hydroxylamine hydrochloride, and regeneration of the aldehyde or ketone,

$$CH_3{\cdot}CH{:}N{\cdot}OH + HCl + H_2O = CH_3{\cdot}CHO + NH_2{\cdot}OH,HCl.$$

They are often converted into readily soluble compounds, such as $CH_3{\cdot}CH{:}N{\cdot}ONa$ and $(CH_3)_2C{:}N{\cdot}OK$, by caustic

alkalis; but they are not otherwise decomposed even by boiling alkalis. Oximes are easily reduced to primary amines (p. 217); as they are generally crystalline, they serve for the *identification* of those ketones and aldehydes which are liquid at ordinary temperatures.

Many oximes unite directly with hydrogen chloride (1 mol.) to form unstable *hydrochlorides*, which are decomposed by water.

The hydrogen atom of the >N·OH group (which is called the *oximido-* or *oximino-*group) may be displaced by alkyl and by acid radicles. These derivatives are produced by the action of alkyl halogen compounds and acid chlorides respectively on the sodium derivative of the oxime. Many oximes exhibit a type of isomerism, the nature of which is discussed later (Part II. p. 462).

One important difference between aldoximes and ketoximes is, that the former are decomposed by acetyl chloride, yielding cyanides or nitriles (p. 321),

$$CH_3{\cdot}CH{:}N{\cdot}OH = CH_3{\cdot}CN + H_2O,$$

whereas the latter are either converted into acetyl derivatives,

$$(CH_3)_2C{:}N{\cdot}OH + CH_3{\cdot}COCl = (CH_3)_2C{:}N{\cdot}O{\cdot}CO{\cdot}CH_3 + HCl,$$

or else undergo a peculiar *intramolecular change* (p. 331) and give alkyl-substituted amides (Part II. p. 464),

$$(CH_3)_2C{:}N{\cdot}OH = CH_3{\cdot}CO{\cdot}NH{\cdot}CH_3.$$

Acetoxime. Methylacetamide.

Hydrazones (or phenylhydrazones).—Aldehydes and ketones react readily with phenylhydrazine (Part II. p. 421), and give compounds which are called *phenylhydrazones*, or simply *hydrazones;* these substances were discovered by E. Fischer, and they are formed according to the equation,

$$>C{:}O + H_2N{\cdot}NH{\cdot}C_6H_5 = >C{:}N{\cdot}NH{\cdot}C_6H_5 + H_2O,$$

Acetaldehyde hydrazone, $CH_3{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5$, and *acetone hydrazone*, $(CH_3)_2C{:}N{\cdot}NH{\cdot}C_6H_5$, for example, are the products obtained from acetaldehyde and acetone respectively. The hydrazones are referred to later (Part II. p. 422); but it may be mentioned here that, like the oximes, they are often decomposed by hot concentrated hydrochloric acid, with regeneration of the aldehyde or ketone, and they may be reduced to *primary amines* (p. 217).

Phenylhydrazine is a very important reagent, as it serves

for the detection of aldehydes and ketones; also for their isolation and identification (p. 301; Part II. p. 423).

Hydrazine, NH_2-NH_2, also reacts with aldehydes and ketones, and compounds called **azines** are produced, in accordance with the equation,

$$>CO + NH_2\cdot NH_2 + >CO = >C{:}N\cdot N{:}C< + 2H_2O.$$

In the preparation of azines the aldehyde or ketone is treated with hydrazine sulphate and sodium carbonate (or sodium acetate) in aqueous alcoholic solution.

Semicarbazones are formed by the interaction of an aldehyde, or ketone, and semicarbazide (Part II. p. 571),

$$>CO + NH_2\cdot NH\cdot CO\cdot NH_2 = >CO{:}N\cdot NH\cdot CO\cdot NH_2 + H_2O.$$

Acetone semicarbazone, for example, separates in colourless crystals when an aqueous solution of acetone is treated with semicarbazide hydrochloride and sodium acetate. As the semicarbazones are usually crystalline, sparingly soluble compounds of high melting-point, semicarbazide is a very important reagent for the detection and identification of aldehydes and ketones.

Cyanohydrins.—Aldehydes and ketones unite directly with hydrogen cyanide, forming *cyanohydrins*,

$$>CO + HCN = >C<^{OH}_{CN},$$

a very important reaction which is often used in synthesising organic compounds (compare pp. 242, 256, 302).

SUMMARY AND EXTENSION.

The **Aldehydes** form a homologous series of the general formula, $C_nH_{2n}O$, or R·CHO, and are derived from the *primary* alcohols by the removal of two atoms of hydrogen from the $-CH_2\cdot OH$ group. The more important members of the series are:—

			B.p.
Formaldehyde,	CH_2O	H·CHO	−21°
Acetaldehyde,	C_2H_4O	$CH_3\cdot CHO$	+20·8°
Propaldehyde,	C_3H_6O	$CH_3\cdot CH_2\cdot CHO$	49°
Butaldehyde,	C_4H_8O	$CH_3\cdot CH_2\cdot CH_2\cdot CHO$	74°
Isobutaldehyde,		$(CH_3)_2CH\cdot CHO$	63°
Valeraldehyde,	$C_5H_{10}O$	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$	102°
Isovaleraldehyde,		$(CH_3)_2CH\cdot CH_2\cdot CHO$	92°
Capraldehyde,	$C_6H_{12}O$	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$	128°
Heptaldehyde, or Œnanthol,	$C_7H_{14}O$	$CH_3\cdot[CH_2]_5\cdot CHO$*	155°

* $[CH_2]_5$ is a convenient way of writing $-CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2-$.

The **Ketones** form a homologous series of the general formula, $C_nH_{2n}O$ or R – CO – R′, and are derived from the *secondary* alcohols by the removal of two atoms of hydrogen from the >CH·OH group. When the alkyl radicles R and R′ are identical the substance is a *simple ketone*, but when R and R′ are different it is a *mixed ketone* (compare ethers, p. 122). The more important ketones are:—

Acetone, or dimethyl ketone	$(CH_3)_2CO$	B.p. 56·5°
Propione, or diethyl ketone	$(C_2H_5)_2CO$	" 103°
Butyrone, or dipropyl ketone	$(C_3H_7)_2CO$	" 144°
Isobutyrone, or di-isopropyl ketone	$(C_3H_7)_2CO$	" 125°
Œnanthone, or dihexyl ketone	$(C_6H_{13})_2CO$	M.p. 30·5°
Laurone	$(C_{11}H_{23})_2CO$	" 69°
Palmitone	$(C_{15}H_{31})_2CO$	" 83°
Stearone	$(C_{17}H_{35})_2CO$	" 88°

A ketone is isomeric with that aldehyde which contains the same number of carbon atoms, and the number of isomeric aldehydes of a given molecular formula is greater than that of the isomeric ketones. Thus, whereas there are four aldehydes of the molecular formula $C_5H_{10}O$—namely, in addition to the two given in the table (p. 141),

$$CH_3\cdot CH_2\cdot CH\begin{matrix}CHO\\CH_3\end{matrix} \quad \text{and} \quad \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CHO\\CH_3\end{matrix}$$

—there are only three ketones—namely,

$$CH_3\cdot CH_2\cdot CO\cdot CH_2\cdot CH_3 \qquad CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_3 \qquad CH_3\cdot CO\cdot CH\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Diethyl Ketone or Propione. Methylpropyl Ketone. Methylisopropyl Ketone.

Both aldehydes and ketones may be regarded as derived from the paraffins, by the substitution of one atom of oxygen for two atoms of hydrogen. In the case of aldehydes, two atoms of hydrogen of one of the CH_3– groups are displaced; but in the case of ketones, the oxygen atom is substituted for two hydrogen atoms of a –CH_2– group.

Nomenclature.—The aldehydes are generally named after the fatty acids which they yield on oxidation, but sometimes they are named after the alcohols from which they may be obtained; thus, formaldehyde and acetaldehyde are sometimes called methaldehyde and ethaldehyde respectively.

The simple ketones, which were first obtained by the dry distillation of a salt of a fatty acid, are usually named after the acid from which they are in this way obtained; acetone, for example, from acetic acid, propione from propionic acid. The mixed ketones are named according to the alkyl-groups which they contain, as exemplified above in the case of the isomerides of the composition,

$C_5H_{10}O$. Aldehydes and ketones in general may also be named after the hydrocarbons from which they are theoretically derived, employing the terminations **al** and **one** respectively, and a numeral —as, for example, propanal (propaldehyde), butanal (butaldehyde), hexan-3-one, $\overset{1}{C}H_3\cdot\overset{2}{C}H_2\cdot\overset{3}{C}O\cdot\overset{4}{C}H_2\cdot\overset{5}{C}H_2\cdot\overset{6}{C}H_3$.

Methods of Preparation.—Aldehydes are prepared by the oxidation of primary alcohols,

$$CH_3\cdot CH_2\cdot OH + O = CH_3\cdot CHO + H_2O;$$

whereas *ketones* are produced from secondary alcohols by a similar treatment,

$$CH_3\cdot CH(OH)\cdot CH_3 + O = CH_3\cdot CO\cdot CH_3 + H_2O.$$

Aldehydes and *ketones* may also be prepared by passing the vapour of an alcohol over reduced copper, heated at 250–320°; primary alcohols thus give hydrogen and an aldehyde, whereas secondary alcohols give hydrogen and a ketone.

Aldehydes may be prepared from the fatty acids by the dry distillation of their calcium salts with *calcium formate*,

$$(CH_3\cdot COO)_2Ca + (H\cdot COO)_2Ca = 2CH_3\cdot CHO + 2CaCO_3,$$
$$(C_3H_7\cdot COO)_2Ca + (H\cdot COO)_2Ca = 2C_3H_7\cdot CHO + 2CaCO_3.$$

In its simplest form this reaction may be considered as being due to the removal of water and carbon dioxide from one molecule of the fatty acid and one molecule of formic acid, thus :—

$$\left.\begin{matrix} R.CO-O-H \\ H.CO-OH \end{matrix}\right\} = R\cdot CHO + CO_2 + H_2O.$$

Ketones may be prepared by the dry distillation of the calcium salts of the fatty acids *alone*,

$$(CH_3\cdot COO)_2Ca = CH_3\cdot CO\cdot CH_3 + CaCO_3.$$

When a mixture of the calcium salts of two fatty acids (other than formic acid) is employed, a mixed ketone is formed,

$$(CH_3\cdot COO)_2Ca + (C_2H_5\cdot COO)_2Ca = 2CH_3\cdot CO\cdot C_2H_5 + 2CaCO_3;$$

Calcium Acetate. Calcium Propionate. Methylethyl Ketone.

at the same time two simple ketones (acetone and propione) are produced by the independent decompositions of the two salts.

This method of formation is rendered clearer if the free acids, instead of their calcium salts, are considered,

$$\left.\begin{matrix} RCO-O-H \\ R'-CO-OH \end{matrix}\right\} = R\cdot CO\cdot R' + CO_2 + H_2O.$$

Ketones, in fact, may be prepared by heating the higher fatty acids with phosphoric anhydride at about 200°,

$$2C_{17}H_{33}\cdot COOH = C_{17}H_{33}\cdot CO\cdot C_{17}H_{33} + CO_2 + H_2O,$$

Stearic Acid. Stearone.

a method especially useful in the preparation of the higher ketones, such as laurone, palmitone, &c. ; ketones of the general formula, $CH_3 \cdot CO \cdot R$, may also be prepared by passing the vapour of an acid, $R \cdot CO \cdot OH$, mixed with acetic acid, over thorium oxide which is heated at 400°.

Aldehydes and ketones are produced by the hydrolysis of those dihalogen derivatives of the paraffins in which both the halogen atoms are united to the same carbon atom. The dihydroxy-derivative, which is the initial product, loses the elements of water, and gives an aldehyde or ketone, as the case may be,

$$>CCl_2 \longrightarrow >C(OH)_2 \longrightarrow >CO + H_2O.$$

A synthetical method for the preparation of ketones consists in treating acid chlorides (1 mol.) with zinc alkyl compounds (1 mol.) ; an additive product is formed, which on decomposition with water yields a ketone,

$$C_2H_5 \cdot C\langle \overset{O}{Cl} + Zn(C_2H_5)_2 = C_2H_5 \cdot CCl\langle \overset{O \cdot Zn \cdot C_2H_5}{C_2H_5}$$

$$C_2H_5 \cdot CCl\langle \overset{O \cdot Zn \cdot C_2H_5}{C_2H_5} + H_2O = C_2H_5 \cdot CO \cdot C_2H_5 + C_2H_6 + Zn\langle \overset{OH}{Cl}.$$

When, however, the additive product is treated with a further quantity (1 mol.) of the zinc alkyl compound, the chlorine atom is displaced by an alkyl-group, and the product then gives a tertiary alcohol on decomposition with water.

Ketones may also be prepared by the hydrolysis of ethyl aceto-acetate and its derivatives, a synthetical method of great practical importance (p. 202).

When hydrocarbons of the acetylene series are heated with water at about 325°, or treated with sulphuric acid or mercuric salts, an aldehyde or a ketone is formed (p. 91).

Physical Properties.—Excluding formaldehyde, which is gaseous at ordinary temperatures, the aldehydes and ketones up to about $C_{11}H_{22}O$ are colourless, mobile, neutral, volatile liquids ; the higher members are solids. Aldehydes have usually a disagreeable, irritating smell, but ketones have generally a rather pleasant odour. The first two or three members of both classes of compounds are readily soluble in water, but the solubility rapidly decreases as the molecular weight increases, and the higher members are insoluble, or nearly so, in water, but readily soluble in alcohol and ether. The sp. gr. of the first member of the series is about 0·78 to 0·79 ; this value gradually increases to about 0·83 and then becomes nearly constant. The boiling-point rises regularly in both homologous series ; but the regularities are only observed when compounds

of similar structure are compared—as, for example, the *normal* aldehydes.

Chemical Properties. — Aldehydes and ketones have many chemical properties in common, because their molecules contain the carbonyl-group, $>CO$, and most of their reactions involve changes in this particular group only. Owing to the presence of this group, they have the power of combining directly under certain conditions with two univalent atoms or groups.

All the lower aldehydes and many* of the lower ketones form crystalline additive compounds when shaken with a concentrated aqueous solution of sodium bisulphite. This property is of great value in purifying aldehydes and ketones, and especially in separating them from substances which do not form 'bisulphite compounds,' as illustrated in the preparation of acetone (p. 135). These 'bisulphite compounds' are soluble in water, but usually insoluble, or nearly so, in alcohol and ether. They may be regarded as salts of *hydroxy-sulphonic acids*,† the compounds formed by aldehyde and acetone respectively being,

$CH_3 \cdot CH(OH) \cdot SO_3Na$ — Sodium Hydroxyethylsulphonate.

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\! C(OH) \cdot SO_3Na.$ — Sodium Hydroxyisopropylsulphonate.

All these compounds are readily decomposed when they are warmed with dilute alkalis or acids, the aldehydes or ketones being regenerated,

$$CH_3 \cdot CH_2 \cdot CH(OH) \cdot SO_3Na + HCl = CH_3 \cdot CH_2 \cdot CHO + NaCl + H_2SO_3.$$

Aldehydes and ketones are readily acted on by reducing agents, such as sodium amalgam and water, zinc and hydrochloric acid, with formation of primary and secondary alcohols respectively,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHO + 2H = CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$$
$$CH_3 \cdot CO \cdot CH_2 \cdot CH_3 + 2H = CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_3.$$

A secondary alcohol is not the sole product of the reduction of ketones, but is usually accompanied by varying quantities of a *di-tertiary* alcohol belonging to the class of *pinacones*. Acetone, for example, yields not only isopropyl alcohol, $CH_3 \cdot CH(OH) \cdot CH_3$, but also *pinacone*,

$$2(CH_3)_2CO + 2H = (CH_3)_2C(OH) \cdot C(OH)(CH_3)_2.$$

The formation of a pinacone may be accounted for by assuming that, during reduction, a substance, $\begin{matrix} R \\ R \end{matrix}\!>\! C \!<^{OH}$, is momentarily produced by the combination of the ketone with one atom of hydrogen. This *hypothetical* inter-

* With few exceptions, only those ketones containing the group, $CH_3 \cdot CO-$, combine readily with $NaHSO_3$.

† A sulphonic acid is an organic acid containing the group, $-SO_2 \cdot OH$ (Part II. p. 427).

mediate product may then combine with another atom of hydrogen to form a secondary alcohol, $\begin{matrix}R\\R\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}OH\\H\end{matrix}$, or two molecules may unite to form a pinacone, $\begin{matrix}R\\R\end{matrix}\!\!>\!C(OH)\cdot(HO)C\!<\!\!\begin{matrix}R\\R\end{matrix}$. Similar products (*di-secondary* alcohols) are formed in the reduction of aldehydes, but in smaller quantities.

Pinacone is decomposed on distillation with dilute sulphuric acid, yielding *pinacoline*,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C(OH)\cdot C(OH)\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}=CH_3\cdot CO\cdot C(CH_3)_3+H_2O,$$

a very remarkable change, which involves the *migration* (the removal from one part of the molecule to another) of a methyl-group. Pinacoline is a colourless liquid, boils at 106°, and has a very strong odour of peppermint. That it has the constitution given above is shown by the facts that on oxidation with chromic acid it yields trimethylacetic acid and carbon dioxide,

$$(CH_3)_3C\cdot CO\cdot CH_3+4O=(CH_3)_3C\cdot COOH+CO_2+H_2O,$$

and that it is formed by the action of zinc methyl on trimethylacetyl chloride, $(CH_3)_3\cdot COCl$. (Compare p. 144).

Aldehydes and ketones are readily acted on by phosphorus pentachloride or pentabromide with formation of dihalogen derivatives of the paraffins, the oxygen atom of the carbonyl-group being displaced by two atoms of halogen. Aldehyde, for example, gives *dichlorethane* or *ethylidene dichloride*, $CH_3\cdot CHCl_2$, and *dibromethane* or *ethylidene dibromide*, $CH_3\cdot CHBr_2$,*

$$CH_3\cdot CHO+PCl_5=CH_3\cdot CHCl_2+POCl_3,$$

and acetone gives *ββ-dichloropropane* or *acetone dichloride*,

$$(CH_3)_2CO+PCl_5=(CH_3)_2CCl_2+POCl_3.$$

The characteristic behaviour of aldehydes and ketones with hydroxylamine, phenylhydrazine, hydrazine, and semicarbazide, has been described above (pp. 138–141).

Aldehydes and ketones combine directly with hydrogen cyanide, forming additive products, termed *hydroxycyanides* or *cyanohydrins*. This reaction may be expressed by the general equation,

$$>CO+HCN=>C\!<\!\!\begin{matrix}OH\\CN\end{matrix},$$

aldehyde, for example, giving *hydroxyethyl cyanide* or *aldehyde cyanohydrin*, $CH_3\cdot CH(OH)\cdot CN$, and acetone, *hydroxyisopropyl cyanide* or *acetone cyanohydrin*, $(CH_3)_2C(OH)\cdot CN$. These compounds are decomposed by alkalis giving hydrogen cyanide and an aldehyde or ketone; but mineral acids hydrolyse them, yielding

* The bivalent group, $CH_3\cdot CH<$, is termed ethylidene.

hydroxycarboxylic acids, the –CN group being transformed into –COOH (p. 315),

$$CH_3 \cdot CH(OH) \cdot CN + 2H_2O = CH_3 \cdot CH(OH) \cdot COOH + NH_3.$$

Aldehydes and ketones are readily acted on by the Grignard reagents, and give products which are decomposed by acids yielding secondary and tertiary alcohols respectively (p. 228).

Aldehydes *differ* from ketones in the following important respects :—They usually undergo oxidation to a fatty acid on exposure to the air, and are readily oxidised by an ammoniacal solution of silver hydroxide, especially in presence of a little potash or soda, a silver mirror being formed. They also reduce alkaline solutions of copper compounds (Fehling's solution). Ketones, on the other hand, are only attacked by powerful oxidising agents, and the difference between their behaviour on oxidation and that of aldehydes is so characteristic that it may be made use of for determining whether a substance of unknown constitution is an aldehyde or a ketone.

Aldehydes, on oxidation, are converted into fatty acids containing *the same number* of carbon atoms as the original compounds,

$$\underset{\text{Propaldehyde.}}{CH_3 \cdot CH_2 \cdot CHO} + O = \underset{\text{Propionic Acid.}}{CH_3 \cdot CH_2 \cdot COOH}.$$

$$\underset{\text{Heptaldehyde.}}{CH_3 \cdot [CH_2]_5 \cdot CHO} + O = \underset{\text{Heptylic Acid.}}{CH_3 \cdot [CH_2]_5 \cdot COOH}.$$

Ketones, on oxidation, are decomposed with formation, usually, of a mixture of acids, each of which contains *a smaller number* of carbon atoms than the original ketone,

$$CH_3 \cdot CO \cdot CH_3 + 4O = CH_3 \cdot COOH + CO_2 + H_2O.$$

$$CH_3 \cdot CO \cdot [CH_2]_4 \cdot CH_3 + 3O = CH_3 \cdot COOH + CH_3 \cdot [CH_2]_3 \cdot COOH.$$

In the case of mixed ketones, several acids may be formed. Methylamyl ketone, for example, might yield acetic acid and valeric acid on oxidation, in which case the molecule would be decomposed as indicated by the dotted line in the above equation, or it might give carbon dioxide and caproic acid, the molecule being attacked in a different manner,

$$CH_3 \cdot CO \cdot [CH_2]_4 \cdot CH_3 + 4O = CH_3 \cdot [CH_2]_4 \cdot COOH + H_2O + CO_2.$$

It frequently happens, therefore, that by the oxidation of mixed ketones several products are formed, the nature of which may afford important evidence as to the constitution of the ketone.

Generally speaking, the oxidation of a mixed ketone follows the rule (Popoff's rule) that the carbonyl-group remains united with the smaller alkyl-group, in which case the decomposition represented in the above

example by the first equation would take place almo t entirely. Popoff's rule, however, does not hold good in all cases.

Aldehydes *differ* from ketones in combining readily with ammonia, forming additive products,

$$\begin{matrix}H\\R\end{matrix}\!\!>\!CO + NH_3 = \begin{matrix}H\\R\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\NH_2\end{matrix}.$$

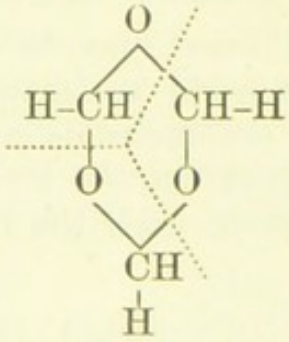
These compounds, of which aldehyde ammonia is an example, are usually crystalline, and very readily soluble in water. They are decomposed on distillation with dilute acids, with regeneration of the aldehyde,

$$R\cdot CH\!<\!\begin{matrix}OH\\NH_2\end{matrix} + HCl = R\cdot CHO + NH_4Cl.$$

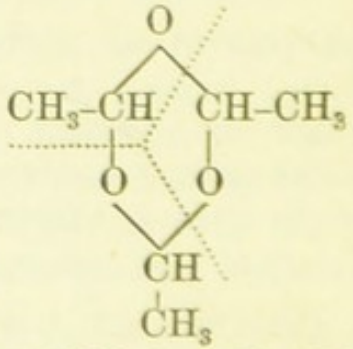
Aldehydes also *differ* from ketones in combining readily with alcohols with elimination of water, to form substances called *acetals*,

$$\begin{matrix}H\\R\end{matrix}\!\!>\!CO + \begin{matrix}HO\cdot C_2H_5\\HO\cdot C_2H_5\end{matrix} = \begin{matrix}H\\R\end{matrix}\!\!>\!C\!<\!\begin{matrix}O\cdot C_2H_5\\O\cdot C_2H_5\end{matrix} + H_2O.$$

Aldehydes, especially the lower members of the series, very readily undergo polymerisation, a property which distinguishes them from ketones in a very striking manner. Polymerisation may take place spontaneously, as in the case of formaldehyde, but usually only on addition of a small quantity of some mineral acid or of some substance, such as $ZnCl_2$, SO_2, &c., which acts in a manner as yet unexplained. The most common form of polymerisation is the combination of three molecules of the aldehyde to form substances such as trioxymethylene, $(CH_2O)_3$, and paracetaldehyde, $(C_2H_4O)_3$, the constitutions of which are probably respectively represented by the formulæ,



Trioxymethylene.



Paracetaldehyde, or Paraldehyde.

The method of combination of the three unsaturated molecules to form a polymeride will be readily understood with the aid of the dotted lines. These polymerides may be decomposed into the original aldehydes under suitable conditions. They do not show the characteristic reactions of aldehydes because they do not

contain the aldehyde group; the misleading names paraldehyde, metaformaldehyde, &c., were given to such substances when their constitutions were unknown.

Aldehydes are generally very unstable in presence of alkalis, by which they are converted into brown resins of unknown nature.

Ketones, as mentioned above, are much more stable than aldehydes; they do not reduce alkaline solutions of silver, copper, &c., do not combine directly with ammonia or with alcohols, and do not polymerise like the aldehydes.

When treated with dehydrating agents, both aldehydes and ketones readily undergo condensation, two or more molecules combining with loss of water, as illustrated in the case of aldehyde (p. 131) and acetone (p. 137). When condensations of this nature occur, the hydrogen atoms of one of the $-CH_2-$ or CH_3- groups, which is in *direct combination* with the carbonyl-group, take part in the reaction.

It is not necessary that the molecules undergoing condensation should be identical; two different ketones, two different aldehydes, or an aldehyde and a ketone, may condense together, always provided that the group, $-CH_2-CO-$, is present in the molecule of one at least of the substances.

CHAPTER IX.

The Fatty Acids.

The fatty acids form a homologous series of the general formula, $C_nH_{2n+1}\cdot CO\cdot OH$, or $C_nH_{2n}O_2$; they may be regarded as derivatives of the paraffins, the alcohols, or the aldehydes.

Paraffins.	Alcohols.	Aldehydes.	Fatty Acids.
$H\cdot CH_3$	$H\cdot CH_2\cdot OH$	$H\cdot CHO$	$H\cdot CO\cdot OH$
$CH_3\cdot CH_3$	$CH_3\cdot CH_2\cdot OH$	$CH_3\cdot CHO$	$CH_3\cdot CO\cdot OH$
$C_2H_5\cdot CH_3$	$C_2H_5\cdot CH_2\cdot OH$	$C_2H_5\cdot CHO$	$C_2H_5\cdot CO\cdot OH$.

The term '*fatty*' was given to the acids of this series because many of the higher members occur in a combined state in natural fats, and resemble fats in physical properties.

Formic acid, CH_2O_2, or $H\cdot CO\cdot OH$, occurs in nature in nettles, ants (*formicæ*), and other living organisms; the sting of an ant or nettle owes part, at least, of its irritating

effect to the presence of formic acid. When nettles or ants are macerated with water and the mixture is distilled, a weak aqueous solution of formic acid collects in the receiver.

Formic acid can be obtained from its elements by simple methods. When a large flask, moistened all over the inside with a concentrated solution of potash, is filled with carbon monoxide and heated in boiling water, the gas is slowly absorbed (as can be shown by providing the flask with a delivery-tube, which dips under mercury) and potassium formate is produced,

$$CO + KOH = H{\cdot}CO{\cdot}OK.$$

When moist carbon dioxide is left in contact with potassium, formate and bicarbonate of potassium are formed, the carbon dioxide being reduced by the nascent hydrogen evolved during the interaction of the potassium and water,

$$2H_2O + 2K = 2KOH + 2H,$$
$$CO_2 + 2H + KOH = H{\cdot}CO{\cdot}OK + H_2O,$$
$$\text{or } 4CO_2 + 4K + 2H_2O = 2H{\cdot}CO{\cdot}OK + 2KHCO_3.$$

The acid may be obtained from the potassium salt by distillation with dilute sulphuric acid.

Formic acid can also be obtained by oxidising methyl alcohol or formaldehyde with platinum black (precipitated platinum),

$CH_3{\cdot}OH + 2O = H{\cdot}CO{\cdot}OH + H_2O$, $H{\cdot}CHO + O = H{\cdot}CO{\cdot}OH$,

by heating hydrocyanic acid with alkalis or mineral acids,

$$HCN + 2H_2O = H{\cdot}CO{\cdot}OH + NH_3,*$$

and by decomposing chloroform with alcoholic potash (p. 182).

Formic acid is prepared by heating oxalic acid with glycerol (glycerin); it can be obtained by heating oxalic acid alone,

$$C_2O_4H_2 = H{\cdot}CO{\cdot}OH + CO_2;$$

but when this is done, a large proportion of the oxalic acid

* When an alkali is used ammonia is liberated, and a salt of formic acid obtained; whereas when a mineral acid is employed, free formic acid and an ammonium salt are produced.

either sublimes without change, or is decomposed into carbon monoxide, carbon dioxide, and water. In presence of glycerol, the anhydrous oxalic acid, produced from the hydrated crystals, $C_2H_2O_4,2H_2O$, is decomposed into carbon dioxide and formic acid; some of this acid distils over with the water and the rest combines with the hydroxide, glycerol, to form the salt, glyceryl formate, or monoformin,

$$C_2O_4H_2,2H_2O = H\cdot CO\cdot OH + CO_2 + 2H_2O,$$
$$C_3H_5(OH)_3 + H\cdot CO\cdot OH = C_3H_5(OH)_2\cdot O\cdot CHO + H_2O.$$

On the addition of a further quantity of the hydrated crystals of oxalic acid, the monoformin is decomposed by the water expelled from the crystals, yielding glycerol and formic acid,

$$C_3H_5(OH)_2\cdot O\cdot CHO + H_2O = C_3H_5(OH)_3 + H\cdot CO\cdot OH.$$

The regenerated glycerol and the anhydrous oxalic acid then interact as before, yielding monoformin, carbon dioxide, and water; the glycerol, like the sulphuric acid in the manufacture of ether (p. 117), is thus able, theoretically, to serve for the preparation of an unlimited quantity of formic acid.

Glycerol (about 50 c.c.) is placed in a retort connected with a condenser, crystallised oxalic acid (about 30 grams) is added, and the mixture is heated to about 100–110°; rather below this temperature, an evolution of carbon dioxide commences, and dilute formic acid distils, but after some time the action ceases. A further quantity of oxalic acid is then added, the temperature of the liquid being kept at 100–110°, when carbon dioxide is again evolved, and a more concentrated solution of formic acid collects in the receiver. The addition of oxalic acid is repeated from time to time, until a sufficient quantity of formic acid has been obtained.

In order to prepare *anhydrous* formic acid, the aqueous distillate is gently warmed with excess of litharge and then heated to boiling; as soon as the litharge ceases to be dissolved, the boiling solution is filtered, and the filtrate is evaporated to a small bulk, when colourless crystals of lead formate are obtained,

$$2H\cdot CO\cdot OH + PbO = (H\cdot CO\cdot O)_2Pb + H_2O.$$

This salt is carefully dried, and about $\frac{1}{20}$ths of it are introduced in the form of coarse powder, between plugs of cotton wool, into the inner tube of an upright Liebig's condenser, which is heated by

passing steam through the outer tube; carefully dried hydrogen sulphide is then led (from above) through the layer of salt, when anhydrous formic acid collects in the receiver,

$$(H\cdot COO)_2Pb + SH_2 = 2H\cdot CO\cdot OH + PbS.$$

This is now warmed for a short time (in a retort connected with a condenser) with the remainder of the dried lead salt, and the acid is then distilled, care being taken to prevent absorption of moisture; this rectification or distillation over lead formate is necessary in order to free the acid from hydrogen sulphide.

Formic acid is a colourless, mobile, hygroscopic liquid of sp. gr. 1·241 at 0°; it solidifies at low temperatures, melting again at 8°, and boiling at 101°. It has a pungent, irritating odour, recalling that of sulphur dioxide, and it blisters the skin like a nettle sting; it is miscible with water and alcohol in all proportions. Formic acid has an acid reaction to litmus, decomposes carbonates, and dissolves certain metallic oxides; it behaves, in fact, like a weak mineral acid. Like the aldehydes, it has reducing properties, and precipitates silver from warm solutions of ammoniacal silver hydroxide, being itself oxidised to carbon dioxide,

$$H\cdot CO\cdot OH + Ag_2O = 2Ag + CO_2 + H_2O.$$

When mixed with concentrated sulphuric acid, it is rapidly decomposed into carbon monoxide and water,

$$H\cdot CO\cdot OH = CO + H_2O,$$

and when heated alone at 160° in closed vessels, it yields carbon dioxide and hydrogen,

$$H\cdot CO\cdot OH = CO_2 + H_2.$$

The **formates,** or salts of formic acid, are prepared by neutralising the acid with alkalis, hydroxides, &c., or by double decomposition; they all dissolve in water, but some, such as the lead and silver salts, are only moderately soluble; they are all decomposed by warm concentrated sulphuric acid, with evolution of carbon monoxide, and by dilute mineral acids, yielding formic acid. The *sodium* salt, H·CO·ONa, and the *potassium* salt H·CO·OK, are deliquescent; when heated at about 250°, they are converted into oxalates with evolution

of hydrogen, a reaction which may be made use of for the preparation of pure hydrogen,

$$2H{\cdot}CO{\cdot}ONa = C_2O_4Na_2 + H_2.*$$

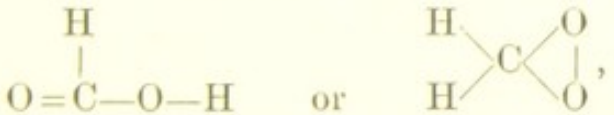
When *ammonium formate* is heated alone at about 230°, it is converted into formamide (p. 169), but when heated with phosphorus pentoxide it gives hydrogen cyanide (p. 316), water being eliminated in both stages,

$$H{\cdot}CO{\cdot}ONH_4 = H{\cdot}CO{\cdot}NH_2 + H_2O,$$
$$H{\cdot}CO{\cdot}NH_2 = HCN + H_2O.\dagger$$

Silver formate, H·CO·OAg, is precipitated in colourless crystals when silver nitrate is added to a *neutral* concentrated solution of a formate; but it is unstable, and quickly darkens when exposed to light or when warmed.

In order to test for formic acid or a formate, the solution, if acid, is neutralised with sodium carbonate, and a portion is warmed with an ammoniacal solution of silver oxide; if a black precipitate of silver is produced, the presence of formic acid is confirmed by evaporating the rest of the neutral solution to dryness, and then warming the residue *very gently* (below 100°) with concentrated sulphuric acid, when carbon monoxide is evolved, and may be ignited at the mouth of the test-tube.

Constitution.—Since formic acid has the molecular formula, CH_2O_2, it must have the constitution,



because these are the only formulæ which can be constructed, provided that the atoms have their normal valencies. But

* When a mixture of sodium formate and powdered arsenic (or an arsenic compound) is heated at about 400°, arsine is formed; the hydrides of antimony, phosphorus, sulphur, and of several other elements may be obtained in a similar manner.

† A mixture of ammonium formate and excess of phosphorus pentoxide is heated in a glass tube and the gaseous products are passed into a solution of potassium hydroxide; the presence of a cyanide in the solution may then be demonstrated in the usual manner (p. 16).

the second formula does not correctly indicate the behaviour of formic acid; it represents the two hydrogen atoms as being in the *same* state of combination, which is very improbable, since one of them is, the other is not, readily displaced by a metal; it does not recall the fact that formic acid behaves in some respects like an aldehyde, and probably, therefore, contains in its molecule the aldehyde-group, $O=\overset{H}{\overset{|}{C}}-$. For these and other reasons, which will be more clearly understood when the case of acetic acid has been considered (p. 159), the constitution of formic acid is represented by the first formula, which is usually written H·CO·OH, or simply H·COOH. From analogy with methyl alcohol and other compounds, it may be assumed that it is the hydrogen atom of the HO– group, and not that directly combined with carbon, which is displaced when the acid forms salts.

Acetic acid, $C_2H_4O_2$, or $CH_3·CO·OH$, occurs in nature in combination with alcohols in the essences or odoriferous, volatile oils of many plants, and is formed during the decay of certain organic substances. It can be produced by gently heating sodium methoxide in an atmosphere of carbon monoxide at about 180°, just as formic acid may be obtained from sodium or potassium hydroxide under similar conditions,

$$CH_3·ONa + CO = CH_3·CO·ONa;$$

also by boiling methyl cyanide (p. 322) with alkalis or mineral acids,

$$CH_3·CN + 2H_2O = CH_3·CO·OH + NH_3;$$

and by exposing alcohol or aldehyde, in contact with platinum black, to the oxidising action of the air,

$$C_2H_6O + 2O = C_2H_4O_2 + H_2O, \qquad C_2H_4O + O = C_2H_4O_2.$$

Acetic acid is prepared on the large scale from the brown aqueous distillate known as *pyroligneous acid*, which is obtained by the destructive distillation of wood (p. 92).

This liquid is first distilled and the vapours are passed through milk of lime, as already described, to separate the methyl alcohol,

acetone, and other volatile neutral substances; the solution of calcium acetate is then evaporated in iron pans, when tarry or 'empyreumatic' matter rises as a scum and is skimmed off. The solution is finally evaporated to dryness, and the calcium salt distilled with concentrated hydrochloric acid from copper vessels, care being taken not to employ excess of acid,

$$(C_2H_3O_2)_2Ca + 2HCl = 2C_2H_4O_2 + CaCl_2.$$

The concentrated aqueous acetic acid which collects in the receiver is now mixed with a little potassium permanganate or dichromate, and again distilled, by which means most of the impurities are oxidised, and commercial acetic acid is obtained.

Vinegar.—When beer, or a weak wine, such as claret, is left exposed to the air, it soon becomes sour, the alcohol which it contains being converted into acetic acid,

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$

This change is not a simple oxidation, as represented by the equation, but a process of fermentation brought about by a living ferment, *mycoderma aceti*. This ferment, being in the atmosphere, soon finds its way into the solution, where it grows and multiplies, and in some way causes the alcohol to combine with the oxygen of the air to form acetic acid. Strong wines, such as port and sherry, do not turn sour on exposure to the air, nor does an aqueous solution of pure alcohol, no matter how dilute, because the ferment is killed by strong alcohol, and cannot live in pure aqueous alcohol, since the latter does not contain nitrogenous substances, mineral salts, &c., which the ferment requires for food, and which are present in beers and wines.

Vinegar is simply a dilute solution of acetic acid, containing colouring matter and other substances, obtained by the acetous fermentation of poor wine or wine residues, of beer which has turned sour, or of other dilute alcoholic liquids; it is prepared by various processes.

In the old *French* or *Orléans* process, a small quantity of wine is placed in large vats covered with perforated lids, the vats having been previously soaked inside with hot vinegar; the ferment soon gets into the wine, and vinegar is produced, the solution gradually

becoming coated with a slimy film, known as 'mother-of-vinegar,' which is simply a mass of the living ferment. After some time more wine is added, the process being repeated at intervals until the vat is about half-full; most of the vinegar is then drawn off, and the operations are repeated with fresh quantities of wine.

In the modern *German* or '*quick vinegar process*,' large vats, provided with perforated sides, and fitted near the top and bottom with perforated discs, are employed, the space between the discs being filled with beech-wood shavings, which are first moistened with vinegar in order that they may become coated with a growth of the ferment; diluted 'raw-spirit,' containing 6–10 per cent. of alcohol, mixed with about 20 per cent. of vinegar, or with beer, or malt extract, to provide food for the ferment, is then poured in at the top, when it slowly trickles through the shavings, in contact with the ferment and with a free supply of air. The liquid which collects at the bottom is again poured over the shavings, the operations being continued until it is converted into vinegar—that is to say, until almost the whole of the alcohol has been oxidised to acetic acid. This process is much more rapid than the French method, since oxidation is hastened by the exposure of a large surface of the liquid; in both processes the fermenting liquid must be kept at a temperature of 25–40°.

Vinegar produced by the French process contains 6–10 per cent. of acetic acid; whereas that produced by the German process from diluted raw-spirit contains only 4–6 per cent. of acetic acid. Vinegar is used for table purposes and in the manufacture of whitelead and verdigris (see below); it is too dilute to be economically employed for the preparation of commercial acetic acid.

Pure acetic acid is prepared by distilling anhydrous sodium acetate with concentrated sulphuric acid; this salt is obtained by neutralising the impure commercial acid with sodium carbonate, and then fusing the recrystallised, hydrated salt, to expel the water. The distillate from this process contains only a small quantity of water, and solidifies, when cooled, to a mass of colourless crystals; it is then termed *glacial acetic acid* in contradistinction to the weaker acid, which does not crystallise so readily. The small quantity of water in glacial acetic acid can be got rid of by separating the crystals from

the more dilute mother-liquors, melting them, and then cooling and filtering again, repeating the processes if necessary.

Anhydrous acetic acid is a colourless, crystalline, hygroscopic solid, which melts at 16·5°, boils at 118°, and has a sp. gr. 1·080 at 0°; it has a pungent, penetrating smell, a burning action on the skin, and a sharp, sour taste; it is inflammable when near its boiling-point, and burns with a feebly luminous flame. It is miscible with water, alcohol, and ether in all proportions, and is an excellent solvent for most organic compounds; it also dissolves many inorganic substances, such as sulphur, iodine, &c., which are insoluble in water. It is a fairly strong acid, and acts readily on certain metals and metallic hydroxides; unlike formic acid, it has not reducing properties. The pure acid does not decolourise a solution of potassium permanganate; if impure, it will probably do so.

Acetic acid is largely used in chemistry laboratories, and in the manufacture of organic dyes, as well as for the preparation of many acetates of considerable commercial importance; the uses of vinegar have been mentioned.

The **acetates**, or salts of acetic acid, are prepared by neutralising the acid with carbonates, hydroxides, &c., or by double decomposition; they are crystalline compounds, soluble in water, and are decomposed by mineral acids with liberation of acetic acid. *Sodium acetate*, $C_2H_3O_2Na,3H_2O$, is extensively used in the laboratory; it dissolves in its water of crystallisation when heated, but as the water is expelled the salt solidifies. The anhydrous salt is hygroscopic, and is used as a dehydrating agent. *Potassium acetate*, $C_2H_3O_2K$, is deliquescent. *Ammonium acetate* is gradually decomposed into acetamide (p. 168) and water when it is distilled. *Silver acetate*, $C_2H_3O_2Ag$, is precipitated in colourless crystals when silver nitrate is added to a concentrated neutral solution of an acetate; it is moderately soluble in cold water, and does not darken on exposure to light. *Lead acetate*, or 'sugar of lead,' $(C_2H_3O_2)_2Pb,3H_2O$, prepared by dissolving litharge in

commercial acetic acid, has a sweet (sugary) astringent taste, and is very poisonous; when its solution is boiled with litharge a soluble basic lead acetate is formed.

Copper acetate, $(C_2H_3O_2)_2Cu,H_2O$, is obtained by dissolving cupric oxide in acetic acid; it is a dark, greenish-blue substance. *Verdigris* is a blue, hydrated, basic copper acetate, $(C_2H_3O_2)_2Cu,Cu(OH)_2$, which is manufactured by leaving sheet-copper in contact with vinegar, or with grape-skins (wine-residues), the sugars in which have undergone fermentation first into alcohol, then into acetic acid. When washed with water, part of the salt dissolves and green verdigris is obtained; both these basic acetates are used as pigments. Copper acetate and copper metarsenite unite to form a beautiful emerald-green, insoluble double salt, $(C_2H_3O_2)_2Cu$, $3Cu(AsO_2)_2$, known as *Schweinfurter green*, *Paris green*, or *emerald green*. This substance was formerly employed in large quantities in colouring wall-papers, carpets, blinds, &c.; but as its dust is poisonous, and as it is liable to decompose in presence of decaying organic matter, with evolution of hydrogen arsenide, its use is now almost abandoned.

Ferrous acetate is prepared on the large scale by dissolving scrap iron in pyroligneous acid; the solution is known in commerce as pyrolignite of iron, 'iron liquor,' or 'black liquor.' *Ferric acetate* is prepared by treating freshly precipitated ferric hydroxide with acetic acid. When a solution of ferric acetate containing traces of other salts is heated, an insoluble basic iron salt is precipitated, and the solution becomes colourless; this property is made use of in the dyeing and 'printing' of cotton, for which purpose 'iron liquor' is used as a mordant. *Aluminium acetate* is prepared by treating a solution of aluminium sulphate with sugar of lead, or calcium acetate, or by dissolving precipitated aluminium hydroxide in acetic acid; its solution is known as 'red liquor,'* and is used as a mordant, because when it is heated it loses acetic acid and gives an insoluble basic salt. *Chromic acetate* is prepared by similar methods, and is also used as a mordant (Part II. p. 639).

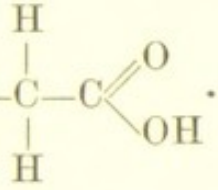
If a solution is to be tested for acetic acid or an acetate, it is boiled with a few drops of strong sulphuric acid, when, if acetic acid is present, its characteristic smell is observed. A fresh portion of the solution is then neutralised, if necessary, with sodium carbonate and evaporated to dryness; the residue

* Because of its use in dyeing alizarin-reds.

is warmed with a few drops of alcohol and a little strong sulphuric acid. If acetic acid is present ethyl acetate (p. 193) is formed, and is recognised by its pleasant, fruity odour (which should be compared with that of alcohol and of ether).

Constitution.—The formation of acetic acid by the oxidation of ethyl alcohol is clearly a process similar to that by which formic acid is produced from methyl alcohol; if, therefore, the two changes take place in a similar manner,

$$H{\cdot}CH_2{\cdot}OH + 2O = H{\cdot}CO{\cdot}OH + H_2O,$$
$$CH_3{\cdot}CH_2{\cdot}OH + 2O = CH_3{\cdot}CO{\cdot}OH + H_2O,$$

the constitution of acetic acid would be expressed by the formula, $CH_3{\cdot}CO{\cdot}OH$, or  .

Again, formic acid is produced when hydrogen cyanide is boiled with mineral acids (p. 317), whilst acetic acid is formed from methyl cyanide under the same conditions; if these two changes are analogous,

$$\left.\begin{array}{c} H{\cdot}CN + 2H_2O = H{\cdot}CO{\cdot}OH + NH_3, \\ CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}CO{\cdot}OH + NH_3, \end{array}\right|$$

the constitution of acetic acid would be represented by the same formula as before.

If now other methods of formation are considered, together with the chemical behaviour of acetic acid, including its various decompositions and its relation to formic acid, it will be seen that the above constitutional formula, and *no other*, affords a satisfactory interpretation or summary of all the facts.

From the numerous arguments which might be advanced in support of this statement, the following may be given. (1) The molecule of acetic acid contains the HO– group, because its behaviour with phosphorus pentachloride is similar to that of alcohols (pp. 94, 99). (2) It contains a

methyl or CH_3– group—that is to say, three of the four atoms of hydrogen are *directly* combined with carbon. This is shown by the fact that three of the four hydrogen atoms behave like those in CH_4, C_2H_6, &c., and are displaceable by free chlorine (p. 169); also by the production of ethane by the electrolysis of potassium acetate (p. 60), a change which can be formulated in a simple manner, only by assuming the presence of a CH_3– group,

$$\begin{matrix} CH_3\cdot CO\cdot OK \\ CH_3\cdot CO\cdot OK \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + \begin{matrix} CO_2 \\ \\ CO_2 \end{matrix} + 2K.$$

Since, then, judging by its chemical behaviour, the molecule of acetic acid contains a CH_3– and an HO– group, it must have the constitution, $CH_3\cdot C\langle^{O}_{OH}$, which confirms the conclusion previously arrived at from other considerations.

The relation between formic and acetic acids, and their similarity in certain chemical properties, are also satisfactorily accounted for by the constitutional formulæ,

$$H\cdot C\langle^{O}_{OH} \quad \text{and} \quad CH_3\cdot C\langle^{O}_{OH},$$

which thus confirm one another. The acids are both represented as containing the univalent group of atoms, $-C\langle^{O}_{OH}$, which has not been met with in any of the *neutral* compounds yet considered; it may be concluded, therefore, that their characteristic *acid* properties are due to the presence of this group. As, moreover, aldehydes contain the group, $-C\langle^{O}_{H}$, but do not contain hydrogen displaceable by metals, it must be the hydrogen atom of the HO– group which is displaced, when the acids form salts. The particular univalent group of atoms common to formic and acetic acids is named the *carboxyl*-group, and is usually written –CO·OH, or simply, for convenience, –COOH.

Homologues of Acetic Acid.—As all the higher members

of the series of fatty acids resemble formic and acetic acids in chemical properties, in their methods of formation, and in their transformations, it is assumed that they all contain a carboxyl-group. With the exception of formic acid, they may, in fact, be regarded as derived from the paraffins, by the substitution of the univalent carboxyl-group for one atom of hydrogen; acetic acid, $CH_3 \cdot COOH$, from methane, CH_4; propionic acid, $C_2H_5 \cdot COOH$, from ethane; and so on. They form, therefore, a homologous series of the general formula, $C_nH_{2n+1} \cdot COOH$, $C_nH_{2n}O_2$, or R·COOH, and are all monobasic or *monocarboxylic* acids.

As in other homologous series, the higher members show isomerism, the number of isomerides theoretically possible, in any given case, being the same as that of the corresponding primary alcohols. The two isomeric acids, butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, and isobutyric acid, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot COOH$, for example, correspond with the two primary alcohols $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$, and $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot OH$, respectively.

Those isomerides which are derived from the normal paraffins (p. 65), by the substitution of -COOH for one atom of hydrogen in a CH_3– group, are termed *normal* acids, as normal butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, normal valeric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$; those which contain the group, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH$– are usually termed *iso*-acids, as, for example, isobutyric acid, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot COOH$, isovaleric acid, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot COOH$, but the term is not used very systematically.

In order to distinguish other isomerides by names, which are also expressive of their constitutions, the acids may be regarded as derived from acetic acid, just as the alcohols may be regarded as derivatives of carbinol (p. 108); the

four isomerides of the molecular formula, $C_5H_{10}O_2$, for example, are named as follows :—

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$

Normal Valeric Acid
(Propylacetic Acid).

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot COOH$

Isovaleric Acid
(Isopropylacetic Acid).

$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH \cdot COOH$

Methylethylacetic Acid.

$\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!C \cdot COOH$

Trimethylacetic Acid.

Propionic acid, $CH_3 \cdot CH_2 \cdot COOH$, occurs in crude pyroligneous acid; it is formed when acrylic acid (p. 291) is reduced with sodium amalgam and water,

$$C_3H_4O_2 + 2H = C_3H_6O_2,$$

and when lactic acid (p. 239) is heated with concentrated hydriodic acid (this reaction takes place in two stages),

$$CH_3 \cdot CH(OH) \cdot COOH + HI = CH_3 \cdot CHI \cdot COOH + H_2O,$$
$$CH_3 \cdot CHI \cdot COOH + HI = CH_3 \cdot CH_2 \cdot COOH + I_2.$$

It is prepared by oxidising propyl alcohol with chromic acid,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH + 2O = CH_3 \cdot CH_2 \cdot COOH + H_2O.$$

Propionic acid is a colourless liquid, boils at 141°, and has a pungent sour smell; it is miscible with water in all proportions. Propionic acid is a mono-carboxylic acid, and closely resembles acetic acid in chemical properties; its salts, the **propionates,** are soluble in water, and of little importance.

There are two acids of the molecular formula, $C_4H_8O_2$. **Normal butyric acid,** $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, occurs in the vegetable and animal kingdoms; in combination with glycerol, it is an important component of butter. It is formed during the decay of animal matter and during the butyric fermentation of lactic acid. When milk is left exposed to the air it turns sour, owing to the lactose or milk-sugar which it contains being converted into lactic acid by an organism, the *lactic ferment*, which is present in the air, and falls into the milk,

$$\underset{\text{Lactose.}}{C_{12}H_{22}O_{11}} + H_2O = 4\underset{\text{Lactic Acid.}}{C_3H_6O_3}$$

The lactic ferment has the power of converting sugars other than lactose into lactic acid. When now a little decaying cheese is added to the sour milk, and the solution is kept neutral by the addition of chalk,* *butyric fermentation* sets in, the lactic acid being converted into butyric acid by the action of another organism, the *butyric ferment*, which is present in the decomposing cheese,

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

Butyric acid is usually prepared by a combination of these two processes of fermentation.

Butyric acid is a thick, sour liquid, boiling at 163°. It has a very disagreeable odour, like that of rancid butter and stale perspiration, in which it occurs; it is miscible with water.

The **butyrates**, or salts of butyric acid, are soluble in water; the *calcium salt*, $(C_4H_7O_2)_2Ca,H_2O$, is more soluble in cold than in hot water, so that when a cold saturated solution is heated, some of the salt separates in crystals, and the solution becomes turbid.

Isobutyric acid, or dimethylacetic acid, $(CH_3)_2CH\cdot COOH$, may be prepared by the oxidation of isobutyl alcohol,

$$(CH_3)_2CH\cdot CH_2\cdot OH + 2O = (CH_3)_2CH\cdot COOH + H_2O.$$

It boils at 155°, and resembles the normal acid very closely, but it is not miscible with water.

The *calcium salt*, $(C_4H_7O_2)_2Ca,5H_2O$, unlike that of normal butyric acid, is more soluble in hot than in cold water.

Of the four isomerides of the molecular formula, $C_5H_{10}O_2$, **isovaleric acid**, or isopropylacetic acid, $(CH_3)_2CH\cdot CH_2\cdot COOH$, and **optically active valeric acid**, or methylethylacetic acid (p. 267),

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH\cdot COOH,$$

are the more important.

These acids occur together in the plant all-heal, or valerian, and in angelica root; the mixture of acids, obtained when the macerated

* The ferment ceases to act if the solution becomes too strongly acid.

plants are distilled with water, is known as valeric or valerianic acid, and is an oily liquid, boiling at about 174°.

A mixture of these two acids may be prepared by oxidising commercial amyl alcohol (p. 111) with chromic acid.

The **hexylic acids**, $C_6H_{12}O_2$, are of little importance; seven of the eight isomerides theoretically possible are known, including normal hexylic acid (caproïc acid).

Normal heptylic acid, $C_7H_{14}O_2$, or $C_6H_{13}\cdot COOH$, one of the seventeen theoretically possible isomerides, of which only eleven are known, is prepared by oxidising castor-oil, or œnanthaldehyde (p. 134), with nitric acid; it is an oily, rather unpleasant-smelling liquid, sparingly soluble in water; it boils at 223°, and, like all the lower members of the series, is readily volatile in steam.

Palmitic acid, $C_{16}H_{32}O_2$, or $C_{15}H_{31}\cdot COOH$, and **stearic acid**, $C_{18}H_{36}O_2$, or $C_{17}H_{35}\cdot COOH$, occur in large quantities in combination with glycerol in animal and vegetable fats and oils (p. 175), from which they are prepared on the large scale, principally for the manufacture of stearin candles; they are colourless, waxy substances melting at 62° and 69° respectively, and are insoluble in water, but soluble in alcohol, ether, &c. Their sodium and potassium salts are soluble in pure water, and are the principal components of soaps (p. 177), but their calcium, magnesium, and other salts are insoluble.

A mixture of these two acids was at one time thought to be a definite compound, and named *margaric acid*; this name is now given to an artificially prepared acid, $C_{17}H_{34}O_2$, or $C_{16}H_{33}\cdot COOH$, which stands between palmitic and stearic acids in the series, and which seems not to occur in nature.

Derivatives of the Fatty Acids.

Acid Chlorides.—When phosphorus pentachloride is added to anhydrous acetic acid an energetic action takes place, and **acetyl chloride**, $CH_3\cdot C\langle{}^{O}_{Cl}$, is formed, with evolution of hydrogen chloride; this change is analogous to that which occurs when an alcohol is treated with phosphorus pentachloride,

$$CH_3\cdot CO\cdot OH + PCl_5 = CH_3\cdot COCl + POCl_3 + HCl,$$
$$CH_3\cdot CH_2\cdot OH + PCl_5 = CH_3\cdot CH_2Cl + POCl_3 + HCl.$$

Phosphorus trichloride and oxychloride also convert acetic acid into acetyl chloride.

Acetyl chloride is prepared by cautiously adding phosphorus trichloride (20 g.) from a tap funnel to *anhydrous* acetic acid (25 g.) contained in a distillation flask connected with a condenser,

$$3CH_3\cdot COOH + 2PCl_3 = 3CH_3\cdot COCl + P_2O_3 + 3HCl.$$

Another method of preparation consists in dropping phosphorus oxychloride (1 mol.) on anhydrous sodium acetate (2 mols.),

$$2CH_3\cdot COONa + POCl_3 = 2CH_3\cdot COCl + NaPO_3 + NaCl.$$

In either case the product is then distilled from a water-bath, and collected in a receiver from which moisture is excluded. Acetyl chloride is a colourless, pungent-smelling liquid, which boils at 55°, and fumes in moist air; it is rapidly decomposed by water, with formation of acetic acid,

$$CH_3\cdot COCl + H_2O = CH_3\cdot COOH + HCl.$$

Acetyl chloride is quickly decomposed not only by water and by alkalis, but also, more or less rapidly, by all compounds containing one or more hydroxyl-groups; the interaction always takes place in such a way that hydrogen chloride is produced, the univalent *acetyl*-group, $CH_3\cdot C\langle^{O}$, displacing the hydrogen of the hydroxyl-group,

$$C_2H_5\cdot OH + CH_3\cdot COCl = C_2H_5\cdot O\cdot CO\cdot CH_3 + HCl,$$
$$C_3H_7\cdot OH + CH_3\cdot COCl = C_3H_7\cdot O\cdot CO\cdot CH_3 + HCl.$$

Acetyl chloride, therefore, may be employed for *detecting the presence of a hydroxyl-group* in the molecule of a compound.

For this purpose the dry substance (in the state of a fine powder, if a solid) is added to excess of acetyl chloride, the mixture or solution is heated for some time (with reflux condenser), and the acetyl chloride is then distilled off on a water-bath. The substance may be recovered unchanged, an

indication that it is not a hydroxy-compound, or it may be converted into a new substance, an *acetyl*-derivative, by the substitution of the acetyl-group for hydrogen.

In the latter case the substance is purified and its composition is ascertained by a combustion;* or, since acetyl-derivatives are generally decomposed by boiling acids and alkalis,

$$C_2H_5\cdot O\cdot CO\cdot CH_3 + KOH = C_2H_5\cdot OH + CH_3\cdot COOK,$$

the quantity of acetic acid formed under these conditions, from a known weight of the substance, may be estimated. The molecular formula of the original substance being known, it is then possible to ascertain how many hydrogen atoms in the molecule have been displaced by acetyl-groups; in other words, how many hydroxyl-groups were contained in the molecule of the original compound.

Example.—A substance of the molecular formula, $C_2H_6O_2$ (glycol, p. 233), is converted by acetyl chloride into a compound which on analysis is found to have the *empirical* formula, $C_3H_5O_2$; this result points to the conclusion that the original compound contains two hydroxyl-groups, and that the *molecular* formula of the product is $C_6H_{10}O_4$ or $C_2H_4O_2(CO\cdot CH_3)_2$. When 0·3 g. of this product is hydrolysed it yields 0·2466 g. of acetic acid. This result proves that the molecule of the original substance contains two hydroxyl-groups.

Determination of Acetyl-Groups.—When the acetyl-derivative is that of a neutral compound it is merely boiled with a known quantity of standard alkali or acid, and the amount of acetic acid which has been formed is then estimated by titration.

In other cases, the acetyl-derivative (about 0·2 g.) is mixed with about 100 c.c. of a 10 per cent. aqueous solution of benzene-sulphonic acid (Part II. p. 430), and the solution is slowly distilled in a current of steam until acetic acid ceases to pass over; the distillate is then titrated with standard alkali.

All the fatty acids except formic acid may be converted into *acid chlorides*, such as *propionyl chloride*, $CH_3\cdot CH_2\cdot COCl$, by the methods described above; the products resemble acetyl chloride in chemical properties. *Acid bromides*, such as $CH_3\cdot COBr$, can be obtained in a similar manner.

Anhydrides.—The hydrogen atom in a carboxyl-group

* When the acetyl-derivative has the same, or nearly the same, percentage composition as the original substance, the number of acetyl-groups in the molecule is determined by the second method.

–COOH, as a rule, is not displaced by the acetyl-group when an acid is treated with acetyl chloride, but when an alkali salt of a fatty acid is heated with acetyl chloride, an acetyl-derivative of the acid is formed,

$$CH_3\cdot COOK + CH_3\cdot COCl = CH_3\cdot CO\cdot O\cdot CO\cdot CH_3 + KCl.$$

The compound obtained from an acetate in this way may be regarded as acetyl oxide, $(CH_3\cdot CO)_2O$, or as an **anhydride** of acetic acid, derived from 2 mols. of the acid by loss of 1 mol. of water, just as ethers are derived from alcohols and inorganic anhydrides from the corresponding acids,

$$\begin{matrix} CH_3\cdot CO\cdot OH \\ CH_3\cdot COO\cdot H \end{matrix} = \begin{matrix} CH_3\cdot CO \\ CH_3\cdot CO \end{matrix}\!\!>O + H_2O$$

$$\begin{matrix} C_2H_5\cdot OH \\ C_2H_5\cdot OH \end{matrix} = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>O + H_2O \qquad \begin{matrix} NO_2\cdot OH \\ NO_2\cdot OH \end{matrix} = \begin{matrix} NO_2 \\ NO_2 \end{matrix}\!\!>O + H_2O.$$

Acetic anhydride, $(CH_3\cdot CO)_2O$, may be prepared by treating the anhydrous alkali acetates (4 mols.) with phosphorus oxychloride (1 mol.); the salt is first acted on by the oxychloride, yielding acetyl chloride (p. 165), which then reacts with more salt, forming acetic anhydride; these two reactions may be summarised in the equation,

$$4CH_3\cdot COONa + POCl_3 = 2(CH_3\cdot CO)_2O + NaPO_3 + 3NaCl.$$

The powdered alkali salt is contained in a distillation flask connected with a condenser, and, when the oxychloride has been cautiously added, the flask is heated in an oil-bath or over the free flame, in order to distil the acetic anhydride; the product is collected in a receiver from which moisture is excluded.

Acetic anhydride is a mobile liquid, boils at 137°, and has an unpleasant, irritating odour; it is decomposed by alkalis, by water, and by all substances which contain the hydroxyl-group, acetyl-derivatives being formed,

$$(CH_3\cdot CO)_2O + H_2O = 2CH_3\cdot COOH,$$

$$(CH_3\cdot CO)_2O + C_2H_5\cdot OH = CH_3\cdot CO\cdot O\cdot C_2H_5 + CH_3\cdot COOH.$$

Acetic anhydride, therefore, like acetyl chloride, may be employed for the detection of hydroxyl-groups in the molecule of a compound.

The operations are carried out as described in the case of acetyl chloride, and the product is examined by methods similar to those already given. The action of acetic anhydride on substances containing hydroxyl-groups is often accelerated by the addition of anhydrous sodium acetate, or of a small quantity of zinc chloride or sulphuric acid.

Other fatty acids, except formic acid, may be converted into anhydrides by treating the acid chloride with the alkali salt of the acid, or by heating excess of the alkali salt with phosphorus oxychloride. If an acid chloride is treated with a salt of a different acid, *mixed anhydrides*, corresponding with the mixed ethers, are obtained. All these anhydrides resemble acetic anhydride in chemical properties.

Amides.—Acetyl chloride and acetic anhydride react not only with compounds containing a hydroxyl-group, but also with anhydrous ammonia; the compound obtained in this way may be regarded as derived from ammonia by the substitution of the acetyl-group for one atom of hydrogen, and it is named acetamide,

$$CH_3{\cdot}COCl + 2NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + NH_4Cl,$$
$$(CH_3{\cdot}CO)_2O + 2NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}CO{\cdot}ONH_4.$$

Acetamide, $CH_3{\cdot}CO{\cdot}NH_2$, may also be produced by treating ethyl acetate (p. 193) with a concentrated aqueous solution of ammonium hydroxide,

$$CH_3{\cdot}CO{\cdot}OC_2H_5 + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH,$$

or by slowly distilling ammonium acetate in a stream of dry ammonia,

$$CH_3{\cdot}CO{\cdot}ONH_4 = CH_3{\cdot}CO{\cdot}NH_2 + H_2O.$$

In the first method the ethyl acetate is left in contact with an equal volume of the ammonium hydroxide solution until it has dissolved,* and the solution is then distilled slowly; the fraction, which passes over from about 200° upwards, solidifies when it is cooled, and is purified by redistillation.

In the second method, only a small proportion of the ammonium acetate is converted into acetamide, and that portion of the distillate boiling above 140° is collected separately and redistilled;

* This operation may require several days.

these operations are repeated several times, and from the fractions collected above 200° the acetamide is isolated by further distillation or by recrystallisation from ether.

Acetamide crystallises in colourless needles, melts at 82°, and boils at 222°. When pure it has only a faint odour, but as usually prepared it has a strong smell of mice; it is readily soluble in water and alcohol. When heated with mineral acids or alkalis, it is decomposed into acetic acid and ammonia, or their salts (compare footnote, p. 150),

$$CH_3{\cdot}CO{\cdot}NH_2 + H_2O = CH_3{\cdot}COOH + NH_3;$$

on distillation with phosphoric anhydride, it loses 1 mol. of water, and is converted into *methyl cyanide* or *acetonitrile*,

$$CH_3{\cdot}CO{\cdot}NH_2 = CH_3{\cdot}CN + H_2O.$$

Formic acid and all the higher fatty acids may be converted into amides by methods similar to those given above; *formamide*, $H{\cdot}CO{\cdot}NH_2$, for example, may be prepared by distilling ammonium formate. These amides closely resemble acetamide in chemical and physical properties, but their solubility in water rapidly diminishes as the molecular weight increases.

Halogen Substitution Products of Acetic Acid.

Since acetic acid, like methyl chloride, is a mono-substitution product of marsh-gas, and contains three atoms of hydrogen combined with carbon, it might be expected to give halogen substitution products, just as does methyl chloride. As a matter of fact, acetic acid yields three substitution products when it is heated with chlorine in direct sunlight,

$$CH_3{\cdot}COOH + Cl_2 = CH_2Cl{\cdot}COOH + HCl,$$
$$CH_3{\cdot}COOH + 2Cl_2 = CHCl_2{\cdot}COOH + 2HCl,$$
$$CH_3{\cdot}COOH + 3Cl_2 = CCl_3{\cdot}COOH + 3HCl.$$

Again, if the constitutions of acetic acid and of these three compounds are correctly represented by these formulæ, it might be inferred that, as the chloro-substitution products still contain the carboxyl-group, they would behave like mono-carboxylic acids, and, like acetic acid, form salts, acid chlorides, anhydrides, &c. This inference, also, is a sound one; the three substitution products are monobasic acids,

similar to acetic acid and to one another in chemical properties; they are reconverted into acetic acid by nascent hydrogen, just as the substitution products of methane or ethane are transformed into the hydrocarbons.

The three chloracetic acids may be prepared by passing chlorine into boiling acetic acid, to which a little iodine has been added. When iodine is present the process can be carried out in absence of sunlight, because the iodine is converted into iodine trichloride, which acts on the acetic acid even in the dark,

$$CH_3\cdot COOH + ICl_3 = CH_2Cl\cdot COOH + HCl + ICl.$$

The iodine chloride is again converted into trichloride by direct combination with chlorine, and so the process continues, a very small quantity of iodine being sufficient to ensure chlorination. The iodine, or rather the iodine chloride, is spoken of as a chlorine *carrier* (Part II. p. 381).

Chloracetic acid, $CH_2Cl\cdot COOH$, melts at 62°, and boils at 185–187°.

Dichloracetic acid, $CHCl_2\cdot COOH$, is a liquid, and boils at 190–191°; it is best prepared by heating chloral hydrate with potassium cyanide (or ferrocyanide) in aqueous solution,

$$KCN + CCl_3\cdot CH(OH)_2 = CHCl_2\cdot COOH + HCN + KCl.$$

Trichloracetic acid, $CCl_3\cdot COOH$, is best prepared by oxidising the corresponding aldehyde, chloral, with concentrated nitric acid,

$$CCl_3\cdot CHO + O = CCl_3\cdot COOH.$$

It melts at 55°, boils at 195°, and is decomposed by hot alkalis into chloroform and a carbonate,

$$CCl_3\cdot COOH + KOH = CHCl_3 + KHCO_3.$$

The *bromacetic* and *iodacetic* acids resemble the chloracetic acids in properties.

The higher fatty acids may be converted into halogen substitution products, which, however, unlike those of acetic acid, exist in isomeric forms. Propionic acid, for example, gives two monochloropropionic acids—namely, α-chloro-propionic acid, $CH_3\cdot CHCl\cdot COOH$, and β-chloro-propionic acid, $CH_2Cl\cdot CH_2\cdot COOH$. For the purpose

of distinguishing between these substitution products, the carbon atoms are lettered α, β, γ, δ, &c., commencing always with that which is combined with the carboxyl-group,

$$\underset{\delta}{CH_3}\cdot\underset{\gamma}{CH_2}\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CH_2}\cdot COOH;$$

the acid of the constitution, $(CH_3)_2CBr\cdot CH_2\cdot COOH$, for example, is named β-bromisopropylacetic acid.

The fatty acids (and other saturated acids) are not readily attacked by any of the halogens (except perhaps by fluorine), but the acid chlorides and bromides, and the anhydrides, are comparatively easily converted into mono-substitution products. In order, therefore, to prepare its halogen derivative, the anhydrous acid is mixed with a small quantity of red phosphorus, and dry chlorine is then passed into or over the mixture, or bromine is slowly added to it from a dropping funnel, gentle heat being afterwards applied in order to complete the interaction (method of Hell and of Volhard). Under these conditions the acid chloride or bromide is first formed, by the action of the halogen phosphorus compound (PCl_3 or PBr_3), or the acid, if dicarboxylic (p. 251), is often converted into its anhydride; substitution then takes place, the halogen displacing one hydrogen atom from the α-position; if there is no hydrogen atom in the α-position—as, for example, in trimethylacetic acid (p. 162)—a halogen derivative is not formed. When the reaction is at an end the product is either treated with water to convert it into the acid, or it is poured into an alcohol to convert it into an ester,

$$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle CBr\cdot COBr + CH_3\cdot OH = \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle CBr\cdot COOCH_3 + HBr;$$

the second method is generally used when the substituted acid is a liquid, because the ester is more easily purified than the acid by fractional distillation.

The α-halogen derivatives of many of the fatty acids may also be prepared by the following method:—Ethyl malonate is converted into a mono-alkyl substitution product (p. 207), the ester is hydrolysed, and the alkylmalonic acid is treated with chlorine or bromine (X), whereby the α-hydrogen atom is easily displaced; the product is then heated in order to convert it into a halogen derivative of a fatty acid. The changes which occur are indicated below.

$$CH_2\left\langle\begin{matrix}COOEt\\COOEt\end{matrix}\right. \rightarrow CHR\left\langle\begin{matrix}COOEt\\COOEt\end{matrix}\right. \rightarrow CHR\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. \rightarrow$$

$$CXR\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. \rightarrow CHXR\cdot COOH.$$

Derivatives containing the halogen in the α- or in other (β, γ, &c.) positions may be prepared indirectly by combining an unsaturated acid with a halogen acid or with a halogen (p. 291); also by displacing the hydroxyl-group of a hydroxy-acid by halogen, with the aid of a halogen acid or a halogen derivative of phosphorus.

The halogen atom or atoms in a halogen substitution product of a fatty acid behave like those in the halogen derivatives of the hydrocarbons, and *not* like those in acid chlorides or bromides; this behaviour is more fully described later (p. 187).

SUMMARY AND EXTENSION.

The Fatty Acids. Carboxy-derivatives of the paraffins of the general formula, R·COOH, or $C_nH_{2n}O_2$.—The more important members of this homologous series are the following :—

	M.p.	B.p.	Sp. gr.
Formic acid, H·COOH,	+ 8·3°	101°	1·241 at 0°
Acetic acid, CH_3·COOH,	+16·5°	118°	1·080 "
Propionic acid, C_2H_5·COOH,	−36°	141°	1·013 "
Butyric acid, C_3H_7·COOH, Normal	− 4°	163°	0·978 "
Butyric acid, C_3H_7·COOH, Iso-	−79°	155°	0·965 "
Valeric acid, C_4H_9·COOH, Normal	−59°	186°	0·957 "
Valeric acid, C_4H_9·COOH, Iso-	−51°	174°	0·947 "
Heptylic acid, C_6H_{13}·COOH, Normal	−10·5°	223°	0·945 "
Lauric acid, $C_{11}H_{23}$·COOH, "	+43·6°	—	0·875 (At the melting-point.)
Myristic acid, $C_{13}H_{27}$·COOH, "	+54°	—	0·862 (At the melting-point.)
Palmitic acid, $C_{15}H_{31}$·COOH, "	+62°	—	0·853 (At the melting-point.)
Stearic acid, $C_{17}H_{35}$·COOH, "	+69°	—	0·845 (At the melting-point.)

It is an interesting fact that lauric acid, and all the higher members named in this table, occur in nature in fats and oils, contain an even number of carbon atoms, and are all normal acids. The higher normal acids containing an odd number of carbon atoms, C_8H_{17}·COOH, $C_{10}H_{21}$·COOH, &c., are known, but they do not occur in nature.

Formic acid is prepared by heating oxalic acid with glycerol, acetic acid from pyroligneous acid, and by the acetous fermentation of alcohol, butyric acid by the butyric fermentation of lactic acid, and palmitic and stearic acids by the hydrolysis of glycerides occurring in fats and oils.

General Methods of Preparation.—(1) Primary alcohols or aldehydes are oxidised,

$$C_2H_5\cdot CH_2\cdot OH + 2\,O = C_2H_5\cdot COOH + H_2O,$$
$$C_6H_{13}\cdot CHO + O = C_6H_{13}\cdot COOH.$$

(2) Alkyl cyanides are heated with alkalis or mineral acids,

$$C_2H_5\cdot CN + 2H_2O = C_2H_5\cdot COOH + NH_3.$$

(3) Those dicarboxylic acids in which the two carboxyl-groups are combined with one and the same carbon atom are decomposed by heat (p. 208),

$$CH_2(COOH)_2 = CH_3\cdot COOH + CO_2.$$

(4) Derivatives of ethyl acetoacetate are hydrolysed (p. 202),

$$CH_3\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5 + 2KOH = C_3H_7\cdot CH_2\cdot COOK + CH_3\cdot COOK + C_2H_5\cdot OH.$$

(5) Dry carbon dioxide is passed into an ethereal solution of a Grignard compound,

$$Mg\begin{matrix}<^{C_2H_5}\\ _{Br}\end{matrix} + CO_2 = C_2H_5\cdot CO\cdot O\cdot MgBr,$$

and the product is decomposed with a dilute acid (p. 228).

Physical Properties. — At ordinary temperatures the lower members (except acetic acid) are liquids, miscible with water, alcohol, and ether, in all proportions. As the molecular weight increases they become more oily in character, gradually lose their pungent smell, and become less readily soluble in water. The higher members, from $C_{10}H_{20}O_2$, are solid, waxy, or fatty substances, have only a faint smell, and are insoluble in water, but soluble in alcohol and ether. The lower members are readily volatile in steam, but the higher members, such as palmitic acid, must be distilled in superheated steam. The first three members are specifically heavier than water, but the specific gravity decreases as the series is ascended (see table). With the exception of the very high members, they boil without decomposing, under ordinary atmospheric pressure, and the boiling-point rises about 19° for every addition of $-CH_2-$ to the molecule in the case of the normal acids. The melting-point also rises, but not continuously; normal acids containing an odd number of carbon atoms melt at a lower temperature than the preceding normal members containing an even number of carbon atoms,

$C_{12}H_{24}O_2$	$C_{13}H_{26}O_2$	$C_{14}H_{28}O_2$	$C_{15}H_{30}O_2$	$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$.
43·6°	40·5°	54°	51°	62°	60°

Chemical Properties.—The fatty acids are very stable, and, with the exception of formic acid, are only with difficulty oxidised or converted into simpler compounds; nevertheless, owing to the presence of the carboxyl-group in their molecules, they readily undergo a variety of double decompositions. They are all monobasic acids, but the acid character becomes less and less pronounced as the molecular weight increases; whereas formic and acetic acids

readily decompose carbonates and dissolve metals and metallic hydroxides, the higher members, such as palmitic and stearic acids, are with difficulty recognised as acids by ordinary tests. The metallic salts of the lower members are soluble in water; but as the series is ascended the solubility decreases, until, in the case of the higher acids, only the alkali salts (soaps) are soluble.

Fatty acids react with alcohols, especially in presence of dehydrating agents, forming esters and water,

$$CH_3{\cdot}COOH + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + H_2O.$$

When treated with phosphorus pentachloride, &c., they are converted into acid chlorides,

$$C_2H_5{\cdot}COOH + PCl_5 = C_2H_5{\cdot}COCl + POCl_3 + HCl.$$

These acid chlorides react readily with hydroxy-compounds, giving esters,

$$C_2H_5{\cdot}COCl + CH_3{\cdot}OH = C_2H_5{\cdot}CO{\cdot}OCH_3 + HCl,$$

and, on distillation with an alkali salt of a fatty acid, they yield anhydrides of the acids,

$$C_2H_5{\cdot}COCl + C_2H_5{\cdot}COOK = (C_2H_5{\cdot}CO)_2O + KCl;$$

when treated with ammonia they give amides,

$$CH_3{\cdot}COCl + NH_3 = CH_3{\cdot}CO{\cdot}NH_2 + HCl.$$

The fatty acids yield halogen substitution products under suitable conditions (p. 170).

From certain salts of the fatty acids, ketones, aldehydes, and paraffins can be prepared; and, as the aldehydes and ketones may be reduced to alcohols, which again may be converted into ethers and olefines, all these compounds may be obtained from the fatty acids. The esters of the fatty acids are also used for the preparation of amides (p. 197) and tertiary alcohols (p. 228).

Different methods by means of which a fatty acid may be converted into the next lower, or higher, homologue are described later (p. 219); but one method, which is based on reactions already studied, may be given here.

When the calcium salt of a fatty acid is heated with calcium acetate, a ketone is formed, and in this process the hydrocarbon radicles of the two acids become united by a carbonyl-group. When this ketone is oxidised, the CH_3–CO– group is converted into acetic acid, and one of the –CH_2– groups of the higher hydrocarbon radicle is oxidised to –CO·OH (p. 147). The net result of these two operations is the conversion of the higher fatty acid into its next lower homologue, as indicated in the following scheme :—

$$R\text{–}CH_2{\cdot}COOH \xrightarrow{(a)} R\text{–}CH_2{\cdot}CO{\cdot}CH_3 \xrightarrow{(a)} R{\cdot}CO{\cdot}OH.$$

This method was employed by Krafft, who started from stearic acid, ($C_{18}H_{36}O_2$), and converted it, step by step, into capric acid, ($C_{10}H_{20}O_2$), which is known to be a normal acid. He thus proved that stearic, margaric, and palmitic acids, as well as all the lower homologues which he obtained in this work, are *normal* acids; the ketone derived from an acid such as $CH_3{\cdot}CHR{\cdot}CO{\cdot}OH$ would *not* yield on oxidation the next lower homologue of the original acid.

Fats, Oils, Soaps, Stearin, and Butter.

Composition of Fats and Oils.—When beef or mutton suet is kneaded in a muslin bag in a basin of hot water, the fat melts and passes out, leaving the membrane or tissue in the bag; the melted fat solidifies on being cooled, and is known as *tallow*. The fat obtained from pig suet, in a similar manner, is much softer, and is called *lard*.

When tallow is heated with water in closed vessels under pressure at about 200°, it is decomposed into glycerol (p. 282) and 'fatty' acids; if the mixture is now distilled in highly superheated steam, these products pass over, and the distillate is an aqueous solution of glycerol, at the surface of which floats the mixture of fatty acids. A similar decomposition takes place, and at lower temperatures, when tallow is heated with dilute sulphuric acid; but a good deal of charring occurs, and the glycerol is more or less decomposed.

All animal fats—such as lard, goose-fat, bone-fat, butter, &c., and the fatty vegetable oils, such as olive-, linseed-, rape-, palm-, and cotton-seed-oil, which are obtained by pressing the seeds or fruit of certain plants—behave in the above manner, and when heated with dilute sulphuric acid or with water, under pressure, they are decomposed into glycerol and a mixture of acids most of which belong to the $C_nH_{2n}O_2$ series (p. 149). The occurrence of these acids in natural fats and oils, and the fact that the higher members of the series resemble fats in physical properties, led to the use of the term 'fatty acid,' which is now applied to all the members of the series.

The chemical compounds of which these fats are com-

posed were investigated by Chevreul, who showed them to be esters (p. 179), formed, together with water, by the combination of the fatty acids with the alcohol, glycerol, which thus acts as a weak basic hydroxide. Glycerol is a *trihydric* alcohol, and it can react with three molecules of a monobasic or monocarboxylic acid, just as can the trihydric hydroxide of bismuth,

$$C_3H_5(OH)_3 + 3CH_3{\cdot}COOH = C_3H_5(O{\cdot}CO{\cdot}CH_3)_3 + 3H_2O,$$
$$Bi(OH)_3 + 3HCl = BiCl_3 + 3H_2O.$$

These esters of glycerol are collectively termed *glycerides*, and are named after the acids from which they are formed. The glyceride formed from acetic acid is called *triacetin;* that from palmitic acid, *tripalmitin;* and that from stearic acid, *tristearin*, and so on.

Now, the chief components of fats and oils are tristearin and tripalmitin, which are *solid* at ordinary temperatures, and a *liquid* glyceride, *trioleïn*, which is formed by the interaction of glycerol and *oleïc acid.** When a fat contains a relatively large proportion of tristearin and tripalmitin it is solid and comparatively hard (tallow) at ordinary temperatures; when, however, it contains a relatively large proportion of trioleïn, it is soft and pasty (lard), or liquid (olive-oil).

These glycerides, like other esters, are decomposed by water and by dilute mineral acids at moderately high temperatures, and are converted into glycerol and an acid; in the case of tristearin, for example,

$$\begin{array}{l} CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ | \\ CH{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ | \\ CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35} \\ \text{Tristearin.} \end{array} + 3H_2O = \begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \\ \text{Glycerol.} \end{array} + 3C_{17}H_{35}{\cdot}COOH. \quad \text{Stearic Acid.}$$

* *Oleïc acid*, $C_{17}H_{33}{\cdot}COOH$ (p. 291), is a liquid at ordinary temperatures. It contains two atoms of hydrogen less than stearic acid, $C_{17}H_{35}{\cdot}COOH$, and is, therefore, an *unsaturated* acid, belonging to a different series; its lead salt is soluble in ether, a property very rarely met with in other lead salts.

Since fats and oils are mixtures of glycerides, they yield mixtures of fatty acids.

Soaps.—When boiled with alkalis, the glycerides are decomposed much more rapidly than by water, and alkali salts of the acids are formed, together with glycerol. In manufacturing soaps, a fat or oil, such as tallow or palm-oil, is heated in an iron-pan with a sufficient quantity of a solution of sodium hydroxide; after some time there is formed a thick, homogeneous, frothy solution, which contains glycerol and the sodium salts of the various acids which were present in the glycerides—that is to say, the sodium salts of stearic, palmitic, and oleïc acids. Some common salt is now added, whereupon the sodium salts separate as a curd from the solution of glycerol and salt, because they are insoluble in salt water. The curd, after having been drained off and allowed to cool, slowly solidifies, and is then known as *hard soap;* it is simply a mixture of the sodium salts of palmitic, stearic, and oleïc acids with water and alkali. When fats or oils are boiled with potash, instead of with caustic soda, similar chemical changes take place, and the potassium salts of the acids are formed; if common salt is then added to the solution, the potassium are partially converted into sodium salts, and a hard soap is finally obtained; if, however, salt is not added, and the homogeneous solution is allowed to cool, it sets to a jelly-like mass of *soft soap*, which is a mixture of the potassium salts of the above-named acids with glycerol and a large percentage of water.

The decomposition of fats and oils in this way, in the process of soap-making, was formerly called *saponification*, and the fats and oils were said to be *saponified*. The term saponification was then applied generally to the analogous decomposition of other esters by alkalis (in spite of the fact that the products were not soaps), but the word *hydrolysis* is now used instead. Hydrolysis may be roughly defined as the decomposition of one compound into two or more, with fixation of the elements of water or of some hydroxide. The

decomposition of glycerides by water, acids, and alkalis, and the changes expressed by the following equations, are examples of hydrolysis,

$$C_2H_3O_2{\cdot}C_2H_5 + H_2O = C_2H_4O_2 + C_2H_5{\cdot}OH \text{ (p. 194)},$$
$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6 \text{ (p. 304)},$$
$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + 2NH_3 \text{ (p. 322)}.$$

Stearin and Glycerol.—Stearin consists principally of a mixture of stearic and palmitic acids, and is manufactured by decomposing tallow and other fats or oils with water, dilute sulphuric acid, or milk of lime, under pressure. The products are distilled in a current of superheated steam—with the addition of a little sulphuric acid if lime has been used—and the pasty mixture of fatty acids is separated from the aqueous solution of glycerol, and pressed in order to squeeze out as much of the liquid oleïc acid as possible. The pressed mass is then gently warmed, and pressed again between warm plates, when a further quantity of oleïc acid is squeezed out, together with some palmitic and stearic acids. The hard mass that remains is called *stearin;* it is mixed with a little paraffin to make it less brittle, and employed in large quantities in the manufacture of stearin candles. The liquid or pasty mass of oleïc, palmitic, and stearic acids which is separated from the stearin, is known as *oleïn*, and is employed for the preparation of soap.

Glycerol (p. 282) is obtained from the aqueous distillate, after the fatty acids have been removed; the solution is decolourised by filtration through charcoal, submitted to redistillation with superheated steam, and finally evaporated to a syrup under reduced pressure.

Considerable quantities of fats and vegetable oils are now hydrolysed on the large scale with the aid of an enzyme (*lipase*) which occurs in castor-oil and in many other oils. The fat or oil (100 parts) is merely left in contact with water (35–40 parts) and lipase (6–7 parts); at the end of about two days, upwards of 90 per cent. of the fat has been hydrolysed, but the action of the enzyme (as in the case of many other enzymes) is reversible, and a condition of equilibrium is attained before hydrolysis is complete. The pro-

ducts (fatty acids, oleïc acid, and glycerol) are treated as described above.

Butter.—Butter, prepared from cream, is a mixture of fat (about 82·5 per cent.), water (about 14·5 per cent.), and small quantities of caseïn, milk-sugar, and salts. Pure butter-fat contains about 92 per cent. of a mixture of tristearin, tripalmitin, and trioleïn, about 7·7 per cent. of tributyrin, and traces of other glycerides, and substances which impart flavour; it differs from all other fats and oils in containing a large proportion of *tributyrin*, the glyceride of butyric acid.

Artificial butter, *margarine* or *oleomargarine*, is prepared from the best ox-suet, which is first freed from membrane or tissue by melting out the fat. After having been left to crystallise for about twenty-four hours at a temperature of 24°, the fat is pressed and is thus separated into solid stearin and liquid oleomargarine. The latter forms a buttery mass when cooled to ordinary temperatures; but as it is not quite soft enough, it is mixed with a small quantity of pea-nut- or sesame-oil and finally churned up with milk to give it a flavour. When carefully prepared it is a wholesome substitute for butter, and no doubt just as nutritious.

CHAPTER X.

Esters.

It has been pointed out that, in some respects, the alcohols behave like metallic hydroxides; they react with acids, forming **esters** (or ethereal salts) and water,

$$C_2H_5\cdot OH + HCl \longleftrightarrow C_2H_5Cl + H_2O,$$
$$C_2H_5\cdot OH + H_2SO_4 \longleftrightarrow C_2H_5\cdot HSO_4 + H_2O,$$
$$CH_3\cdot OH + CH_3\cdot COOH \longleftrightarrow CH_3\cdot COOCH_3 + H_2O.$$

These reactions are *reversible;* esters are hydrolysed by water, with formation of an alcohol and an acid. In the preparation of an ester, therefore, the presence of water must be avoided, and the other conditions of the experiment must be so chosen

that the reaction proceeds as far as possible in the desired direction (compare p. 195).

Halogen Esters and other Halogen Derivatives of the Paraffins.

The halogen esters of the monohydric alcohols are identical with the *halogen mono-substitution products of the paraffins*, and may be obtained either from the alcohols or from the paraffins; they form homologous series of the general formula, $C_nH_{2n+1}\cdot X$, where X = Cl, Br, or I.

Methyl chloride,	CH_3Cl	Methyl bromide,	CH_3Br	Methyl iodide,	CH_3I
Ethyl "	C_2H_5Cl	Ethyl "	C_2H_5Br	Ethyl "	C_2H_5I
Propyl "	C_3H_7Cl	Propyl "	C_3H_7Br	Propyl "	C_3H_7I

The di-, tri-, &c. halogen substitution products of the paraffins, such as methylene dichloride, CH_2Cl_2, chloroform, $CHCl_3$, iodoform, CHI_3, and carbon tetrachloride, CCl_4, are not usually regarded as esters, because the corresponding di-, tri-, or polyhydric alcohols are not known; but as such halogen compounds are closely related to the halogen esters, they are conveniently considered in this chapter.

Methyl chloride, or chloromethane, CH_3Cl, is one of the four substitution products obtained by treating methane with chlorine in sunlight, and is formed in *small* quantities when methyl alcohol is heated with *concentrated* hydrochloric acid,

$$CH_3\cdot OH + HCl = CH_3Cl + H_2O.$$

It is prepared by passing hydrogen chloride into methyl alcohol containing anhydrous zinc chloride (Groves' process), as described in the case of ethyl chloride (p. 184); also by heating methyl alcohol with sodium chloride and concentrated sulphuric acid.

It is a colourless gas, which liquefies below −24° under ordinary atmospheric pressure. It burns with a green-edged flame, is moderately easily soluble in water, and when heated with water or aqueous alkalis under pressure it is converted into methyl alcohol,

$$CH_3Cl + H_2O = CH_3\cdot OH + HCl.$$

Methyl chloride is employed on the large scale in the preparation of organic dyes, and the compressed gas is also used for the production of a low temperature; for these purposes it is manufactured by heating crude trimethylamine hydrochloride (p. 216) with hydrochloric acid,

$$N(CH_3)_3,HCl + 3HCl = 3CH_3Cl + NH_4Cl.$$

The halogen esters, *methyl bromide*, CH_3Br (b.p. 4·5°), and *methyl iodide*, CH_3I (b.p. 42°), are prepared by methods similar to those employed in the case of the corresponding ethyl esters (pp. 184–186), which they closely resemble in chemical properties.

Methylene dichloride, CH_2Cl_2, is prepared by reducing chloroform with zinc and hydrochloric acid in alcoholic solution,

$$CHCl_3 + 2H = CH_2Cl_2 + HCl;$$

it is a colourless, heavy liquid, boiling at 41°.

Chloroform, or trichloromethane, $CHCl_3$, is formed when methane, methyl chloride, or methylene dichloride is treated with chlorine in sunlight, and when many simple organic substances containing oxygen, such as ethyl alcohol, acetone, &c., are heated with bleaching-powder, which acts as an oxidising as well as a chlorinating agent (see below).

Chloroform may be prepared by distilling alcohol or acetone with bleaching-powder.

Some strong bleaching-powder (about 450 grams) is made into a cream with about 1½ litres of water and placed in a large flask connected with a condenser; alcohol, methylated spirit, or acetone (about 100 c.c.) is then gradually added, and the flask is *cautiously* heated on a water-bath; a vigorous reaction usually sets in, and a mixture of chloroform, water, and alcohol or acetone distils. If the operation has been successful, the chloroform collects as a heavy oil at the bottom of the receiver; but if too much alcohol or acetone is present, the chloroform must be precipitated by adding water. It is then separated with the aid of a funnel, washed with water, shaken once or twice with a little concentrated sulphuric acid, which frees it from water, alcohol, &c., and redistilled from a water-bath.

The changes which occur in the preparation of chloroform from alcohol are complex. It is probable that aldehyde is first formed by oxidation, and then converted into chloral, which is decomposed by the calcium hydroxide

present in the bleaching-powder (or produced during the reaction), yielding chloroform and calcium formate. When acetone is employed, trichloracetone is probably formed in the first place; this compound is then decomposed by the calcium hydroxide, giving chloroform and calcium acetate,

$$2CH_3{\cdot}CO{\cdot}CCl_3 + Ca(OH)_2 = 2CHCl_3 + (CH_3{\cdot}COO)_2Ca.$$

The chloroform prepared in this way is impure; the pure substance is best prepared by warming chloral or chloral hydrate (p. 133) with a solution of sodium hydroxide, and then isolating the product in the manner just described,

$$\cdot CCl_3{\cdot}CHO + NaOH = CHCl_3 + H{\cdot}COONa.$$

Chloroform is a heavy, pleasant-smelling liquid of sp. gr. 1·5 at 15°, and boils at 61°; when heated it burns with a green-edged flame, but it is not inflammable at ordinary temperatures. It is readily decomposed by warm alcoholic potash, yielding potassium formate and chloride,

$$CHCl_3 + 4KOH = H{\cdot}COOK + 3KCl + 2H_2O.$$

If a drop of chloroform is added to a mixture of aniline (Part II. p. 402) and alcoholic potash, and the solution is gently warmed, an intensely nauseous smell is observed, owing to the formation of *phenylcarbylamine* or *phenylisocyanide*,*

$$CHCl_3 + 3KOH + C_6H_5{\cdot}NH_2 = C_6H_5{\cdot}NC + 3KCl + 3H_2O.$$

This reaction affords a very delicate test for chloroform (and for primary amines, p. 210), and it is known as the **carbylamine reaction** (p. 212).

Chloroform is extensively employed in surgery as an anæsthetic, its vapour when inhaled causing unconsciousness (Simpson). For this purpose pure chloroform must be employed, as the impure substance is dangerous, and produces bad after-effects.† Pure chloroform gives no precipitate

* The experiment should be performed in a test-tube, with *one drop* only of aniline, and the contents of the test-tube should afterwards be carefully poured into the sink-pipe, in a draught closet if possible.

† In the presence of air, chloroform gradually undergoes decomposition, especially under the influence of light, carbonyl chloride (phosgene gas, $COCl_2$), and hydrochloric acid being produced, $CHCl_3 + O = COCl_2 + HCl$. As carbonyl chloride is very poisonous, all chloroform required for anæsthetic purposes should be kept in the dark in a well-stoppered bottle; a

with silver nitrate, and does not darken when it is shaken with concentrated sulphuric acid or with a strong solution of potassium hydroxide.

Carbon tetrachloride, or tetrachloromethane, CCl_4, the final product of the action of chlorine on CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$, is prepared by passing chlorine into boiling chloroform in sunlight, or by passing chlorine into carbon disulphide in presence of iodine which acts as a chlorine carrier (Part II. p. 381),

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2;$$

in the latter case the sulphur dichloride is got rid of, after a preliminary distillation, by shaking the product with caustic soda, and the carbon tetrachloride is purified by redistillation. Carbon tetrachloride is a very heavy, pleasant-smelling liquid, boiling at 76–77°; on treatment with nascent hydrogen, it is successively converted into $CHCl_3$, CH_2Cl_2, CH_3Cl, and CH_4. It is decomposed by hot alcoholic potash,

$$CCl_4 + 6KOH = 4KCl + K_2CO_3 + 3H_2O.$$

Iodoform, or triiodomethane, CHI_3, a halogen tri-substitution product of methane, is closely related to chloroform, and may be considered here. It is formed when ethyl alcohol (but *not* methyl alcohol), acetone, aldehyde, and other compounds containing oxygen united with a $CH_3{\cdot}C\equiv$ group are warmed with iodine and an aqueous solution of an alkali hydroxide or alkali carbonate; the changes which occur are doubtless similar to those which take place in the preparation of chloroform.

All ketones which contain the group, $CH_3{\cdot}CO-$, yield iodoform under the above conditions, the $-CO-$ group being converted into $-COOH$, the CH_3- group into iodoform. If bromine is used instead of iodine, a similar change occurs, and *bromoform*, $CHBr_3$ (b.p. 151°), separates; this reaction is of considerable practical importance, and is often used for the conversion of a ketone into an acid containing one atom of carbon less than the parent substance.

little alcohol (up to 1 per cent.) is generally added in order to decompose any carbonyl chloride which might be formed, $COCl_2 + 2C_2H_5{\cdot}OH = 2HCl + CO(OC_2H_5)_2$ (*ethyl carbonate*).

Iodoform is prepared by gradually adding iodine (2 parts) to an aqueous solution of sodium carbonate (2 parts) and acetone, or alcohol (1 part), which is heated at 60–80°; the precipitated iodoform is separated by filtration, and purified by recrystallisation from dilute alcohol. It crystallises in lustrous, yellow, six-sided plates, melts at 120°, and has a peculiar, very characteristic odour; it sublimes readily, and is volatile in steam. It is used in medicine and surgery as an antiseptic.

Ethyl chloride, or chlorethane, C_2H_5Cl, is formed when ethane is treated with chlorine in sunlight, and when alcohol is heated with concentrated hydrochloric acid, or treated with phosphorus pentachloride, or trichloride, at ordinary temperatures,

$$C_2H_5{\cdot}OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

Ethyl chloride is prepared by Groves' process—namely, by passing dry hydrogen chloride into a flask containing absolute alcohol, to which about half its weight of anhydrous zinc chloride has been added,

$$C_2H_5{\cdot}OH + HCl \longleftrightarrow C_2H_5Cl + H_2O.$$

The zinc chloride probably combines with the water which is formed, and thus prevents the reversal of the reaction. The flask is connected with a reflux condenser and is provided with a safety tube. As soon as the solution is saturated with hydrogen chloride, it is gently warmed on the water-bath, when ethyl chloride and alcohol pass off; the alcohol vapour is cooled in passing through the condenser, and the liquid runs back into the flask. The gaseous ethyl chloride is passed through three wash-bottles containing water, dilute potash, and concentrated sulphuric acid respectively, by which means it is freed from hydrogen chloride, alcohol, and moisture; the pure ethyl chloride is then collected in a U-tube immersed in a freezing mixture.

Ethyl chloride may also be prepared by warming a mixture of absolute alcohol, concentrated sulphuric acid, and sodium chloride; the sulphuric acid not only acts on the common salt, forming hydrogen chloride, but also combines with the

water which is generated, and thus prevents the reversal of the reaction.

Ethyl chloride is a colourless, very volatile liquid, boiling at 12·5°; it burns with a greenish, smoky flame, and is only sparingly soluble in water, but it is miscible with alcohol, ether, &c. When heated with water or potash under pressure, it yields ethyl alcohol,

$$C_2H_5Cl + H_2O = C_2H_5{\cdot}OH + HCl;$$

on treatment with chlorine in sunlight, it gives di-, tri-, &c. substitution products of ethane. It does not give an immediate precipitate with an aqueous solution of silver nitrate, but from a warm *alcoholic* solution of this salt, silver chloride is quickly precipitated and ethyl nitrate remains in solution,

$$C_2H_5Cl + AgNO_3 = C_2H_5{\cdot}NO_3 + AgCl.$$

Ethyl bromide, or bromethane, C_2H_5Br, is formed when alcohol is heated with concentrated hydrobromic acid, or treated with phosphorus tribromide or pentabromide, at ordinary temperatures,

$$C_2H_5{\cdot}OH + PBr_5 = C_2H_5Br + POBr_3 + HBr.$$

It may be prepared by adding coarsely powdered potassium bromide (50 parts) to a cold mixture of alcohol (30 parts) and concentrated sulphuric acid (50 parts) and then distilling slowly; the hydrogen bromide which is generated reacts with the alcohol, and the excess of sulphuric acid combines with the water which is thus formed.

The materials are placed in a distillation flask, which is connected with a condenser, and, in order to avoid loss of ethyl bromide by evaporation, the other end of the condenser dips under water contained in the receiver. The heavy oil is separated with the aid of a funnel, and shaken with a dilute solution of potassium hydroxide to free it from bromine, hydrobromic acid, and alcohol; it is then washed with water, dried with calcium chloride, and purified by distillation.

Ethyl bromide is a colourless, pleasant-smelling, heavy liquid, and boils at 38°; it resembles ethyl chloride in its

behaviour towards water, potassium hydroxide, and silver nitrate.

Ethyl iodide, or iodethane, C_2H_5I, is formed when alcohol is heated with concentrated hydriodic acid; it is prepared by gradually adding iodine (65 grams), in small quantities at a time, to a mixture of alcohol (25 grams) and red phosphorus (5 grams), and then distilling from a water-bath,

$$3C_2H_5{\cdot}OH + P + 3I = 3C_2H_5I + H_3PO_3.$$

The product is purified exactly as described in the case of ethyl bromide.

Ethyl iodide is a colourless, pleasant-smelling, highly refractive, very heavy, liquid, boiling at 72°; on exposure to light it slowly turns yellow or brown, owing to the separation of iodine, a phenomenon which is observed in the case of nearly all organic compounds containing iodine. In chemical properties it closely resembles ethyl chloride and ethyl bromide.

Other halogen esters or halogen mono-substitution products of the paraffins, such as **propyl bromide**, C_3H_7Br, **butyl iodide**, C_4H_9I, &c., may be prepared by methods similar to those given above.

All the halogen *mono*-substitution products of the paraffins are classed together as **alkyl halogen compounds**; they are very much used in the preparation of other substances and are constantly referred to later. They are all colourless, neutral, pleasant-smelling liquids, and most of them are specifically heavier than water, in which they are practically insoluble; their physical properties, however, depend greatly on the halogen which they contain, as will be seen from the data given in the following table:—

	Sp. gr. at 0°	B.p.		Sp. gr. at 0°	B.p.
Methyl chloride, CH_3Cl	—	−22°	Ethyl chloride, C_2H_5Cl	0·921	12·5°
Methyl bromide, CH_3Br	1·73	+ 4·5°	Ethyl bromide, C_2H_5Br	1·47	38°
Methyl iodide, CH_3I	2·33	42°	Ethyl iodide, C_2H_5I	1·975	72°

The alkyl halogen compounds resemble one another very closely in chemical properties, and the following are some of

their more important reactions:—They are reduced by nascent hydrogen giving paraffins (p. 56), and they react with sodium giving paraffins (p. 60). They are slowly decomposed, or hydrolysed (p. 177), by boiling water and by *aqueous* alkalis, yielding the alcohols,

$$C_3H_7Br + KOH = C_3H_7{\cdot}OH + KBr;$$

but when boiled with *alcoholic* potash, they are converted into olefines,

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

They do not react readily with silver nitrate in aqueous solution, but when they are heated with this, or with other silver salts, or with an alkali salt, in alcoholic solution, they undergo double decomposition and give *esters*,

$$C_2H_5Br + AgC_2H_3O_2 = C_2H_5{\cdot}C_2H_3O_2 + AgBr,$$
$$CH_3I + AgNO_3 = CH_3{\cdot}NO_3 + AgI.$$

They combine directly with magnesium in presence of ether, giving a very important class of compounds (the Grignard reagents), of which a description is given later (p. 226).

The monohalogen derivatives of propane and of the higher paraffins show isomerism. There are, for example, two compounds of the molecular formula, C_3H_7I, corresponding with the two alcohols, $C_3H_7{\cdot}OH$—namely, *normal propyl iodide*, $CH_3{\cdot}CH_2{\cdot}CH_2I$ (b.p. 102°), and *isopropyl iodide*, $CH_3{\cdot}CHI{\cdot}CH_3$ (b.p. 89·5°). The monohalogen derivatives of butane also correspond with the four isomeric alcohols; two of them, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X$ and $CH_3{\cdot}CH_2{\cdot}CHX{\cdot}CH_3$, are derived from normal butane, the other two, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{\cdot}CH_2X$ and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CX{\cdot}CH_3$, from isobutane.

Esters of Nitric Acid.

The esters of nitric acid are formed when the alkyl halogen compounds are heated with silver nitrate in alcoholic solution,

$$CH_3I + AgNO_3 = CH_3{\cdot}NO_3 + AgI;$$

they are also produced, together with nitrites (see below), when the alcohols are treated with concentrated nitric acid,

$$C_3H_7{\cdot}OH + HNO_3 = C_3H_7{\cdot}NO_3 + H_2O.$$

Ethyl nitrate, $C_2H_5 \cdot NO_3$, is formed when alcohol is treated with ordinary concentrated nitric acid,

$$C_2H_5 \cdot OH + HNO_3 = C_2H_5 \cdot NO_3 + H_2O;$$

but oxidation also occurs, and so much heat is developed that unless care is taken the reaction becomes almost explosive in violence; even when the mixture is cooled, only a comparatively small quantity of ethyl nitrate is produced, owing to the acid oxidising some of the alcohol and being itself reduced to nitrous acid, which then reacts with the alcohol and gives rise to ethyl nitrite. If, however, the nitric acid is previously mixed with a little urea (p. 330), a substance which decomposes nitrous acid,

$$CO(NH_2)_2 + 2NO \cdot OH = CO_2 + 3H_2O + 2N_2,$$

the reaction takes place quietly, and ethyl nitrate is the principal product.

For these reasons ethyl nitrate is prepared by gradually adding alcohol (not more than 30 grams) to half its volume of nitric acid (sp. gr. 1·4), to which about 5 grams of urea have been added; the mixture is then *very slowly* heated on a water-bath in a large retort provided with a condenser. The mixture of ethyl nitrate, alcohol, and acid which collects in the receiver is shaken with water in a separating-funnel, and the heavy oil is separated, dried with calcium chloride, and distilled from a water-bath.

Ethyl nitrate is a colourless liquid of sp. gr. 1·11 at 20°, and boils at 87°; it has a pleasant, fruity odour, and is almost insoluble in water, but readily soluble in alcohol, &c. It burns with a luminous flame, and when dropped on a hot surface it sometimes explodes. It is slowly hydrolysed by boiling water, quickly by hot alkalis, yielding alcohol and nitric acid or a nitrate,

$$C_2H_5 \cdot NO_3 + H_2O = C_2H_5 \cdot OH + HNO_3.$$

On reduction with tin and hydrochloric acid it yields *hydroxylamine*,

$$C_2H_5 \cdot NO_3 + 6H = C_2H_5 \cdot OH + NH_2 \cdot OH + H_2O.$$

Methyl nitrate, $CH_3 \cdot NO_3$ (b.p. 66°), and the higher homologues closely resemble ethyl nitrate in properties.

Esters of Nitrous Acid.

The esters of nitrous acid are produced by the action of nitrous acid on the alcohols,

$$C_2H_5\cdot OH + HNO_2 = C_2H_5\cdot NO_2 + H_2O.$$

They may be prepared by saturating the alcohols with the gases evolved by the interaction of arsenious oxide and nitric acid,* or by distilling alcohol with sodium nitrite and sulphuric acid, or with copper and nitric acid.†

Ethyl nitrite, $C_2H_5\cdot NO_2$, is prepared by adding a mixture of alcohol and dilute sulphuric acid to a solution of potassium nitrite; the product is separated, dried over calcium chloride, and distilled.

When concentrated nitric acid (3 c.c.) is dropped slowly into a cold mixture of alcohol (20 c.c.) and concentrated sulphuric acid (2 c.c.), and the solution is carefully distilled with copper turnings (about 4 grams), the distillate consists of a mixture of ethyl nitrate, alcohol, and oxidation products of the latter; when diluted with alcohol, it is employed in medicine as 'sweet spirit of nitre.'

Ethyl nitrite is a colourless liquid of sp. gr. 0·947 at 15·5°; it boils at 17°, and has a pleasant, fruity odour like that of apples; it is insoluble in water, and is readily hydrolysed by boiling water or dilute alkalis,

$$C_2H_5\cdot NO_2 + KOH = C_2H_5\cdot OH + KNO_2.$$

Methyl nitrite, $CH_3\cdot NO_2$, is a gas; the higher homologues resemble ethyl nitrite. *Amyl nitrite*, $C_5H_{11}\cdot NO_2$, for example, prepared by distilling commercial amyl alcohol (p. 111) with nitric acid,‡ is a liquid boiling at 96°; it is used in medicine in cases of *angina pectoris*.

Nitro-paraffins.—When ethyl iodide is warmed with *silver* nitrite, silver iodide is precipitated, and when the liquid product is fractionally distilled it yields *two* substances. One of these boils at 17° and is identical with ethyl nitrite; the other boils at 114° and is called *nitro-ethane*.

* $As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$.

† $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + 2H_2O + 2HNO_2$.

‡ Some of the amyl alcohol is oxidised and the nitric is reduced to nitrous acid.

Ethyl nitrite and nitro-ethane are *isomeric*, and the formation of both compounds, therefore, may be expressed by the equation,

$$C_2H_5I + AgNO_2 = C_2H_5 \cdot NO_2 + AgI;$$

but whereas the former is an ester of nitrous acid, $HO \cdot N:O$, and has the constitution, $C_2H_5 \cdot O \cdot N:O$, the structure of nitro-ethane must be represented by the formula, $C_2H_5 \cdot N\langle^{O}_{O}$.

Compounds, similar to nitro-ethane in constitution, and isomeric with the corresponding nitrites, may be obtained from other halogen esters in the above manner; they were discovered by V. Meyer, and are termed *nitro-paraffins*, because they are derived from the paraffins by the substitution of the nitro-group, $-N\langle^{O}_{O}$, for one atom of hydrogen.

The nitro-paraffins are colourless, pleasant-smelling liquids, and distil without decomposing, but their boiling-points are much higher than those of the corresponding nitrites, as illustrated by the case of ethyl nitrite and nitro-ethane. They differ entirely from the nitrites in chemical behaviour; the nitro-paraffins may dissolve in, but are not decomposed by, caustic alkalis, whereas the nitrites, like all other esters, undergo hydrolysis, yielding an alcohol and a nitrite.

The nitro-paraffins are converted into amines on reduction,

$$C_2H_5 \cdot NO_2 + 6H = C_2H_5 \cdot NH_2 + 2H_2O,$$

whilst the nitrites yield hydroxylamine (p. 188) or ammonia, and an alcohol,

$$C_2H_5 \cdot O \cdot N:O + 6H = C_2H_5 \cdot OH + NH_3 + H_2O.$$

It is on facts such as these that the structural formulæ given above are based: the reactions of the alkyl nitrites show that the alkyl radicle is directly united with *oxygen*, whereas those of the nitro-paraffins show equally clearly that the alkyl-group is directly united with nitrogen; but there is no satisfactory explanation of how both types of compounds are formed by the interaction of silver nitrite and an alkyl halogen compound (compare p. 323). All the nitro-paraffins which contain the group, $-CH_2 \cdot NO_2$ or $>CH \cdot NO_2$, are converted into soluble salts by aqueous solutions of the alkali hydroxides. These salts are derived from acids which are isomeric with the nitro-paraffins. Nitro-ethane, $CH_3 \cdot CH_2 \cdot N\langle^{O}_{O}$, for example, gives a sodium salt of the constitution, $CH_3 \cdot CH = N\langle^{O}_{ONa}$, which is derived from the acid,

$CH_3 \cdot CH = N\langle^{O}_{OH}$, and which is probably formed in the manner indicated below,

$$CH_3 \cdot CH_2 \cdot N\langle^{O}_{O} + NaOH \longrightarrow CH_3 \cdot CH_2 \cdot N(OH)(ONa)(=O)$$

$$\longrightarrow CH_3 \cdot CH = N(=O)(ONa) + H_2O.$$

Although the sodium salts are stable, the corresponding acids are unstable, and cannot, as a rule, be isolated, as they undergo intramolecular or isomeric change into nitro-paraffins; compounds such as the nitro-paraffins which, not being themselves acids, are yet capable of undergoing a (reversible) change in structure and thus giving acids, are called *pseudo-acids*.

Nitro-methane, $CH_3 \cdot NO_2$, is formed with development of heat when methyl iodide is treated with silver nitrite, and the product in this case does not contain the isomeric nitrite. It may be prepared by heating potassium chloracetate with potassium nitrite in aqueous solution,

$$CH_2Cl \cdot COOK + KNO_2 = CH_2(NO_2) \cdot COOK + KCl$$
$$CH_2(NO_2) \cdot COOK + H_2O = CH_3 \cdot NO_2 + KHCO_3.$$

It is a colourless liquid (b.p. 101°), and with a solution of sodium hydroxide, it gives a soluble sodium salt, $CH_2 = N\langle^{O}_{ONa}$.

Esters of Sulphuric Acid.

Dibasic acids, such as sulphuric acid, form two classes of esters with alcohols—namely, alkyl hydrogen esters, corresponding with the metal hydrogen sulphates, and normal alkyl esters, corresponding with the normal metallic sulphates,

Ethyl hydrogen sulphate, $\frac{C_2H_5}{H}\rangle SO_4$ Ethyl sulphate, $(C_2H_5)_2SO_4$.

Potassium hydrogen sulphate, $\frac{K}{H}\rangle SO_4$ Potassium sulphate, K_2SO_4.

Ethyl hydrogen sulphate, ethylsulphuric acid, or *sulphovinic acid* (from sulphuric acid and spirit of wine), $C_2H_5 \cdot HSO_4$, is formed when ethylene is passed into fuming sulphuric acid, or heated with ordinary sulphuric acid,

$$C_2H_4 + H_2SO_4 = C_2H_5 \cdot HSO_4.$$

It is prepared by heating alcohol with concentrated sulphuric acid,

$$C_2H_5\cdot OH + H_2SO_4 = C_2H_5\cdot HSO_4 + H_2O.$$

A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated at 100° for about an hour, when some of the alcohol is converted into ethyl hydrogen sulphate. The solution is then cooled, diluted with water, and treated with a slight excess of barium carbonate, when barium sulphate and barium ethylsulphate are formed,

$$2C_2H_5\cdot HSO_4 + BaCO_3 = (C_2H_5\cdot SO_4)_2Ba + CO_2 + H_2O.$$

The barium sulphate and excess of barium carbonate are separated by filtration, and the cold solution of barium ethylsulphate is treated with dilute sulphuric acid, as long as a precipitate is produced, and filtered again from the barium sulphate,

$$(C_2H_5\cdot SO_4)_2Ba + H_2SO_4 = 2C_2H_5\cdot HSO_4 + BaSO_4.$$

The filtrate is now free from sulphuric acid; it is evaporated at ordinary temperatures under reduced pressure, when alcohol and water pass off, and ethyl hydrogen sulphate remains as a thick, sour liquid.

Ethyl hydrogen sulphate has an acid reaction, decomposes carbonates, and is, in fact, like potassium hydrogen sulphate, a monobasic acid, since it contains one atom of hydrogen displaceable by metals. The *potassium* salt, $C_2H_5\cdot KSO_4$, may be prepared by neutralising the acid with potassium carbonate; also by treating a solution of the barium salt with potassium carbonate, filtering, and evaporating; it is a colourless, crystalline, neutral compound, readily soluble in water. The *barium* salt, $(C_2H_5\cdot SO_4)_2Ba$, is also readily soluble in water, so that ethylsulphuric acid does not give a precipitate with barium chloride.

Ethyl hydrogen sulphate is a very important substance, as it is an intermediate product in the conversion of alcohol into ethylene and into ether, and of ethylene into alcohol. It is hydrolysed by boiling water, and for this reason it cannot be obtained from its aqueous solution by evaporation at 100°,

$$C_2H_5\cdot HSO_4 + H_2O = C_2H_5\cdot OH + H_2SO_4;$$

when heated with alcohol it gives ether,

$$C_2H_5\cdot HSO_4 + C_2H_5\cdot OH = (C_2H_5)_2O + H_2SO_4;$$

and when heated alone, or with concentrated sulphuric acid, it yields ethylene,

$$C_2H_5\cdot HSO_4 = C_2H_4 + H_2SO_4.$$

Other alcohols react with sulphuric acid, yielding *alkyl hydrogen sulphates*, corresponding with ethyl hydrogen sulphate; these compounds closely resemble ethyl hydrogen sulphate in properties, undergo similar decompositions, and are frequently used in preparing other substances.

Dimethyl sulphate, $(CH_3)_2SO_4$, is prepared by treating methyl alcohol with sulphuric anhydride at temperatures below 0°; the methyl hydrogen sulphate which is thus produced is afterwards heated under reduced pressure, whereon the normal ester distils over,

$$2CH_3\cdot HSO_4 = (CH_3)_2SO_4 + H_2SO_4.$$

It is a colourless, heavy, *poisonous* liquid, boiling at 188°, and it is slowly hydrolysed by cold water, giving methyl alcohol and methyl hydrogen sulphate. When a substance which contains –OH, $-NH_2$, or >NH groups is treated with dimethyl sulphate and an aqueous solution of an alkali hydroxide, the hydrogen atoms of these groups are displaced by methyl-groups; hence methyl sulphate is often used, instead of methyl iodide, in *methylating* organic compounds.

Diethyl sulphate, $(C_2H_5)_2SO_4$, is of less importance; it may be prepared by warming silver sulphate with ethyl iodide,

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI.$$

It is a colourless liquid, and boils at 208°, decomposing slightly.

Esters of Organic Acids.

Ethyl acetate, $C_2H_3O_2\cdot C_2H_5$, or $CH_3\cdot CO\cdot OC_2H_5$, is formed when acetyl chloride or acetic anhydride is treated with alcohol,

$$CH_3\cdot COCl + C_2H_5\cdot OH = CH_3\cdot COOC_2H_5 + HCl,$$
$$(CH_3\cdot CO)_2O + C_2H_5\cdot OH = CH_3\cdot COOC_2H_5 + CH_3\cdot COOH;$$

also when a metallic salt of acetic acid is heated with a halogen ester of ethyl alcohol,

$$CH_3\cdot COOAg + C_2H_5Br = CH_3\cdot COOC_2H_5 + AgBr,$$

and when alcohol is heated with glacial acetic acid,

$$CH_3\cdot COOH + C_2H_5\cdot OH \longleftrightarrow CH_3\cdot COOC_2H_5 + H_2O.$$

It is prepared by gradually adding a mixture of equal volumes of alcohol and acetic acid to a mixture of equal volumes of alcohol

and concentrated sulphuric acid, heated at about 140° in a flask connected with a condenser; this process, like that by which ether is prepared, is theoretically continuous, the alcohol and sulphuric acid combining to form ethyl hydrogen sulphate, which then interacts with acetic acid, forming ethyl acetate and sulphuric acid,

$$C_2H_5\cdot OH + H_2SO_4 = C_2H_5\cdot HSO_4 + H_2O$$
$$C_2H_5\cdot HSO_4 + C_2H_4O_2 = C_2H_3O_2\cdot C_2H_5 + H_2SO_4.$$

The distillate is shaken with a concentrated solution of sodium chloride containing some sodium carbonate, when the alcohol and acetic acid dissolve, and the ethyl acetate separates as an oil; the ester is dried over anhydrous calcium chloride, and purified by fractional distillation.

Ethyl acetate is a colourless, mobile liquid, having a pleasant, fruity odour, and boiling at 77°; it is specifically lighter than water, in which it is moderately easily soluble. It is readily hydrolysed by hot alkalis, more slowly by hot mineral acids, and by water,

$$CH_3\cdot COOC_2H_5 + H_2O = CH_3\cdot COOH + C_2H_5\cdot OH.$$

When treated with concentrated ammonia, it yields acetamide and alcohol,

$$CH_3\cdot COOC_2H_5 + NH_3 = CH_3\cdot CO\cdot NH_2 + C_2H_5\cdot OH.$$

Since ethyl acetate has a rather characteristic smell, and is formed when acetic acid or any of its salts is warmed with alcohol and concentrated sulphuric acid, the presence of acetic acid or an acetate may be readily detected by this reaction, the so-called 'acetic-ether' test.

Although, on the whole, the esters of mineral acids resemble one another in chemical properties, they are derived from acids of such diverse characters that differences in behaviour are only to be expected. The esters of carboxylic acids, on the other hand, are derived from acids of a similar nature, and therefore resemble one another very closely in properties, and may be prepared by similar methods.

The esters of organic (and of inorganic) acids may be produced by treating an alcohol with the chloride or anhydride of the acid,

$$C_3H_7\cdot COCl + CH_3\cdot OH = C_3H_7\cdot COOCH_3 + HCl,$$

and by heating a metallic salt of the acid with an alkyl halogen compound,

$$C_2H_5\cdot COOAg + CH_3I = C_2H_5\cdot COOCH_3 + AgI.$$

The latter method is principally used when only a small quantity of acid is at disposal; the acid is converted into its silver salt, the latter is warmed with the alkyl halogen compound, in a flask provided with a reflux condenser, and the ester is separated from the silver halide by filtration; a readily volatile solvent, such as ether, may be used to dissolve the ester, if necessary.

Esterification.—Esters in general are formed when an alcohol is mixed with an acid; but the change, which is a gradual one, is never complete, because the reaction is reversible. When the interaction has proceeded for a certain time, the quantity of ester which is decomposed by the water present is equal to that formed in the same time by the interaction of the acid and the alcohol; in other words, a condition of equilibrium is established when the two changes represented by the equations,

$$CH_3\cdot OH + C_2H_4O_2 = C_2H_3O_2\cdot CH_3 + H_2O,$$
$$C_2H_3O_2\cdot CH_3 + H_2O = CH_3\cdot OH + C_2H_4O_2,$$

balance one another. This is usually expressed by writing the equation thus,

$$CH_3\cdot OH + C_2H_4O_2 \longleftrightarrow C_2H_3O_2\cdot CH_3 + H_2O,$$

to indicate that the change takes place in either direction, and the process represented by reading the equation from left to right, is generally called *esterification* (the reverse process, hydrolysis).

The proportion of alcohol which is converted into ester depends on the nature of the alcohol and of the acid, and on their relative quantities (molecular concentrations); it is independent of the temperature, but the higher the temperature the sooner the condition of equilibrium is attained. These facts were established by Berthelot and by Menschutkin.

Now, if the water produced during esterification could be removed, or otherwise prevented from decomposing the ester,

the desired change should take place far more completely. This consideration led to the use of 'dehydrating agents' in the preparation of esters, substances such as zinc chloride, hydrogen chloride, or sulphuric acid being added to the mixture of alcohol and acid to 'bind' the water and prevent it from decomposing the ester. In practice, the results of doing this are very satisfactory, and the two methods usually employed in preparing esters of organic acids are (*a*) by passing *dry* hydrogen chloride into a boiling mixture of the acid and alcohol contained in a flask provided with a reflux condenser; (*b*) by warming a mixture of the acid and alcohol with concentrated sulphuric acid. In both these processes, when the object is to convert as large a proportion as possible of the acid into its ester, the alcohol is used in considerable excess.

The action of the mineral acids during esterification is not yet thoroughly understood; in the case of sulphuric acid, an alkyl hydrogen sulphate is doubtless formed as an intermediate product (compare p. 193), and the sulphuric acid probably combines with the water which is formed, giving a hydroxide such as $SO(OH)_4$; hydrogen chloride may also possibly combine with water.

The isolation of the ester is sometimes accomplished by distillation, as in the case of ethyl acetate; as a rule, however, when esterification is at an end the excess of alcohol is distilled from a water-bath, the residue is poured into water, and the ester is separated with a separating-funnel or (if a solid) by filtration. It is washed with a solution of sodium carbonate, to free it from acid, and is then dried and distilled, or recrystallised.

Esters are usually colourless, neutral, pleasant-smelling liquids, sparingly soluble or insoluble in water;* as a rule, they distil unchanged under atmospheric pressure, and are volatile in steam. The hydrogen esters, such as ethyl hydrogen oxalate, may be non-volatile under atmospheric pressure, and readily soluble in water.

All esters are decomposed by aqueous mineral acids and

* Methyl oxalate (p. 247) is a noteworthy exception, as it is a solid and dissolves readily in water.

alkalis (sometimes even by water), the change which they undergo being spoken of as hydrolysis (p. 177),

$$CH_3{\cdot}COOC_3H_7 + KOH = CH_3{\cdot}COOK + C_3H_7{\cdot}OH,$$
$$2H{\cdot}COOCH_3 + Ba(OH)_2 = (H{\cdot}COO)_2Ba + 2CH_3{\cdot}OH.$$

The rapidity with which hydrolysis takes place depends on the temperature and concentration of the solution, as well as on the nature of the ester and of the hydrolysing agent; as a rule, potassium, sodium, and barium hydroxides are the most powerful hydrolysing agents. Since, however, esters are generally insoluble in water, they are not attacked very quickly by aqueous alkalis or mineral acids; for this reason it is usual to employ *alcoholic* potash (in which the esters are soluble), when the only object is to bring about hydrolysis.

The *identification* of esters, as such, is usually impossible because they are generally liquids, and a determination of the boiling-point is insufficient for such a purpose; it is necessary, therefore, to hydrolyse the ester with boiling aqueous potash, and then to separate and identify the *alcohol* and the *acid* which have been produced.

The esters of organic acids yield amides on treatment with concentrated aqueous or alcoholic ammonia,

$$C_3H_7{\cdot}COOCH_3 + NH_3 = C_3H_7{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}OH,$$

whereas the halogen esters give amines with alcoholic ammonia (p. 210),

$$C_2H_5I + NH_3 = C_2H_5{\cdot}NH_2{,}HI.$$

The esters of organic acids afford excellent examples of isomerism; ethyl formate, $H{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3$, for example, is isomeric with methyl acetate, $CH_3{\cdot}CO{\cdot}O{\cdot}CH_3$; propyl formate, $H{\cdot}COOC_3H_7$, is isomeric with ethyl acetate, $CH_3{\cdot}COOC_2H_5$, and with methyl propionate, $C_2H_5{\cdot}COOCH_3$, and so on.

Many esters occur in the fruit, flower, and other parts of plants, and it is to their presence in many cases that the scent of the part is due; many are prepared artifically for flavouring sweets, pastry, perfumes, &c. Amyl acetate, $CH_3{\cdot}COOC_5H_{11}$, for example, prepared from commercial amyl alcohol, has a strong smell of pears, and is known as 'pear-oil;' methyl butyrate, $C_3H_7{\cdot}COOCH_3$, is sold as 'pine-apple-oil,' and isoamyl isovalerate as 'apple-oil.'

CHAPTER XI.

Synthesis of Fatty Acids and Ketones with the aid of Ethyl Acetoacetate and Ethyl Malonate.

In the whole domain of organic chemistry few compounds have been more extensively used for synthetical purposes than ethyl acetoacetate and ethyl malonate; one of the more important uses to which these substances have been put is the synthesis of a great number of fatty acids and ketones, many of which could have been prepared only with great difficulty by other methods.

Ethyl acetoacetate, $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$,* the ethyl ester of **acetoacetic acid,** is formed when ethyl acetate is warmed with sodium, and the product decomposed with dilute acids. The final result is that two molecules of ethyl acetate combine with loss of 1 molecule of alcohol (compare p. 204),

$$CH_3 \cdot CO \cdot OC_2H_5 + H \cdot CH_2 \cdot COOC_2H_5 = CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5 + C_2H_5 \cdot OH.$$

Sodium (30 grams), in the form of fine wire or shavings, is added to dry ethyl acetate (300 grams) contained in a flask connected with a reflux condenser. As soon as the vigorous action, which sets in, has subsided, the flask is heated on a water-bath until bright particles of sodium no longer make their appearance when the flask is vigorously shaken.

The thick brownish semi-solid product, which consists of the sodium derivative of ethyl acetoacetate (and of sodium ethoxide), is allowed to cool, and then treated with dilute (1:4) hydrochloric acid, until the solution is distinctly acid to test-paper. An equal volume of a saturated solution of salt is now added, and the oily layer is separated from the aqueous solution, dried over anhydrous calcium chloride, and fractionated. At first some unchanged ethyl acetate passes over, but the thermometer then rises rapidly to about 160°; the fraction boiling between 175° and 185°, which consists of

* Et is used to represent C_2H_5– in this and in many of the following formulæ for the sake of clearness.

nearly pure ethyl acetoacetate, and weighs 40–50 grams, is collected separately. In the preparation of large quantities of ethyl acetoacetate, the crude product is distilled under reduced pressure, otherwise some decomposition occurs.

Ethyl acetoacetate is a colourless liquid, boiling at 181°, and having an agreeable, fruity odour; it is sparingly soluble in water, but readily in alcohol and ether. The alcoholic solution assumes a beautiful *violet colour* on the addition of ferric chloride.

Although neutral to litmus, ethyl acetoacetate possesses some of the properties of an acid; it dissolves in dilute aqueous solutions of the alkalis, and is reprecipitated on the addition of acids, but it is insoluble in solutions of the alkali carbonates.

These properties are due to the fact that the molecule of ethyl acetoacetate contains a hydrogen atom which is displaceable by certain metals under certain conditions.

The **sodium derivative**, $CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOEt$,* may be prepared by boiling a solution of ethyl acetoacetate, in ether or benzene, with sodium for several hours,

$$2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOEt + 2Na = 2CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOEt + H_2;$$

the sodium derivative is gradually formed as a colourless (or yellowish) crystalline mass, which is readily soluble in water and alcohol; it rapidly deliquesces in moist air, and undergoes decomposition when its aqueous solution is boiled. A *solution* of the sodium derivative is easily obtained by mixing ethyl acetoacetate with a cold alcoholic solution of sodium ethoxide,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOEt + NaO{\cdot}C_2H_5 = CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOEt + C_2H_5{\cdot}OH.$$

When shaken with a saturated solution of copper acetate, ethyl acetoacetate forms a green crystalline *copper derivative*, $(C_6H_9O_3)_2Cu$.

* This formula may be used for the sake of simplicity; although it does *not* express the constitution of the sodium derivative (p. 204), the reactions of this compound are more easily followed when this formula is employed.

This property of forming metallic derivatives is due to the presence in the molecule of the group, –CO–CH_2–CO– ; all substances which contain this, or the group, –CO–CHR–CO–, yield derivatives with sodium, frequently also with other metals.

The sodium derivative of ethyl acetoacetate reacts readily with alkyl halogen compounds, with formation of a sodium halogen salt and a *mono-alkyl derivative* of ethyl acetoacetate. Thus methyl iodide and the sodium derivative of ethyl acetoacetate, give ethyl *methyl*acetoacetate,

$$CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + \mathbf{Me}I\ ^* =$$
$$CH_3\cdot CO\cdot CH\mathbf{Me}\cdot COOC_2H_5 + NaI,$$

whereas propyl bromide gives ethyl *propyl*acetoacetate, $CH_3\cdot CO\cdot CH\mathbf{Pr}\cdot COOC_2H_5$, and so on.

All the *mono*-alkyl derivatives of ethyl acetoacetate contain the group, –CO–CHR–CO, and, therefore, are capable of forming sodium compounds such as

$$CH_3\cdot CO\cdot CNaMe\cdot COOC_2H_5,\ CH_3\cdot CO\cdot CNaPr\cdot COOC_2H_5,$$

&c., on treatment with sodium or sodium ethoxide.

From these sodium compounds, by the action of alkyl halogen compounds, *di-alkyl derivatives* of ethyl acetoacetate are produced thus,

$$CH_3\cdot CO\cdot CNaMe\cdot COOC_2H_5 + \mathbf{Et}Br =$$
$$CH_3\cdot CO\cdot C\mathbf{Et}Me\cdot COOC_2H_5 + NaBr.$$

Ethyl *Ethylmethyl*acetoacetate.

$$CH_3\cdot CO\cdot CNaPr\cdot COOC_2H_5 + \mathbf{Pr}I =$$
$$CH_3\cdot CO\cdot C\mathbf{Pr}Pr\cdot COOC_2H_5 + NaI.$$

Ethyl *Dipropyl*acetoacetate.

It is thus possible to obtain a number of *mono-* or *di-alkyl* derivatives of ethyl acetoacetate, but the mono-alkyl derivative must always be prepared in the first place ; the introduction of both the alkyl-groups cannot be carried out in one operation, because ethyl acetoacetate does *not* form a disodium derivative.

* The symbols Me, &c., are used here for the sake of clearness.

The synthesis of the alkyl substitution products of ethyl acetoacetate is usually carried out as follows :—The theoretical quantity of sodium (1 atom) is dissolved in 10–12 times its weight of absolute alcohol, and the solution of sodium ethoxide is thoroughly cooled. The ethyl acetoacetate, or the mono-substituted ethyl acetoacetate (1 mol.), and a slight excess of the alkyl halogen compound (1 mol.), are now gradually added to the solution of the sodium ethoxide, which is well cooled during the operation. The mixture is then carefully heated on a water-bath in a flask connected with a reflux condenser until it becomes neutral to litmus-paper. In order to isolate the product, the alcohol is distilled from a brine-bath, the residue is mixed with water to dissolve the precipitated sodium salt, and the product is extracted with ether. The ethereal solution is washed with water and dried with anhydrous calcium chloride; the ether is then distilled off, and the residual oil purified by fractional distillation.

The following are some of the more important mono- and di-substitution products of ethyl acetoacetate, with their boiling-points :

		B.p.
Ethyl *methyl*acetoacetate,	$CH_3 \cdot CO \cdot CHMe \cdot COOC_2H_5$	187°
Ethyl *dimethyl*acetoacetate,	$CH_3 \cdot CO \cdot CMe_2 \cdot COOC_2H_5$	184°
Ethyl *ethyl*acetoacetate,	$CH_3 \cdot CO \cdot CHEt \cdot COOC_2H_5$	198°
Ethyl *diethyl*acetoacetate,	$CH_3 \cdot CO \cdot CEt_2 \cdot COOC_2H_5$	218°
Ethyl *propyl*acetoacetate,	$CH_3 \cdot CO \cdot CHPr^{\alpha} \cdot COOC_2H_5$	209°
Ethyl *isopropyl*acetoacetate,	$CH_3 \cdot CO \cdot CHPr^{\beta} \cdot COOC_2H_5$	201°

The *mono*-substituted ethyl acetoacetates resemble ethyl acetoacetate in chemical behaviour, and give a characteristic bluish-violet colouration with ferric chloride. The *di*-substituted ethyl acetoacetates, however, do *not* contain a hydrogen atom displaceable by metals, and do not give the violet ferric chloride reaction.

One of the more important changes which ethyl acetoacetate and its derivatives undergo is that which takes place when they are treated with alkalis or mineral acids. Alkalis *at ordinary temperatures* simply hydrolyse the esters with formation of the alkali salts of the corresponding acids,

$$CH_3 \cdot CO \cdot CH_2 \cdot COOEt + KOH = CH_3 \cdot CO \cdot CH_2 \cdot COOK + Et \cdot OH.$$

Potassium Acetoacetate.

The free acids are obtained by acidifying the solutions and extracting with ether; these *β-ketonic* acids,* however, are very

* The ketonic oxygen atom is here combined with the β-carbon atom (compare p. 171).

unstable, and decompose, in many cases at ordinary temperatures, but always when heated, yielding carbon dioxide and a ketone,

$$CH_3\cdot CO\cdot CH_2\cdot COOH = CH_3\cdot CO\cdot CH_3 + CO_2,$$
$$CH_3\cdot CO\cdot CEt_2\cdot COOH = CH_3\cdot CO\cdot CHEt_2 + CO_2.$$

When *heated* with alkalis, ethyl acetoacetate and its derivatives are decomposed in two ways, the course of the decomposition depending to a great extent on the nature and concentration of the alkali used.

Boiling *dilute* alcoholic potash converts these substances into *ketones*, with separation of potassium carbonate (**ketonic hydrolysis**),

$$CH_3\cdot CO\cdot CH_2\vdots COOEt + 2KOH = CH_3\cdot CO\cdot CH_3 + K_2CO_3 + Et\cdot OH,$$

$$CH_3\cdot CO\cdot C\mathbf{Et}_2\vdots COOEt + 2KOH = CH_3\cdot CO\cdot CH\mathbf{Et}_2 + K_2CO_3 + Et\cdot OH.$$

Ketonic hydrolysis is also brought about by boiling dilute mineral acids. When, however, *strong* alcoholic potash is employed, the decomposition takes place in quite a different manner, the potassium salt of a fatty acid being the principal product (**acid hydrolysis**),

$$CH_3\cdot CO\vdots CH_2\cdot COOEt + 2KOH = 2CH_3\cdot COOK + Et\cdot OH,$$

$$CH_3\cdot CO\vdots C\mathbf{Et}_2\cdot COOC_2H_5 + 2KOH = CH_3\cdot COOK + \mathbf{Et}_2CH\cdot COOK + C_2H_5\cdot OH.$$

Potassium Diethylacetate.

Ethyl acetoacetate, therefore, is a very important compound, as with its aid many fatty acids and many ketones (containing the group, $CH_3\cdot CO-$), can be synthetically prepared.

Example.—If an *acid* of the constitution, $(C_2H_5)(C_3H_7)CH\cdot COOH$ —namely, ethylpropylacetic acid—were required, ethyl *ethyl*acetoacetate, $CH_3\cdot CO\cdot CH(C_2H_5)\cdot COOC_2H_5$, might be first prepared; the sodium derivative of this substance would then be treated with propyl iodide, and the ethyl *ethylpropyl*acetoacetate, $CH_3\cdot CO\cdot C(C_2H_5)(C_3H_7)\cdot COOC_2H_5$, so formed, would be heated with *strong* alcoholic potash,

$$CH_3{\cdot}CO{\cdot}C(C_2H_5)(C_3H_7){\cdot}COOC_2H_5 + 2KOH = CH_3{\cdot}COOK + CH(C_2H_5)(C_3H_7){\cdot}COOK + C_2H_5{\cdot}OH.$$

Example.—If a *ketone* of the constitution, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_4H_9$—namely, butyl acetone—were required, ethyl butylacetoacetate, $CH_3{\cdot}CO{\cdot}CH(C_4H_9){\cdot}COOC_2H_5$, would be prepared by treating the sodium compound of ethyl acetoacetate with butyl iodide; this product would then be decomposed with boiling *dilute* alcoholic potash or dilute sulphuric acid,

$$CH_3{\cdot}CO{\cdot}CH(C_4H_9){\cdot}COOC_2H_5 + 2KOH = CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_4H_9 + K_2CO_3 + C_2H_5{\cdot}OH.$$

The acid and the ketonic hydrolysis of ethyl acetoacetate and its derivatives always take place to some extent simultaneously, whether weak or strong alkali is used. It is not possible, for instance, to decompose an ethyl acetoacetate derivative with strong alkali without a small amount of ketone being formed, and when dilute alkali is used a certain quantity of the salt of a fatty acid is invariably produced; nevertheless, the relative quantities of the products depend very largely on the concentration of the alkali employed.

Constitution of Ethyl Acetoacetate.—On hydrolysis with cold alkalis, ethyl acetoacetate is converted into a salt of acetoacetic acid, and when this acid is gently warmed it is decomposed into acetone and carbon dioxide; it may be assumed, therefore, that acetoacetic acid has the constitution, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$, and its ester, ethyl acetoacetate, may be represented by the formula, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$.

That ethyl acetoacetate contains a ketonic-group, –CO–, seems to be proved by many facts; it reacts with hydroxylamine and with phenylhydrazine, combines with sodium bisulphite and with hydrogen cyanide, and on reduction it is converted into β-hydroxybutyric acid, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$, or its ethyl ester. In many of its reactions, however, ethyl acetoacetate behaves as if it contained a hydroxyl-group, and had the constitution represented by the formula, $CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5$.

Ever since ethyl acetoacetate was discovered by Geuther in 1863, chemists have been trying to explain its formation from ethyl acetate, and to decide which of the two possible formulæ (given above) should be used to express its constitution. The fact that ethyl acetoacetate contains a hydrogen atom displaceable by sodium, whilst ethyl acetate does not, seemed to show that the

former, like ethyl alcohol, contained a *hydroxyl*-group, a view which was confirmed by the knowledge that in the vast majority of organic compounds hydrogen *directly united with carbon* is not displaceable by metals. At first sight it might seem absurd to represent the sodium derivative by the formula, $CH_3{\cdot}C(ONa){:}CH{\cdot}COOEt$, because when this compound reacts with alkyl halogen compounds the alkyl-group does not become united to *oxygen* but to *carbon;* this difficulty, however, was avoided by the further assumption that the first change consisted in a direct addition of the alkyl halogen compound to the unsaturated sodium derivative, giving an unstable product which immediately underwent decomposition,

$$CH_3{\cdot}C(ONa){:}CH{\cdot}COOEt + MeI = CH_3{\cdot}CI(ONa){\cdot}CMeH{\cdot}COOEt,$$
$$CH_3{\cdot}CI(ONa){\cdot}CMeH{\cdot}COOEt = CH_3{\cdot}CO{\cdot}CMeH{\cdot}COOEt + NaI.$$

A similar assumption—namely, the formation of an unstable intermediate product—may also be made to explain the action of sodium on ethyl acetate (Claisen); in the first place, sodium ethoxide is probably produced by the action of the metal on traces of alcohol contained in, or formed from, the ester; combination then ensues between the sodium ethoxide and the ethyl acetate (which strictly speaking is an unsaturated compound), giving an unstable derivative of ortho-acetic acid, $CH_3{\cdot}C(OH)_3$,

$$CH_3{\cdot}COOEt + NaOEt = CH_3{\cdot}C(OEt)_2{\cdot}ONa;$$

this additive product then condenses with ethyl acetate, giving alcohol and the sodium derivative of ethyl acetoacetate (*ethyl hydroxycrotonate*),

$$CH_3{\cdot}C(OEt)_2{\cdot}ONa + CH_3{\cdot}COOEt =$$
$$CH_3{\cdot}C(ONa){:}CH{\cdot}COOEt + 2Et{\cdot}OH.$$

Further investigation has shown that 'ethyl acetoacetate' is a mixture of two *different* substances, which are easily converted one into the other. At ordinary temperatures it consists almost entirely of a compound of the constitution, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, but contains a small proportion of the isomeric hydroxy-compound, $CH_3{\cdot}C(OH){:}CH{\cdot}COOEt$. These isomeric substances are in equilibrium with one another, but are readily converted one into the other in presence of various solvents or reagents, and a new condition of equilibrium is established. On the addition of sodium ethoxide, for example, the *hydroxy*-compound is converted into its sodium derivative, the equilibrium is disturbed, and the ketonic form passes into the hydroxy-isomeride, so that ultimately the whole of the ester is converted into a sodium derivative of the above constitution. On the addition of an acid to this sodium

derivative, the regenerated hydroxy-compound passes into the ketone until equilibrium is attained.

Many substances which, like ethyl acetoacetate, contain the group, $R-CO-CH_2-$, or $R\cdot CO\cdot CH<$, behave in a similar manner and readily pass into *isomeric* hydroxy-compounds, $R-C(OH)=CH-$ or $R\cdot C(OH)=C<$, which may be reconverted into the keto-derivatives; such isomerides differ from isomeric compounds generally in the readiness with which they are changed one into the other by heat or by the action of various chemical agents, and are termed *tautomeric* forms or *tautomerides*. When, as in the case of ethyl acetoacetate, it is known that the two tautomerides are capable of existence, they are further distinguished as *desmotropic* forms or *isodynamic isomerides*. The hydroxy-form is usually known as the '*enol*' modification, the isomeride being named the '*keto*' form. When one of the tautomeric forms is more stable than the other under ordinary conditions, the latter is often called the *labile* modification; but, as a rule, it is difficult to say which is the more stable form, as it all depends on the conditions under which the tautomerides are placed. The enol form, as a rule, gives a violet colouration with ferric chloride, but the keto form does not (unless it is converted into the enol by the reagent).

Other Ketonic Acids.

Pyruvic acid, or acetylformic acid, $CH_3\cdot CO\cdot COOH$, is formed by the destructive distillation of tartaric acid (p. 255),

$$\begin{matrix}CH(OH)\cdot COOH\\ |\\ CH(OH)\cdot COOH\end{matrix} = CH_3\cdot CO\cdot COOH + CO_2 + H_2O.$$

It is an oily, sour-smelling liquid, distils at 165–170°, and is soluble in water in all proportions. It reacts with hydroxylamine, and gives with phenylhydrazine in aqueous solution a very sparingly soluble phenylhydrazone, $CH_3\cdot C(N_2HC_6H_5)\cdot COOH$. When treated with sodium amalgam and water, pyruvic acid is reduced to lactic acid (p. 239),

$$CH_3\cdot CO\cdot COOH + 2H = CH_3\cdot CH(OH)\cdot COOH.$$

Levulic acid (β-acetylpropionic acid), $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$, is produced when fructose, glucose, sucrose, starch, and various other carbohydrates containing 6, or a multiple of 6, carbon atoms are boiled with dilute hydrochloric acid.

It melts at 33·5° and boils at 239°; it is very soluble in water, reacts readily with hydroxylamine and phenylhydrazine, and when reduced with sodium amalgam and water it yields the sodium salt of γ-hydroxyvaleric acid, $CH_3\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COOH$. Levulic

acid is isomeric with methylacetoacetic acid or *a*-acetylpropionic acid, $CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}COOH$; its name is derived from that of levulose (fructose), a sugar from which it was first obtained.

a-Ketonic acids, such as pyruvic acid, and γ-ketonic acids, such as levulic acid, show a behaviour very different from that of β-ketonic acids, such as acetoacetic acid; they are *not* decomposed when they are heated moderately strongly, and their esters do *not* contain hydrogen displaceable by metals.

Ethyl malonate, $CH_2(COOC_2H_5)_2$, does not belong to the same class of substances as ethyl acetoacetate, but it may be conveniently considered in this chapter on account of its employment in the synthesis of fatty acids.

When potassium chloracetate is digested with potassium cyanide in aqueous solution, potassium cyano-acetate is produced,

$$CH_2Cl{\cdot}COOK + KCN = CH_2(CN){\cdot}COOK + KCl.$$

This salt, on hydrolysis with hydrochloric acid, yields malonic acid (p. 248),

$$CH_2(CN){\cdot}COOK + 2HCl + 2H_2O = CH_2(COOH)_2 + KCl + NH_4Cl;$$

but when the dry potassium cyanoacetate is mixed with alcohol and the mixture is saturated with hydrogen chloride, the acid which is formed is esterified and ethyl malonate is produced,

$$CH_2(CN){\cdot}COOK + 2HCl + 2C_2H_5{\cdot}OH = CH_2(COOC_2H_5)_2 + KCl + NH_4Cl.$$

Preparation.—Chloracetic acid (100 grams) is dissolved in water (200 c.c.) and neutralised with potassium carbonate (76 grams); potassium cyanide (75–80 grams) is then added, and the mixture is heated in a large porcelain basin until a vigorous reaction commences.* As soon as this has subsided the solution is evaporated on a sand-bath, the thick, semi-solid residue being constantly stirred with a thermometer until the temperature reaches 135°; the solid cake of potassium chloride and cyanoacetate is powdered, transferred to a flask, an equal weight of absolute alcohol added, and the boiling mixture saturated with dry hydrogen chloride (compare p. 196). When cold, the solution is poured into twice or thrice its volume of ice-water; the product is then

* These operations are carried out in a fume chamber.

extracted with ether, and the ethereal solution is washed with water and dried with calcium chloride. The crude oil, which remains when the ether is distilled off, is purified by fractional distillation; the portion boiling at 195–200° consists of practically pure ethyl malonate (b.p. 198°), and has a pleasant fruity odour.

Ethyl malonate, $CH_2<^{CO\cdot OC_2H_5}_{CO\cdot OC_2H_5}$, like ethyl acetoacetate, contains the group, $-CO\cdot CH_2\cdot CO-$, and forms a sodium derivative when it is treated with the metal or with sodium ethoxide,

$$2CH_2(COOC_2H_5)_2 + 2Na = 2CHNa(COOC_2H_5)_2 + H_2,$$
$$CH_2(COOC_2H_5)_2 + C_2H_5\cdot ONa = CHNa(COOC_2H_5)_2 + C_2H_5\cdot OH.$$

Unlike ethyl acetoacetate, it does not dissolve in aqueous alkalis, because its alkali derivatives are decomposed by water, and it does not give a colouration with ferric chloride.

The sodium derivative of ethyl malonate reacts readily with alkyl halogen compounds, yielding alkyl derivatives of ethyl malonate,

$$CHNa(COOC_2H_5)_2 + \mathbf{Et}I = CH\mathbf{Et}(COOC_2H_5)_2 + NaI;$$

Ethyl *Ethyl*malonate.

these mono-substitution derivatives, like those of ethyl acetoacetate, are capable of forming sodium derivatives, which, by further treatment with alkyl halogen compounds, yield di-substitution derivatives of ethyl malonate,

$$CH\mathbf{Et}(COOC_2H_5)_2 + NaOEt = CNa\mathbf{Et}(COOC_2H_5)_2 + Et\cdot OH,$$
$$CNa\mathbf{Et}(COOC_2H_5)_2 + \mathbf{Pr}I = C\mathbf{PrEt}(COOC_2H_5)_2 + NaI.$$

Ethyl *Propylethyl*malonate.

In this way a great number of derivatives may be obtained, the syntheses being carried out exactly as described in the case of the substitution products of ethyl acetoacetate.

Ethyl malonate and its derivatives are hydrolysed by boiling alcoholic potash with formation of the potassium salts of the corresponding acids,

$$CH\mathbf{Et}(COOC_2H_5)_2 + 2KOH = CH\mathbf{Et}(COOK)_2 + 2C_2H_5\cdot OH,$$

Potassium Ethylmalonate.

$$C\mathbf{EtPr}(COOC_2H_5)_2 + 2KOH = C\mathbf{EtPr}(COOK)_2 + 2C_2H_5\cdot OH.$$

Potassium Ethylpropylmalonate.

Malonic acid and the dicarboxylic acids derived from it are rapidly and quantitatively decomposed at about 200°, with evolution of carbon dioxide and formation of fatty acids. This behaviour is shown by *all* acids which contain two carboxyl-groups directly combined with the *same* carbon atom (p. 249),

$$CH_2(COOH)_2 = CH_3{\cdot}COOH + CO_2,$$

$$C\mathbf{EtPr}(COOH)_2 = C\mathbf{EtPr}H{\cdot}COOH + CO_2.$$

Ethylpropylmalonic Acid. Ethylpropylacetic Acid.

Ethyl malonate, therefore, is of the utmost service in the synthesis of fatty acids, and, indeed, is more used for this purpose than ethyl acetoacetate, because, in the case of the latter, ketones are always formed on hydrolysis as by-products.

Example.—Normal valeric acid, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is to be prepared synthetically. In the first place, the sodium derivative of ethyl malonate is heated with propyl iodide, and the resulting ethyl propylmalonate, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2$, is hydrolysed with boiling alcoholic potash. The propylmalonic acid obtained from the potassium salt is heated at about 200°, or distilled, when it decomposes into normal valeric acid and carbon dioxide,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH)_2 = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + CO_2.$$

The examples already given will afford some indication of the great usefulness of ethyl acetoacetate and of ethyl malonate in synthesising fatty acids and ketones, but there are many other synthetical operations in which these important esters are employed. Their sodium derivatives react readily, not only with alkyl halogen esters, but also with *acid chlorides*, &c., such as acetyl chloride,

$$CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOEt + CH_3{\cdot}COCl = CH_3{\cdot}CO{\cdot}CH(CO{\cdot}CH_3){\cdot}COOEt + NaCl$$

$$CHNa(COOEt)_2 + CH_3{\cdot}COCl = CH(CO{\cdot}CH_3)(COOEt)_2 + NaCl,$$

and with halogen derivatives of esters, such as ethyl chloracetate (compare p. 249); the compounds thus obtained undergo hydrolysis in much the same way as the simple alkyl-derivatives of the two esters.

Cyanoacetic acid, $CN{\cdot}CH_2{\cdot}COOH$, is obtained in the form of its potassium salt in the preparation of ethyl malonate (p. 206), and may be isolated by decomposing the salt with ice-cold concentrated

hydrochloric acid, filtering from potassium chloride, and evaporating the filtrate under reduced pressure. It melts at 69° and decomposes at about 165°, giving methyl cyanide and carbon dioxide. **Ethyl cyanoacetate**, $CN{\cdot}CH_2{\cdot}COOEt$ (b.p. 207°), like ethyl malonate, contains a hydrogen atom which is displaceable by sodium, and the *sodium derivative*, $CN{\cdot}CHNa{\cdot}COOEt$, is often used for synthetical purposes.

Ethyl oxalacetate, $COOEt{\cdot}CH_2{\cdot}CO{\cdot}COOEt$, is prepared by adding ethyl acetate to ethyl oxalate in presence of sodium; the *sodium derivative*, which is thus formed (by a reaction similar to that which occurs in the preparation of ethyl acetoacetate, p. 204), is decomposed with dilute sulphuric acid, and the ester is fractionally distilled under reduced pressure (b.p. 131–132°, 24 mm.). It gives an intense red colouration with an alcoholic solution of ferric chloride, and resembles ethyl acetoacetate in undergoing both ketonic and acid hydrolysis; thus, when it is heated with 10 per cent. sulphuric acid it gives pyruvic acid (p. 205), alcohol, and carbon dioxide, whereas with boiling alcoholic potash it yields alcohol and the potassium salts of acetic and oxalic acids.

CHAPTER XII.

Alkyl Compounds of Nitrogen, Phosphorus, Arsenic, Silicon, Magnesium, Zinc, Mercury, &c.

Amines.

Many of the compounds described in the preceding pages may be conveniently considered as derivatives of simple inorganic compounds; the alcohols and ethers, for example, may be regarded as derivatives of water, the mercaptans and sulphides as derivatives of hydrogen sulphide,

$H{\cdot}O{\cdot}H$	$C_2H_5{\cdot}OH$	$C_2H_5{\cdot}O{\cdot}C_2H_5$
$H{\cdot}S{\cdot}H$	$C_2H_5{\cdot}SH$	$C_2H_5{\cdot}S{\cdot}C_2H_5$.

In a similar manner the hydrides of many other elements may be directly or indirectly converted into organic compounds by the substitution of one or more alkyl-groups for an equivalent quantity of hydrogen; from ammonia, for example, a very

important class of strongly basic substances, termed **amines**, may be obtained, and these compounds are distinguished as *primary*, *secondary*, or *tertiary* amines, according as 1, 2, or 3 atoms of hydrogen in ammonia have been displaced by alkyl-groups.

Primary.	*Secondary.*
Methylamine, $NH_2 \cdot CH_3$	Dimethylamine, $NH(CH_3)_2$
Ethylamine, $NH_2 \cdot C_2H_5$	Diethylamine, $NH(C_2H_5)_2$
Propylamine, $NH_2 \cdot C_3H_7$	Dipropylamine, $NH(C_3H_7)_2$

Tertiary.

Trimethylamine, $N(CH_3)_3$
Triethylamine, $N(C_2H_5)_3$
Tripropylamine, $N(C_3H_7)_3$

In addition to the amines, alkyl derivatives of ammonium hydroxide, such as *tetrethylammonium hydroxide*, $N(C_2H_5)_4 \cdot OH$, are known; these compounds are strong basic hydroxides, which with acids give salts, such as *tetrethylammonium iodide*, $N(C_2H_5)_4I$, just as ammonium hydroxide gives ammonium iodide. The methods of formation and general characters of the amines, and of the tetra-alkylammonium derivatives, may be illustrated by a description of the ethyl compounds.

Ethylamine, $NH_2 \cdot C_2H_5$, was first obtained by the distillation of ethyl isocyanate (p. 325) with potash (Würtz),

$$CO{:}N \cdot C_2H_5 + 2KOH = NH_2 \cdot C_2H_5 + K_2CO_3.$$

It is produced (together with *di-* and *tri*-ethylamine and a tetrethylammonium derivative) when ethyl chloride, bromide, or iodide, is heated at about 100° in closed vessels with alcohol which has been saturated with ammonia (Hofmann); the halogen acid produced during the interaction combines with the amine, forming a salt,

$$C_2H_5I + NH_3 = C_2H_5 \cdot NH_2, HI.$$

Ethylamine is prepared by cautiously mixing propionamide (1 mol.) with bromine (1 mol.), and then slowly adding a 10 per cent. solution of potassium hydroxide (1 mol.) until the

colour of the bromine disappears; the solution of the propiobromamide which is thus produced,

$$C_2H_5\cdot CO\cdot NH_2 + Br_2 + KOH = C_2H_5\cdot CO\cdot NHBr + KBr + H_2O,$$

is now slowly added to excess of a concentrated solution of potassium hydroxide (3 mols.), when the bromamide is converted into ethylamine (Hofmann),

$$C_2H_5\cdot CO\cdot NHBr + 3\,KOH = C_2H_5\cdot NH_2 + KBr + K_2CO_3 + H_2O.$$

In the latter operation the temperature is allowed to rise to about 68°, and the solution is kept at this temperature until it becomes colourless. The liquid is then distilled, and the ethylamine is collected in hydrochloric acid. The acid solution is evaporated to dryness, and the residue is extracted with alcohol; ammonium chloride remains, and crystals of ethylamine hydrochloride are obtained when the filtered alcoholic solution is concentrated. *Methylamine hydrochloride* is prepared in a similar manner from acetamide.

Ethylamine is a colourless, mobile, inflammable liquid of sp. gr. 0·689 at 15°, and boils at 18·7°; it is soluble in water in all proportions, and the solution, like the liquid itself, has a pungent, slightly fish-like odour, distinguishable from that of ammonia only with difficulty. An aqueous solution of ethylamine might, in fact, be easily mistaken for a solution of ammonia, so closely do they resemble one another in properties; the former, like the latter, has a strongly alkaline reaction, and gives, especially when warmed, a pungent-smelling gas, which fumes when brought into proximity with concentrated hydrochloric acid; it precipitates metallic hydroxides from solutions of their salts, and neutralises acids, forming salts, which are readily soluble in water. Ethylamine, therefore, is an organic *base*, and its basic properties are even more pronounced than those of ammonia; it is very hygroscopic, and readily absorbs carbon dioxide from the air, forming with it a salt.*

Although, speaking generally, ethylamine is very stable, it

* Probably not a carbonate, but a carbamate (p. 330), $CO<^{NH\cdot C_2H_5}_{OH}, C_2H_5\cdot NH_2$.

is rapidly converted into ethyl alcohol on treatment with nitrous acid in aqueous solution, nitrogen being liberated,

$$C_2H_5\cdot NH_2 + HO\cdot NO = C_2H_5\cdot OH + H_2O + N_2;$$

this reaction is analogous to that which occurs when ammonia and nitrous acid (ammonium nitrite) are heated together,

$$NH_4NO_2 \text{ or } NH_3 + HO\cdot NO = 2H\cdot OH + N_2.$$

A solution of ethylamine hydrochloride is mixed with hydrochloric acid, and a solution of sodium nitrite is added slowly by means of a thistle funnel which passes to the bottom of the acid solution; a rapid effervescence sets in, and the gas which is evolved is colourless and contains little, if any, nitrous anhydride. When the solution is subsequently distilled, the presence of ethyl alcohol in the distillate may be proved by the usual methods (p. 99).

Ethylamine is also quickly changed when it is warmed with chloroform and alcoholic potash, and is converted into *ethylcarbylamine* (p. 322),

$$C_2H_5\cdot NH_2 + CHCl_3 + 3KOH = C_2H_5\cdot NC + 3KCl + 3H_2O.$$

The intensely disagreeable smell of the product * is at once recognisable, and affords a sure indication of the presence of a primary amine (Hofmann's carbylamine reaction). The two reactions just mentioned are characteristic of all *primary amines*, and are of great practical importance; the first is employed for the conversion of the primary amines into alcohols, the second for their detection.

Ethylamine is a monacid base, and, like ammonia, forms salts by direct combination, in virtue of the possible quinquevalency of the nitrogen atom; these salts are all soluble in water, and some of them, like those of ammonia, sublime readily, even at ordinary temperatures; they usually differ from ammonium salts in being soluble in alcohol, a property which is frequently made use of in isolating the amine.

Ethylamine hydrochloride, $C_2H_5\cdot NH_3Cl$, or $C_2H_5\cdot NH_2$, HCl, as usually written, crystallises in large plates, melts at

* Compare footnote, p. 182.

about 80°, and is deliquescent. The *normal sulphate*, $2C_2H_5\cdot NH_2,H_2SO_4$, has similar properties. The halogen salts, like those of ammonia, form complex salts with many other metallic halogen salts; of these compounds the *platinichlorides* and the *aurichlorides* are important, and they correspond with the complex ammonium salts of similar composition,

Ethylamine platinichloride,	$(C_2H_5\cdot NH_2)_2, H_2PtCl_6$
Ammonium platinichloride,	$(NH_3)_2, H_2PtCl_6$
Ethylamine aurichloride,	$C_2H_5\cdot NH_2, HAuCl_4$
Ammonium aurichloride,	$NH_3, HAuCl_4$.

The platinichlorides and aurichlorides are usually yellow, orange, or red, and are generally much more sparingly soluble in water than the hydrochlorides; for the latter reason they are often used in detecting and isolating the amines; on ignition they give a residue of pure metal.

Diethylamine, $NH(C_2H_5)_2$, is formed when ethyl iodide is heated with alcoholic ammonia, just as described in the case of ethylamine; one molecule of the hydrogen iodide, which is produced, combines with the base to form a salt, and the other unites with the excess of ammonia,

$$2C_2H_5I + NH_3 = NH(C_2H_5)_2,HI + HI.$$

Diethylamine is a colourless, inflammable liquid, boiling at 56°; it is a stronger base than ethylamine, which it resembles very closely in smell, solubility, &c., and also in forming simple and complex salts. It is readily distinguished from ethylamine, inasmuch as it does *not* give the carbylamine reaction; its behaviour with nitrous acid is also totally different from that of ethylamine, since, instead of being converted into an alcohol, it yields *diethylnitrosamine*,

$$(C_2H_5)_2NH + HO\cdot NO = (C_2H_5)_2N\cdot NO + H_2O.$$

A concentrated aqueous solution of sodium nitrite is added gradually to a concentrated solution of diethylamine hydrochloride in hydrochloric acid; the diethylnitrosamine separates as an oil,

because it is not readily soluble in water and does not form salts with acids.

All *secondary amines* behave in this way; that is to say, on treatment with nitrous acid, they are converted into *nitrosamines* by the substitution of the univalent nitroso-group, –NO, for the atom of hydrogen which is directly united with nitrogen.

When a nitrosamine is mixed with phenol (Part II. p. 439) and concentrated sulphuric acid, it gives a dark-green solution which, when diluted with water, becomes red, and with excess of alkali assumes a beautiful and intense blue or green colour; this reaction (*Liebermann's nitroso-reaction*) affords a means of detecting, not only a nitrosamine, but also a secondary amine, as the latter is convertible into the former.

Diethylamine hydrochloride, $(C_2H_5)_2NH$, HCl, is colourless, and readily soluble in water; its *platinichloride*, $[(C_2H_5)_2NH]_2$, H_2PtCl_6, and *aurichloride*, $(C_2H_5)_2NH$, $HAuCl_4$, are orange, and less readily soluble.

Triethylamine, $N(C_2H_5)_3$, like the primary and secondary amines, is produced when ethyl iodide is heated with alcoholic ammonia,

$$3C_2H_5I + NH_3 = N(C_2H_5)_3,HI + 2HI.$$

It is a pleasant-smelling liquid, boiling at 89°, and except that it is more sparingly soluble in water, it resembles the primary and secondary compounds in most ordinary properties. It does *not* give the carbylamine reaction, and is *not* acted on by nitrous acid at ordinary temperatures, so that it is readily distinguished from the primary and secondary amines; other *tertiary amines* resemble triethylamine in these respects. The salts of triethylamine correspond with those of the other bases.

The salts of primary, secondary, and tertiary amines are all decomposed by alkalis and by alkali carbonates; when excess of the alkali is used, and heat is applied, the amine volatilises and, as in the case of ammonium salts, the (reversible) reaction proceeds to completion.

Quaternary Ammonium Derivatives.

Triethylamine, and other tertiary amines, combine directly with one molecule of an alkyl halogen compound, yielding salts corresponding with those of ammonium,

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I \qquad NH_3 + HI = NH_4I.$$

The bases corresponding with these salts are non-volatile, and therefore they are not expelled when the salt is heated with an aqueous solution of potassium hydroxide; when, however, aqueous solutions of the salts are shaken with freshly precipitated silver hydroxide, a silver halide is formed, and hydroxides, corresponding with ammonium hydroxide, may be isolated by evaporating the filtered solutions,

$$N(C_2H_5)_4I + Ag{\cdot}OH = N(C_2H_5)_4{\cdot}OH + AgI,$$
$$NH_4I + Ag{\cdot}OH = NH_4{\cdot}OH + AgI.$$

The hydroxides obtained in this way are termed *quaternary ammonium bases*, or *tetralkylammonium hydroxides;* although they are similar in type to ammonium hydroxide, they differ from the latter in several important respects, and resemble rather the hydroxides of sodium and potassium.

Tetrethylammonium hydroxide, $N(C_2H_5)_4{\cdot}OH$, for example, is a crystalline, deliquescent substance; it has a strong alkaline reaction, absorbs carbon dioxide from the air, and liberates ammonia from ammonium salts; when strongly heated it is resolved into triethylamine and ethyl alcohol, or its decomposition products,

$$N(C_2H_5)_4{\cdot}OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

The salts of tetrethylammonium hydroxide, such as the iodide (see above), may of course be obtained by treating the hydroxide with acids; they are crystalline and readily soluble in water.

The tetralkylammonium halogen salts undergo decomposition or dissociation on dry distillation, yielding a tertiary amine and an alkyl halogen salt, just as ammonium chloride dissociates into ammonia and hydrogen chloride,

$$N(C_2H_5)_4Cl = N(C_2H_5)_3 + C_2H_5Cl \qquad NH_4Cl = NH_3 + HCl.$$

Under ordinary circumstances the halogen ester, being much more volatile than the tertiary amine, can be separated from the latter before recombination takes place.

In a similar manner the halogen salts of *some* tertiary amines may be converted into secondary, and those of secondary into primary, amines,

$$N(CH_3)_3,HCl = N(CH_3)_2H + CH_3Cl$$
$$N(CH_3)_2H,HCl = N(CH_3)H_2 + CH_3Cl.$$

The three ethylamines and the tetrethylammonium compounds may be taken as typical examples of the several classes of alkyl-derivatives of ammonia; the corresponding methyl bases, and those of the higher alkyl radicles, are prepared by methods so similar to those described in the case of the ethylamine compounds, and have chemical properties so closely resembling those of the latter, that a description of individual compounds is unnecessary.

Methylamine, $NH_2 \cdot CH_3$, *dimethylamine*, $NH(CH_3)_2$, and *trimethylamine*, $N(CH_3)_3$, are usually produced in small quantities during the decomposition of nitrogenous organic substances, and occur in herring brine, the last named especially in relatively large proportions. Dimethylamine and trimethylamine are prepared on the large scale by the distillation of the waste products obtained in refining beet-sugar, and are used in considerable quantities for various technical purposes; trimethylamine hydrochloride is used in the preparation of methyl chloride (p. 181, and above).

The physical properties of the amines undergo a gradual change with increasing molecular weight, just as is the case in other series; the boiling-points of the first four *normal* primary amines may be taken as an illustration.

Methylamine, $CH_3 \cdot NH_2$	B.p.	$-6°$
Ethylamine, $C_2H_5 \cdot NH_2$	"	$+19°$
Propylamine, $C_3H_7 \cdot NH_2$	"	$49°$
Butylamine, $C_4H_9 \cdot NH_2$	"	$76°$

The amines, like other compounds, show isomerism; there are, for example, four compounds of the molecular formula, C_3H_9N, —namely, normal *propylamine*, $CH_3 \cdot CH_2 \cdot CH_2 \cdot NH_2$, *isopropylamine*, $(CH_3)_2CH \cdot NH_2$, *methylethylamine*, $CH_3 \cdot NH \cdot C_2H_5$, and *trimethylamine*, $(CH_3)_3N$. It will be seen that the name of each of these isomerides expresses the structure of the compound.

Preparation of Amines.—Two important general methods which are used for the preparation of amines have already been described—namely, those which were discovered by Hofmann (p. 210). The first of these methods gives primary, secondary, and tertiary amines, as well as the tetralkylammonium derivatives, whereas the second method (the decomposition of the amides with bromine and potash) gives a *primary* amine only.

Primary amines are also prepared by the following methods :—

An oxime (or a hydrazone) is reduced with zinc dust and acetic acid, or, in the case of an oxime, with sodium and alcohol,

$$(CH_3)_2C{:}NOH + 4H = (CH_3)_2CH{\cdot}NH_2 + H_2O.$$

An alkyl cyanide is reduced with zinc and sulphuric acid, or with sodium and alcohol,

$$CH_3{\cdot}CN + 4H = CH_3{\cdot}CH_2{\cdot}NH_2.$$

A nitro-paraffin is reduced with stannous chloride and hydrochloric acid, or with zinc and an acid,

$$C_2H_5{\cdot}NO_2 + 6H = C_2H_5{\cdot}NH_2 + 2H_2O.$$

In all these methods the solution of the product, if acid, is made strongly alkaline, and the liberated base is distilled in steam, and collected in hydrochloric acid ; the solution is then evaporated to dryness, and the hydrochloride is distilled with powdered caustic potash.

The compounds formed by the combination of aldehydes with ammonia are also reduced to amines when they are treated with zinc and hydrochloric acid in the cold,

$$CH_3{\cdot}CH(OH){\cdot}NH_2 + 2H = CH_3{\cdot}CH_2{\cdot}NH_2 + H_2O;$$

but it is unusual for the hydroxyl-group to be displaced by hydrogen under such conditions, and a change of this kind is generally brought about only by heating the compound with hydriodic acid (pp. 240, 293, 302).

Secondary and *tertiary* amines are obtained, as already stated, by heating the alkyl bromides or iodides with alcoholic ammonia; but as primary bases and tetralkylammonium compounds are also formed, the separation of the four products is a troublesome matter. For this reason it is often more

convenient to prepare the primary amine by one of the methods given above, and then to heat it with the theoretical quantity of the alkyl bromide or iodide and excess of potassium hydroxide, when reactions such as the following occur :—

$$C_2H_5\cdot NH_2 + C_2H_5I + KOH = (C_2H_5)_2NH + KI + H_2O,$$
$$(C_2H_5)_2NH + C_2H_5I + KOH = (C_2H_5)_3N + KI + H_2O,$$
$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI.$$

A primary may thus be converted into a secondary base, and the latter into a tertiary base, which finally may form a tetralkylammonium salt.

Even when the theoretical quantity of the alkyl halogen compound is used, the product may be a mixture of secondary, tertiary, and quaternary bases. The two amines may be distilled off in steam, and the distillate neutralised with some acid ; the mixture of salts is then submitted to fractional crystallisation. The platinichlorides and aurichlorides are often used for this purpose, also the sparingly soluble compounds which most amines form with picric acid (Part II. p. 442).

The solution which contains the quaternary hydroxide is neutralised with hydrochloric acid and evaporated to dryness ; the tetralkylammonium chloride may then be separated from the potassium salts by extracting the residue with alcohol.

A tertiary base may generally be separated from a secondary base by converting the latter into its nitroso-derivative (p. 214), and extracting this *neutral* product from the *acid* solution with ether ; the tertiary base is then liberated with potassium hydroxide and distilled in steam, whilst the secondary base may be recovered by decomposing the nitroso-derivative with boiling hydrochloric acid,

$$(C_2H_5)N\cdot NO + H_2O = (C_2H_5)_2\cdot NH + HO\cdot NO.$$

A tertiary base may also be separated from a primary or secondary base by making use of the fact that the two latter react readily with *acid chlorides*, giving *neutral substituted amides*,

$$C_2H_5\cdot NH_2 + CH_3\cdot COCl = C_2H_5\cdot NH\cdot CO\cdot CH_3 + HCl$$
$$(C_2H_5)_2NH + CH_3\cdot COCl = (C_2H_5)_2N\cdot CO\cdot CH_3 + HCl,$$

whereas a tertiary base is not acted on ; by extracting the acid solution of the product, the neutral amide is removed and the salt of the tertiary base remains in the solution.

Identification of Amines.—In order to find out whether a

given amine is a primary, secondary, or tertiary base, Hofmann's carbylamine reaction (p. 212) is first tried. If this test gives no result, the base is dissolved in hydrochloric acid and an aqueous solution of sodium nitrite is gradually added; the separation of an oily nitrosamine (which can be further characterised by Liebermann's reaction, p. 214), proves the presence of a secondary amine. A tertiary base does not give either of these reactions, and does not react with acid chlorides.

As most amines are liquid, and consequently difficult to identify as such, except by a determination of the boiling-point, it is generally necessary to convert the base into some crystalline derivative, which can then be identified by its melting-point; for this purpose the platinichloride, aurichloride, picrate (see above), acetyl derivative, or benzoyl derivative (Part II. p. 472) may be employed, and an analysis of the platinichloride or aurichloride may also be made if necessary (pp. 33, 34).

The Ascent and Descent of a Homologous Series.

A member of any homologous series may be transformed into the next higher or next lower homologue, a process which is commonly spoken of as 'passing up' or 'passing down' the series, as the case may be. As several homologous series have now been studied, some examples may be given of how such transformations may be brought about. A given fatty acid may be transformed into the next *higher* homologue in the following manner:—The calcium salt of the acid is distilled with calcium formate, and the resulting aldehyde is converted into the corresponding alcohol by reduction; the alcohol is then transformed into the iodide, the latter is treated with potassium cyanide, and the resulting cyanide is hydrolysed with alkalis or mineral acids,

$$\underset{\text{Acetic Acid.}}{CH_3\cdot COOH} \longrightarrow \underset{\text{Acetaldehyde.}}{CH_3\cdot CHO} \longrightarrow \underset{\text{Ethyl Alcohol.}}{CH_3\cdot CH_2\cdot OH} \longrightarrow \underset{\text{Ethyl Iodide.}}{CH_3\cdot CH_2I} \longrightarrow \underset{\text{Ethyl Cyanide.}}{CH_3\cdot CH_2\cdot CN} \longrightarrow \underset{\text{Propionic Acid.}}{CH_3\cdot CH_2\cdot COOH.}$$

The cyanide may be converted into the acid in another way;

it is first reduced to the amine, the amine is converted into the alcohol, and the latter is oxidised through the aldehyde to the fatty acid,

$$\underset{\text{Ethyl Cyanide.}}{CH_3\cdot CH_2\cdot CN} \longrightarrow \underset{\text{Propylamine.}}{CH_3\cdot CH_2\cdot CH_2\cdot NH_2} \longrightarrow \underset{\text{Propyl Alcohol.}}{CH_3\cdot CH_2\cdot CH_2\cdot OH} \longrightarrow \underset{\text{Propaldehyde.}}{CH_3\cdot CH_2\cdot CHO} \longrightarrow \underset{\text{Propionic Acid.}}{CH_3\cdot CH_2\cdot COOH.}$$

A given fatty acid may be transformed into the next *lower* homologue in the following manner:—The acid is converted into its amide (p. 168), and the amide is treated with bromine and potassium hydroxide in aqueous solution (p. 210); the resulting amine is converted into the alcohol, which is then oxidised, through the aldehyde, to the fatty acid,*

$$\underset{\text{Propionic Acid.}}{CH_3\cdot CH_2\cdot COOH} \longrightarrow \underset{\text{Propionamide.}}{CH_3\cdot CH_2\cdot CO\cdot NH_2} \longrightarrow \underset{\text{Ethylamine.}}{CH_3\cdot CH_2\cdot NH_2} \longrightarrow \underset{\text{Ethyl Alcohol.}}{CH_3\cdot CH_2\cdot OH} \longrightarrow \underset{\text{Acetaldehyde.}}{CH_3\cdot CHO} \longrightarrow \underset{\text{Acetic Acid.}}{CH_3\cdot COOH.}$$

It need hardly be pointed out that although a fatty acid is taken as the starting-point in the above examples, any of the other compounds referred to would serve equally well, and that the same methods would be applicable for the ascent or descent of the homologous series of alcohols, aldehydes, amines, &c. All the reactions employed in these transformations are *general reactions*, which should be carefully studied.

Phosphines.

Since phosphorus and nitrogen belong to the same natural family of elements, it might be expected that phosphine (hydrogen phosphide), PH_3, like ammonia, would be capable of yielding substitution products analogous to the amines. As a matter of fact, the **phosphines**, or alkyl substitution products of hydrogen phosphide, may be obtained by heating the alkyl iodides with phosphonium iodide in presence of zinc oxide (which combines with the hydrogen iodide produced in the reaction). In the case of

* Another method of passing down the series of fatty acids has already been given (p. 174).

ethyl iodide, for example, salts of *ethylphosphine* and *diethylphosphine*, corresponding with those of the primary and secondary amines respectively, are formed,

$$2PH_4I + 2C_2H_5I + ZnO = 2[PH_2 \cdot C_2H_5, HI] + ZnI_2 + H_2O$$
$$PH_4I + 2C_2H_5I + ZnO = PH(C_2H_5)_2, HI + ZnI_2 + H_2O.$$

Tertiary phosphines, such as *triethylphosphine*, are *not* produced under the above conditions, but may be prepared by heating the alkyl iodides with phosphonium iodide alone; as in the case of the corresponding amines, the tertiary phosphines combine with alkyl iodides, forming salts of quaternary bases, such as *tetrethylphosphonium iodide*, so that the product is a mixture of two organic compounds,

$$PH_4I + 3C_2H_5I = P(C_2H_5)_3, HI + 3HI$$
$$P(C_2H_5)_3 + C_2H_5I = P(C_2H_5)_4I.$$

With the exception of *methylphosphine*, $PH_2 \cdot CH_3$, which is a gas, the primary, secondary, and tertiary phosphines are colourless, volatile, highly refractive, very unpleasant-smelling liquids; they differ from the amines in smell, in being, as a rule, insoluble, or only sparingly soluble, in water (PH_3, unlike NH_3, is only sparingly soluble), and in readily undergoing oxidation on exposure to the air; in many cases so much heat is developed during this process that the compound takes fire—that is to say, many of the phosphines are spontaneously inflammable. When tertiary phosphines undergo slow oxidation in presence of air, they are converted into stable oxides, such as *triethylphosphine oxide*, $P(C_2H_5)_3O$.*

Although hydrogen phosphide is only a feeble base compared with ammonia, and forms salts, such as phosphonium iodide, PH_4I, which are decomposed even by water, each successive substitution of an alkyl-group for an atom of hydrogen is accompanied by an increase in basic properties, just as in the case of the amines. Salts of the primary phosphines, such as *ethylphosphine hydriodide*, $PH_2 \cdot C_2H_5, HI$, are almost, if not quite, as unstable as those of hydrogen phosphide, and are decomposed into acid and base on treatment with water; they may thus be separated from the more stable salts of the secondary and tertiary phosphines, such as *diethylphosphine hydriodide*, $PH(C_2H_5)_2, HI$, and *triethylphosphine hydriodide*, $P(C_2H_5)_3, HI$, which are not acted on by water, as a rule, but are readily decomposed by alkali hydroxides. Salts of the tetralkylphosphonium compounds, such as *tetrethylphosphonium iodide*, $P(C_2H_5)_4I$, are not acted on by water, but on treatment

* Tertiary amines give similar oxidation products, termed *oxamines*, on treatment with hydrogen peroxide.

with moist silver hydroxide they are converted into *quaternary phosphonium hydroxides*,

$$P(C_2H_5)_4I + Ag{\cdot}OH = P(C_2H_5)_4{\cdot}OH + AgI.$$

These compounds have a *strong* alkaline reaction, readily absorb carbon dioxide, and dissolve freely in water; they are, in fact, similar in properties to the hydroxides of the fixed alkalis, and their salts are much more stable than the phosphine salts, just as those of the corresponding tetralkylammonium bases are more stable than those of ammonia.

Derivatives of Arsenic, Antimony, and Bismuth.

The hydrogen atoms of the hydrides of arsenic and antimony, and the chlorine atoms of bismuth trichloride, may be (indirectly) displaced by alkyl-groups. The principal alkyl compounds of these elements correspond with the *tertiary* amines, and have the compositions, AsR_3, SbR_3, and BiR_3, respectively, but *primary* and *secondary* arsines, $As(CH_3)H_2$ and $As(CH_3)_2H$, are also known.

The tertiary arsines and stibines can be converted into quaternary *arsonium* and *stibonium* derivatives, but the tertiary bismuthines do not give compounds of this type.

The tertiary **arsines** are obtained by treating arsenious chloride with the zinc alkyl compounds (p. 229), or by heating the alkyl iodides with sodium arsenide,

$$2AsCl_3 + 3Zn(C_2H_5)_2 = 2As(C_2H_5)_3 + 3ZnCl_2,$$
$$AsNa_3 + 3CH_3I = As(CH_3)_3 + 3NaI.$$

Triethylarsine, $As(C_2H_5)_3$, is a colourless, very unpleasant-smelling, highly poisonous liquid, and is only sparingly soluble in water; it fumes in the air, and takes fire when heated, but does not ignite spontaneously. It differs from the amines and phosphines in being a *neutral* compound, and, like hydrogen arsenide, it does not form salts with acids; it combines readily with alkyl iodides, forming salts of *quaternary arsonium hydroxides*,

$$As(C_2H_5)_3 + C_2H_5I = As(C_2H_5)_4I.$$

Tetrethylarsonium iodide, $As(C_2H_5)_4I$, is crystalline, and,

like other quaternary salts, it reacts with silver hydroxide, giving **tetrethylarsonium hydroxide,**

$$As(C_2H_5)_4I + Ag{\cdot}OH = As(C_2H_5)_4{\cdot}OH + AgI.$$

This substance is a strong basic hydroxide, like the corresponding derivatives of nitrogen and phosphorus.

The tertiary arsines and stibines resemble the tertiary phosphines in readily undergoing oxidation on exposure to the air, with formation of oxides, such as *triethylarsine oxide*, $As(C_2H_5)_3O$.

Tertiary arsines combine directly with two atoms of a halogen, forming compounds, such as triethylarsine dichloride, $As(C_2H_5)_3Cl_2$; these substances are decomposed when they are heated, yielding an alkyl halogen compound and a *halogen derivative* of a secondary arsine,

$$As(C_2H_5)_3Cl_2 = As(C_2H_5)_2Cl + C_2H_5Cl.$$

These halogen derivatives of the secondary compounds also combine with one molecule of a halogen,

$$As(C_2H_5)_2Cl + Cl_2 = As(C_2H_5)_2Cl_3,$$

and when the products are heated they are decomposed into *dihalogen derivatives* of primary arsines,

$$As(C_2H_5)_2Cl_3 = As(C_2H_5)Cl_2 + C_2H_5Cl.$$

Certain derivatives of dimethylarsine were investigated by Bunsen, and are of historical interest.

Dimethylarsine oxide, or **cacodyl oxide,** $\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\!\!>\!O$, is formed when a mixture of equal parts of arsenious oxide and potassium acetate is submitted to dry distillation; during the operation highly poisonous gases are evolved, and an oily liquid collects in the receiver,

$$As_4O_6 + 8CH_3{\cdot}COOK = 2As_2(CH_3)_4O + 4K_2CO_3 + 4CO_2.$$

This liquid has an intensely obnoxious smell,* and is excessively poisonous, for which reasons its preparation, except in *minute* quantities, should not be attempted; its formation, however, may be used, with proper precautions, as a test for acetates, as the substance is very readily recognised by its smell.

Cacodyl oxide boils at 120°, and is insoluble in water; the

* The name cacodyl is derived from the Greek κακώδης, 'stinking.'

substance prepared in the above-mentioned manner is spontaneously inflammable owing to the presence of cacodyl, but the pure compound is not. In chemical properties cacodyl oxide resembles the feebly basic metallic oxides; it has a neutral reaction, but reacts readily with acids, forming salts, such as *cacodyl chloride* and *cacodyl cyanide*, $As(CH_3)_2{\cdot}CN$,

$$\left.\begin{matrix}As(CH_3)_2\\ As(CH_3)_2\end{matrix}\right\rangle O + 2HCl = 2As(CH_3)_2Cl + H_2O.$$

When cacodyl chloride is heated with zinc in an atmosphere of carbon dioxide, it yields **cacodyl** or diarsenic tetramethyl, a change which is analogous to the formation of ethane from methyl iodide,

$$2As(CH_3)_2Cl + Zn = As(CH_3)_2{-}As(CH_3)_2 + ZnCl_2,$$
$$2CH_3I + 2Na = CH_3{-}CH_3 + 2NaI.$$

Cacodyl, like the oxide, is a colourless, excessively poisonous liquid, and has an intensely disagreeable smell; it takes fire on exposure to the air.

Cacodylic acid, $(CH_3)_2AsO{\cdot}OH$, is formed when cacodyl oxide is oxidised with mercuric oxide,

$$\left.\begin{matrix}As(CH_3)_2\\ As(CH_3)_2\end{matrix}\right\rangle O + 2HgO + H_2O = 2(CH_3)_2AsO{\cdot}OH + 2Hg;$$

it is a crystalline, odourless substance, and seems to be non-poisonous.

Organic Silicon Compounds.

Organic derivatives of silicon, which correspond with some of the more important types of carbon compounds, are known —as, for example, the *silicohydrocarbons*, SiR_4, the *silicyl chlorides*, SiR_3Cl, the (tertiary) *silicols*, $SiR_3{\cdot}OH$, the *silicones*, R_2SiO, and the *silicic acids*, $R{\cdot}SiO{\cdot}OH$. The silicohydrocarbons are very similar to the hydrocarbons in general behaviour, but in the case of compounds in which the silicon atom is directly united to a halogen, or to an oxygen atom, the silicon derivative and the corresponding carbon compound differ widely in properties, and the relationship is analogous to that between silicon tetrachloride and carbon tetrachloride, or between silica and carbon dioxide, as the case may be.

Silicon tetramethyl, $Si(CH_3)_4$, is produced when silicon tetrachloride is heated with zinc methyl,

$$SiCl_4 + 2Zn(CH_3)_2 = Si(CH_3)_4 + 2ZnCl_2.$$

It is a colourless, mobile, volatile liquid, boiling at 30°, and has properties very similar to those of tetramethylmethane.

Silicon tetrethyl, $Si(C_2H_5)_4$, may be obtained by treating silicon tetrachloride with zinc ethyl, and also by heating a mixture of silicon tetrachloride and ethyl bromide, dissolved in ether, with sodium,

$$SiCl_4 + 4C_2H_5Br + 8Na = Si(C_2H_5)_4 + 4NaCl + 4NaBr;$$

it boils at 153°, and closely resembles the normal paraffin, nonane, C_9H_{20}, in properties, for which reason it is sometimes named *silicononane*.

Silicononane is not acted on by nitric acid or caustic alkalis, but when it is treated with chlorine it yields the substitution product, *silicononyl chloride*, $Si(C_2H_5)_3 \cdot C_2H_4Cl$, a colourless liquid, boiling at 185°; this chloride closely resembles the alkyl chlorides in properties, whereas *triethylsilicyl chloride*, $SiEt_3Cl$, like silicon tetrachloride, is rapidly and completely hydrolysed by water, giving *triethylsilicol*, $SiEt_3 \cdot OH$.

Organic Derivatives of the Metals.

Many of the metals form alkyl compounds, although their hydrides are unknown. These alkyl derivatives are named 'organo-metallic' compounds, but there is no sharp division between them and the alkyl derivatives of other elements, just as there is none between the metals and the non-metals. If, in fact, the alkyl compounds of elements belonging to the same natural family are considered, it will be evident that they show a *gradual* change in properties, just as do other derivatives of these elements. The compounds of the elements of the fourth group, for example, such as

$$C(CH_3)_4 \quad Si(CH_3)_4 \quad Sn(CH_3)_4 \quad Pb(CH_3)_4,$$

may be divided into two fairly distinct classes; but in the case of those of the elements of the fifth group,

$$N(CH_3)_3 \quad P(CH_3)_3 \quad As(CH_3)_3 \quad Sb(CH_3)_3 \quad Bi(CH_3)_3,$$

it is hard to say which of them, if any, should be classed as organo-metallic compounds.

The zinc alkyl compounds, discovered by Frankland, have been of the greatest service in the past in the synthesis of various types of organic compounds, of which many examples have already been given; their place has now been taken by certain magnesium compounds, the *Grignard reagents*, which are far more easily prepared and are far less troublesome to work with.*

The Grignard Reagents.

Magnesium ethyl bromide, $Mg<^{C_2H_5}_{Br}$, or MgEtBr, may be described as an example of a Grignard reagent. It is formed, with development of heat, when ethyl bromide (1 mol.) is added to magnesium (1 atom) in presence of pure ether; the metal gradually disappears, and when the solution is evaporated it gives a colourless, crystalline, very hygroscopic substance, which may be regarded as a compound of magnesium ethyl bromide and ether of the composition, $MgEtBr, (C_2H_5)_2O$.

In all those reactions in which magnesium ethyl bromide (or another Grignard reagent) is employed, it is unnecessary to isolate the crystalline compound; an *ethereal solution* of the reagent is used, and as the combined ether appears to

* In 1899 it was found by Barbier that when methylheptenone, $(CH_3)_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, is brought into contact with methyl iodide in presence of magnesium and ether, a reaction occurs and dimethylheptenol, $(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(OH)(CH_3)_2$, can be isolated, after the product has been treated with an acid. These observations suggested that magnesium methyl iodide, $CH_3{\cdot}MgI$, had been formed and had subsequently reacted with the methylheptenone in the same manner as zinc methyl was known to react with ketones.

As it was also known that zinc methyl unites with anhydrous ether to form a compound, $Zn(CH_3)_2, (C_2H_5)_2O$, Barbier's observations led Grignard, in 1903, to investigate the action of magnesium on methyl iodide and similar compounds in presence of ether. The magnesium alkyl halides which were thus discovered, and analogous compounds which have since been obtained, are known as the Grignard reagents.

play no part in the chemical change, it is not represented in the equations for the reactions.

The solution is prepared as follows:—Clean dry magnesium (1 atom) in the form of powder or filings is placed in a flask provided with a reflux condenser, and is covered with 5–10 times its weight of pure ether; a small quantity (1–2 c.c.) of the alkyl halogen compound (1 mol.) is then added. If after 1–5 minutes a visible reaction sets in, it is then only necessary to continue the addition of the alkyl halide at such a rate that the reaction does not become too violent; but it is often advisable, and sometimes essential, to keep the solution at 0° to 10° during the operation. If a reaction does not set in spontaneously, the flask is gently warmed, or a small quantity of a solution of magnesium ethyl bromide, prepared in a test-tube, is poured into the flask; the reaction having been started, the addition of the requisite alkyl halogen compound is then continued as before. In order to ensure success, all the reagents and the apparatus must be perfectly dry, and the ether should be previously distilled over sodium and then over phosphorus pentoxide, in order to free it from water and alcohol.

Magnesium ethyl iodide, MgEtI, resembles the corresponding bromide; **magnesium methyl iodide**, MgMeI, and **magnesium propyl bromide**, MgPrBr, are also common Grignard reagents; but in addition to those named here, many others are used, more especially those derived from aromatic halogen compounds (Part II. p. 390).

The principal reactions of the Grignard reagents are the following:—

(1) They are attacked by water, by alcohols, and by primary or secondary amines yielding *hydrocarbons*,

$$MgEtBr + H_2O = C_2H_6 + MgBr{\cdot}OH,$$
$$MgMeI + C_2H_5{\cdot}OH = CH_4 + C_2H_5{\cdot}O{\cdot}MgI,$$
$$MgMeI + (C_2H_5)_2NH = CH_4 + (C_2H_5)_2N{\cdot}MgI.$$

(2) They absorb dry oxygen, and the products yield *alcohols* (or phenols, Part II. p. 437) when they are treated with a mineral acid,

$$2MgRBr + O_2 = 2MgBr(OR),$$
$$MgBr(OR) + H_2O = R{\cdot}OH + MgBr{\cdot}OH.$$

(3) They absorb carbon dioxide, and the products yield carboxylic acids when they are treated with a mineral acid,

$$MgEtBr + CO_2 = C_2H_5{\cdot}CO{\cdot}O{\cdot}MgBr,$$
$$C_2H_5{\cdot}CO{\cdot}O{\cdot}MgBr + HCl = C_2H_5{\cdot}CO{\cdot}OH + MgClBr.$$

The ethereal solution is saturated with pure, dry carbon dioxide, and the ether is then distilled off; the carboxylic acid is liberated with dilute sulphuric acid and distilled off, or extracted with ether.

If the initial product is heated with excess of the Grignard reagent, a tertiary alcohol may be formed; the reactions in this case are similar to those which occur in the conversion of an ester into a tertiary alcohol (see below).

(4) They attack most substances which contain a carbonyl-group and give an additive product; the latter yields an *alcohol* when it is treated with a mineral acid. Aldehydes are thus converted into *secondary alcohols*,

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!CO + MgEtBr = \begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}O{\cdot}MgBr\\Et\end{matrix}$$

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}O{\cdot}MgBr\\Et\end{matrix} + HCl = \begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\Et\end{matrix} + MgClBr,$$

whereas ketones, $\begin{matrix}R\\R\end{matrix}\!\!>\!CO$, give *tertiary alcohols*, $\begin{matrix}R\\R\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\Et\end{matrix}$, in a similar manner. When the carbonyl-group is that of an ester, the first product is probably a ketone,

$$CH_3{\cdot}CO{\cdot}OEt + MgMeI = CH_3{\cdot}CO{\cdot}Me + MgI{\cdot}OEt,$$

which then reacts with a further quantity of the Grignard compound, as shown above; esters, therefore, give *tertiary alcohols*.

Acid chlorides and amides also yield tertiary alcohols in a similar manner, but the esters of orthoformic acid give aldehydes,

$$CH(OC_2H_5)_3 + MgRI = R{\cdot}CH(OC_2H_5)_2 + C_2H_5{\cdot}O{\cdot}MgBr$$
$$R{\cdot}CH(OC_2H_5)_2 + H_2O = R{\cdot}CHO + 2C_2H_5{\cdot}OH.$$

(5) They react with the halides of many metals and of many non-metals, and yield alkyl, or alkyl halogen, derivatives of the element,

$$SiCl_4 + MgEtBr = SiEtCl_3 + MgClBr,$$
$$SiEtCl_3 + MgEtBr = SiEt_2Cl_2 + MgClBr,$$
$$SnBr_4 + 4MgEtBr = SnEt_4 + 4MgBr_2.$$

Compounds of this kind have been obtained from the halides of phosphorus, arsenic, antimony, silicon, tin, lead, mercury, thallium, and gold.

It will be seen from the above examples that the Grignard reagents are of very great importance; their use in synthetic work has led to a rapid development of organic chemistry in recent years.

In many cases the actual preparation of the Grignard reagent is unnecessary, and the desired synthesis may be brought about by the method employed by Barbier (footnote, p. 226). It is also possible in many cases to use zinc, instead of magnesium, a method which was employed long ago by Reformatsky.

Alkyl Compounds of Zinc and of Mercury.

Zinc ethyl, $Zn(C_2H_5)_2$, is prepared by heating zinc with ethyl iodide in an atmosphere of carbon dioxide; the first product is a colourless, solid substance (*zinc ethiodide*),

$$Zn + C_2H_5I = Zn\begin{matrix}<^{C_2H_5}\\ _{I}\end{matrix};$$

but at higher temperatures a second change occurs, and zinc ethyl is formed,

$$2Zn\begin{matrix}<^{C_2H_5}\\ _{I}\end{matrix} = Zn(C_2H_5)_2 + ZnI_2.$$

Zinc filings (100 grams) and an equal weight of ethyl iodide are placed in a flask connected with a reflux condenser, and the air is completely expelled from the apparatus by passing a stream of dry carbon dioxide through a narrow tube which runs through the condenser to the bottom of the flask. The condenser is then quickly fitted with a cork through which passes a tube, dipping under mercury, in order to prevent access of air; the materials and the apparatus must be perfectly dry.

The flask is now heated on a water-bath, when an evolution of gas (butane) takes place, and the white intermediate product is gradually formed; after two or three hours' time the interaction is at an end. When cold, the flask is quickly fitted with a cork

and glass tubes (just as in an ordinary wash-bottle), and the smaller tube is connected with a condenser; the flask is then heated in an oil-bath, and the zinc ethyl is distilled, a stream of dry carbon dioxide being passed through the longer tube into the apparatus during the whole operation; the distillate is collected in a vessel which can be easily sealed.

Zinc ethyl is a colourless liquid (b.p. 118°); it inflames spontaneously on exposure to the air, burning with a luminous, greenish flame, and emitting clouds of zinc oxide. It decomposes water with great energy, yielding ethane and zinc hydroxide,

$$Zn(C_2H_5)_2 + 2H_2O = 2C_2H_6 + Zn(OH)_2,$$

and it is also decomposed by alcohol, but not so quickly as by water,

$$Zn(C_2H_5)_2 + 2C_2H_5{\cdot}OH = 2C_2H_6 + Zn\begin{<}{OC_2H_5}{OC_2H_5}.$$

Zinc ethyl reacts readily with all substances containing the hydroxyl-group, and also with almost all halogen compounds, whether organic or inorganic, as, for example, with acid chlorides (p. 144), alkyl halogen compounds (p. 69), and metallic chlorides (see below); for these reasons, it has been extensively used in the synthesis of paraffins, ketones, tertiary alcohols, &c., as well as in the preparation of various organo-metallic compounds.

Zinc methyl, $Zn(CH_3)_2$, resembles zinc ethyl and boils at 46°.

Mercuric ethyl, $Hg(C_2H_5)_2$, is formed when zinc ethyl is treated with mercuric chloride,

$$Zn(C_2H_5)_2 + HgCl_2 = Hg(C_2H_5)_2 + ZnCl_2,$$

and when ethyl iodide is shaken with sodium amalgam,

$$HgNa_2 + 2C_2H_5I = Hg(C_2H_5)_2 + 2NaI.$$

It is a colourless liquid, of sp. gr. 2·44, and boils at 159°; it is not spontaneously inflammable at ordinary temperatures, does not oxidise on exposure to the air, and is not decomposed by water, in which it is only sparingly soluble; both the liquid and its vapour are highly poisonous.

On treatment with halogen acids, mercuric ethyl is converted into salts, analogous in some respects to the halogen salts of the alkali metals,

$$Hg(C_2H_5)_2 + HCl = Hg\begin{matrix}<^{C_2H_5}\\ _{Cl}\end{matrix} + C_2H_6.$$

These salts are also formed by the direct union of mercury and alkyl halogen compounds at ordinary temperatures, especially in sunlight,

$$Hg + C_2H_5I = Hg\begin{matrix}<^{C_2H_5}\\ _{I}\end{matrix}.$$

They react with moist silver hydroxide, and are converted into *hydroxides*, just as sodium iodide, for example, gives sodium hydroxide,

$$Hg\begin{matrix}<^{C_2H_5}\\ _{I}\end{matrix} + AgOH = Hg\begin{matrix}<^{C_2H_5}\\ _{OH}\end{matrix} + AgI.$$

The hydroxides thus formed are thick, caustic liquids, readily soluble in water; they have an *alkaline* reaction, neutralise acids, liberate ammonia from its salts, and precipitate metallic hydroxides from their salts. Here, as in the case of compounds of nitrogen, phosphorus, arsenic, &c., the substitution of alkyl-groups for hydrogen (or hydroxyl) is accompanied by a marked increase in basic properties; mercuric (hydr)oxide is a comparatively feeble base.

Of the other organo-metallic compounds, those of tin, lead, and aluminium may be mentioned. Tin and lead form compounds, such as $Sn(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$, $Pb(C_2H_5)_4$ and $Pb_2(C_2H_5)_6$, in which the metal is quadrivalent; stannous ethyl, $Sn(C_2H_5)_2$, corresponding with stannous chloride, is also known. Aluminium appears only to give alkyl compounds, such as $Al(CH_3)_3$ and $Al(C_2H_5)_3$, in which the metal is tervalent.

As the alkyl derivatives of many metals, unlike the great majority of metallic compounds, are volatile, their molecular weights can be determined from their vapour densities, and in this way the valencies of the metals in the compounds may be established.

CHAPTER XIII.

The Glycols and their Oxidation Products.

It may be assumed, as a general rule, that the changes which any particular group of atoms in a molecule is capable of undergoing, are to some extent independent of the nature of the other groups with which this particular group is combined; at the same time, however, it must be remembered that the behaviour of every atom or group in a molecule is influenced by the other atoms or groups, and depends, therefore, on the nature of the molecule as a whole.

As an example, the case of ethane, $CH_3 \cdot CH_3$, may be considered. This hydrocarbon, as already shown, may be successively transformed into ethyl chloride, $CH_3 \cdot CH_2Cl$, ethyl alcohol, $CH_3 \cdot CH_2 \cdot OH$, and acetic acid, $CH_3 \cdot CO \cdot OH$, by changes in which only *one* of the methyl-groups takes part,

$$\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ CH_2Cl \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ CH_2 \cdot OH \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ COOH \end{matrix};$$

it might be supposed, therefore, that the *other* methyl-group should be capable of undergoing the same modifications, compounds such as $CH_2Cl \cdot CH_2Cl$ (ethylene dichloride), $CH_2(OH) \cdot CH_2 \cdot OH$ (dihydroxyethane), and $COOH \cdot COOH$ (oxalic acid) being formed,

$$\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} \rightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} \rightarrow \begin{matrix} CH_2 \cdot OH \\ | \\ CH_2 \cdot OH \end{matrix} \rightarrow \begin{matrix} COOH \\ | \\ COOH \end{matrix}.$$

Such reactions, in fact, may be brought about, and it is thus possible to obtain various series of *di*-substitution products of the paraffins, the members of which show, on the whole, a close relationship with the corresponding *mono*-substitution products.

The **glycols**, or dihydroxy-derivatives of the paraffins, discovered by Würtz in 1856, afford an example of this

point; they form a homologous series of the general formula $C_nH_{2n}(OH)_2$, and are closely related to the monohydric alcohols.

Ethylene glycol, $C_2H_4(OH)_2$, is the simplest glycol, and corresponds with ethyl alcohol, the compound, methylene glycol, $CH_2(OH)_2$, which would correspond with methyl alcohol, being unknown. Ethylene glycol is formed in small quantities when ethylene is oxidised with a cold, dilute alkaline solution of potassium permanganate,

$$C_2H_4 + H_2O + O = C_2H_4(OH)_2.$$

It is prepared by heating ethylene dibromide, or ethylene dichloride, with dilute aqueous alkalis, or alkali carbonates, the change which occurs being similar to that which takes place in the formation of ethyl alcohol from ethyl bromide,

$$C_2H_4Br_2 + 2KOH = C_2H_4(OH)_2 + 2KBr.$$

For this purpose potassium carbonate (138 grams) is dissolved in water (1 litre), ethylene dibromide (188 grams) is added, and the mixture is boiled in a flask connected with a reflux condenser. The insoluble oily dibromide is slowly converted into ethylene glycol, which passes into solution, so that the change is known to be complete when globules of oil are no longer visible. The solution is then slowly evaporated on a water-bath,* to expel most of the water, the semi-solid residue is extracted with alcoholic ether (which precipitates potassium bromide, but dissolves the glycol), and the glycol is isolated from the filtered solution by fractional distillation.

Ethylene glycol is a thick, colourless liquid, and has a rather sweet taste; it boils at 197·5°, and is miscible with water and alcohol in all proportions, but is only sparingly soluble in ether. It reacts with sodium at ordinary temperatures, yielding *sodium glycol*, $C_2H_5O_2Na$, one atom of the metal displacing one atom of hydrogen; if this substance is then heated with sodium, hydrogen is again evolved, and *disodium glycol*, $C_2H_4O_2Na_2$, is formed by a repetition of the substitution process. These sodium derivatives, like those of the monohydric alcohols, are colourless, crystal-

* If the solution is boiled, a considerable quantity of the glycol escapes with the steam.

line, and hygroscopic, and are readily decomposed by water, giving glycol,

$$C_2H_4O_2Na_2 + 2H_2O = C_2H_6O_2 + 2NaOH.$$

From its behaviour with sodium, it might be assumed that the molecule of glycol contains hydroxyl-groups, and that it gives *di*-substitution products (whereas the monohydric alcohols yield only mono-substitution products) because it contains *two* hydroxyl-groups. If this were so, it might be expected that glycol, like alcohol, would be readily attacked by the chlorides and bromides of phosphorus, giving *di*-halogen compounds; this is indeed the case. When glycol is treated with phosphorus pentabromide it is converted into ethylene dibromide, whereas with phosphorus pentachloride it yields the dichloride,

$$C_2H_4(OH)_2 + 2PBr_5 = C_2H_4Br_2 + 2POBr_3 + 2HBr.$$

Again, it has been shown that ethyl alcohol and other hydroxy-compounds react with acetic anhydride and with acetyl chloride, so that if glycol contains two hydroxyl-groups it should be converted into a *di*-acetyl-derivative; this also is the fact, since *glycol diacetate* is obtained when glycol is heated with acetic anhydride,

$$C_2H_4(OH)_2 + 2(CH_3{\cdot}CO)_2O = C_2H_4(O{\cdot}CO{\cdot}CH_3)_2 + 2C_2H_4O_2.$$

Glycol diacetate is also formed when ethylene dibromide is heated with silver acetate,

$$C_2H_4Br_2 + 2C_2H_3O_2Ag = C_2H_4(C_2H_3O_2)_2 + 2AgBr;$$

this ester is hydrolysed by boiling alkalis, yielding ethylene glycol, which was first obtained by Würtz in this way.

Constitution of Glycol.—The facts already stated show clearly that glycol contains two hydroxyl-groups; the only matter requiring further attention, therefore, is whether these two groups are combined with the same or with different carbon atoms—that is to say, whether glycol has the constitution, $CH_3{\cdot}CH(OH)_2$ or $HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. This point is easily decided, because ethylene dibromide has the constitu-

tion, $CH_2Br{\cdot}CH_2Br$, and its conversion into glycol must be regarded as a simple process of substitution; glycol, therefore, may be represented by the formula, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ or $\begin{matrix}CH_2{\cdot}OH\\ |\\ CH_2{\cdot}OH\end{matrix}$. This conclusion is confirmed by a study of the behaviour of glycol on oxidation and under other conditions, and of its relations to other compounds.

Homologues of Ethylene Glycol.—The higher glycols, or dihydroxy-derivatives of the paraffins—as, for example, *αβ-propylene glycol*, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, and *αγ*-butylene glycol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$—are named after the unsaturated hydrocarbons of the olefine series, from which they may be regarded as derived. As they exist in isomeric forms, these are distinguished by employing α, β, γ, &c. to denote the positions of the hydroxyl-groups, commencing at the *terminal* carbon atom (compare p. 171).

The glycols are neutral, thick liquids, similar to ethylene glycol in properties; they are usually prepared by treating the olefines with bromine, and decomposing the dibromo-additive products obtained in this way with boiling solutions of an alkali carbonate (compare also pinacones, p. 145).

The great advantage of employing constitutional formulæ is well illustrated by the case of ethylene glycol. From a consideration of its method of formation and of one or two of its reactions, it may be concluded that glycol has the constitution, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. Assuming this to be so, its behaviour under given conditions can then be foretold with tolerable certainty, from the facts established in the case of ethyl alcohol, because *the constitutional formula is a summary of the whole chemical behaviour of a compound.* Ethylene glycol contains two $-CH_2{\cdot}OH$ groups, each of which is similar to that in ethyl alcohol; it may be supposed, then, that those properties of ethyl alcohol which are dependent on the presence of this group will also be exhibited by glycol. Since, for example, alcohol acts like a metallic hydroxide, and forms salts with one molecule of a monobasic acid, ethylene glycol, which contains *two* hydroxyl-groups, should

behave as a *di*acid hydroxide, and form salts with *two* molecules of a monobasic acid.

When hydrogen chloride is passed into glycol heated at about 100°, *ethylene chlorohydrin* is formed,

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH + HCl = CH_2Cl{\cdot}CH_2{\cdot}OH + H_2O,$$

and when this product is heated with hydrogen chloride at a higher temperature, ethylene dichloride is produced,

$$CH_2Cl{\cdot}CH_2{\cdot}OH + HCl = CH_2Cl{\cdot}CH_2Cl + H_2O,$$

changes which are strictly analogous to the conversion of alcohol into ethyl chloride.

Ethylene chlorohydrin is identical with the compound formed by the direct combination of ethylene and hypochlorous acid (p. 82), and similarly *propylene chlorohydrin*, $CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}OH$, can be obtained from propylene glycol or from propylene. These chlorohydrins are usually readily acted on by alkalis, and are converted into oxides by loss of one molecule of hydrogen chloride,

$$\begin{matrix} CH_2{\cdot}OH \\ | \\ CH_2Cl \end{matrix} + KOH = \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O + KCl + H_2O.$$

Ethylene Oxide.

$$\begin{matrix} CH_2{\cdot}OH \\ | \\ CHCl \\ | \\ CH_3 \end{matrix} + KOH = \begin{matrix} CH_2 \\ | \\ CH \\ | \\ CH_3 \end{matrix}\!\!>\!O + KCl + H_2O.$$

Propylene Oxide.

Ethylene oxide is isomeric with aldehyde, C_2H_4O; it is a liquid, boils at 13·5°, and is slowly decomposed by water, being converted into glycol.

When ethyl alcohol is carefully oxidised, it is first converted into aldehyde (the group, $-CH_2{\cdot}OH$, being transformed into $-CHO$) and then into acetic acid (by the oxidation of the $-CHO$ group to $-COOH$). Since, therefore, glycol contains two $-CH_2{\cdot}OH$ groups, each of which may undergo these changes, it might be foretold that, on oxidation, glycol would probably yield several compounds, according as one or both the $-CH_2{\cdot}OH$ groups were attacked. This also is the fact; on oxidation with nitric acid glycol yields the following compounds :—

$CH_2 \cdot OH$	$CH_2 \cdot OH$	CHO	CHO	$COOH$
CHO	$COOH$	CHO	$COOH$	$COOH$
Glycollic Aldehyde.*	Glycollic Acid.	Glyoxal.	Glyoxylic Acid.	Oxalic Acid.

These examples show clearly that, the constitution of any substance having been ascertained from a study of some of its reactions, its behaviour under given conditions may be foretold with tolerable certainty; for this reason *the general reactions of particular groups and the constitutional formulæ of compounds are most important matters to bear in mind.*

Glyoxal, $CHO \cdot CHO$, is produced by the oxidation of glycol, but it is usually prepared by slowly oxidising alcohol or aldehyde with nitric acid,

$$CH_3 \cdot CHO + 2O = CHO \cdot CHO + H_2O.$$

It is an amorphous substance, readily soluble in alcohol and ether; it shows all the properties of an aldehyde, reduces ammoniacal silver oxide, and combines with sodium hydrogen sulphite to form a crystalline compound of the composition, $C_2H_2O_2$, $2NaHSO_3, H_2O$. It also reacts with hydroxylamine and with phenylhydrazine, giving the compounds, $HO \cdot N{:}CH \cdot CH{:}N \cdot OH$ and $C_6H_5NH \cdot N{:}CH \cdot CH{:}N \cdot NHC_6H_5$.

Hydroxycarboxylic Acids.

Glycollic acid, or **hydroxyacetic acid,** $HO \cdot CH_2 \cdot COOH$, may be produced by the oxidation of glycol, $HO \cdot CH_2 \cdot CH_2 \cdot OH$, just as acetic acid is produced by the oxidation of alcohol, $CH_3 \cdot CH_2 \cdot OH$,

$$\begin{matrix} CH_2 \cdot OH \\ | \\ CH_2 \cdot OH \end{matrix} + 2O = \begin{matrix} CH_2 \cdot OH \\ | \\ COOH \end{matrix} + H_2O.$$

But as several oxidation products are formed, the isolation of the acid is very troublesome.

It is also formed when amino-acetic acid (glycine, p. 329) is treated with nitrous acid, a reaction exactly analogous to the conversion of ethylamine into ethyl alcohol,

* This, the first oxidation product of glycol, is obtained when glycol is oxidised with hydrogen peroxide in presence of a ferrous salt; other glycols and polyhydric alcohols give hydroxy-aldehydes under the same conditions (p. 283).

$$\begin{matrix}CH_2\cdot NH_2\\ |\\ COOH\end{matrix} + HO\cdot NO = \begin{matrix}CH_2\cdot OH\\ |\\ COOH\end{matrix} + H_2O + N_2.$$

Glycollic acid is prepared by boiling the potassium salt of chloracetic acid with water, when the hydroxyl-group is substituted for one atom of chlorine, just as in the formation of alcohol from ethyl chloride,

$$\begin{matrix}CH_2Cl\\ |\\ COOK\end{matrix} + H_2O = \begin{matrix}CH_2\cdot OH\\ |\\ COOH\end{matrix} + KCl.$$

The solution is evaporated to dryness, and the residue extracted with acetone, which dissolves the glycollic acid, but not the potassium chloride.

Glycollic acid is a crystalline, hygroscopic substance, and melts at 80°; it is readily soluble in water, alcohol, and ether.

Since its constitution is established by its methods of formation it is almost unnecessary to describe at length the chemical behaviour of glycollic acid, because this is summarised in its constitutional formula.

Glycollic acid contains one carboxyl-group; therefore, like the fatty acids, it is a monobasic acid and forms salts with metallic hydroxides and with alcohols.

Glycollic acid also contains one $-CH_2\cdot OH$ group; therefore it behaves like a primary alcohol, as well as like an acid. On oxidation, for example, it yields glyoxylic acid and oxalic acid, just as alcohol gives aldehyde and acetic acid,

$$\begin{matrix}CH_2\cdot OH\\ |\\ COOH\end{matrix} + O = \begin{matrix}CHO\\ |\\ COOH\end{matrix} + H_2O,$$

$$\begin{matrix}CH_2\cdot OH\\ |\\ COOH\end{matrix} + 2O = \begin{matrix}COOH\\ |\\ COOH\end{matrix} + H_2O.$$

Even when the hydrogen atom of the carboxyl-group has been displaced, glycollic acid still contains one atom of hydrogen, which, like that in alcohols, may be displaced by the alkali metals and by the acetyl-group; ethyl glycollate, for example, is readily converted into an acetyl-derivative on treatment with acetyl chloride,

$$\begin{matrix}CH_2\cdot OH\\ |\\ COOC_2H_5\end{matrix} + CH_3\cdot COCl = \begin{matrix}CH_2\cdot O\cdot CO\cdot CH_3\\ |\\ COOC_2H_5\end{matrix} + HCl.$$

Homologues of Glycollic Acid.—Glycollic acid is hydroxyacetic acid, or acetic acid in which a hydroxyl-group has been substituted for one atom of hydrogen; as other fatty acids yield similar hydroxy-derivatives, a homologous series of *hydroxy-carboxylic acids* may be obtained.*

The more important members of the series are:—

Glycollic acid, or hydroxyacetic acid, $HO\cdot CH_2\cdot COOH$.
Lactic acid, or hydroxypropionic acid, $CH_3\cdot CH(OH)\cdot COOH$.

These compounds may also be regarded as oxidation products of the glycols; just as glycollic acid is formed by oxidising ethylene glycol, so the higher members of the series may be obtained from the corresponding glycols by oxidising a $-CH_2\cdot OH$ group to $-COOH$.

Two isomeric hydroxy-derivatives of propionic acid are known—namely, α- and β-hydroxypropionic acids; these two isomerides are related to propionic acid, in the manner shown by the following formulæ:—

$CH_3\cdot CH_2\cdot COOH$
Propionic Acid.

$CH_3\cdot CH(OH)\cdot COOH$
α-Hydroxypropionic or Lactic Acid.

$CH_2(OH)\cdot CH_2\cdot COOH.$
β-Hydroxypropionic or Hydracrylic Acid.

Lactic acid (α-hydroxypropionic acid), $CH_3\cdot CH(OH)\cdot COOH$, is formed during the lactic fermentation of sugars, starch, and other substances, and occurs in sour milk.

It can be obtained by methods analogous to those given in the case of glycollic acid—namely, by oxidising $\alpha\beta$-propylene glycol with nitric acid,

$$CH_3\cdot CH(OH)\cdot CH_2\cdot OH + 2O = CH_3\cdot CH(OH)\cdot COOH + H_2O;$$

* The lowest member of this series, carbonic acid or hydroxyformic acid, $HO\cdot COOH$, is only stable in aqueous solution, and this is true also of the corresponding glycol, $CH_2(OH)_2$, which possibly exists in aqueous solutions of formaldehyde,

$$H\cdot CHO + H_2O = H\cdot CH(OH)_2.$$

by heating α-chloro- or α-bromo-propionic acid with water, dilute aqueous alkalis, or silver hydroxide,

$$CH_3{\cdot}CHBr{\cdot}COOH + H_2O = CH_3{\cdot}CH(OH){\cdot}COOH + HBr,$$

and by treating α-amino-propionic acid with nitrous acid,

$$CH_3{\cdot}CH(NH_2){\cdot}COOH + HO{\cdot}NO = CH_3{\cdot}CH(OH){\cdot}COOH + N_2 + H_2O.$$

It is prepared by the lactic fermentation of sugar (see butyric acid, p. 162), or by heating sucrose or glucose with alkalis.

Lactic acid is a thick, sour liquid, miscible with water, alcohol, and ether in all proportions; it cannot be distilled, as it undergoes decomposition into aldehyde, water, carbon monoxide, and other products. When heated with dilute sulphuric acid it is decomposed into aldehyde and formic acid, a fact which shows that, compared with the fatty acids, lactic acid is very unstable,

$$CH_3{\cdot}CH(OH){\cdot}COOH = CH_3{\cdot}CHO + H{\cdot}COOH.$$

Lactic acid is a monocarboxylic acid, and forms metallic salts and esters.

Calcium lactate, $(C_3H_5O_3)_2Ca$, $5H_2O$, and *zinc lactate*, $(C_3H_5O_3)_2Zn$, $3H_2O$, are crystalline, and are readily soluble in hot water. *Ethyl lactate*, $CH_3{\cdot}CH(OH){\cdot}COOC_2H_5$, is a neutral liquid, but, since it contains a $>CH(OH)$ group, it yields metallic derivatives with potassium and sodium, and, like other hydroxy-compounds, it reacts with acetyl chloride, giving *ethyl acetyl-lactate*, $CH_3{\cdot}CH(O{\cdot}C_2H_3O){\cdot}COOC_2H_5$, an ester derived from acetyl-lactic acid, $CH_3{\cdot}CH{<}^{O{\cdot}CO{\cdot}CH_3}_{COOH}$.

Lactic acid also contains the group, $>CH{\cdot}OH$, and shows, therefore, the reactions of a secondary alcohol. When, for example, it is heated with concentrated hydrobromic acid, it is converted into α-bromo-propionic acid, just as isopropyl alcohol gives isopropyl bromide,

$$CH_3{\cdot}CH(OH){\cdot}COOH + HBr = CH_3{\cdot}CHBr{\cdot}COOH + H_2O;$$

with concentrated hydriodic acid, however, it yields propionic

acid, because the α-iodo-propionic acid which is first produced is reduced by excess of hydrogen iodide (footnote, p. 57),

$$CH_3{\cdot}CHI{\cdot}COOH + HI = CH_3{\cdot}CH_2{\cdot}COOH + I_2.$$

On oxidation with potassium permanganate, lactic acid again behaves like a secondary alcohol, and is converted into pyruvic acid, just as isopropyl alcohol gives acetone,

$$CH_3{\cdot}CH(OH){\cdot}COOH + O = CH_3{\cdot}CO{\cdot}COOH + H_2O.$$

Sarcolactic acid, or *paralactic acid*, $C_3H_6O_3$, occurs in animals, more especially in the muscle juices, and is best prepared from extract of meat. It has the same constitution as lactic acid, because it undergoes the same chemical changes, but it differs from ordinary lactic acid in being optically active (p. 266).

Hydracrylic acid (β-hydroxypropionic acid), $CH_2(OH){\cdot}CH_2{\cdot}COOH$, is not formed during lactic fermentation, but may be obtained by reactions exactly similar to those which give the corresponding α-acid—namely, by oxidising αγ-propylene glycol, and by boiling β-chloro-, bromo-, or iodo-propionic acid, $CH_2X{\cdot}CH_2{\cdot}COOH$, with water or weak aqueous alkalis.

It is a thick, sour syrup, and when heated alone or with moderately dilute sulphuric acid, it is converted into *acrylic acid* (p. 291), with loss of the elements of water, a change analogous to the conversion of ethyl alcohol into ethylene,

$$CH_2(OH){\cdot}CH_2{\cdot}COOH = CH_2{:}CH{\cdot}COOH + H_2O.$$

In many respects hydracrylic behaves like lactic acid; it is a monocarboxylic acid, but also contains a $-CH_2{\cdot}OH$ group, so that it shows the reactions of a primary alcohol as well as those of a monobasic acid; on oxidation with chromic acid, for example, it yields *malonic acid* (p. 248),

$$CH_2(OH){\cdot}CH_2{\cdot}COOH + 2O = COOH{\cdot}CH_2{\cdot}COOH + H_2O.$$

Constitutions of the Hydroxypropionic Acids.—The methods of formation and the chemical behaviour of lactic acid and of hydracrylic acid show that both compounds are hydroxymonocarboxylic acids of the molecular composition, $C_3H_6O_3$; as only two such acids—namely,

$$\underset{\text{I.}}{CH_3{\cdot}CH(OH){\cdot}COOH} \text{ and } \underset{\text{II.}}{CH_2(OH){\cdot}CH_2{\cdot}COOH},$$

are theoretically possible, all that is necessary is to determine which of these formulæ represents the one and which the other acid. This point, of course, is already settled if the constitutions of the chloro-propionic or amino-propionic acids, or those of the oxidation products of the hydroxy-acids, are known; if, however, this were not the case, the following syntheses of the hydroxy-acids establish their constitutions.

When aldehyde is treated with hydrocyanic acid direct combination occurs, and the product is converted into lactic acid when it is heated with hydrochloric acid,

$$CH_3\cdot CH(OH)\cdot CN + 2H_2O = CH_3\cdot CH(OH)\cdot COOH + NH_3.$$

Lactic acid, therefore, is represented by formula I., a conclusion which is fully borne out by all other facts.

When ethylene is treated with an aqueous solution of hypochlorous acid, ethylene chlorohydrin is formed (p. 82); this compound reacts with potassium cyanide in dilute alcoholic solution, giving ethylene cyanohydrin,

$$CH_2(OH)\cdot CH_2Cl + KCN = CH_2(OH)\cdot CH_2\cdot CN + KCl,$$

which, when boiled with mineral acids, is converted into hydracrylic acid,

$$CH_2(OH)\cdot CH_2\cdot CN + 2H_2O = CH_2(OH)\cdot CH_2\cdot COOH + NH_3.$$

Hydracrylic acid, therefore, is represented by formula II.

Since, moreover, aldehyde and ethylene may be prepared from their elements, this is also true as regards the two hydroxypropionic acids.

Lactic acid and hydracrylic acid are sometimes called *ethylidene-lactic acid* and *ethylenelactic acid* respectively; these names serve to recall the facts that lactic acid contains the ethylidene group, $CH_3\cdot CH<$, hydracrylic acid, the ethylene group, $-CH_2\cdot CH_2-$.

Lactides.—Since lactic acid is an alcohol, as well as an acid, two molecules of lactic acid may react with one another to form an ester-like compound of the constitution, $CH_3\cdot CH<\begin{matrix}COOH\\O\cdot CO\cdot CH(OH)\cdot CH_3\end{matrix}$, and this product, in an analogous manner, may give a substance of

the constitution, $CH_3 \cdot CH\begin{cases} CO\text{—}O \\ O \cdot CO \cdot \underset{|}{C}H \cdot CH_3 \end{cases}$. Both these compounds are formed when lactic acid is heated; the former is called *lactyl-lactic acid;* the latter, *lactide.*

Other α-hydroxy-acids may give rise to similar compounds, and those derivatives which correspond with lactide in structure are classed as *lactides;* glycollic acid, for example, may be transformed into a lactide, $O\begin{cases} CH_2 \cdot CO \\ CO \cdot CH_2 \end{cases}O$, which is distinguished as *glycolide.*

Lactones.—The higher homologues of the hydroxy-propionic acids may be prepared by reducing the corresponding ketonic acids (many of which may be synthesised from ethyl acetoacetate, p. 198), and by other methods. The α-acids, such as *α-hydroxybutyric acid*, $CH_3 \cdot CH_2 \cdot CH(OH) \cdot COOH$ (obtained by treating an aqueous solution of α-bromobutyric acid with silver oxide), are generally converted into lactides (see above) when they are heated alone. The β-acids, such as *β-hydroxybutyric acid* (p. 203), behave like hydracrylic acid, and when heated alone they give αβ-unsaturated acids, of which crotonic acid (p. 291) is an example. The γ-acids, such as *γ-hydroxyvaleric acid*, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot COOH$ (prepared by reducing levulic acid, p. 205), undergo yet a different type of change and pass spontaneously into ester-like compounds, which are classed as *lactones;* γ-hydroxyvaleric acid, for example, gives *γ-valerolactone,*

$$CH_3 \cdot CH(OH) \cdot [CH_2]_2 \cdot COOH = CH_3 \cdot CH\begin{cases} O\text{—}CO \\ CH_2 \cdot CH_2 \end{cases} + H_2O.$$

δ-Hydroxy-acids behave in a similar manner, and give δ-lactones.

The lactones are usually liquids which may be distilled under atmospheric pressure; they are neutral substances and resemble esters in some respects. They are slowly hydrolysed by water (until a condition of equilibrium is reached); but they are readily and completely hydrolysed by alkali hydroxides, giving alkali salts of the hydroxy-acids.

Dicarboxylic Acids.

Glycollic acid, $CH_2(OH) \cdot COOH$, being derived from ethylene glycol, $CH_2(OH) \cdot CH_2 \cdot OH$, by the oxidation of *one* of the $-CH_2 \cdot OH$ groups, it might be concluded that the *other* $-CH_2 \cdot OH$ group would be capable of undergoing a similar change; this is found to be so, since on oxidation glycollic acid is converted into oxalic acid, $COOH \cdot COOH$.

As, moreover, other glycols, such as $\alpha\gamma$-propylene glycol, $CH_2(OH)\cdot CH_2\cdot CH_2\cdot OH$, which contain two $-CH_2\cdot OH$ groups, behave in the same way as ethylene glycol, it is possible to prepare a homologous series of *dicarboxylic* acids of the general formula, $C_nH_{2n}(COOH)_2$. These compounds may also be considered as derived from the fatty acids by the substitution of the carboxyl-group for one atom of hydrogen, and since they contain two such groups, they are dibasic acids.

The more important members of this homologous series are :

Oxalic acid.....$C_2H_2O_4$ or $\begin{matrix}COOH\\|\\COOH\end{matrix}$

Malonic acid .....$C_3H_4O_4$ or $CH_2<\begin{matrix}COOH\\COOH\end{matrix}$

Succinic acid.....$C_4H_6O_4$ or $\begin{matrix}CH_2\cdot COOH\\|\\CH_2\cdot COOH\end{matrix}$

Isosuccinic acid.....$C_4H_6O_4$ or $CH_3\cdot CH<\begin{matrix}COOH\\COOH\end{matrix}$

Glutaric acid.....$C_5H_8O_4$ or $COOH\cdot[CH_2]_3\cdot COOH$ *

Adipic acid.....$C_6H_{10}O_4$ or $COOH\cdot[CH_2]_4\cdot COOH$ *

Oxalic acid, $C_2H_2O_4$, or $\begin{matrix}COOH\\|\\COOH\end{matrix}$, occurs in rhubarb (*rheum*), the dock (*rumex*), sorrel (*oxalis acetosella*), and other plants, usually in the form of its potassium hydrogen salt, or as calcium oxalate; when sorrel is ground up with water, the filtered solution gives with calcium chloride a precipitate of calcium oxalate. Oxalic acid is formed when alcohol, glycol, sucrose, fats, and a great many other organic substances are oxidised with nitric acid, and may be obtained by numerous reactions, of which the following are instructive.

Its sodium salt is formed when sodium is heated at about 350° in an atmosphere of carbon dioxide,

$$2CO_2 + 2Na = C_2O_4Na_2,$$

and when sodium formate is heated at about 250°,

$$2H\cdot COONa = C_2O_4Na_2 + H_2;$$

* Compare footnote, p. 141.

it is also produced (in the form of its ammonium salt), together with many other compounds, when an aqueous solution of cyanogen (p. 314) is kept for some time, a change which is analogous to the conversion of methyl cyanide into acetic acid,

$$\left.\begin{array}{l}\mathrm{CN}\\ \mathrm{CN}\end{array}\right. + 4\mathrm{H_2O} = \left.\begin{array}{l}\mathrm{CO{\cdot}ONH_4}\\ \mathrm{CO{\cdot}ONH_4}\end{array}\right..$$

Each of these three reactions affords a means of synthesising oxalic acid from its elements, since carbon dioxide, formic acid, and cyanogen may be obtained from their elements.

Oxalic acid may be prepared by gently warming sucrose (cane-sugar) with about six times its weight of concentrated nitric acid.

The operation is performed in a good draught-cupboard, and as soon as brown fumes appear the heating is temporarily discontinued, in spite of which oxidation proceeds very vigorously; after some time the solution is evaporated, a little more nitric acid being added, if necessary, to ensure complete oxidation. The product, when practically free from nitric acid, is dissolved in a little water, and the crystals of oxalic acid which separate are purified by recrystallisation from water; further quantities may be obtained by evaporating the acid mother-liquors.

Oxalic acid is prepared on the large scale from sawdust, which consists of organic compounds (cellulose, lignin, &c.) similar in composition to sucrose; when heated with alkalis, these compounds undergo a profound decomposition.

The sawdust is made into a paste with a concentrated solution of the hydroxides of sodium and potassium, and then heated in iron pans at about 240°; afterwards the mass is extracted with water, the solution of potassium and sodium oxalates is boiled with lime, and the precipitated calcium oxalate is washed with water and decomposed with dilute sulphuric acid,

$$\mathrm{C_2O_4Ca + H_2SO_4 = C_2O_4H_2 + CaSO_4};$$

the solution of oxalic acid is then filtered from the calcium sulphate and evaporated to crystallisation. The acid obtained in this way contains small quantities of potassium and sodium hydrogen oxalates, from which it is separated only with great difficulty,

and on ignition it gives a residue of alkali carbonates; the pure acid is most conveniently prepared from sucrose.

The formation of oxalic acid from sawdust and from sucrose cannot be expressed by a simple equation; in both cases a complex molecule containing –CH(OH)·CH(OH)– groups undergoes simultaneous decomposition and oxidation.

Oxalic acid crystallises in colourless hydrated prisms, $C_2H_2O_4,2H_2O$; it is readily soluble in alcohol and moderately so in water, but is only sparingly soluble in ether. When quickly heated, it melts at about 100° and loses its water of hydration; the anhydrous acid sublimes at about 150°, but if heated more strongly it decomposes into carbon dioxide and formic acid (p. 150) or its decomposition products,

$$C_2O_4H_2 = H{\cdot}COOH + CO_2 = H_2O + CO + CO_2;$$

the anhydrous acid is very hygroscopic, and a powerful dehydrating agent.

Oxalic acid is decomposed by concentrated sulphuric acid, but only when the mixture is heated moderately strongly (distinction from formic acid),

$$C_2O_4H_2 = CO_2 + CO + H_2O;$$

it is a feeble reducing agent, precipitates gold from its solutions, and is readily oxidised by *warm* potassium permanganate (or chlorine water), by which it is converted into carbon dioxide and water; this reaction is employed for the volumetric estimation of oxalic acid and also in standardising permanganate solutions,

$$C_2O_4H_2 + O = 2CO_2 + H_2O.$$

Oxalic acid has an acid reaction, decomposes carbonates, and dissolves certain metallic oxides; it is a *dibasic* acid. The salts of the alkali metals are readily soluble in hot water, but most of the other salts are sparingly soluble or insoluble.

Ammonium oxalate, $C_2O_4(NH_4)_2,H_2O$, is decomposed, giving oxamide, when it is carefully heated, just as ammonium acetate yields acetamide,

$$\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} = \begin{matrix} CO{\cdot}NH_2 \\ | \\ CO{\cdot}NH_2 \end{matrix} + 2H_2O;$$

when heated with phosphoric anhydride it gives cyanogen (p. 314).

Potassium oxalate, $C_2O_4K_2,H_2O$, is readily soluble in water, but *potassium hydrogen oxalate*, C_2O_4KH, a salt which occurs in many plants, is more sparingly soluble; the latter forms with oxalic acid a crystalline compound of the composition, C_2O_4KH, $C_2O_4H_2$, $2H_2O$, known as 'salts of sorrel,' or potassium quadroxalate; this salt is used in removing iron-mould and ink-stains, as it converts the iron compounds into soluble iron potassium oxalate.

Silver oxalate, $C_2O_4Ag_2$, is obtained in crystals when silver nitrate is added to a neutral solution of an oxalate; it is only sparingly soluble in water, and the dry salt explodes when it is quickly heated, leaving a residue of silver.

Calcium oxalate, C_2O_4Ca,H_2O, occurs in crystals in the cells of various plants, and is obtained as a white precipitate when a solution of a calcium salt is added to a neutral or ammoniacal solution of an oxalate; it is insoluble in water, and also in *acetic acid*.

Oxalic acid and its salts are used to a considerable extent in dyeing, in photography (as developers), and in analytical chemistry. The metallic salts are all decomposed when they are heated with concentrated sulphuric acid, giving carbon dioxide, carbon monoxide, water, and a sulphate; they are also decomposed when they are heated alone, but in neither case is there any appreciable charring. Oxalic acid and its soluble salts are very *poisonous*.

The detection of oxalic acid or of an oxalate is chiefly based on (*a*) the behaviour of the dry substance when it is heated alone or with sulphuric acid; (*b*) the behaviour of the neutral solution with calcium chloride, and the insolubility of the precipitate in acetic acid.

Methyl oxalate, $C_2O_4(CH_3)_2$, is a colourless, crystalline compound, melting at 54°, and is easily prepared by heating anhydrous oxalic acid with methyl alcohol; it is readily hydrolysed by alkalis and by boiling water, and is sometimes employed in the preparation of pure methyl alcohol (p. 93).*

* Compare also footnote, p. 196.

Ethyl oxalate, $C_2O_4(C_2H_5)_2$, can be obtained in a similar manner; it is a pleasant-smelling liquid, boiling at 186°, and sparingly soluble in water. It is a curious fact that the methyl esters of organic acids are frequently crystalline, even when the ethyl, propyl, butyl, &c., esters are liquid at ordinary temperatures.

The *constitution* of oxalic acid is established by its formation from glycol, glycollic acid, and formates; it is a dibasic acid, and therefore contains two carboxyl-groups.

Oxalic acid, like other compounds which are very rich in oxygen, is comparatively unstable; its *anhydride* is unknown, and when the acid is treated with phosphorus pentachloride, instead of yielding the chloride, COCl–COCl, as might have been expected, it is decomposed into water and the oxides of carbon.

Oxamide, $\begin{matrix}CO\cdot NH_2\\ |\\ CO\cdot NH_2\end{matrix}$, is formed as an intermediate product in the conversion of cyanogen into ammonium oxalate (p. 315), also when ammonium oxalate is heated. It is prepared by shaking methyl or ethyl oxalate with concentrated ammonia, a general method for the preparation of amides from esters (p. 197),

$$C_2O_4(C_2H_5)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2C_2H_5\cdot OH.$$

It is colourless, crystalline, and insoluble in water; when heated with water, alkalis, or mineral acids, it is converted into oxalic acid or an oxalate, a change exactly analogous to that undergone by acetamide (p. 169),

$$C_2O_2(NH_2)_2 + 2H_2O = C_2O_4H_2 + 2NH_3.$$

Malonic acid, $CH_2(COOH)_2$, the next homologue of oxalic acid, has already been mentioned, and the preparation of its ethyl ester from chloracetic acid has been described (p. 206).

If, instead of the ethyl ester, the free acid is required, the product of the action of potassium cyanide on potassium chloracetate is mixed with twice its volume of concentrated hydrochloric acid, and the solution is saturated with hydrogen chloride; the clear liquid is then decanted from the precipitated potassium chloride, evaporated to dryness on a water-bath, and the malonic acid extracted from the residue with ether.

It was first prepared by oxidising malic acid (p. 253); hence

its name. Malonic acid is a colourless, crystalline substance, readily soluble in water; it melts at 132°, and at higher temperatures decomposes into acetic acid and carbon dioxide,

$$CH_2(COOH)_2 = CH_3{\cdot}COOH + CO_2.$$

All other dicarboxylic acids, in which *both* the carboxyl-groups are united to *one and the same* carbon atom, are decomposed in a similar manner, when they are heated alone or in aqueous solution (at 100–200°).

Succinic acid, $C_4H_6O_4$, or $\begin{matrix}CH_2{\cdot}COOH\\ |\\ CH_2{\cdot}COOH\end{matrix}$, occurs in amber, and also in smaller quantities in lignite (fossil wood), in many plants, and in certain animal secretions. It is formed during the alcoholic fermentation of sugar, and in several other fermentation processes; also when fats are oxidised with nitric acid.

It can be obtained from its elements in the following manner:—Acetylene, which can be prepared from carbon and hydrogen, is reduced to ethylene (p. 73); the latter is converted into ethylene dibromide (p. 79), and this compound is boiled with potassium cyanide in aqueous alcoholic solution; the *ethylene dicyanide* which is thus formed,

$$C_2H_4Br_2 + 2KCN = C_2H_4(CN)_2 + 2KBr,$$

is decomposed by boiling alkalis or mineral acids, giving succinic acid and ammonia (compare footnote, p. 150),

$$\begin{matrix}CH_2{\cdot}CN\\ |\\ CH_2{\cdot}CN\end{matrix} + 4H_2O = \begin{matrix}CH_2{\cdot}COOH\\ |\\ CH_2{\cdot}COOH\end{matrix} + 2NH_3.$$

Succinic acid may also be prepared synthetically from ethyl acetoacetate (or ethyl malonate) and ethyl chloracetate,

$$CH_3{\cdot}CO{\cdot}\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}HNa + CH_2Cl{\cdot}COOC_2H_5 = CH_3{\cdot}CO{\cdot}\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}H{\cdot}CH_2{\cdot}COOC_2H_5 + NaCl$$

$$CH_3{\cdot}CO{\cdot}\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}H{\cdot}CH_2{\cdot}COOC_2H_5 + 3KOH =$$

(Acid Hydrolysis, p. 202.)

$$\begin{matrix}CH_2{\cdot}CH_2{\cdot}COOK\\ |\\ COOK\end{matrix} + CH_3{\cdot}COOK + 2C_2H_5{\cdot}OH.$$

Succinic acid is usually prepared by distilling amber from iron retorts; the dark-brown, oily distillate is evaporated, and the dirty-brown, crystalline residue of succinic acid is purified by recrystallisation from hot dilute nitric acid.

Succinic acid crystallises in colourless prisms, melts at 185°, and sublimes readily; it has an acid, unpleasant taste, and is only sparingly soluble in cold water, alcohol, and ether. It is a dibasic acid, and its salts, the **succinates**, with the exception of those of the alkalis, are sparingly soluble or insoluble in water.

The *constitution* of succinic acid is established by its formation from ethylene dibromide, and by the fact that the only alternative formula for a dicarboxylic acid of the molecular composition, $C_4H_6O_4$, must be assigned to isosuccinic acid (p. 252).

Succinic anhydride, $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!O$, is formed when succinic acid is distilled, but a large proportion of the acid passes over unchanged. It is prepared by heating the acid with phosphorus oxychloride for some time and then distilling; the oxychloride combines with the water which is produced, and thus prevents the reconversion of the anhydride into the acid; phosphorus pentoxide, acetyl chloride, or some other dehydrating agent may be used in the place of the oxychloride.

Succinic anhydride is a colourless, crystalline substance, and melts at 120°; it resembles the anhydrides of the fatty acids in chemical properties, and when boiled with water or alkalis it is reconverted into succinic acid or a succinate.

In the formation of succinic anhydride *one* molecule of the acid loses one molecule of water, whereas in the case of the anhydride of a fatty acid *two* molecules of the acid take part in the formation of the product,

$$\begin{matrix}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix} = \begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!O + H_2O,$$

$$\begin{matrix}CH_3\cdot COOH\\ \\ CH_3\cdot COOH\end{matrix} = \begin{matrix}CH_3\cdot CO\\ \\ CH_3\cdot CO\end{matrix}\!\!>\!O + H_2O.$$

Many other dicarboxylic acids give anhydrides which are of the same type as succinic anhydride, and which are called *inner* anhydrides.

Succinyl chloride, $\begin{matrix}CH_2\cdot COCl\\ |\\ CH_2\cdot COCl\end{matrix}$, is formed when succinic acid is treated with two molecules of phosphorus pentachloride,* the interaction recalling that which occurs in the formation of acetyl chloride,

$$\begin{matrix}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix} + 2PCl_5 = \begin{matrix}CH_2\cdot COCl\\ |\\ CH_2\cdot COCl\end{matrix} + 2POCl_3 + 2HCl.$$

It is a colourless liquid, boils at 190°, and resembles acetyl chloride in chemical properties; like the latter, it is decomposed by water, alkalis, and hydroxy-compounds, yielding succinic acid or a succinate.

Succinamide, $\begin{matrix}CH_2\cdot CO\cdot NH_2\\ |\\ CH_2\cdot CO\cdot NH_2\end{matrix}$, is prepared by shaking ethyl succinate with concentrated ammonia; it is a crystalline substance, melts at 242–243°, and is only very sparingly soluble in cold water. When heated with water it is slowly converted into ammonium succinate, just as oxamide is converted into ammonium oxalate,

$$\begin{matrix}CH_2\cdot CO\cdot NH_2\\ |\\ CH_2\cdot CO\cdot NH_2\end{matrix} + 2H_2O = \begin{matrix}CH_2\cdot COONH_4\\ |\\ CH_2\cdot COONH_4\end{matrix}.$$

Succinamide cannot be obtained by distilling ammonium succinate, although oxamide and acetamide are produced by the distillation of the corresponding ammonium salts; this fact shows that it is not always safe to judge by analogy, since compounds very closely related in constitution may, in certain respects, behave very differently. When, in fact, ammonium succinate or succinamide is heated, it is converted into succinimide.

Succinimide, $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!NH$, is also formed when succinic anhydride is heated in a stream of dry ammonia; it is readily soluble in water, from which it crystallises with one molecule of water, the

* The product is probably a mixture of succinyl chloride and a dichloro-substitution derivative of succinic anhydride of the constitution, $\begin{matrix}CH_2\cdot CCl_2\\ |\\ CH_2-CO\end{matrix}\!\!>\!O$.

anhydrous substance melting at 126°. When boiled with water, alkalis, or mineral acids, it is converted into succinic acid,

$$\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!NH + 2H_2O = \begin{matrix}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix} + NH_3.$$

The constitution of succinimide, as expressed by the above formula, is based principally on its methods of formation; it may be regarded as a di-substitution product of ammonia—that is to say, as ammonia in which two atoms of hydrogen have been displaced by the bivalent *succinyl*-group, $\begin{matrix}CH_2\cdot CO-\\ |\\ CH_2\cdot CO-\end{matrix}$, just as an amide is a mono-substitution product of ammonia. Many other dicarboxylic acids yield *imides* similar in constitution to succinimide.

Although succinimide is not an acid in the ordinary sense of the word, has a neutral reaction, and does not decompose carbonates, it contains one atom of hydrogen displaceable by metals. When, for example, a solution of potash in alcohol is added to an alcoholic solution of succinimide, a crystalline derivative, *potassium succinimide*, $\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!NK$, is produced; this compound reacts with silver nitrate, giving *silver succinimide*, and the latter, on treatment with ethyl iodide, yields *ethyl succinimide*,

$$\begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!NAg + C_2H_5I = \begin{matrix}CH_2\cdot CO\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!N\cdot C_2H_5 + AgI.$$

It has been pointed out that a hydrogen atom in the group, –CO–CH_2–CO–, is displaceable by certain metals, as in the cases of ethyl acetoacetate and ethyl malonate. The behaviour of succinimide, and of other imides, shows that the hydrogen atom of an imido-group, >NH, is also displaceable by metals when the imido-group is directly united with two >CO groups. In both types of compounds the metallic derivatives may be regarded as substitution products of the tautomeric enolic forms, –C(OH):CH– and –C(OH):N–, respectively (p. 205).

Isosuccinic acid, $CH_3\cdot CH(COOH)_2$, is isomeric with succinic acid; it may be prepared by treating an alcoholic solution of the sodium derivative of ethyl malonate with methyl iodide, and hydrolysing the product, a reaction which shows that isosuccinic acid is methyl-malonic acid,

$$CHNa(COOC_2H_5)_2 + CH_3I = CH_3\cdot CH(COOC_2H_5)_2 + NaI.$$

It is a crystalline substance, sublimes readily, and melts at 130°; it does not form an anhydride, and when heated alone, or with

water, it is decomposed into propionic acid and carbon dioxide, just as malonic acid gives acetic acid and carbon dioxide,

$$CH_3 \cdot CH(COOH)_2 = CH_3 \cdot CH_2 \cdot COOH + CO_2.$$

Four acids of the composition, $C_5H_8O_4$, are known—namely,

$CH_2 < \begin{matrix} CH_2 \cdot COOH \\ CH_2 \cdot COOH \end{matrix}$

Glutaric Acid.

$CH_3 \cdot CH(CH_2 \cdot COOH) \cdot COOH$

Pyrotartaric Acid or Methylsuccinic Acid.

$CH_3 \cdot CH_2 \cdot CH < \begin{matrix} COOH \\ COOH \end{matrix}$

Ethylmalonic Acid.

$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > C < \begin{matrix} COOH \\ COOH \end{matrix}$

Dimethylmalonic Acid.

Adipic acid, $C_6H_{10}O_4$, is of some importance, and is often obtained by oxidising fats with nitric acid; it may be produced synthetically by heating β-iodo-propionic acid with finely divided silver, just as ethane may be obtained by treating methyl iodide with sodium or zinc,

$$2CH_2I \cdot CH_2 \cdot COOH + 2Ag = COOH \cdot [CH_2]_4 \cdot COOH + 2AgI;$$

it is a crystalline substance, melting at 148°.

Hydroxydicarboxylic Acids.

With the exception of oxalic acid, the dicarboxylic acids just considered are capable of yielding substitution products in exactly the same way as are the fatty acids; malonic acid, for example, may be converted into chloromalonic acid, $CHCl(COOH)_2$, hydroxymalonic acid, $HO \cdot CH(COOH)_2$, &c.; succinic acid, into bromosuccinic acid, $COOH \cdot CHBr \cdot CH_2 \cdot COOH$, dibromosuccinic acid, $COOH \cdot CHBr \cdot CHBr \cdot COOH$, hydroxysuccinic acid, $COOH \cdot CH(OH) \cdot CH_2 \cdot COOH$, dihydroxysuccinic acid, $COOH \cdot CH(OH) \cdot CH(OH) \cdot COOH$, and so on. Some of these compounds—namely, the hydroxy-derivatives—occur in nature, and for this and other reasons are of considerable importance.

Malic acid (monohydroxysuccinic acid), $\begin{matrix} CH(OH) \cdot COOH \\ CH_2 \cdot COOH \end{matrix}$, occurs, not only in the free state, but also in the form of salts, in many plants, more especially in (unripe) apples, from which it derives its name (*acidum malicum*), in grapes, and in the berries of the mountain-ash. It may be obtained by boiling

bromosuccinic acid with water and silver hydroxide, a reaction analogous to the formation of lactic acid from α-bromo-propionic acid,

$$\begin{matrix}\mathrm{CHBr{\cdot}COOH}\\ |\\ \mathrm{CH_2{\cdot}COOH}\end{matrix} + \mathrm{Ag{\cdot}OH} = \begin{matrix}\mathrm{CH(OH){\cdot}COOH}\\ |\\ \mathrm{CH_2{\cdot}COOH}\end{matrix} + \mathrm{AgBr}.$$

As, therefore, bromosuccinic acid may be prepared by brominating succinic acid (p. 171), and succinic acid may be synthesised in the manner already described (p. 249), it is possible to obtain malic acid from its elements.

Malic acid may be produced by treating aminosuccinic or aspartic acid (a compound which may be obtained indirectly from asparagus*) with nitrous acid, just as lactic acid may be prepared from α-amino-propionic acid,

$$\begin{matrix}\mathrm{CH(NH_2){\cdot}COOH}\\ |\\ \mathrm{CH_2{\cdot}COOH}\end{matrix} + \mathrm{HO{\cdot}NO} = \begin{matrix}\mathrm{CH(OH){\cdot}COOH}\\ |\\ \mathrm{CH_2{\cdot}COOH}\end{matrix} + \mathrm{N_2} + \mathrm{H_2O}.$$

Malic acid is usually prepared from the juice of unripe berries of the mountain-ash.

The expressed juice is boiled with milk of lime and the crystalline, sparingly soluble calcium salt, $C_4H_4O_5Ca,H_2O$, which is precipitated, is dissolved in hot dilute nitric acid; the calcium hydrogen malate, $(C_4H_5O_5)_2Ca,6H_2O$, which separates in crystals, is then decomposed with the theoretical quantity of oxalic acid, and the filtered solution is evaporated.

Malic acid is crystalline, deliquescent, and melts at 100°; it is readily soluble in water and alcohol, but only sparingly in ether. Its metallic salts and esters are of little importance.

Many of the reactions of malic acid may be foretold from a consideration of its constitution, which is established by its methods of formation. Since, for example, it is a hydroxy-derivative of succinic acid, it might be expected that, on reduction with hydriodic acid at a high temperature, it would be converted into succinic acid, just as lactic acid is converted into propionic acid; also that, when heated with hydrobromic

* *Asparagine*, $COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH_2$, the amide of aspartic acid, occurs in asparagus; when it is boiled with acids or alkalis it is converted into aspartic acid (aminosuccinic acid), $COOH{\cdot}CH(NH)_2{\cdot}CH_2{\cdot}COOH$.

acid, it would yield bromosuccinic acid, a change which would be analogous to the conversion of lactic into bromopropionic acid. Both these changes actually take place,

$$COOH{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH + 2HI = COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + H_2O + I_2,$$

$$COOH{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH + HBr = COOH{\cdot}CHBr{\cdot}CH_2{\cdot}COOH + H_2O.$$

Although the malic acid obtained from plants undergoes exactly the same chemical changes as that prepared from bromosuccinic acid, the two acids are not identical in all respects; they differ principally in their action on polarised light, the naturally occurring acid being optically active (p. 266).

When malic acid is heated for a long time at 130°, it does not form malic anhydride, as might have been expected from the behaviour of succinic acid, but is slowly converted into *fumaric acid* and water,

$$\begin{matrix} CH(OH){\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{matrix} = \begin{matrix} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{matrix} + H_2O;$$

if now the fumaric acid is distilled, some passes over unchanged, and the rest is converted into *maleïc anhydride* and water,

$$\begin{matrix} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{matrix} = \begin{matrix} CH{\cdot}CO \\ \| \\ CH{\cdot}CO \end{matrix}\!\!>\!O + H_2O.$$

Maleïc anhydride is decomposed by boiling water, giving *maleïc acid*, which has the same constitution as fumaric acid—that is to say, both compounds are unsaturated dicarboxylic acids of the constitution, $COOH{\cdot}CH{:}CH{\cdot}COOH$; the existence of these two isomerides, and other cases of isomerism of a similar kind, are accounted for by the theory of stereochemical isomerism proposed by van't Hoff and Wislicenus (p. 279).

Tartaric acid, $\begin{matrix} CH(OH){\cdot}COOH \\ | \\ CH(OH){\cdot}COOH \end{matrix}$ (dihydroxysuccinic acid), is one of the more commonly occurring vegetable acids, and is contained in grapes, in the berries of the mountain-ash, and in other fruits; during the later stages of the fermentation of grape-juice a considerable quantity of 'argol,' or impure

potassium hydrogen tartrate, is deposited, and it is from this salt that the tartaric acid of commerce is prepared.

The crude, coloured deposit is first recrystallised from hot water, and its aqueous solution is then boiled with chalk, when insoluble calcium tartrate is precipitated and normal potassium tartrate remains in solution,

$$2C_4H_5O_6K + CaCO_3 = C_4H_4O_6Ca + C_4H_4O_6K_2 + CO_2 + H_2O;$$

the calcium salt is separated, and the solution is treated with calcium chloride, when a further quantity of calcium tartrate is precipitated,

$$C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl.$$

The calcium tartrate from these two operations is washed with water, and decomposed with the theoretical quantity of dilute sulphuric acid; finally, the filtered solution of the tartaric acid is evaporated to crystallisation.

Tartaric acid can be obtained from succinic acid, and, therefore, from its elements, by reactions similar to those employed in the synthesis of malic acid; dibromosuccinic acid is first prepared by treating succinic acid with bromine and red phosphorus (compare p. 171), and two hydroxyl-groups are then substituted for the two atoms of bromine in the usual way—namely, by heating the dibromo-derivative with water and silver hydroxide,*

$$\begin{matrix} CHBr\cdot COOH \\ | \\ CHBr\cdot COOH \end{matrix} + 2Ag\cdot OH = \begin{matrix} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{matrix} + 2AgBr.$$

Tartaric acid may also be obtained synthetically from glyoxal (p. 237), which, like other aldehydes, combines directly with hydrogen cyanide,

$$\begin{matrix} CHO \\ | \\ CHO \end{matrix} + 2HCN = \begin{matrix} CH(OH)\cdot CN \\ | \\ CH(OH)\cdot CN \end{matrix};$$

the dicyanohydrin thus produced is decomposed by mineral acids, giving tartaric acid,† just as ethylene dicyanide yields succinic acid,

* The tartaric acid obtained in this way is optically inactive, and is a mixture of racemic acid and mesotartaric acid (p. 275).

† This acid is also optically inactive, and is said to consist of racemic acid (p. 275).

$$\begin{matrix}\mathrm{CH(OH)\cdot CN}\\ |\\ \mathrm{CH(OH)\cdot CN}\end{matrix} + 4\mathrm{H_2O} = \begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{matrix} + 2\mathrm{NH_3}.$$

Tartaric acid (obtained from argol) forms large transparent crystals, and is readily soluble in water and alcohol, but insoluble in ether; it melts at about 167°, but not sharply, owing to decomposition taking place.

When heated for a long time at about 150°, it is converted into tartaric anhydride, $C_4H_4O_5$, and several other compounds, and on dry distillation it chars and yields a variety of products, among others, pyruvic acid (p. 205) and pyrotartaric acid (p. 253).

Tartaric acid, like other dicarboxylic acids, forms both normal and hydrogen salts, some of which are of considerable importance.

Normal *potassium tartrate*, $C_4H_4O_6K_2,\frac{1}{2}H_2O$, is readily soluble in cold water, in which respect it differs from *potassium hydrogen tartrate*, $C_4H_5O_6K$, which is only sparingly soluble. The latter is precipitated * when *excess* of tartaric acid is added to a concentrated neutral solution of a potassium salt (test for potassium), and also when an aqueous solution of normal potassium tartrate is treated with a mineral acid,

$$C_4H_4O_6K_2 + HCl = C_4H_5O_6K + KCl;$$

it is known in commerce as 'argol' or 'cream of tartar.'

Potassium sodium tartrate, $C_4H_4O_6KNa,4H_2O$ ('Rochelle salt'), is obtained when a solution of potassium hydrogen tartrate is neutralised with sodium carbonate, and then concentrated; it forms large transparent crystals, and is employed in the preparation of Fehling's solution (p. 296).

Calcium tartrate, $C_4H_4O_6Ca,4H_2O$, is precipitated when a solution of a calcium salt is added to a neutral solution of a tartrate; it is readily soluble in potash, but is reprecipitated when the solution is boiled, a behaviour which is made use of in testing for tartaric acid.

Tartar emetic, $C_4H_4O_6K(SbO),\frac{1}{2}H_2O$ (potassium antimonyl tartrate), is prepared by heating potassium hydrogen tartrate

* The precipitation is hastened by stirring the solution with a glass rod.

with antimonious oxide and water; it is readily soluble in water, and is used as an emetic and as a mordant.

The detection of tartaric acid or of a tartrate is based (*a*) on the fact that the solid compound rapidly chars when heated alone, giving an odour of burnt sugar; it also chars when heated with concentrated sulphuric acid, sulphur dioxide and oxides of carbon being evolved; (*b*) on the behaviour of the neutral solution with an ammoniacal solution of silver oxide, from which a mirror of silver is deposited, when the mixture is warmed; (*c*) on the behaviour of the neutral solution with calcium chloride (in the cold), and on the solubility of the precipitate in potash.

That the *constitution* of tartaric acid is expressed by the formula given above is shown by the methods of formation of the acid; it is a dihydroxy-derivative of succinic acid, just as malic acid is a monohydroxy-derivative of the same compound.

On reduction with hydriodic acid, tartaric acid is converted first into malic, then into succinic acid,

$$\begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{matrix} + 2\mathrm{HI} = \begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH_2\cdot COOH}\end{matrix} + \mathrm{H_2O} + \mathrm{I_2},$$

$$\begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{matrix} + 4\mathrm{HI} = \begin{matrix}\mathrm{CH_2\cdot COOH}\\ |\\ \mathrm{CH_2\cdot COOH}\end{matrix} + 2\mathrm{H_2O} + 2\mathrm{I_2};$$

whereas, when heated with concentrated hydrobromic acid, it yields dibromosuccinic acid, as was to be expected,

$$\begin{matrix}\mathrm{CH(OH)\cdot COOH}\\ |\\ \mathrm{CH(OH)\cdot COOH}\end{matrix} + 2\mathrm{HBr} = \begin{matrix}\mathrm{CHBr\cdot COOH}\\ |\\ \mathrm{CHBr\cdot COOH}\end{matrix} + 2\mathrm{H_2O}.$$

Four distinct modifications of tartaric acid are known—namely, dextrotartaric acid (the compound obtained from argol), levotartaric acid, racemic acid, and mesotartaric acid. These four compounds have the *same constitution*—that is to say, they are all dihydroxy-derivatives of succinic acid, and are represented by the formula,

$$\mathrm{COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH};$$

they differ, however, in certain *physical* properties, as, for example, in crystalline form, solubility, &c., but more especially in their behaviour towards polarised light; the relationship between these physically different modifications is discussed in the next chapter.

Hydroxytricarboxylic Acids.

Citric Acid, $C_6H_8O_7$, like tartaric acid, occurs in the free state in the juice of many fruits; it is found in comparatively large quantities in lemons, in smaller quantities in unripe currants, gooseberries, raspberries, and other fruit.

It is prepared on the large scale from lemon-juice, which is first boiled, in order to coagulate and precipitate albuminous matter, and then neutralised with calcium carbonate; the calcium salt, which is precipitated from the hot solution, is washed with water, decomposed with the theoretical quantity of dilute sulphuric acid, and the filtrate from the calcium sulphate is evaporated to crystallisation.

It is also prepared by fermenting glucose solutions with *citromycetes*.

Citric acid forms large transparent crystals, which contain one molecule of water and melt at 100°, but do not lose their water until about 130°; it is readily soluble in water and fairly so in alcohol, but insoluble in ether. Like tartaric acid, and several other organic acids, it has the property of preventing the precipitation of certain metallic hydroxides from solutions of their salts. Solutions of ferric chloride and of zinc sulphate, for example, do not give a precipitate with potassium or ammonium hydroxide if citric acid is present; on account of this property, citric acid and tartaric acid are employed in analytical chemistry and in calico-printing.

Citric acid is a tricarboxylic acid, and, like phosphoric acid, it forms three classes of salts—as, for example, the three potassium salts, $C_6H_5O_7K_3$, $C_6H_6O_7K_2$, and $C_6H_7O_7K$, all of which are readily soluble in water. *Calcium citrate*, $(C_6H_5O_7)_2Ca_3,4H_2O$, is not precipitated when a solution of a calcium salt is added to a neutral, dilute solution of a citrate,

because it is readily soluble in cold water; on the application of heat, however, a crystalline precipitate is produced, as the salt is less soluble in hot than in cold water. This behaviour, and the fact that the precipitate is insoluble in potash, distinguishes citric from tartaric acid. When heated alone, citric acid chars and gives irritating vapours, but no smell of burnt sugar is noticed; it also differs from tartaric acid, inasmuch as it does not immediately char when it is gently heated with concentrated sulphuric acid.

Citric acid may be obtained synthetically by a series of reactions, which show it to be a hydroxytricarboxylic acid of the constitution,

$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH. \\ | \\ CH_2\cdot COOH \end{array}$$

Symmetrical dichloracetone, $CH_2Cl\cdot CO\cdot CH_2Cl$, which may be obtained by oxidising glyceryl *aa*-dichlorohydrin (p. 285) with chromic acid, combines with hydrogen cyanide, forming the cyanohydrin, $(CH_2Cl)_2C<^{OH}_{CN}$; this product, like other compounds containing the –CN group, is converted into a carboxylic acid, $(CH_2Cl)_2C<^{OH}_{COOH}$, by boiling mineral acids. The two atoms of chlorine in this acid may now be displaced by –CN groups by heating the potassium salt of the acid with potassium cyanide in aqueous solution,

$$\begin{array}{l} CH_2Cl \\ | \\ C(OH)\cdot COOK \\ | \\ CH_2Cl \end{array} + 2KCN = \begin{array}{l} CH_2\cdot CN \\ | \\ C(OH)\cdot COOK \\ | \\ CH_2\cdot CN \end{array} + 2KCl,$$

and this dicyano-derivative may then be converted into citric acid by boiling it with hydrochloric acid,

$$\begin{array}{l} CH_2\cdot CN \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot CN \end{array} + 4H_2O = \begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + 2NH_3.$$

This view of the constitution of citric acid is borne out by all the reactions of the compound; it is shown to contain one hydroxyl-

group by the fact that ethyl citrate, $C_3H_4(OH)(COOC_2H_5)_3$, yields a monacetyl-derivative with acetyl chloride. When heated alone at 175°, citric acid is converted into *aconitic acid*, just as malic is converted into fumaric acid,

$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} = \begin{array}{l} CH\cdot COOH \\ \| \\ C\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + H_2O\,;$$

when carefully warmed with sulphuric acid, it yields *acetone-dicarboxylic* acid, with evolution of carbon monoxide,

$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} = \begin{array}{l} CH_2\cdot COOH \\ | \\ CO \\ | \\ CH_2\cdot COOH \end{array} + CO + H_2O,$$

and on reduction with hydriodic acid it is converted into

$$\begin{array}{l} CH_2\cdot COOH \\ | \\ CH\cdot COOH. \\ | \\ CH_2\cdot COOH \end{array}$$

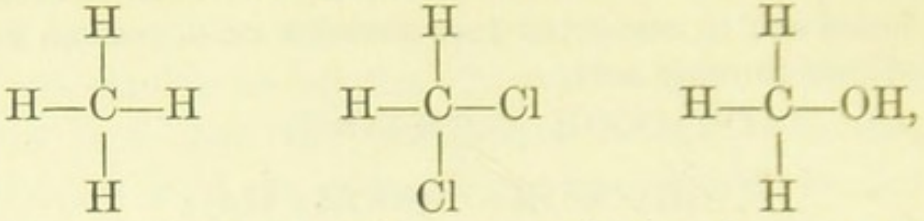
tricarballylic acid,

CHAPTER XIV.

Stereo-Isomerism.

The constant use of structural formulæ in studying carbon compounds was strongly recommended in an early chapter, because, as such formulæ are based on the chemical behaviour of the substances which they represent, they summarise the chemical properties of those substances, whereas the ordinary molecular formulæ express little, and are besides more difficult to remember. The limited significance of structural or constitutional formulæ was also explained; the lines which are drawn between any two symbols simply express the conclusion that, as far as can be ascertained experimentally, the particular atoms represented by those symbols are directly united.

When, therefore, formulæ such as the following,



are employed, it must not be supposed that they are intended to give any idea whatever of the actual form of the molecule, or to indicate that all the atoms in the molecule lie in one plane; the latter assumption would be entirely unsupported, and, moreover, is shown to be untenable by many considerations, some of which will be mentioned later.

Now, as the study of organic compounds advanced and more attention was paid to *constitution*, isomeric substances—the existence of which could not be explained with the aid of the ordinary graphic or structural formulæ—were discovered; as an instance of this, the classical example of tartaric acid may be considered.

Tartaric acid, $C_4H_6O_6$, obtained from grape-juice is *optically active*—that is to say, its solutions have the property of rotating the plane of polarisation of polarised light. The mother-liquors which are obtained in the purification of this tartaric acid contain an acid, originally called para-tartaric acid, but now known as *racemic acid*, which is proved to have the same structural formula as tartaric acid, because it is identical with the latter in *chemical* properties; racemic acid, however, differs from tartaric acid in *physical* properties, and its solutions have *no action* on polarised light.

The nature of polarised light, and the instrument (the *polarimeter*) which is employed in the examination of optically active compounds, are described in text-books on physics; but for those who are unacquainted with the use of a polarimeter the following notes may be given.

When the monochromatic light, obtained by heating *fused* sodium chloride in a Bunsen flame, is examined with a polarimeter, and the scale of the instrument is set at the zero, an illuminated disc, divided by a vertical line, is observed,* and the two halves of

* This is the ordinary two-field instrument.

this disc are equally bright; if the vertical line is not sharply defined, the focus must be adjusted with the aid of the eye-piece. When now a polarimeter tube filled with a solution of an optically active substance is placed in the instrument (in the hollow bed) and the focus is adjusted, one-half of the illuminated disc becomes darker than the other. With the aid of the milled screw-head (which is usually placed horizontally) the movable graduated circle, to which the eye-piece is fixed, is turned either to the right or to the left, according as the substance is dextro- or levo-rotatory, until a point is reached at which the two halves of the disc again become equally illuminated. The angle, through which the graduated circle has been turned from the zero, is read from the scale, and is the angle of rotation ($+$ or $-\alpha_D$). Satisfactory observations can be made only when the solution is perfectly clear and the light is good; 5–10 observations are made, and the average result is taken: the zero of the instrument should be similarly checked.

The *specific rotation* of a substance is the angle of rotation (α), which is produced by a column of the substance 1 decimetre in length, divided by the specific gravity of the substance, and is represented by $[\alpha]_D$;* hence $[\alpha]_D = \frac{\alpha_D}{l \times \text{sp. gr.}}$, where l is the length, in decimetres, of the column in the polarimeter tube (usually 2 decimetres).

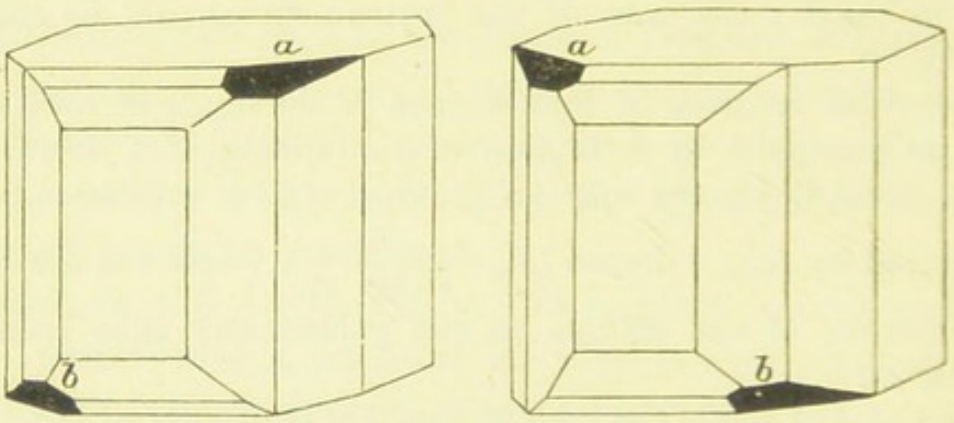
In the case of solids the specific rotation is usually determined in solution; observations are made with a solution of known concentration, and the rotation which would be produced by a solution containing 1 gram of the substance in 1 c.c. of the solution is then calculated. For this purpose a weighed quantity (usually about 0·5 g.) of the solid is washed into a 20 or 25 c.c. flask, with the aid of the solvent, the flask is filled to the graduation mark, the contents are thoroughly mixed, and the polarimeter tube is then filled. The specific rotation is calculated from the formula, $[\alpha]_D = \frac{\alpha_D \times 100}{l \times p}$, where p is the weight of the substance in 100 c.c. of the solution. The specific rotation varies with the solvent and with the temperature. The *molecular rotation*, $[M]_D$, of a substance is $\frac{[\alpha]_D \times \text{M.Wt.}}{100}$.

From these two acids, sodium ammonium salts having

* The letter D refers to the bright line in the spectrum of sodium (see table of spectra, *Inorganic Chemistry*, Kipping and Perkin).

the composition, $C_4H_4O_6NaNH_4,4H_2O$, were obtained; these salts, like the acids themselves, differed in their action on polarised light, the salt of tartaric acid being *dextrorotatory*, that of racemic acid being optically *inactive*, in aqueous solution.

At one time it was thought that this was the only difference between the two salts, but in 1848 Pasteur discovered the fact that the two salts also differed in crystalline form; he found that *all* the perfect or well-grown crystals of the salt obtained from tartaric acid had certain small faces or facets (*a*, *b*) arranged in one particular manner, as shown in the crystal D (fig. 24), in which these



D L

Fig. 24.

particular faces are darkened; the crystals of the salt obtained from racemic acid, on the other hand, were of *two kinds*, the one being identical with those of the salt of tartaric acid, the other having the particular faces (*a*, *b*) arranged as shown in the crystal L (fig. 24).

The two kinds of crystals obtained from racemic acid were, in fact, found to be related to one another as an object, such as the hand, is related to its mirror-image; a left hand, held before a mirror, gives an image which is a right hand, and *vice versâ*; similarly, a D crystal (fig. 24), if held before a mirror, gives an image identical with the L crystal viewed directly.

Having observed the existence of two kinds of crystals,

Pasteur picked out a number of each from the mixture and placed them in two heaps; he then dissolved the two kinds separately in water and examined the solutions in the polarimeter. One solution was *dextrorotatory*—that is, rotated the plane of polarisation of polarised light to the right—the other was *levorotatory*.

This highly important discovery was carefully followed up by Pasteur, who next found that one of the sodium ammonium salts (the dextrorotatory one) gave an acid identical with ordinary tartaric acid in every respect, whereas the other salt—namely, the levorotatory one—gave an acid identical with ordinary tartaric acid, except that its solution rotated the plane of polarisation of polarised light to the *left*, to exactly the same extent as a solution of tartaric acid of the same concentration rotated it to the *right*. Further, by heating the cinchonine salt of tartaric acid, Pasteur obtained another form of tartaric acid (mesotartaric acid),* which, like racemic acid, is optically *inactive*, but from which only one kind of sodium ammonium salt was formed, this salt also being different from those previously obtained. *Four* tartaric acids thus came to be known, and yet, judging from their chemical behaviour, they all had the same constitutional formula, COOH·CH(OH)·CH(OH)·COOH.

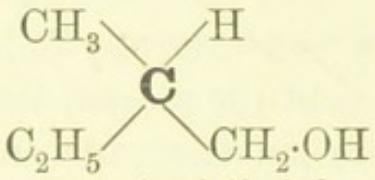
A simple explanation of this and of similar cases of isomerism was advanced in 1874 by Le Bel and van't Hoff, almost simultaneously and independently.

These chemists were led to conclude that optical activity in the case of dissolved substances depends on *molecular structure*, and that a substance is optically active only when its molecule contains at least one carbon atom which is directly united with *four different* atoms or groups.

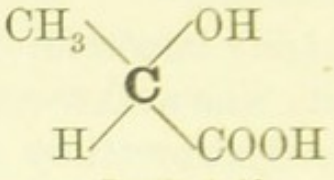
If the following graphic formulæ of various optically active compounds are examined, it will be seen that in every case

* It was subsequently found that this acid is more conveniently obtained by heating dextrotartaric acid with a little water at 165° (p. 276).

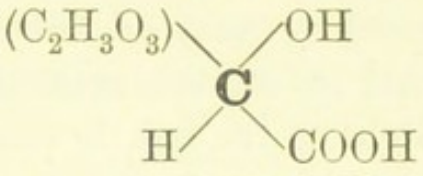
there is (at least) one carbon atom in the molecule—namely, that printed in heavy type—which is thus directly united with four different atoms or groups; such an atom is termed an **asymmetric** carbon atom, and any molecule which contains such an atom is an asymmetric molecule.



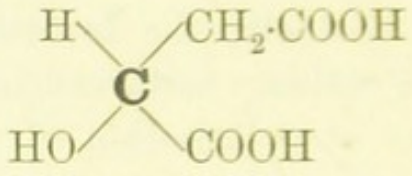
Active Amyl Alcohol.



Lactic Acid.



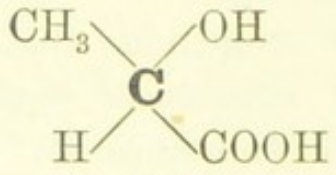
Tartaric Acid.



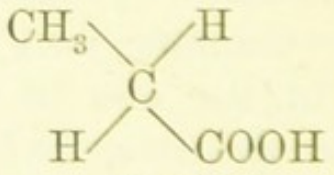
Malic Acid.

That this property of rotating the plane of polarisation of polarised light is due to the asymmetry of the molecule is now established by the fact that all optically active carbon compounds of known constitution contain an asymmetic group, and also by the fact that if by any means the asymmetric character of the molecule is destroyed, the power of rotating the plane of polarisation also disappears.

Sarcolactic acid (p. 241), for example, is optically active, but when it is reduced with hydrogen iodide it yields propionic acid, which is inactive, because it does not contain a carbon atom united with four different atoms or groups,

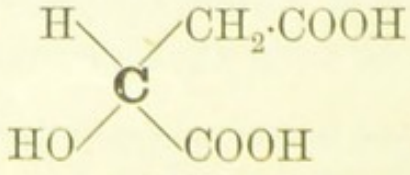


Active.

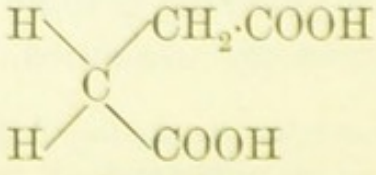


Inactive.

Malic acid, again, is optically active, but on reduction inactive succinic acid is formed,

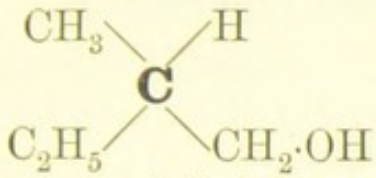


Active.

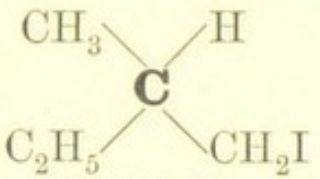


Inactive.

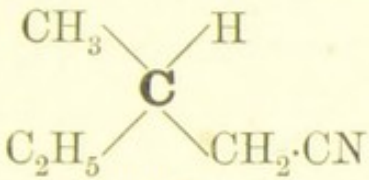
A still more instructive case is afforded by active amyl alcohol (p. 111), and the following derivatives of this alcohol,



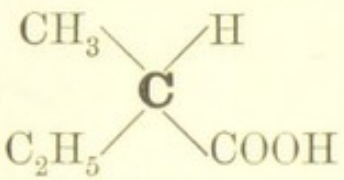
Amyl Alcohol.



Amyl Iodide.

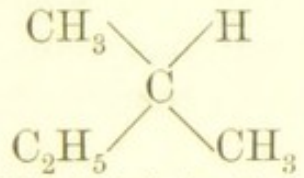


Amyl Cyanide.



Methylethylacetic Acid.

These substances, prepared from active amyl alcohol by the usual series of reactions, are themselves optically active, because they still contain an asymmetric grouping; when, however, the iodide is reduced to the hydrocarbon,



Dimethylethylmethane.

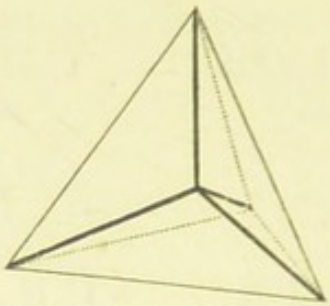
the asymmetric character of the molecule vanishes, and a substance is formed which is optically inactive.

The relation between the asymmetry of the molecule and the property of rotating the plane of polarisation of polarised light is now supported by such weighty evidence that it may be regarded as established.

The next point in Le Bel and van't Hoff's theory concerns the *arrangement in space* of the four atoms or groups united to a quadrivalent carbon atom.

According to this theory, each of the several atoms or groups, with which a carbon atom is united, is situated at some point on one of four different lines, which are symmetrically arranged in the space around the carbon atom. It may be supposed, therefore, that the carbon atom is situated at the centre of an imaginary regular tetrahedron, and that its four valencies (by virtue of which it unites with four atoms

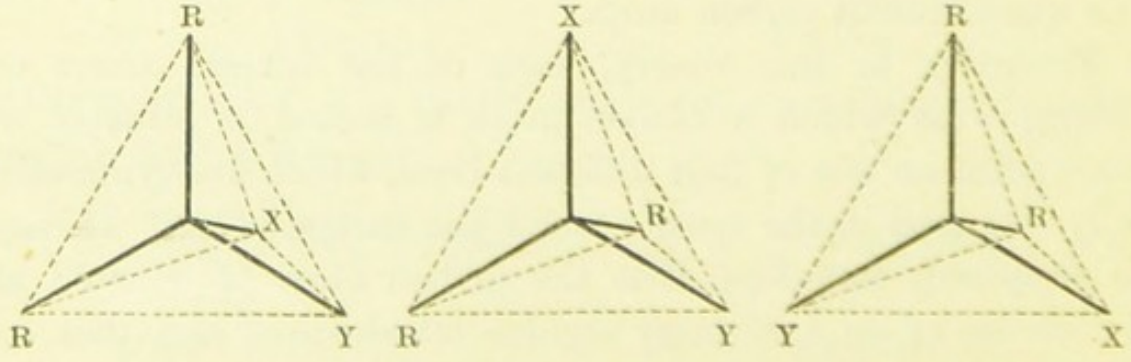
or groups) act in the directions of straight lines, drawn from the centre of the tetrahedron to the four corners, as represented by the dark lines in the following figure :—



This view of the arrangement in space of the groups united to the carbon atom not only explains the existence of isomerides such as those referred to above, but also accounts satisfactorily for other facts observed in the study of carbon compounds ; the application of Le Bel and van't Hoff's theory to such compounds generally may now be considered, and the following conclusions drawn therefrom.

(1) A compound of the type, CR_3X (where R and X represent any atom or group)—as, for example, CH_3Cl, $CHCl_3$, $CH_3{\cdot}OH$, $CH_3{\cdot}COOH$, &c.—can exist in *one* form only, because whichever corner of the tetrahedron is occupied by X, the result is the same.

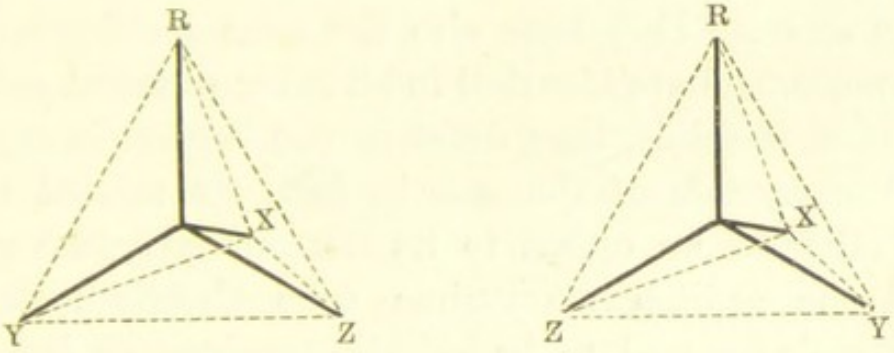
(2) A compound of the type, CR_2XY (that is to say, one in which any two atoms or groups are identical)—as, for example, CH_2ClBr, CH_2Cl_2, $CH(CH_3)_2{\cdot}OH$—can exist in *one* form only ; arrangements at the corners of the tetrahedron such as the following,



which may appear to be different on paper, are in reality identical.

Points such as these can only be clearly understood by actually handling models made to represent arrangements of this kind;* it will then be seen that whatever attempts are made to vary the positions of the different atoms R, R, X, Y, only one arrangement is possible, the apparent difference which exists on paper vanishing at once when the models are turned about.

(3) Compounds of the type, CRXYZ—in which the carbon atom is united with four different atoms or groups—may exist in *two*, but only two, different forms, which may be represented by the following figures:—



In working with the models, the red, white, blue, and yellow balls are first attached to the two rubber carbon models, in such a way as to produce identical arrangements; any two of the balls in one of the models are then interchanged. The two arrangements which are thus obtained are different.

These two arrangements, moreover, are related to one another, in the same way as an *object* to its *mirror-image*—that is to say, if one be held before a mirror, the positions of X, Y, and Z in relation to R, in the mirror-image, will be

* In order to facilitate the study of stereochemistry, sets of models similar to those recommended by Friedländer have been specially prepared, at the authors' request, by Messrs Baird & Tatlock (14 Cross Street, Hatton Garden, London, E.C.), from whom they may be obtained at a cost of eighteenpence. Such sets contain sufficient models for the study of the isomerism of the tartaric acids, but larger sets suitable for the study of the sugars may also be obtained.

identical with those in the other model viewed directly; for the sake of convenience, one of these arrangements may be distinguished by + or *d*, the other by − or *l*, the actual choice being immaterial.

Returning to the case of the simple optically active substances—namely, those containing *only one* asymmetric carbon atom—it is now known that they invariably exist in two optically active forms, one of which is dextrorotatory (*d* or +), the other levorotatory (*l* or −) to exactly the same extent. These two forms may be represented by the figures just given, and they are called *optical* (physical, or stereochemical) *isomerides*. The two optical isomerides have the same chemical properties and the same constitution, and their molecules differ only as regards the arrangement of their atoms in space. They have also the same melting-point and boiling-point, and are identical in all other physical properties, except that, if solids, they differ in one respect in crystalline form; the crystals of the one, in fact, are related to those of the other as an object to its mirror-image, just as in the case of the sodium ammonium salts already referred to. Such crystals are said to be *enantiomorphous* or *hemihedral*, and the *d*- and *l*-compounds which form these crystals are said to be *enantiomorphously related* to one another.

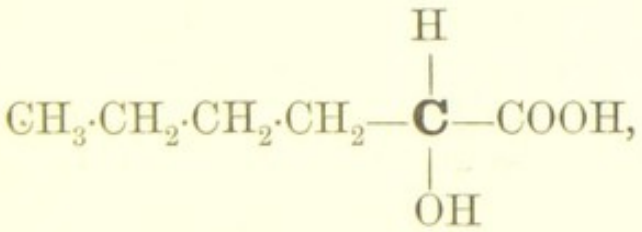
When any substance containing *one* asymmetric carbon atom is prepared synthetically, the product is found to be optically *inactive*. When, for example, lactic acid is produced from acetaldehyde (p. 242), or malic acid from (inactive) bromosuccinic acid (p. 254), the product in each case has no action on polarised light.

This is due to the fact that the product contains equal quantities of the *d*- and *l*-forms, and the action on polarised light of the one is exactly counterbalanced by that of the other. By simply dissolving together equal quantities of the *d*- and *l*-forms, and then evaporating the solution, an inactive product, identical with that produced synthetically, is obtained.

Compounds of this kind, which consist of exactly equal quantities of the *d*- and *l*-forms, are called *externally compensated* or *dl*-compounds.

When an externally compensated or *dl*-compound is a solid, it often differs very considerably from the active forms in physical properties; it may have a different melting-point (usually a higher one), different solubility, different density, and a different *crystalline form*. Such a crystallographic combination of the *d*- and *l*-forms is termed a *racemic* compound. Sometimes, however, the *d*- and *l*-forms of solids do not give a racemic compound, but remain as a mere mixture; when, for example, a solution containing the sodium ammonium salts of both *d*- and *l*-tartaric acids is evaporated at ordinary temperatures, the crystals of the two salts are deposited separately, side by side. Such a product is termed a *dl*-mixture.

In the case of compounds containing only *one* asymmetric carbon group, no matter how many carbon atoms the molecule may contain, or what the nature of the other atoms may be, so long as only one of the carbon atoms is combined with four different atoms or groups, the compound exists only in the above three optically different forms—namely *d*-, *l*-, and externally compensated; a substance of the constitution,



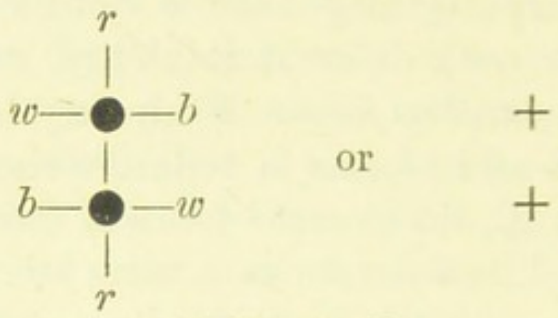
for example, would not form a larger number of optical isomerides than a simple substance such as lactic acid.

When, however, a compound contains *two* asymmetric carbon-groups, a larger number of modifications may exist, as will be seen by constructing models in the following manner:

I. Make two *identical* asymmetric carbon groups, **C**, *r*, *b*, *w*, *y*,* each of which, for convenience, may be designated +; now

* The letters *r*, *b*, *w*, and *y* refer respectively to the red, blue, white, and yellow balls in the sets of models.

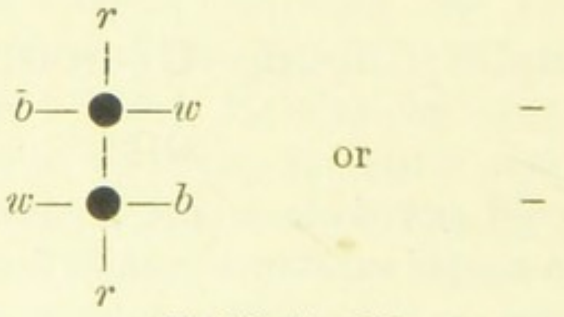
remove y from both models, join the two free ends by means of the rod, and lay the model on the table, so that the two red balls point upwards. This is one possible modification, a plane figure of which may be obtained by pressing the red balls outwards on the table, when it will appear like this,



Modification I.

The removal of one of the balls, representing one of the atoms or groups, and the substitution for it of the more complex group (**C**, r, b, w), still leaves each carbon atom asymmetric; in other words, each is now combined with the four different groups (r), (b), (w), and (C, r, b, w), instead of with (r), (b), (w), and (y).

II. Repeat the above operations, starting, however, with two *identical* asymmetric carbon-groups, **C**, r, b, y, w, which are the mirror-images of those taken in I., and which may, therefore, be called $-$; the plane representation of this model will be,

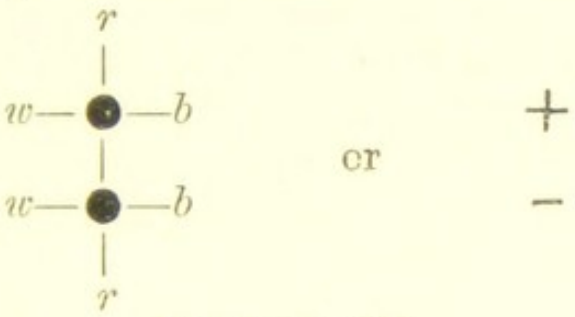


Modification II.

This form is quite different from I., and the one cannot possibly be made to coincide with the other; if, for example, II. is turned over, although the positions of b and w will correspond with those in I., r and r will now point downwards in II., whereas they pointed upwards in I.; if, in fact, this model (II.) is held before a mirror, it will be seen that it is

not identical with its mirror-image, but that its mirror-image *is* identical with I. viewed directly.

III. If, now, two *different* asymmetric carbon-groups, C, *r*, *b*, *w*, *y*, and C, *r*, *b*, *y*, *w*, or + and −, are joined in the same manner as before, another modification will be obtained, which is quite different from I. and II., and which may be represented thus,



Modification III.

No other form different from these three can be constructed. It is evident, then, that a compound containing *two* asymmetric carbon atoms may form *three* distinct modifications. One of these (I.) will be dextrorotatory, because it contains two *identical* (+) asymmetric carbon atoms; the other (II.) will be levorotatory to exactly the same extent, because it contains two *identical* (−) asymmetric carbon atoms. The third form, on the other hand, will be optically inactive; the molecule which it represents contains two *different* asymmetric carbon atoms, one + and the other − but otherwise identical, and consequently the dextrorotatory action of the one is exactly counterbalanced by the levorotatory action of the other; in other words, the rotatory power of one *part* of this molecule is compensated or neutralised by that of the other part; such a compound is said to be inactive by *internal compensation*.

There is, however, a fourth modification which has not yet been considered in the present case; by dissolving equal quantities of the two active (*d*- and *l*-) forms, and then evaporating the solution, an externally compensated or *dl*-modification may be obtained, just as in the case of compounds which contain one asymmetric carbon atom.

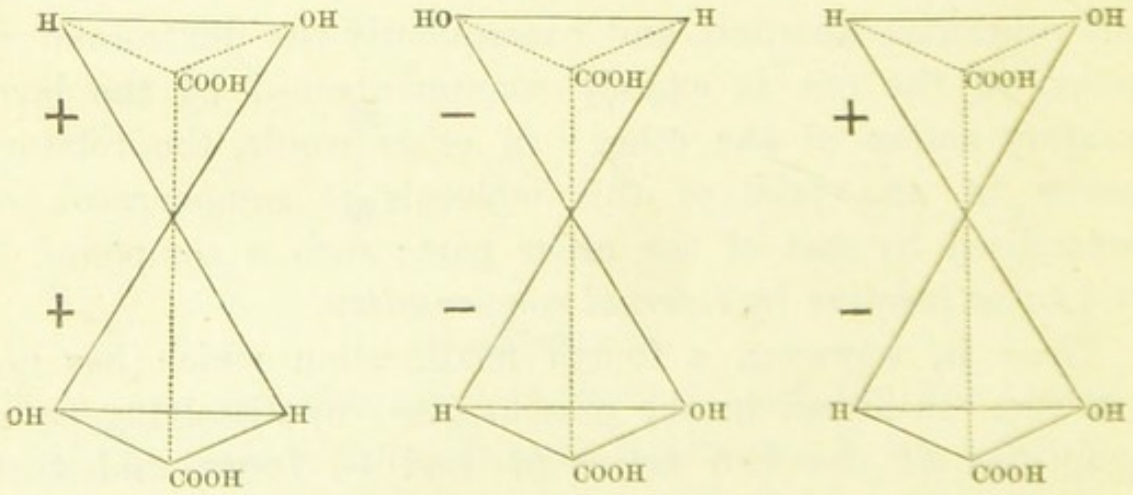
In order to decide which two of the above three forms represent the active (*d*- and *l*-) modifications of the substance, it is only necessary to determine which two models behave to each other as object to mirror-image. This will be found to be the case with the forms I. and II., which, therefore, are the active forms; on the other hand, the form III. is identical with its own mirror-image, and, therefore, is inactive.

The same conclusions are arrived at by disconnecting and then comparing the asymmetric carbon atoms, when it is easy to see that one of the models is composed of two *different* arrangements; this, therefore, is the form which is inactive by internal compensation.

Optical Isomerism of the Tartaric Acids.

One of the better known examples of optical isomerism in substances containing two asymmetric carbon atoms is that of the tartaric acids, investigated by Pasteur. Tartaric acid, COOH·**C**H(OH)·**C**H(OH)·COOH, contains two carbon atoms, each of which is united with four different atoms or groups—namely, {COOH}, {H}, {OH}, and {CH(OH)·COOH}, and consequently, as just shown, there should be four physically isomeric forms of this acid.

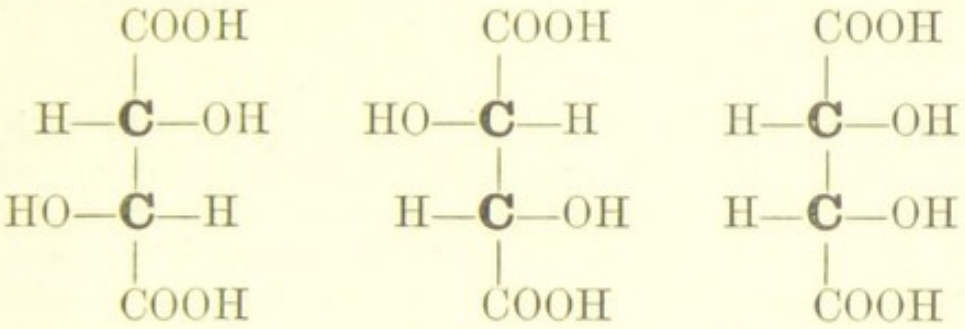
These four modifications—namely, dextrotartaric, levotartaric, mesotartaric, and racemic acid—are all known, and the first three compounds may be represented with the aid of the tetrahedral models as follows:—



d-Tartaric Acid. *l*-Tartaric Acid. Mesotartaric Acid.

For ordinary purposes the *configurations* represented above

may be more conveniently symbolised by using projections of these models, which correspond with those already employed (pp. 272, 273).



d-Tartaric Acid. *l*-Tartaric Acid. Mesotartaric Acid.

Dextrotartaric acid and levotartaric acid are the two optically active forms. The one rotates the plane of polarisation to the right, whereas the other rotates it to the left; but in all other respects they are identical, except for the differences in crystalline form already mentioned. They possess the same melting-point and the same solubility in a given solvent; their metallic salts have the same composition, and crystallise with the same number of molecules of water. Their esters boil at the same temperature; all their salts, like the acids themselves, are optically active to the same extent, but in opposite directions.

Mesotartaric acid, $C_4H_6O_6$, is the *simple* optically inactive form of tartaric acid; that is to say, it is inactive by internal compensation.

It differs from the two optically active forms in many respects—as, for example, in melting-point, solubility, and crystalline form. It might, in fact, be regarded as a totally different substance from an examination of its *physical* properties and of those of its salts, although in *chemical* properties it is identical with the active forms. Mesotartaric acid *cannot be resolved into two optically active modifications*, because all the molecules of which it is composed are alike.

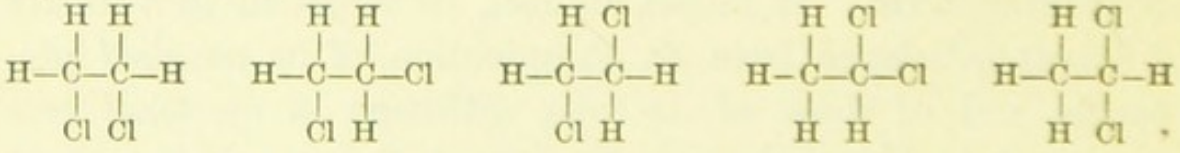
Racemic acid, or *dl*-tartaric acid, is simply a crystallographic union of equal quantities of dextro- and levo-tartaric acids, and is inactive by external compensation. It is obtained

when a solution of equal quantities of the two active modifications is evaporated, and it *can be separated again into these two forms* by certain methods given below. Racemic acid behaves as if it were a distinct substance, so far as *physical* properties are concerned.

Racemic acid or *dl*-tartaric acid is obtained, together with meso-tartaric acid, when 'tartaric acid' (dihydroxysuccinic acid) is prepared by any synthetical process; also when *d*- or *l*-tartaric acid is heated with water at 165°. Many optically active compounds are more or less readily converted into the corresponding *dl*-mixtures when they are heated alone, or in solution, or treated with various reagents. This change is termed *racemisation*, and is due to the transformation of some of the *d*- or *l*-groups into the optically isomeric arrangements.

It will be seen from the above examples that the existence of optical isomerides, and the number of such modifications, is in complete accordance with the theory of Le Bel and van't Hoff, and a great many other cases might be mentioned in which the agreement is also perfect.

The view that the atoms or groups united to carbon are not arranged in one plane (as represented in ordinary structural formulæ) is also strongly supported by considerations based on the phenomenon of structural isomerism, because such an arrangement of the atoms or groups would render possible the existence of isomerides in cases where experience has shown that isomerism does not occur; in the case of the compound, $C_2H_4Cl_2$, for example, two structural isomerides—namely, $CH_3 \cdot CHCl_2$ and $CH_2Cl \cdot CH_2Cl$—are known, in accordance with theory; were all the atoms arranged in one plane, the following *five* isomeric compounds should be capable of existence,

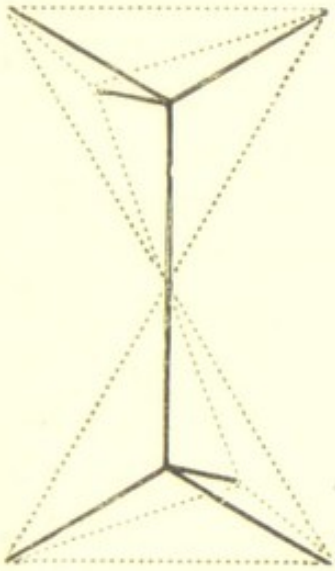


As the number of asymmetric carbon atoms in the molecule of any compound increases, the number of optical isomerides becomes larger; a substance such as saccharic acid (p. 297), for example,

COOH·**C**H(OH)·**C**H(OH)·**C**H(OH)·**C**H(OH)·COOH,

which contains four asymmetric carbon atoms, is capable of existing in ten optically isomeric forms. Many other examples of optical isomerism occur among the polyhydric alcohols (p. 292) and among the carbohydrates and their derivatives (p. 293; and Part II. p. 599).

An examination of the models of substances containing two asymmetric carbon atoms—or, in fact, of those of any substances derived from the model shown below—might lead to the supposition that such substances might exist in many modifications.



In the first place, the model could be arranged as shown in the figure. If, then, one of the carbon atoms were slowly rotated about an axis, the model would pass through an infinite number of forms, all of which would be different, because they would represent different relative positions in space of the atoms constituting the molecule.

This difficulty, however, is only apparent. In a compound represented by this model (atoms or groups are supposed to be attached to the corners of the tetrahedra), the atoms or groups united with one of the carbon atoms would exert attraction or repulsion on those united with the other; if, then, the carbon atoms are capable of *free rotation* about an axis, a certain position of equilibrium, which is the resultant of all the forces, would be attained. This position might be disturbed by the application of heat, &c., but on the removal of the disturbing element the original form would be restored, so that, under given conditions, the compound exists in one form only, unless, of course, it contains one or more asymmetric carbon atoms.

Resolution of Externally Compensated Compounds.

The externally compensated form of tartaric acid and the corresponding varieties of other asymmetric substances—namely, those which are inactive because they are composed of equal quantities of the *d*- and *l*-forms—may generally be resolved into their optically active (enantiomorphously related) components by various methods.

One important method, discovered by Pasteur, consists in fractionally crystallising the salt formed from an externally compensated acid or base with an optically *active* substance. This method depends on the fact that the *d*- and *l*-components of the externally compensated compound form, with one and the same optically active substance, salts which *differ in solubility*, and which, therefore, may be separated by fractional crystallisation in the ordinary way. When, for example, racemic acid is combined with the optically active *d*-base, cinchonine (Part II. p. 542), the product consists of two salts, which may be represented by [*d*-acid, *d*-base] and [*l*-acid, *d*-base] respectively; these two salts may be separated from one another, and the dextro- and levo-acids may then be obtained from the salts. In a similar manner the inactive modification of coniine (Part II. p. 543) may be resolved into its components by the fractional crystallisation of the salt which it forms with *d*-tartaric acid.

Another method, also discovered by Pasteur, has already been described (p. 264): if a solution of the sodium ammonium salt, prepared from racemic (*dl*-tartaric) acid, is allowed to crystallise slowly at a temperature below 28°, enantiomorphous crystals (right- and left-handed, as shown in the fig., p. 264) are deposited, and if the crystals are sufficiently large and well-formed they may be distinguished and sorted from one another. This method of separation, however, is seldom applicable, because, as a rule, the two active components form a racemic compound, or, if deposited separately, their crystals are not sufficiently well defined to be distinguishable. Racemic acid itself cannot be resolved by this method.

Another method, quite different in principle from the foregoing,

depends on the fact that if certain organisms, such as yeast or *penicillium glaucum*, are placed in a solution of a *dl*-substance, they may bring about the decomposition of one of the optical isomerides, the result being that, after a time, the solution contains the other modification only (compare Part II. p. 618).

dl-Alcohols, such as methylethyl carbinol, CHMeEt·OH, may be resolved into their optically active components by the following method:—The *dl*-alcohol is converted into an acid ester with the aid of a dicarboxylic acid, such as phthalic acid (Part II. p. 478); the acid ester, $CHMeEt{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is then combined with an alkaloid, or some other optically active base, and the two components of the salt are separated by fractional crystallisation, as described above. The *d*- and *l*-acid esters are separately regenerated from the salts and the *d*- and *l*-alcohols are finally obtained by hydrolysing the esters.

dl-Aldehydes and *dl*-ketones may be resolved with the aid of an optically active derivative of hydrazine. The *dl*-compound gives two different hydrazones, just as a *dl*-acid gives two different salts with an optically active base, and the two products may be separated by fractional crystallisation.

Optically active derivatives of quinquevalent nitrogen and phosphorus, and of quadrivalent sulphur, selenium and silicon have been prepared. In the case of nitrogen, tetralkylammonium salts of the type, $NR_1R_2R_3R_4X$ (where R_1, R_2, R_3, and R_4 represent *different* hydrocarbon radicles, and X a halogen atom), are treated in aqueous solution with the silver salt of an optically active acid. The product, like that formed from a *dl*-acid and an optically active base, consists of two components (*d*A*d*B and *d*A*l*B *or* *l*A*d*B and *l*A*l*B, as the case may be), which may be separated by fractional crystallisation. The halogen salts, regenerated from these components, are optically active and enantiomorphously related.

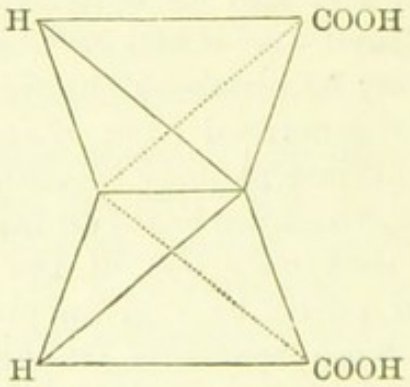
In all the above resolution methods, which are based on fractional crystallisation, the general rule is that only one of the active compounds is obtained in a state of purity by a given process—namely, the one which forms the more sparingly soluble component.

Stereo-isomerism of Unsaturated Compounds.

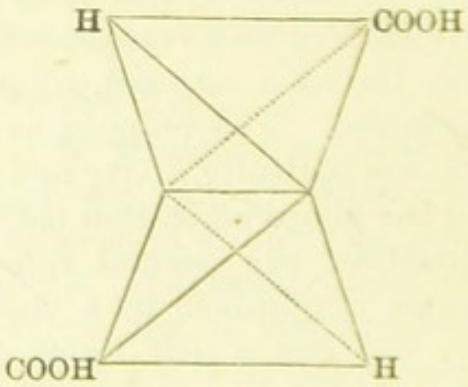
The occurrence of isomerism among certain unsaturated compounds was observed long ago, but for many years a satisfactory explanation of the existence of such isomerides could not be given.

Fumaric acid and maleïc acid, for example, are both unsaturated compounds of the constitution, COOH·CH:CH·COOH (p. 255); their isomerism is not *structural*—that is to say, it is not due to the atoms being in a different state of combination—as is proved by their methods of formation and by their whole chemical behaviour; and yet the isomerides differ considerably in properties, both physical and chemical. Maleïc acid, for example, is readily converted into an anhydride, whereas fumaric acid does not give an anhydride of its own, but on distillation it gives water and maleïc anhydride.

This and similar cases of isomerism among unsaturated compounds were explained by van't Hoff and Wislicenus as follows:—Unsaturated compounds contain (at least) two carbon atoms united together by two valencies of each. Representing the molecule of such a compound of the type $CR_2:CR_2$ with the aid of the tetrahedral models, it will be seen that when two corners of the one tetrahedron are joined to two corners of the other (to represent the double binding) the four groups, R, now lie in *one plane*. If, then, all the four groups, or any three of them, are identical, or if any two united with one and the same carbon atom are identical, only one arrangement is possible; if, however, the compound is of the type $CRX:CR_1X_1$—that is to say, if each of the carbon atoms is combined with two different atoms or groups—then *two* isomerides, represented respectively by the following figures, are possible, and it makes no difference whether R and R_1, or X and X_1, are identical or different:—



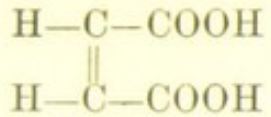
Maleïc Acid.



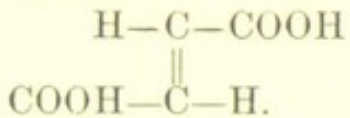
Fumaric Acid.

The existence of maleïc and fumaric acids, therefore, is explained, and as maleïc acid readily forms an anhydride, whereas fumaric acid does not, it may be represented by the first formula, in which the carboxyl-groups appear to be more suitably situated for anhydride formation than in the second. For ordinary purposes, the

projections of such models are employed and the *configurations* of the two acids are expressed in the following manner :—



Maleïc Acid.



Fumaric Acid.

On reduction, maleïc and fumaric acids give one and the same product—namely, succinic acid, $COOH \cdot CH_2 \cdot CH_2 \cdot COOH$—because as soon as the carbon atoms become singly bound they regain the property of free rotation, and by the mutual actions of the different atoms and groups *the* position of equilibrium is attained (compare p. 277).

Isomerism such as that of these two acids is generally called *stereo-isomerism*, and the compounds are referred to as the *cis*- and *trans*-isomerides respectively ; the *cis*-isomeride is that in which identical atoms or groups are in juxtaposition.

Several other examples of stereo-isomerism of this type are given later (Part II. p. 486).

CHAPTER XV.

Trihydric and Polyhydric Alcohols.

It has been shown that it is possible to convert a paraffin first into a monohydric alcohol, and then into a dihydric alcohol, or glycol, by the substitution of hydroxyl-groups for atoms of hydrogen ; ethane, for example, may be converted into ethyl alcohol and ethylene glycol, propane into propyl alcohol and propylene glycol.

In a similar manner those paraffins containing three or more carbon atoms may be converted into **trihydric alcohols**, compounds which stand in the same relation to the glycols as the latter to the monohydric alcohols,

Propyl Alcohol. $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$ Propylene Alcohol. $CH_3 \cdot CH(OH) \cdot CH_2 \cdot OH$

Propenyl Alcohol. $CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$.

As, however, the preparation of such trihydric alcohols from

the paraffins is a matter of very considerable difficulty, their study has necessarily been very limited except in the case of glycerol, which, from its occurrence in such large quantities in natural fats and oils, has offered exceptional opportunities for investigation.

Glycerol, $CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH$ (glycerin, propenyl alcohol, or trihydroxypropane), has been previously referred to as one of the unimportant products of the alcoholic fermentation of sugar, and its preparation from fats and oils, which consist essentially of tripalmitin, tristearin, and triolein (esters of glycerol) has been described.

The concentrated glycerol, obtained as already stated (p. 178), may be further purified and freed from water by distillation under reduced pressure, the first fractions, which contain the water, being collected separately.

Glycerol may be obtained from its elements by the following series of reactions:—Acetylene, obtained by Berthelot's synthetical method or from calcium carbide, is converted into acetaldehyde (p. 87), and the latter is oxidised to acetic acid, from which acetone is prepared in the usual manner (p. 135); this ketone is first converted into isopropyl alcohol (p. 135) and then into propylene (p. 79). This olefine unites directly with bromine, yielding propylene dibromide, and from the latter, by heating with bromine in presence of iron (Part II. p. 381), *propenyl tribromide*, $CH_2Br\cdot CHBr\cdot CH_2Br$, is obtained. The three bromine atoms in this compound are next displaced by acetyl-groups with the aid of silver acetate (p. 195), and the product, *propenyl* or *glyceryl acetate*, is hydrolysed with aqueous or alcoholic potash. The complete synthesis of glycerol may be summarised as follows:—

$$C_2H_2 \rightarrow CH_3\cdot CHO \rightarrow CH_3\cdot COOH \rightarrow CH_3\cdot CO\cdot CH_3 \rightarrow CH_3\cdot CH(OH)\cdot CH_3$$
$$\rightarrow CH_3\cdot CH{:}CH_2 \rightarrow CH_3\cdot CHBr\cdot CH_2Br \rightarrow CH_2Br\cdot CHBr\cdot CH_2Br$$
$$\rightarrow CH_2(OAc)\cdot CH(OAc)\cdot CH_2\cdot OAc^* \rightarrow CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH.$$

Glycerol is a colourless, crystalline substance, melting at 17°; as ordinarily prepared, however, it is a thick syrup of sp. gr. about 1·26, and does not solidify readily, owing to the presence of water and traces of other impurities. It boils at 290° under atmospheric pressure, without decomposing;

* $CH_3\cdot CO-$ is represented by Ac in this formula.

if, however, it contains even traces of salts it undergoes slight decomposition, so that in such cases it must first be distilled in a current of superheated steam. Glycerol is very hygroscopic; it mixes with water and with alcohol in all proportions, but it is insoluble in ether, a property which is common to most substances which contain many hydroxyl-groups. It has a distinctly sweet taste; this property also seems to be conditioned by the presence of hydroxyl-groups, as is shown by the fact that other trihydric alcohols, and to an even greater extent the tetra-, penta-, and hexa-hydric alcohols, are sweet, sugar-like compounds.

Glycerol readily undergoes decomposition into acroleïn and water (p. 290),

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O;$$

this change takes place to a slight extent when impure glycerol is distilled, but much more readily and completely when glycerol is heated with potassium hydrogen sulphate or phosphorus pentoxide.

Glycerol, like glycol, yields a variety of oxidation products, according to the conditions under which it is treated; when carefully oxidised with dilute nitric acid, it is converted into *glyceric acid*, a change analogous to the formation of glycollic acid from glycol,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 2O = CH_2(OH)\cdot CH(OH)\cdot COOH + H_2O;$$

under other conditions, however, it is usually oxidised to a mixture of glycollic, oxalic, and carbonic acids,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 4O = CH_2(OH)\cdot COOH + CO_2 + 2H_2O,$$

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 6O = COOH\cdot COOH + CO_2 + 3H_2O.$$

In presence of ferrous sulphate, glycerol is readily oxidised by an aqueous solution of hydrogen peroxide, and is converted into glycerose (p. 300); other polyhydric alcohols, under these conditions, are oxidised in a similar manner.

Glycerol is extensively used in the preparation of nitroglycerin (p. 286) and toilet-soaps, also for filling gas-meters; it is used in smaller quantities in medicine and as an antiputrescent in preserving food materials.

Derivatives of Glycerol.—If it were known that glycerol is a trihydric alcohol of the constitution given above, its behaviour under various conditions might be foretold with a good prospect of success, from analogy with that of ethyl alcohol and of glycol. The fact, for example, that glycerol contains hydrogen, displaceable by sodium, was only to be expected, and, just as in the case of glycol, only one atom of hydrogen is displaced at ordinary temperatures; the product, $C_3H_5(OH)_2 \cdot ONa$, is hygroscopic, and is immediately decomposed by water.

Again, the behaviour of glycerol with acids is analogous to that of alcohol and of glycol; when heated with acetic acid, for example, glycerol yields the ester, *triacetin*, or *glyceryl acetate*, and water,

$$C_3H_5(OH)_3 + 3CH_3 \cdot COOH = C_3H_5(O \cdot CO \cdot CH_3)_3 + 3H_2O.$$

It is obvious, however, that triacetin is not the only ester which may be produced by the interaction of glycerol and acetic acid, because, being a *triacid* base, glycerol may yield compounds, such as *monacetin* and *diacetin*, by the displacement of only one, or of two, atoms of hydrogen,

$$C_3H_5(OH)_3 + CH_3 \cdot COOH = C_3H_5(OH)_2 \cdot O \cdot CO \cdot CH_3 + H_2O,$$
$$C_3H_5(OH)_3 + 2CH_3 \cdot COOH = C_3H_5(O \cdot CO \cdot CH_3)_2 \cdot OH + 2H_2O.$$

These three compounds may all be prepared by heating glycerol with acetic acid, the higher the temperature and the larger the relative quantity of acetic acid employed, the larger the proportion of triacetin produced. Acetic anhydride acts more readily than acetic acid, but gives the same three products.

Chlorohydrins.—The action of concentrated hydrochloric acid on glycerol is similar to that of acetic acid; at moderately high temperatures, and with relatively small quantities

of the acid, one atom of chlorine is substituted for one hydroxyl-group, and *glyceryl chlorohydrin* is formed, just as ethylene glycol is converted into ethylene chlorohydrin,

$$C_3H_5(OH)_3 + HCl = C_3H_5Cl(OH)_2 + H_2O\ ;$$

with excess of hydrochloric acid, however, *glyceryl dichlorohydrin* is produced,

$$C_3H_5(OH)_3 + 2HCl = C_3H_5Cl_2{\cdot}OH + 2H_2O.$$

Glyceryl trichloride,* $CH_2Cl{\cdot}CHCl{\cdot}CH_2Cl$ (propenyl trichloride), cannot easily be obtained by heating glycerol with hydrochloric acid, but may be prepared by treating the dichlorohydrin with phosphorus pentachloride,

$$C_3H_5Cl_2{\cdot}OH + PCl_5 = C_3H_5Cl_3 + POCl_3 + HCl\ ;$$

it is a colourless liquid, boiling at 158°, and smells like chloroform.

Two isomeric glyceryl chlorohydrins and two isomeric dichlorohydrins are known,

$CH_2(OH){\cdot}CH(OH){\cdot}CH_2Cl$	$CH_2(OH){\cdot}CHCl{\cdot}CH_2{\cdot}OH$
α-Chlorohydrin.	β-Chlorohydrin.
$CH_2Cl{\cdot}CH(OH){\cdot}CH_2Cl$	$CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OH$
αα-Dichlorohydrin.	αβ-Dichlorohydrin.

Glyceryl *α-chlorohydrin* is formed, together with small quantities of the β-compound, when glycerol is heated at 100° with hydrochloric acid ; it is an oil, soluble in water. Glyceryl *β-chlorohydrin* can be obtained by treating allyl alcohol (p. 287) with hypochlorous acid.

Glyceryl *αα-dichlorohydrin* is produced when glycerol is heated with a solution of hydrogen chloride in glacial acetic acid ; on oxidation with chromic acid it yields symmetrical dichloracetone, $CH_2Cl{\cdot}CO{\cdot}CH_2Cl$.

Glyceryl *αβ-dichlorohydrin* is obtained by treating allyl alcohol (p. 287) with chlorine ; on oxidation with nitric acid it gives αβ-dichloropropionic acid, $CH_2Cl{\cdot}CHCl{\cdot}COOH$. When treated with potash, both the αα- and the αβ-chlorohydrin yield *epichlorohydrin*, $CH_2Cl{-}CH{<}\overset{CH_2}{O}$, (compare ethylene oxide, p. 236).

* The name *glyceryl*, or *propenyl*, is given to the group of atoms, $-CH_2{-}\overset{|}{C}H{-}CH_2-$, which may be regarded as a tervalent radicle.

When glycerol is treated with acetyl chloride it does not yield triacetin, as might have been expected, but glyceryl *chlorohydrin* diacetate,

$$C_3H_5(OH)_3 + 2CH_3{\cdot}COCl = C_3H_5Cl(O{\cdot}CO{\cdot}CH_3)_2 + H_2O + HCl.$$

This behaviour, although apparently abnormal, is not really so; in the first place, the glycerol is converted into a *diacetyl*-derivative in the usual manner,

$$C_3H_5(OH)_3 + 2CH_3{\cdot}COCl = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + 2HCl,$$

and the hydrogen chloride, produced during the reaction, then acts on the diacetyl-derivative, just as it does on other monohydric alcohols,

$$C_3H_5(O{\cdot}CO{\cdot}CH_3)_2{\cdot}OH + HCl = C_3H_5(O{\cdot}CO{\cdot}CH_3)_2Cl + H_2O.$$

Ethylene glycol and other di- and poly-hydric alcohols show a similar behaviour.

Nitro-glycerin, $C_3H_5(O{\cdot}NO_2)_3$ (glyceryl trinitrate, or propenyl trinitrate), is the glyceryl ester of nitric acid. It is prepared by slowly adding pure glycerol drop by drop, or in a fine stream, to a *well-cooled* mixture of concentrated sulphuric acid (4 parts) and nitric acid of sp. gr. 1·52 (1 part); the solution is run into cold water, and the nitro-glycerin, which is precipitated as a heavy oil, is washed well with water and left to dry in the air.*

It is a colourless oil of sp. gr. 1·6, has a sweetish taste, and is poisonous; although readily soluble in ether, it is only sparingly soluble in alcohol, and insoluble in water, so that, as regards solubility, its behaviour is widely different from that of glycerol, a fact which shows the influence of hydroxyl-groups in a very distinct manner. It explodes with great violence when it is suddenly heated or subjected to percussion, but when ignited with a flame it burns without explosion, and is even rather difficult to ignite.

Nitro-glycerin is readily hydrolysed by boiling alkalis, and is converted into glycerol and a nitrate,†

$$C_3H_5(O{\cdot}NO_2)_3 + 3KOH = C_3H_5(OH)_3 + 3KNO_3;$$

* Nitro-glycerin is an extremely dangerous substance, and its preparation is safe only to expert chemists.

† An alkali nitrite is also formed owing to reduction, the glycerol undergoing partial oxidation.

on reduction with ammonium sulphide it yields glycerol and ammonia,

$$C_3H_5(O{\cdot}NO_2)_3 + 12H_2S = C_3H_5(OH)_3 + 3NH_3 + 6H_2O + 12S.$$

In these two reactions the behaviour of nitro-glycerin is exactly analogous to that of ethyl nitrate, $CH_3{\cdot}CH_2{\cdot}O{\cdot}NO_2$, but quite different from that of nitro-ethane, $CH_3{\cdot}CH_2{\cdot}NO_2$, which, as previously stated, is not decomposed by alkalis, and on reduction yields amino-ethane or ethylamine; since, moreover, groups of atoms in a similar state of combination show a similar behaviour, it is clear that nitro-glycerin, like ethyl nitrate, is an ester, and not a nitro-derivative; in other words, the nitro-groups, $(-NO_2)$, in nitro-glycerin are directly combined with oxygen, and not with carbon. The name nitro-glycerin, therefore, is misleading; but, being so well known, it is employed here instead of the more correct names, glyceryl trinitrate or propenyl trinitrate.

Nitro-glycerin is extensively employed as an explosive, sometimes alone, sometimes in the form of *dynamite*, which is simply a mixture of nitro-glycerin and kieselguhr, a porous, earthy powder, consisting of the siliceous remains of small marine animals; the object of absorbing the nitro-glycerin with kieselguhr is to render it less liable to explode, and, consequently, safer to handle and to transport. The presence of acids in nitro-glycerin makes it liable to undergo spontaneous decomposition and explosion; great care, therefore, must be taken to wash it thoroughly. Nitro-glycerin is also employed, mixed with gun-cotton (p. 311), as blasting-gelatine, and in the preparation of smokeless gunpowder (cordite); it is used in medicine in cases of heart disease.

Unsaturated Compounds related to Glycerol.

Allyl alcohol, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, is formed and distils over when anhydrous glycerol is slowly heated to about 260° with crystallised oxalic acid. The glycerol is first converted into monoformin, with evolution of carbon dioxide, water, and a little formic acid (p. 151),

$$C_3H_5(OH)_3 + C_2H_2O_4 = C_3H_5(OH)_2{\cdot}O{\cdot}CHO + CO_2 + H_2O,$$
$$C_3H_5(OH)_2{\cdot}O{\cdot}CHO + H_2O = C_3H_5(OH)_3 + H{\cdot}COOH,$$

and as the temperature rises the rest of the monoformin undergoes decomposition, giving allyl alcohol,

$$CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot O\cdot CHO = CH_2(OH)\cdot CH{:}CH_2 + CO_2 + H_2O.$$

The liquid which passes over from about 220–260° is collected separately, and is redistilled; the portion which then boils below about 105° contains the allyl alcohol. This fraction is treated with anhydrous potassium carbonate, to free it from water, and is fractionated again. In the first operation, the thermometer dips into the *liquid*, but in the other distillations the temperature of the vapour is taken in the usual way.

Allyl alcohol is also produced when acroleïn (acraldehyde, p. 290) is reduced with nascent hydrogen, a change which is exactly analogous to the formation of alcohol from aldehyde,

$$CH_2{:}CH\cdot CHO + 2H = CH_2{:}CH\cdot CH_2\cdot OH.$$

It is a colourless, neutral liquid, boils at 96–97°, and has a very irritating smell; it is miscible with water, alcohol, and ether in all proportions.

Allyl alcohol is an unsaturated compound, and has therefore not only the properties of a primary alcohol, but also those of unsaturated compounds in general. Its alcoholic character is shown by the following facts:—It dissolves sodium with evolution of hydrogen,

$$2CH_2{:}CH\cdot CH_2\cdot OH + 2Na = 2CH_2{:}CH\cdot CH_2\cdot ONa + H_2,$$

forms esters with acids,

$$CH_2{:}CH\cdot CH_2\cdot OH + HCl = CH_2{:}CH\cdot CH_2Cl + H_2O,$$

and on oxidation is converted, first into acroleïn, then into acrylic acid,

$$CH_2{:}CH\cdot CH_2\cdot OH + O = CH_2{:}CH\cdot CHO + H_2O,$$
$$CH_2{:}CH\cdot CH_2\cdot OH + 2O = CH_2{:}CH\cdot COOH + H_2O.$$

In all these reactions its behaviour is so closely analogous to that of ethyl alcohol and other primary alcohols that it must be concluded that allyl alcohol contains the group, $-CH_2\cdot OH$. That it is an unsaturated compound is shown by its behaviour towards chlorine and bromine, with which it combines

directly, forming glyceryl $\alpha\beta$-dichloro- or $\alpha\beta$-dibromohydrin, isomeric with the corresponding $\alpha\alpha$- compounds obtained by treating glycerol with halogen acids,

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + Br_2 = CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH.$$

Allyl iodide, $CH_2{:}CH{\cdot}CH_2I$, is an unsaturated ester, related to allyl alcohol in the same way as ethyl iodide to ethyl alcohol. It may be obtained by treating allyl alcohol with iodine and phosphorus, but is more conveniently prepared from glycerol.

Iodine (10 parts) is mixed with glycerol (15 parts) in a large retort connected with a condenser, and the air is displaced by carbon dioxide, which is passed through the apparatus during the experiment. *Small* pieces of dry phosphorus (6 parts) are added from time to time, the mixture is *very gently* warmed if necessary to start the reaction, and the allyl iodide is afterwards distilled.

It is probable that the glycerol is first converted into the tri-iodide, $CH_2I{\cdot}CHI{\cdot}CH_2I$, which then undergoes decomposition into iodine and allyl iodide; if excess of phosphorus and iodine are employed, isopropyl iodide is formed,

$$CH_2{:}CH{\cdot}CH_2I + HI = CH_2{:}CH{\cdot}CH_3 + I_2,$$
$$CH_2{:}CH{\cdot}CH_3 + HI = CH_3{\cdot}CHI{\cdot}CH_3.$$

Allyl iodide is a colourless liquid, boiling at 101°, and has an odour of garlic; it resembles ethyl iodide in many respects, but has also the properties of an unsaturated compound. When heated with potassium sulphide in alcoholic solution, it is converted into *allyl sulphide* (see below), just as ethyl iodide gives ethyl sulphide,

$$2CH_2{:}CH{\cdot}CH_2I + K_2S = (CH_2{:}CH{\cdot}CH_2)_2S + 2KI.$$

Allyl bromide, $CH_2{:}CH{\cdot}CH_2Br$, may be obtained by treating allyl alcohol with phosphorus tribromide; it is a heavy liquid, and boils at 70–71°.

Allyl sulphide occurs in nature in many Cruciferæ, but is especially abundant in garlic (*Allium sativum*), from which it is obtained by distilling the macerated plant with water; it is known, therefore, as *oil of garlic*. It is a colourless, very unpleasant-smelling liquid, boiling at 140°. Another allyl-

derivative—namely, allyl isothiocyanate—occurs in nature in considerable quantities in black mustard-seeds, and is known as *oil of mustard* (p. 327).

Acroleïn, or **acraldehyde**, CH_2:CH·CHO, is formed during the partial combustion of fats, and when impure glycerol is distilled under ordinary pressure; also when allyl alcohol undergoes oxidation. It is prepared by distilling glycerol with potassium hydrogen sulphate,

$$C_3H_5(OH)_3 = C_3H_4O + 2H_2O.$$

Acroleïn is an aldehyde, and its relationship to allyl alcohol is the same as that of aldehyde to ethyl alcohol; it is a colourless liquid, boils at 52°, and has an exceedingly irritating and disagreeable odour, like that of scorched fat; it produces sores when brought in contact with the skin, and its vapour causes a copious flow of tears. Like other aldehydes, it reduces ammoniacal solutions of silver hydroxide with formation of a mirror, and readily undergoes polymerisation into an amorphous, brittle substance named *disacryl;* it also gives the aldehyde reaction with rosaniline, but on the other hand it does not combine with sodium hydrogen sulphite. On reduction it yields allyl alcohol; on exposure to the air, or on treatment with silver oxide, it readily undergoes oxidation, yielding acrylic acid. That it is an unsaturated compound is shown by the fact that it combines directly with bromine, forming an additive product of the composition,

$$CH_2Br·CHBr·CHO.$$

Crotonaldehyde, CH_3·CH:CH·CHO, is a homologue of acraldehyde; it is obtained by heating acetaldehyde with dilute hydrochloric acid, or with a solution of zinc chloride, aldol being formed as an intermediate product (p. 131),

$$2CH_3·CHO = CH_3·CH(OH)·CH_2·CHO$$
$$CH_3·CH(OH)·CH_2·CHO = CH_3·CH:CH·CHO + H_2O.$$

It boils at 104–105°, and closely resembles acraldehyde in properties; on reduction it yields, first, *crotonalcohol*, CH_3·CH:CH·CH_2·OH, and then butyl alcohol, $CH_3·CH_2·CH_2·CH_2·OH$; on oxidation it gives *crotonic acid*, CH_3·CH:CH·COOH.

Acrylic acid, CH_2:CH·COOH, the oxidation product of allyl alcohol and of acroleïn, may also be obtained from hydracrylic acid (p. 241), which on distillation loses the elements of water,

$$CH_2(OH)\cdot CH_2\cdot COOH = CH_2{:}CH\cdot COOH + H_2O,$$

a change analogous to the formation of ethylene from alcohol; acrylic acid is also produced when β-bromopropionic acid is treated with alcoholic potash, just as ethylene is formed from ethyl bromide,

$$CH_2Br\cdot CH_2\cdot COOH = CH_2{:}CH\cdot COOH + HBr.$$

Acrylic acid is a liquid at ordinary temperatures, and boils at 139–140°; it smells like acetic acid, is miscible with water in all proportions, and its solutions have an acid reaction. It is a monocarboxylic acid, and forms metallic salts and esters just as do the fatty acids; it differs from the latter, however, in being an unsaturated compound, as is shown by its forming additive products. It combines directly with bromine, giving $\alpha\beta$-dibromopropionic acid,

$$CH_2{:}CH\cdot COOH + Br_2 = CH_2Br\cdot CHBr\cdot COOH;$$

with halogen acids, yielding β-halogen derivatives* of propionic acid,

$$CH_2{:}CH\cdot COOH + HCl = CH_2Cl\cdot CH_2\cdot COOH,$$

and with nascent hydrogen giving propionic acid,

$$CH_2{:}CH\cdot COOH + 2H = CH_3\cdot CH_2\cdot COOH.$$

Crotonic acid, $CH_3\cdot CH{:}CH\cdot COOH$, the next homologue of acrylic acid, may be obtained by methods similar to those mentioned in the case of acrylic acid—namely, by oxidising crotonalcohol or crotonaldehyde, by heating β-hydroxybutyric acid, $CH_3\cdot CH(OH)\cdot CH_2\cdot COOH$, and by treating α-bromobutyric acid with alcoholic potash. It melts at 72°, and resembles acrylic acid in general behaviour.

Oleïc acid, $C_{18}H_{34}O_2$, one of the higher members of the acrylic series, has been previously mentioned (p. 176). It melts at 14° and is odourless, but it oxidises on exposure to the air and becomes rancid.

* This behaviour is abnormal, as the halogen usually combines with that carbon atom which is combined with the *least* number of hydrogen atoms (p. 82).

On oxidation with permanganate it first gives *dihydroxystearic acid*, $C_{18}H_{34}O_2(OH)_2$, and then *azelaïc acid*, $COOH\cdot[CH_2]_7\cdot COOH$,

$$C_{18}H_{34}O_2(OH)_2 + 5O = 2COOH\cdot[CH_2]_7\cdot COOH + H_2O;$$

on reduction with hydriodic acid it is transformed into stearic acid. These facts prove that oleïc acid has the constitution $CH_3\cdot[CH_2]_7\cdot CH=CH\cdot[CH_2]_7\cdot COOH$.

Polyhydric Alcohols.

The existence of tetra-, penta-, and hexa-hydric alcohols, which theoretically should be obtained from the higher paraffins by the substitution of four, five, or six hydroxyl-groups for an equivalent quantity of hydrogen, just as glycerol is derived from propane, was of course to be expected; nevertheless, owing to the difficulties which would be met with in the actual synthesis of such complex substances from the paraffins, or from other compounds, it is highly probable that they might still have been unknown, were it not that many of them occur in nature, and may also be prepared from products of the vegetable kingdom by simple processes.

Erythritol, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$, for example, is a tetrahydric alcohol which occurs in many lichens and in certain seaweeds. *Arabitol* and *xylitol* are *optically isomeric* pentahydric alcohols of the constitution,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH;$$

they may be respectively prepared by reducing *arabinose* and *xylose*, two sugars which occur in various vegetable products, with sodium amalgam and water.

Hexahydric alcohols, such as *mannitol*, *sorbitol*, and *dulcitol*, also occur in nature; these three compounds are *identical* in constitution, and they may all be represented by the formula,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH;$$

they are *optically isomeric* (p. 270; and Part II. p. 606).

Mannitol is found in manna, the dried sap of a species of ash, from which it may be extracted with boiling alcohol; it may also be obtained by reducing mannose or fructose

(pp. 297, 298) with sodium amalgam and water. It is a colourless, crystalline substance, has a sweet taste, and is readily soluble in water and hot alcohol, but insoluble in ether. When carefully oxidised with nitric acid it yields the aldehyde, mannose, and the ketone, fructose; on reduction with hydriodic acid it is converted into (secondary)* hexyl iodide, a derivative of normal hexane,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH + 11HI = CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHI\cdot CH_3 + 6H_2O + 5I_2.$$

This conversion of mannitol (sorbitol and dulcitol) into a derivative of *normal* hexane is a fact of great importance, as it throws light on the constitution not only of mannitol, but also on that of the monosaccharoses (p. 302) in general; since the latter yield one or other of these hexahydric alcohols on reduction with sodium amalgam and water, it is proved that they also are derivatives of *normal* hexane, and not of some secondary or tertiary paraffin, isomeric with hexane.

The constitution of mannitol is further established by the usual methods; that it contains six hydroxyl-groups is shown by the fact that it yields a hexacetyl-derivative, $C_6H_8(O\cdot CO\cdot CH_3)_6$, and a hexanitrate, $C_6H_8(O\cdot NO_2)_6$. As, moreover, it is known from experience that in all stable hydroxy-compounds one carbon atom does not unite with more than one hydroxyl-group, each of the six hydroxyl-groups in mannitol must be combined with a different carbon atom.

CHAPTER XVI.

The Carbohydrates.

The term 'carbohydrate' was originally used to denote certain naturally occurring substances, composed of carbon, hydrogen, and oxygen, in which the ratio of hydrogen to oxygen was the same as in water, because such compounds might be represented as composed of carbon and water in

* The term 'secondary' denotes the fact that the iodide may be regarded as a derivative of a secondary (hexyl) alcohol,

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3.$$

different proportions; the formula of glucose, $C_6H_{12}O_6$, for example, might be written $6C + 6H_2O$, a mode of expression which, if employed now, would be both useless and misleading.

In the course of time many derivatives of these natural products, and many other compounds more or less closely related to them, have been obtained from natural sources, or prepared in the laboratory, and have been classed as carbohydrates; the term, therefore, can hardly be defined, as it embraces compounds which differ widely in constitution.

The carbohydrate-group is one of the more important in organic chemistry, as it includes many of the principal components of plants. To this group belong (*a*) the *sugars*, substances which are of great value as food-stuffs and as sources of alcohol, and to which the sweetness of fruits is due; (*b*) the *starches*, the most abundant of all foods; and (*c*) the *celluloses*, substances of which the cell membranes and tissues of plants are principally composed, and which in the form of cotton, paper, wood, &c., are of the greatest importance in daily life.

The Sugars.

The *sugars* described in the following pages may be classed into two groups: (*a*) the *mono-saccharoses* having the molecular formula, $C_6H_{12}O_6$, and (*b*) the *di-saccharoses* having the molecular formula, $C_{12}H_{22}O_{11}$; the former are not decomposed by very dilute acids, but the latter readily undergo hydrolysis, yielding two molecules of the same or of different mono-saccharoses.

MONO-SACCHAROSES.

Glucose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]^*_4\cdot CHO$, also called **dextrose,** or **grape-sugar,** is found in large quantities in grapes—hence its name, grape-sugar; when the grapes are dried in the sun, in the preparation of raisins, the glucose

* Compare footnote, p. 141.

in the juice is deposited in hard, brownish-coloured nodules. Glucose is more frequently met with associated with fructose, and mixtures of these sugars occur in the juices of a great many sweet fruits, in the roots and leaves of many plants, and in honey. Glucose may be prepared by decomposing sucrose (cane-sugar) with dilute acids (p. 304) and recrystallising the product (invert sugar) from alcohol, when the more readily soluble fructose remains in solution.

A mixture of alcohol (1 litre, 90 per cent.) and concentrated hydrochloric acid (40 c.c.) is heated at about 50°, and powdered sucrose (350 grams) is added in small portions, the whole being well stirred during the operation. The mixture is kept at 50° for two hours, then allowed to cool, and crystallisation is promoted by stirring the solution, or, better, by adding to it a crystal of glucose. After some days the crystals are collected and purified by recrystallisation from 80 per cent. alcohol.

Glucose crystallises with 1 mol. H_2O in warty masses which liquefy at 86°, but the anhydrous substance melts at 146°; it is almost insoluble in absolute alcohol, but it dissolves in about its own weight of water at ordinary temperatures. It is not so sweet as sucrose. It is not carbonised when it is gently warmed with sulphuric acid (distinction from sucrose).

Glucose is dextrorotatory *—that is, it has in solution the property of rotating the plane of polarisation of polarised light to the *right*—hence the name dextrose by which it was formerly known. The quantity of glucose in solution may be estimated by determining the angle of rotation which is produced by a column of the liquid of known length. The apparatus used for this purpose is called a *saccharimeter* or *polarimeter* (p. 262).

Glucose is a strong reducing agent, and quickly precipitates gold, silver, and platinum from warm solutions of their salts. When a solution of glucose to which potassium hydroxide has been added, is mixed with a solution of copper sulphate, a deep-blue liquid is obtained; but when this solution is boiled, a bright-red precipitate of cuprous oxide, Cu_2O, is

* For $C_6H_{12}O_6$, $[\alpha]_D$ +52·6° in 10 per cent. aqueous solution.

deposited, and the solution becomes colourless if sufficient glucose is present; as, moreover, a given quantity (1 molecule) of glucose always reduces exactly the same quantity (approximately 5 molecules) of cupric to cuprous oxide, this behaviour affords a method of *estimating* glucose by titration.

The *standard* solution used for this purpose is known as *Fehling's solution*, and, as it is rather unstable, it is best prepared, as required, by mixing equal quantities of the following solutions:—(1) 34·6 grams of hydrated copper sulphate, made up to 500 c.c. with water; (2) 173 grams of Rochelle salt and 60 grams of sodium hydrate, made up to 500 c.c. with water. 10 c.c. of the deep-blue solution thus obtained are completely reduced by 0·05 gram of glucose, or by 0·0475 gram of sucrose (after inversion). In the estimation of a sugar, the solution of the latter is slowly added to a known volume of the Fehling's solution, which is kept at about 100°, until the blue colour is discharged.

Glucose ferments readily with yeast in dilute aqueous solution at a temperature of about 20–30°, yielding principally alcohol and carbon dioxide,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2;$$

but at the same time small quantities of glycerol, succinic acid, and other substances are formed.

Glucose combines readily with certain metallic hydroxides, forming *glucosates*, such as calcium glucosate, $C_6H_{11}O_6Ca{\cdot}OH$, and barium glucosate, $C_6H_{11}O_6Ba{\cdot}OH$; these compounds are readily soluble in water, and are decomposed by carbonic acid, with regeneration of glucose.

Glucose is slowly transformed into a pentacetyl-derivative, $C_5H_6(O{\cdot}CO{\cdot}CH_3)_5{\cdot}CHO$, when it is warmed with acetic anhydride and a little zinc chloride; this fact shows that its molecule contains five hydroxyl-groups, and glucose, therefore, is a *pentahydric alcohol*; it has also the properties of an *aldehyde*, and its constitution is expressed by the formula,

$$CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CHO,$$

which is based on a number of facts, only a few of which can be given here.

On reduction with sodium amalgam in aqueous solution, it is converted into the primary alcohol, *sorbitol*,

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CHO + 2H = CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH;$$

whereas, on oxidation with bromine water, it yields *gluconic acid*, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot COOH$. These changes are clearly analogous to those undergone by acetaldehyde, and the fact that gluconic acid and glucose contain the same number of carbon atoms in their molecules shows that glucose is an aldehyde and not a ketone (p. 147). Powerful oxidising agents, such as nitric acid, convert glucose into *saccharic acid*, $COOH\cdot[CH\cdot OH]_4\cdot COOH$, the $-CH_2\cdot OH$ group, as well as the –CHO group, undergoing oxidation; on further oxidation, oxalic acid is formed. Glucose, like other aldehydes, reacts readily with hydroxylamine and with phenylhydrazine, with formation of the oxime, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH{:}N\cdot OH$, and the hydrazone (p. 300), $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH{:}N_2H\cdot C_6H_5$, respectively.

Mannose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH(OH)]_4\cdot CHO$, is closely related to glucose, with which it is optically isomeric; it is obtained by oxidising mannitol with nitric acid, and by hydrolysing *seminin* (contained in various vegetable products, such as ivory-nuts) with dilute sulphuric acid.

When glucose is left in contact with a little caustic alkali, in aqueous solution, it is partly transformed into fructose, and the latter is partly transformed into mannose; these reactions are reversible and are summarised in the following scheme,

$$\text{Glucose} \longleftrightarrow \text{Fructose} \longleftrightarrow \text{Mannose}.$$

Galactose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CHO$, is formed by the hydrolysis of lactose, together with glucose, from which it may be separated by crystallisation from water. It is also formed by boiling certain gums with dilute sulphuric acid.

It crystallises in prisms and melts at 168°; it is optically isomeric with glucose and mannose, and its solutions are dextrorotatory, and ferment readily with yeast.

When oxidised with nitric acid, it yields *mucic acid*, $COOH\cdot[CH\cdot OH]_4\cdot COOH$, which is optically isomeric with saccharic acid. It interacts with phenylhydrazine, yielding galactosazone (p. 301),

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(N_2HC_6H_5)\cdot CH{:}N_2HC_6H_5,$$

and on reduction with sodium amalgam and water it is converted into the corresponding alcohol, *dulcitol*, $CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH$, which is optically isomeric with mannitol and sorbitol (p. 292).

Fructose, $C_6H_{12}O_6$, or $CH_2(OH)\cdot[CH\cdot OH]_3\cdot CO\cdot CH_2\cdot OH$, also called **levulose,** occurs, together with glucose, in most sweet fruits and in honey; it may be prepared from invert sugar (p. 305) by taking advantage of the fact that it forms with calcium hydroxide a compound which is sparingly soluble in water, whereas that of glucose (p. 296) is readily soluble.

Invert sugar (10 grams) is dissolved in water (50 c.c.), the solution is well cooled with ice, and slaked lime (6 grams) is stirred into the solution in small quantities at a time. The sparingly soluble lime compound of fructose is collected on a filter, washed with a little water, well pressed, and then suspended in water and decomposed with carbon dioxide; the filtrate, on evaporation, yields nearly pure fructose as a transparent syrup.

Fructose is also prepared from *inulin*, $(C_6H_{10}O_5)n$, a starch which occurs in many plants, especially in dahlia tubers.* An aqueous solution of inulin is heated on a water-bath for one hour, with a few drops of sulphuric acid,

$$(C_6H_{10}O_5)n + nH_2O = nC_6H_{12}O_6.$$

The sulphuric acid is then removed by precipitation with barium hydroxide, and the solution is evaporated at 80°. On the addition of a crystal of fructose, the syrup slowly solidifies, and the crystals may then be purified by recrystallisation from alcohol.

Fructose separates from alcohol in crystals, and melts at 95°; it is more soluble in water and in alcohol than glucose, and its taste is just about as sweet as that of the latter. Fructose is *levorotatory* †—hence the name 'levulose' by which it was formerly known.

* Inulin also occurs in artichokes and in chicory. It is readily soluble in hot water, and is coloured *yellow* by iodine.

† $[\alpha]_D$ −93° in 10 per cent. aqueous solution.

Fructose ferments with yeast, but less rapidly than glucose; consequently, during the fermentation of a solution of invert sugar (p. 305) the glucose is decomposed first, and the operation can be stopped at a point when the solution contains only fructose; by the further action of yeast, however, the fructose also undergoes fermentation, yielding the same products as glucose.

Fructose is a strong reducing agent, and reduces Fehling's solution more rapidly than, although to exactly the same extent as, glucose. This behaviour is due to the presence of the group, $-CO\cdot CH_2\cdot OH$, and all those ketonic alcohols which contain this group, like the aldehydes, are strong reducing agents.

Fructose has the properties of a *pentahydric alcohol*, as well as those of a *ketone*, and its constitution is expressed by the formula,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH.$$

When warmed with acetic anhydride and zinc chloride, it yields a pentacetyl-derivative, $C_6H_7O(O\cdot CO\cdot CH_3)_5$, a fact which shows that its molecule contains five hydroxyl-groups. It is reduced by sodium amalgam and water more readily than glucose, mannitol and sorbitol being formed,

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot CO\cdot CH_2\cdot OH + 2H =$$
$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot CH(OH)\cdot CH_2\cdot OH,$$

just as acetone, under similar treatment, yields isopropyl alcohol. When oxidised with nitric acid or bromine water, it yields tartaric acid and glycollic acid,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH + 4O =$$
$$COOH\cdot CH(OH)\cdot CH(OH)\cdot COOH + COOH\cdot CH_2\cdot OH + H_2O;$$

whereas, when boiled with mercuric oxide in aqueous solution, it is oxidised to trihydroxybutyric acid and glycollic acid,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH + 2O =$$
$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH + COOH\cdot CH_2\cdot OH.$$

This behaviour shows that fructose is a ketone, and not an aldehyde; it does not, like glucose, yield on oxidation an acid containing the same number of carbon atoms, but is decomposed in a variety of ways, giving products which throw light on its constitution.

Fructose, like other ketones, reacts with hydroxylamine, yielding the oxime, $CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(N\cdot OH)\cdot CH_2\cdot OH$, and also with phenylhydrazine (see below).

Glucose and fructose have been prepared synthetically from formaldehyde and also from glycerol. When an aqueous solution of formaldehyde is treated with milk of lime at ordinary temperatures, a sugar-like substance called *methylenitan* (Butlerow) or *formose* (Loew) is produced. Methylenitan and formose consist of mixtures of various sugars of the composition, $C_6H_{12}O_6$, produced by the polymerisation of formaldehyde,

$$6CH_2O = C_6H_{12}O_6.$$

From these mixtures E. Fischer isolated a sugar, which he called *α-acrose;* and from this sugar, by a series of operations briefly described later (Part II. p. 615), he succeeded in preparing both glucose and fructose.

α-Acrose was also obtained by E. Fischer and Tafel from *glycerose*, which is a mixture of *glyceraldehyde*, $CH_2(OH)\cdot CH(OH)\cdot CHO$, and *dihydroxyacetone*, $CH_2(OH)\cdot CO\cdot CH_2\cdot OH$, prepared by carefully oxidising glycerol with bromine water or dilute nitric acid; when glycerose is treated with caustic soda it undergoes condensation, giving a mixture of sugars, among others, α-acrose.

Action of Phenylhydrazine on Glucose and Fructose.

When glucose and fructose are treated with phenylhydrazine (1 mol.), they yield hydrazones, just as do other aldehydes and ketones (p. 140),

$$^*M\cdot CH(OH)\cdot CHO + C_6H_5\cdot NH\cdot NH_2 =$$

Glucose.

$$M\cdot CH(OH)\cdot CH{:}N_2HC_6H_5 + H_2O,$$

Glucosephenylhydrazone.

$$M\cdot CO\cdot CH_2\cdot OH + C_6H_5\cdot NH\cdot NH_2 = M\cdot C(N_2HC_6H_5)\cdot CH_2\cdot OH + H_2O.$$

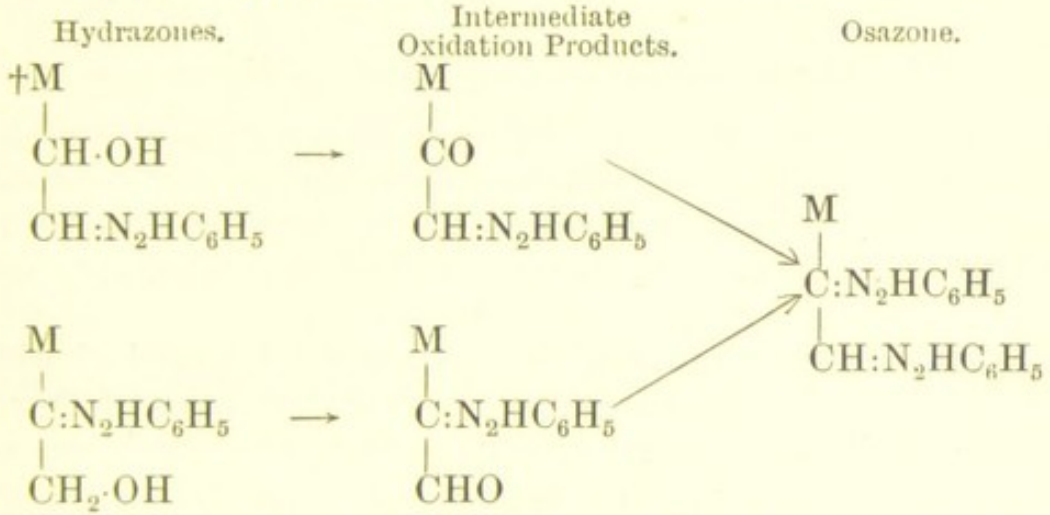
Fructose. Fructosephenylhydrazone.

The group, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)$-, which takes no part in the reaction, is represented by M, for the sake of clearness.

These hydrazones, when heated with excess of phenylhydrazine, undergo oxidation, the $>CH\cdot OH$ group of the one and the $-CH_2\cdot OH$ group of the other being transformed into $>CO$ and $-CHO$ respectively, by loss of hydrogen, which reduces some of the phenylhydrazine to aniline (Part II. p. 402) and ammonia,

$$C_6H_5\cdot NH\cdot NH_2 + 2H = C_6H_5\cdot NH_2 + NH_3.$$

The ketone or aldehyde thus formed then reacts with a second molecule of phenylhydrazine, with formation of an *osazone*.*



Although the hydrazones of glucose and fructose are quite distinct substances, they yield one and the same osazone; this fact proves that the two sugars differ in constitution only as regards the two groups which take part in the formation of the osazone.

Many other sugars yield hydrazones or osazones according as 1 mol., or excess, of phenylhydrazine is employed. The hydrazones are usually readily soluble in water, but the osazones are only sparingly soluble; the latter, therefore, are of the greatest service, not only in the detection and identification of a sugar, but also as offering a means of separating it from a mixture (Part II. p. 615).

When treated with strong hydrochloric acid, the osazones are decomposed with separation of phenylhydrazine hydrochloride, and formation of *osones*, substances which contain the group, $-CO\cdot CHO$, and which are therefore *both* ketones *and* aldehydes,

$$M\cdot C(N_2HC_6H_5)\cdot CH:N_2HC_6H_5 + 2HCl + 2H_2O =$$
Glucosazone.

$$M\cdot CO\cdot CHO + 2C_6H_5\cdot NH\cdot NH_2,\ HCl.$$
Glucosone.

As, moreover, osones may be reduced to sugars with the aid of zinc dust and acetic acid, the osazones, also, may be indirectly recon-

* The practical details of the preparation of an osazone are given later (Part II. p. 423).

† See footnote, p. 300.

verted into sugars. A given osazone, however, does not necessarily yield the sugar from which it was derived; glucosazone, for example, yields first glucosone and then fructose, the group $-CO\cdot CHO$ in the osone being converted into $-CO\cdot CH_2\cdot OH$,

$$\underset{\text{Glucosone.}}{M\cdot CO\cdot CHO} + 2H = \underset{\text{Fructose.}}{M\cdot CO\cdot CH_2\cdot OH}.$$

This series of reactions, therefore, affords a means of converting glucose into fructose (E. Fischer).

The Constitutions of the Mono-saccharoses.

That the mono-saccharoses are either aldehydes (aldoses) or ketones (ketoses) is shown by their behaviour on oxidation and reduction, and also by the fact that they react with phenylhydrazine, hydroxylamine, &c.; that they contain five hydroxyl-groups is proved by their conversion into pentacetyl-derivatives.

Their constitutions are further determined by a method which was worked out by Kiliani, and which is based on the following reactions:—The mono-saccharoses, like the simpler aldehydes and ketones, combine directly with hydrogen cyanide, forming cyanohydrins,

$$M\cdot CHO + HCN = M\cdot CH(OH)\cdot CN$$
$$M\cdot CO\cdot CH_2\cdot OH + HCN = M\cdot C(OH)(CN)\cdot CH_2\cdot OH,$$

and these products are converted into polyhydric *acids* on hydrolysis with a mineral acid,

$$M\cdot CH(OH)\cdot CN + 2H_2O = M\cdot CH(OH)\cdot COOH + NH_3$$
$$M\cdot C(OH)(CN)\cdot CH_2\cdot OH + 2H_2O = M\cdot C(OH)(COOH)\cdot CH_2\cdot OH + NH_3.$$

When these polyhydric acids are heated at a high temperature with a large excess of hydriodic acid and a little red phosphorus, all the hydroxyl-groups in the molecule are displaced by hydrogen atoms—that is to say, complete reduction of all the $>CH\cdot OH$ and $-CH_2\cdot OH$ groups is effected, and a fatty acid is obtained. In the case of the polyhydric acid prepared from glucose cyanohydrin, this change is represented by the equation,

$$CH_2(OH)\cdot[CH\cdot OH]_4\cdot CH(OH)\cdot COOH + 12HI =$$
$$CH_3\cdot[CH_2]_4\cdot CH_2\cdot COOH + 6H_2O + 6I_2,$$

and *normal* heptylic acid is obtained; whereas from the corresponding polyhydric acid prepared from fructose cyanohydrin, methylbutylacetic acid, an isomeride of normal heptylic acid, is formed,

$$CH_2(OH)\cdot[CH\cdot OH]_3\cdot C(OH)(COOH)\cdot CH_2\cdot OH + 12HI =$$
$$CH_3\cdot[CH_2]_3\cdot CH(COOH)\cdot CH_3 + 6H_2O + 6I_2.$$

These facts show that glucose is an aldehyde and a derivative of

normal hexane. Had it been a ketone, the polyhydric acid produced from it could not have contained the group, $-CH(OH)\cdot COOH$, but must have contained the group, $\begin{matrix}-CH(OH)\\-CH(OH)\end{matrix}\!>\!C(OH)\cdot COOH$; this, on reduction, would have been transformed into

$$\begin{matrix}-CH_2\\-CH_2\end{matrix}\!>\!CH\cdot COOH,$$

and consequently the fatty acid finally produced would not have been normal heptylic acid, but one of its isomerides. Obviously, also, the conversion of fructose into methylbutylacetic acid, taken in conjunction with other facts, shows that this sugar is a ketone and not an aldehyde, and that its constitution is expressed by the formula already given (p. 298). In addition to this evidence, the fact that glucose and fructose may be converted into secondary hexyl iodide (p. 293) shows them to be derivatives of normal hexane.

Both galactose and mannose are aldehydes (aldoses), identical with glucose in constitution.

DI-SACCHAROSES.

Sucrose, or **cane-sugar,** $C_{12}H_{22}O_{11}$, is very widely distributed in nature; it occurs in large quantities in the ripe sugar-cane (15–20 per cent.) and in beetroot (some kinds of which contain as much as 16 per cent.), in smaller quantities in strawberries, pine-apples, and other fruits.

Practically the whole of the sucrose of commerce is manufactured from beetroot and from the sugar-cane; the processes of extraction are much the same in both cases, and expensive apparatus is required in order to obtain the largest possible yield of crystallised sucrose.

The sugar-canes are crushed in hydraulic presses; but the beetroots are cut into slices, and the sugar is extracted by a diffusion process. The expressed juice, or the sugar solution, is heated with about 1 per cent. of milk of lime in order to neutralise acids present, and to coagulate the vegetable proteïns which are always contained in the extract and which would undergo fermentation. The solution is treated with carbon dioxide in order to precipitate any excess of lime, boiled with animal charcoal in order to decolourise it as far as possible, and filtered; it is then evaporated under reduced pressure, in an apparatus heated with steam, until

the syrup is of such a consistency that it deposits crystals on being cooled. These crystals are separated from the brown mother-liquor (*molasses*, or treacle) in a centrifugal machine, and purified by recrystallisation from water.

The molasses still contain about 50 per cent. of sucrose, which does not crystallise from the syrup even on further evaporation, owing to the presence of impurities; nearly the whole of this sucrose, however, can be profitably extracted by adding strontium hydroxide ($\frac{1}{2}$ mol.), and separating the insoluble strontium sucrosate (see below) from the dark mother-liquor by filtration. This precipitate is suspended in water, decomposed with carbon dioxide, and the filtrate from the strontium carbonate is evaporated to a syrup; the impurities having been removed, the sucrose separates in a crystalline form. The annual production of sucrose is now about 16 million tons.

Sucrose crystallises from water in large four-sided prisms (sugar-candy), and is soluble in one-third of its weight of water at ordinary temperatures, but is only sparingly soluble in alcohol. It melts at about 160–161°, and does not immediately crystallise when it is cooled again, but solidifies to a pale-yellow, glassy mass, called *barley-sugar*, which, however, becomes opaque and crystalline in the course of time. At about 200–210° sucrose loses water, and is gradually converted into a brown mass, called *caramel*, which is largely used for colouring liqueurs, soups, gravies, &c.

Warm concentrated sulphuric acid chars sucrose; when a strong aqueous solution of sucrose is mixed with an equal volume of concentrated sulphuric acid, the mixture blackens and the carbonaceous product froths up, owing to the evolution of steam, carbon dioxide, and sulphur dioxide.

Sucrose is readily hydrolysed by dilute mineral acids, with formation of equal quantities of glucose and fructose,

$$\underset{\text{Sucrose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Now, since fructose rotates the plane of polarisation to the left to a somewhat greater extent than glucose rotates it to the right, the product, which consists of equal parts of glucose and fructose, is slightly levorotatory. When, there-

fore, a solution of sucrose, which is *dextrorotatory*,* is boiled with acids, the resulting solution is *levorotatory*—that is to say, the direction of the rotation has been reversed or 'inverted.' Hence the hydrolysis of sucrose is usually called *inversion*, and the mixture of glucose and fructose is called *invert sugar*.

Invert sugar comes on the market as a somewhat brownish mass, and is extensively used in the manufacture of preserves, confectionery, &c., as well as for the preparation of alcohol.

Sucrose does not reduce Fehling's solution (p. 296); when it is boiled for a long time with hydrochloric acid (sp. gr. 1·1) it yields levulic acid (p. 205). The action of yeast on a solution of sucrose has already been explained (p. 102); the enzyme, *invertase*, which is present in the yeast, converts the sucrose into glucose and fructose, and then the enzyme, *zymase*, brings about alcoholic fermentation.

When boiled with acetic anhydride and sodium acetate, sucrose is converted into *octacetylsucrose*, $C_{12}H_{14}O_3(O{\cdot}CO{\cdot}CH_3)_8$, and therefore its molecule contains eight hydroxyl-groups; this fact, and the behaviour of sucrose on hydrolysis, show that it is formed, together with one molecule of water, by the combination of one molecule of glucose with one molecule of fructose.

Sucrose reacts readily with certain hydroxides, such as those of calcium, barium, and strontium, with formation of metallic compounds, called sucrosates (*saccharosates*), in which one or more of the hydrogen atoms of the hydroxyl-groups in the sucrose is displaced by a basic radicle such as –Ca·OH. These sucrosates are produced by adding the metallic hydroxide to the sucrose solution. They are readily decomposed by much water and by carbon dioxide into sucrose and the hydroxide or carbonate of the metal.

Strontium sucrosate, $C_{12}H_{20}(SrOH)_2O_{11}$, is a granular substance of great commercial importance, owing to its use in separating sucrose from molasses (p. 304).

Maltose, $C_{12}H_{22}O_{11}$, is produced together with dextrin

* $[\alpha]_D = +66{\cdot}5°$ in 10 per cent. aqueous solution.

(p. 310) by the action of malt on starch; this change may be roughly represented by the equation,

$$3(C_6H_{10}O_5)n + nH_2O = nC_{12}H_{22}O_{11} + nC_6H_{10}O_5,$$

and, as already stated in describing the manufacture of alcohol and spirituous liquors, it is brought about by an enzyme, *diastase*, which is contained in the malt.

Preparation of Maltose.—Potato starch (1 kilo) is heated with water (4 litres) on a water-bath until it forms a paste; the product is cooled to 60°, malt (60 grams) is added, and the mixture is kept at this temperature for an hour. The solution is then heated to boiling, filtered, and evaporated to a syrup, which crystallises on the addition of a crystal of maltose; the crude substance is washed with alcohol, and then recrystallised from this solvent.

Maltose crystallises with one molecule of water in needles, and is very soluble in water, the solution being strongly dextrorotatory;* it reduces Fehling's solution, and ferments readily with yeast (p. 102). When boiled with dilute sulphuric acid, it is converted into glucose *only*,

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6,$$

a change which indicates that maltose is a condensation product of the latter.

Maltose reacts with phenylhydrazine, yielding *maltosazone*, $C_{12}H_{20}O_9(N_2HC_6H_5)_2$, and gives with acetic anhydride *octacetyl-maltose*, $C_{12}H_{14}O_3(C_2H_3O_2)_8$.

Lactose, or *milk-sugar*, $C_{12}H_{22}O_{11}$, so far, has been found in the animal kingdom only. It occurs in the milk of all mammals to the extent of about 4 per cent., and is obtained as a by-product in the manufacture of cheese.

When milk is treated with rennet the *caseïn* separates, and lactose remains in solution; on evaporation, the crude sugar is deposited in crystals, which are readily purified by re-crystallisation from water.

Lactose crystallises with one molecule of water and dissolves in six parts of water at ordinary temperatures; it

* For $C_{12}H_{22}O_{11},H_2O$, $[\alpha]_D + 139°$ in 10 per cent. aqueous solution.

is very much less sweet than sucrose, and is dextrorotatory.* It reduces Fehling's solution, but much more slowly than does glucose. Lactose does not ferment readily with yeast, but it rapidly undergoes lactic fermentation (p. 162) under suitable conditions. It is decomposed, by boiling dilute sulphuric acid, into *glucose* and *galactose*,

$$\underset{\text{Lactose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Galactose.}}{C_6H_{12}O_6}.$$

When oxidised with nitric acid, it yields a mixture of saccharic and mucic acids, both of which have the constitution $COOH{\cdot}[CH{\cdot}OH]_4{\cdot}COOH$; but whereas saccharic acid is dextrorotatory, mucic acid is optically inactive.

POLY-SACCHAROSES.

Starch, dextrin, and cellulose are all highly complex substances, the molecules of which seem to consist of combinations of the molecules of the mono- or di-saccharoses, with loss of the elements of water; they are therefore classed together as *poly-saccharoses*.

Starch, or amylum, $(C_6H_{10}O_5)n$, is widely distributed throughout the vegetable world, and is found in almost all the organs of plants in the form of grains or nodules.

It occurs in large quantities in all kinds of grain, as, for example, in rice, barley, and wheat, and also in tubers, such as potatoes and arrowroot. In Europe, starch is manufactured principally from potatoes, but sometimes also from wheat, maize, and rice.

The potatoes are well washed, crushed, and macerated with water in fine sieves, when the starch passes through with the water, leaving a pulp, consisting of gluten, cellulose, and other substances. The milky liquid deposits the starch as a paste, which is repeatedly washed by decantation, and then slowly dried.

The grain is first soaked in warm water, then ground in a mill, and the product is run into a large vat, where it is allowed to undergo lactic fermentation. During this process the sugar in the grain is converted into lactic, butyric, and acetic acids, and the

* For $C_{12}H_{22}O_{11},H_2O$, $[\alpha]_D + 52{\cdot}5°$ in 10 per cent. aqueous solution.

gluten (see below) is brought into a less tenacious condition, which favours the subsequent washing of the starch, an operation which is carried out in the manner described above.

Starch is a white powder, which, when examined under the miscroscope, is seen to be made up of peculiarly striated

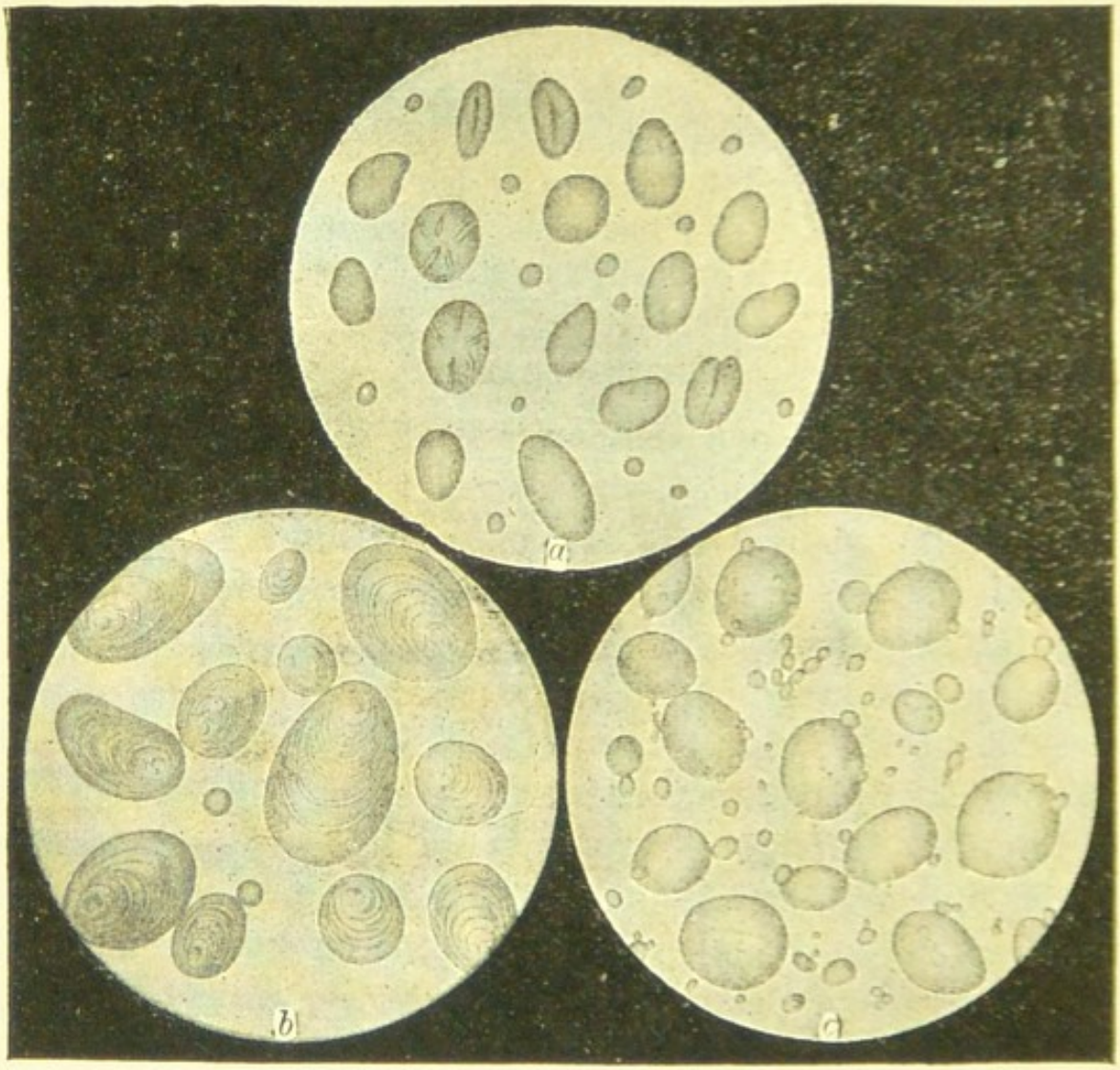


Fig. 25.

(*a*) Barley Starch ; (*b*) Potato Starch ; (*c*) Wheat Starch.

granules, having a definite shape and structure. Granules from different plants vary very much in appearance and in size, as shown above* (magnified 350 diameters), those of potato starch being comparatively large, those of barley starch considerably smaller.

* From *The Microscope in the Brewery.*

Starch is insoluble in cold water, but when heated with water the granules swell up and then burst. The contents of the cells, or the *granulose*, dissolves, but the cell-wall, or *starch cellulose*, is insoluble, and can be separated by filtration; on the addition of alcohol to the filtrate, the granulose is precipitated as an amorphous powder, which is known as *soluble starch*.

The gelatinous mass obtained when starch is heated with water is called *starch paste*, and is largely used for stiffening linen and calico goods, and also as a substitute for gum. It is best prepared by rubbing starch into a thin paste with cold water, and then adding a considerable quantity of boiling water.

Characteristic of starch is the brilliant blue colour, which is produced when a solution of iodine is added to starch paste, or to its solution in water; the colour disappears when the solution is heated, but reappears when the temperature falls again.

When boiled with dilute acids, starch is first converted into *dextrin*, $(C_6H_{10}O_5)n$, and then into *glucose*,

$$(C_6H_{10}O_5)n + nH_2O = nC_6H_{12}O_6.$$

Malt extract, which contains the enzyme, *diastase*, decomposes starch at 60–70°, with formation of *dextrin* and *maltose*,

$$3C_6H_{10}O_5 + H_2O = C_6H_{10}O_5 + C_{12}H_{22}O_{11},$$

a process which, as already mentioned (p. 103), is of the utmost importance in the manufacture of alcohol and of spirituous liquors from grain.

Since the molecule of starch is probably produced by the combination of n molecules of a monosaccharose, with elimination of $n-1$ molecules of water, its empirical formula is probably $n(C_6H_{12}O_6) - (n-1)H_2O$, and not $C_6H_{10}O_5$. As, however, n is doubtless a very large number, possibly greater than 200, the formula, $C_6H_{10}O_5$, gives the composition of starch very closely, and also serves to express its decomposi-

tion into dextrin and maltose. The empirical formula of dextrin (and that of cellulose) may be written in the same way as that of starch, but n is obviously a smaller number in the case of the dextrin formula than in that of starch.

Glycogen, or animal starch, $(C_6H_{10}O_5)n$, occurs in the liver, muscle, and white corpuscles, and is a substance of great physiological importance. It resembles ordinary starch in that it is a white, tasteless, odourless powder; but it gives a red colouration with iodine, and is almost entirely soluble in water to an opalescent liquid; on hydrolysis with dilute mineral acids it yields glucose.

Gluten.—Wheaten flour contains about 70 per cent. of starch and 10 per cent. of a sticky, nitrogenous substance called *gluten*. An approximate separation of these two components may be brought about by kneading flour in a thin calico bag under water, when the starch passes through with the water, forming a milky liquid, from which the starch is slowly deposited. The gluten remains in the bag as a tenacious, sticky, gray mass, which soon decomposes and smells disagreeably.

Both starch and gluten are very valuable food-stuffs.

Dextrin, $(C_6H_{10}O_5)n$, is the name given to the substance, or mixture of substances, obtained as an intermediate product in the conversion of starch into glucose (see above). It is produced by heating starch to about 210°, or by treating it with dilute acids or with malt extract.

Dextrin is a colourless, amorphous substance, soluble in water, and is largely used as a substitute for gum; when boiled with dilute acids it is converted into *glucose*.

Dextrin is probably a mixture of various substances (amylodextrins, maltodextrins), the compositions of which are approximately expressed by the *empirical* formula, $C_6H_{10}O_5$.

Cellulose, $(C_6H_{10}O_5)n$, like starch, occurs very widely distributed throughout the vegetable kingdom. It is the principal component of cell membrane and of wood, and constitutes, indeed, the framework of all vegetable tissues.

Linen, cotton-wool, hemp, and flax, which have been freed from inorganic matter by repeated extraction with acids, consist of almost pure cellulose; a less impure form may be

obtained by extracting Swedish filter-paper with hydrofluoric acid, in order to remove traces of silica, washing well with water, and drying at 100°.

Cellulose is insoluble in all the ordinary solvents, but it dissolves in an ammoniacal solution of cupric oxide (Schweitzer's reagent). It is reprecipitated from this solution on the addition of acids, in the form of a jelly, which, when washed with water and dried, is obtained in the form of an amorphous powder.

Concentrated sulphuric acid gradually dissolves cellulose, and if the solution is diluted with water and boiled, dextrin and ultimately dextrose are produced. It is thus possible to obtain sugar, and also alcohol, from wood.

When unsized paper is immersed in concentrated sulphuric acid for a few seconds, and is then washed with water and dilute ammonia, and again with water, it is converted into a tough substance called *parchment paper* on account of its resemblance to parchment. Such paper serves as a convenient substitute for animal membrane, and is used for a variety of purposes.

Cellulose gives on analysis results agreeing with the formula, $C_6H_{10}O_5$, but its molecular formula is certainly very much greater than this, and is therefore written $(C_6H_{10}O_5)n$, or $(C_{12}H_{20}O_{10})n$.

When heated with acetic anhydride at 180°, it yields *cellulose hexacetate*, $C_{12}H_{14}O_4(O{\cdot}CO{\cdot}CH_3)_6$, a white flocculent mass.

Gun-Cotton, Cordite, Artificial Silk.—When *purified* cotton-wool is treated with nitric acid, or, better, with a mixture of nitric and sulphuric acids, nitrates of cellulose of variable composition are produced, according to the quantity and concentration of the acids employed, and the length of time during which they are allowed to act.

If cotton-wool is soaked in ten parts of a mixture of one part of nitric acid (sp. gr. 1·5) and three parts of concentrated sulphuric acid for twenty-four hours, and is then thoroughly

washed the product is *gun-cotton.** This substance has, approximately, the composition, $C_{12}H_{14}(NO_3)_6O_4$, and is, therefore, cellulose hexa-nitrate. It is insoluble in a mixture of alcohol and ether.

Gun-cotton burns rapidly and quietly, without smoke, when a flame is applied to it, but when fired with a detonator it explodes with great violence; it is used as an explosive, either alone or mixed with nitro-glycerin, the mixture being known as *ballistite* or blasting-gelatin.

Cordite is a mixture of gun-cotton and nitro-glycerin, made into a gelatinous mass by the addition of acetone and vaseline, and then worked into threads; it is used as a smokeless powder.

Celluloid is a mixture of cellulose nitrates (principally the lower nitrates) and camphor, which has been heated at about 110° under great pressure; although readily combustible, it is not explosive.

When treated with nitric and sulphuric acids for a short time only, cellulose is converted principally into *tetra-nitrate*, $C_{12}H_{16}(NO_3)_4O_6$, and *penta-nitrate*, $C_{12}H_{15}(NO_3)_5O_5$, both of which dissolve in a mixture of alcohol and ether; a solution of the mixed nitrates in alcohol and ether constitutes *collodion*, which is largely used for photographic and other purposes.

The nitrates of cellulose are decomposed by alkalis, yielding nitrates of the alkalis and cellulose; they are, therefore, true esters and not nitro-derivatives (p. 287).

Artificial silk is the name given to various fibres which are now manufactured in large quantities from wood-cellulose; these materials have many of the physical properties of natural silk (the product of the silkworm), but differ entirely from the latter in composition.

In the manufacture of artificial silk, wood-pulp is heated

* Gun-cotton is best dried with the aid of alcohol; it is dangerous to heat it, even at relatively low temperatures. The dry substance *may* be exploded by friction.

under pressure with a solution of calcium hydrogen sulphite (or is treated in other ways) in order to free it from gum, oil, &c. The purified cellulose is then dissolved in an ammoniacal solution of cupric oxide; or it is converted into cellulose nitrates, or acetates, or xanthogenates (*viscose*), and solutions of these derivatives in some suitable solvent are prepared. The solution of the cellulose, or of one of the derivatives just named, is then forced through capillary tubes into some liquid which precipitates the cellulose or cellulose-derivative from its solution; the precipitate is thus obtained in the form of very fine fibres, which are then spun and made into fabrics.*

Artificial silk is highly lustrous and can be easily dyed, but in strength and durability the products manufactured up to the present time are not equal to natural silk.

CHAPTER XVII.

Cyanogen Compounds and their Derivatives.

The cyanogen compounds contain the univalent radicle, cyanogen, –C:N (Gay-Lussac), and may be considered as derivatives of cyanogen, $(CN)_2$; in many respects they are closely related to the corresponding halogen-derivatives, although they contain the univalent *group of atoms*, –CN, in the place of a *single atom* of halogen, (–Cl), as shown by the following examples,

Cl_2, HCl, KCl, AgCl, $HgCl_2$, HO·Cl, C_2H_5·Cl
$(CN)_2$, HCN, KCN, AgCN, $Hg(CN)_2$, HO·CN, C_2H_5·CN.

This fact brings out very clearly the meaning of the term 'radicle;' the univalent group, –CN,† plays much the same

* The material made from cellulose nitrates is first 'de-nitrated' with ammonium sulphide, &c.; otherwise it would remain highly inflammable.

† Cy is sometimes used to represent the cyanogen radicle, –CN.

part as the atom of chlorine, just as the radicle ammonium may play the part of a single atom of an alkali metal.

Cyanogen, $N{\equiv}C{-}C{\equiv}N$, is produced when ammonium oxalate is strongly heated with phosphoric anhydride,

$$NH_4OOC{\cdot}COONH_4 = N{\equiv}C{-}C{\equiv}N + 4H_2O,$$

a reaction which shows that cyanogen is the nitrile (p. 322) of oxalic acid.

A mixture of anhydrous ammonium oxalate and phosphoric anhydride is heated in a glass tube sealed at one end, and the products are collected in a solution of potassium hydroxide (see below); the latter is then tested for cyanide (p. 16).

Cyanogen is prepared* by heating silver cyanide or mercuric cyanide (p. 319) in a hard glass tube, the gas being collected over mercury,

$$Hg(CN)_2 = Hg + C_2N_2.$$

During the operation a considerable quantity of a brown amorphous substance, $(CN)n$, called *paracyanogen*, is produced; this compound is a polymeride of cyanogen, and when heated at a high temperature it is completely resolved into cyanogen gas, just as trioxymethylene (metaformaldehyde) is converted into formaldehyde under like conditions (p. 126).

Cyanogen is also prepared by heating potassium cyanide with cupric sulphate in aqueous solution; the cupric cyanide, which is first precipitated, undergoes decomposition into cyanogen and cuprous cyanide (compare behaviour of potassium iodide with cupric sulphate),

$$4KCN + 2CuSO_4 = (CN)_2 + 2CuCN + 2K_2SO_4.$$

Cyanogen is a colourless, easily liquefiable gas; it has a peculiar smell, is excessively *poisonous*, and burns with a characteristic purple or peach-coloured flame, yielding carbon dioxide and nitrogen.

It is moderately soluble in water, readily in alcohol, but its aqueous solution soon decomposes, and a brown amorphous

* Owing to the highly poisonous character of cyanogen and many of its derivatives, great care should be observed in their preparation.

precipitate ('azulmic acid') is deposited; the solution then contains ammonium oxalate and other substances.

When cyanogen is treated with hydrochloric acid, it is first converted into oxamide, and then into oxalic acid (and ammonium chloride),

$$N{\equiv}C{-}C{\equiv}N + 2H_2O = NH_2{\cdot}CO{\cdot}CO{\cdot}NH_2,$$
$$NH_2{\cdot}CO{\cdot}CO{\cdot}NH_2 + 2H_2O = HOOC{\cdot}COOH + 2NH_3;*$$

these changes are the reverse of those which occur when ammonium oxalate is heated with phosphoric anhydride.

All substances which contain the cyanogen-group behave in a similar manner, and are converted on hydrolysis into carboxylic acids or their salts, *amides* being formed as intermediate products; *this is a very important general reaction.*

Cyanogen is readily absorbed by a solution of potassium hydroxide, potassium cyanide and cyanate being produced,

$$C_2N_2 + 2KOH = KCN + KOCN + H_2O,$$

just as potassium chloride and hypochlorite are formed from chlorine and potassium hydroxide,

$$Cl_2 + 2KOH = KCl + KOCl + H_2O.$$

Cyanogen chloride, CNCl, is formed by the action of chlorine on a solution of hydrogen cyanide,

$$HCN + Cl_2 = CNCl + HCl.$$

It is a very poisonous liquid, boils at 15·5°, and readily undergoes spontaneous polymerisation into *cyanuric chloride*, $C_3N_3Cl_3$, which melts at 146°, and is decomposed by aqueous alkalis, yielding cyanuric acid,

$$C_3N_3Cl_3 + 3H_2O = C_3N_3(OH)_3 + 3HCl.$$

Cyanuric acid is a crystalline tribasic acid; on distillation it is converted into cyanic acid (p. 323).

Hydrogen cyanide (hydrocyanic or prussic acid), H·C:N, was discovered by Scheele, and is found in the free state in plants, sometimes in considerable quantities; more frequently it occurs in combination with glucose and benzaldehyde in

* Compare footnote, p. 150.

the form of a glucoside,* known as *amygdalin.* Bitter almonds and cherry-kernels contain this glucoside; when they are macerated and kept in contact with water, the amygdalin is decomposed by an enzyme, *emulsin*,† into hydrogen cyanide, benzaldehyde, and glucose,

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde.}}{C_7H_6O} + HCN + 2\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

Hydrogen cyanide is formed when carbon is heated very strongly (at 2000°) in a mixture of hydrogen and nitrogen. It is also produced when ammonium formate is heated with phosphoric anhydride; this change is analogous to the formation of cyanogen from ammonium oxalate, and may be demonstated in a similar manner (p. 314),

$$H{\cdot}COONH_4 = HCN + 2H_2O.$$

Hydrocyanic acid is prepared by distilling potassium cyanide, or, more usually, potassium ferrocyanide, with dilute sulphuric acid,

$$KCN + H_2SO_4 = KHSO_4 + HCN,$$

$$\underset{\text{Potassium Ferrocyanide.}}{2K_4Fe(CN)_6} + 3H_2SO_4 = 6HCN + \underset{\text{Ferrous Potassioferrocyanide.}}{FeK_2Fe(CN)_6} + 3K_2SO_4;$$

in the latter reaction, only half of the potassium ferrocyanide yields hydrogen cyanide.

Powdered potassium ferrocyanide (10 parts) is mixed with concentrated sulphuric acid (7 parts) previously diluted with water (10–40 parts, according to the desired strength of the hydrocyanic acid), and the mixture is distilled from a retort connected with a condenser. The anhydrous acid may be prepared from the aqueous solution thus obtained by fractional distillation and dehydration over calcium chloride, but very special precautions must be taken to avoid accidents with this readily volatile poison.

Anhydrous hydrogen cyanide is a colourless liquid; it boils at 25°, and solidifies in a freezing mixture to colourless

* The term *glucoside* is applied to all those vegetable products which, on treatment with acids or alkalis, yield a sugar, or some closely allied carbohydrate, and one or more other substances (frequently phenols or aromatic aldehydes) as decomposition products (compare Part II. p. 619).

† Emulsin occurs naturally in bitter almonds and cherry-kernels.

crystals, which melt at −12°; it has an odour similar to that of oil of bitter almonds, and burns with a pale blue flame, with formation of carbon dioxide, water, and nitrogen. It is a terrible poison, very small quantities of the liquid or of its vapour being sufficient to cause death.*

Hydrogen cyanide dissolves readily in water, but the solution rapidly decomposes, with separation of a brown substance, and the liquid then contains ammonium formate and other compounds,

$$HCN + 2H_2O = H{\cdot}COONH_4.$$

This hydrolysis takes place only slowly if a trace of some mineral acid is present, more quickly if the solution is heated with mineral acids or alkalis.

On reduction with nascent hydrogen, hydrogen cyanide is converted into methylamine,

$$HCN + 4H = CH_3{\cdot}NH_2.$$

The *constitution* of hydrogen cyanide may be expressed by the formula H·C⋮N for the following reasons:—The acid is produced from ammonium formate, by a change similar to that by which methyl cyanide is formed from ammonium acetate (p. 322),

$$H{\cdot}COONH_4 = H{\cdot}CN + 2H_2O,$$
$$CH_3{\cdot}COONH_4 = CH_3{\cdot}CN + 2H_2O;$$

when heated with alkalis it is converted into formic acid, just as methyl cyanide is converted into acetic acid,

$$H{\cdot}CN + 2H_2O = H{\cdot}COOH + NH_3,$$
$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + NH_3.$$

As, moreover, many facts show that the methyl-group in methyl cyanide and in acetic acid is directly united with carbon, it would seem probable that the hydrogen atom in hydrogen cyanide is in a similar state of combination.

Hydrogen cyanide is sometimes called formonitrile, the nitrile of formic acid; the name of a nitrile is derived from that of the acid into which the nitrile is converted by hydrolysing agents.

* As an antidote, hydrogen peroxide may be used.

Hydrocyanic acid is a feeble acid, and scarcely reddens blue litmus. It forms salts with the hydroxides (but not with the carbonates) of potassium, sodium, and many other metals; the alkali salts are decomposed by carbon dioxide with liberation of the acid, for which reason potassium cyanide, for example, in contact with moist air, always smells of hydrogen cyanide.

Potassium cyanide, KCN, may be obtained synthetically by gently heating potassium in cyanogen. It is prepared on the large scale by strongly heating potassium ferrocyanide alone, or with potassium carbonate, out of contact with the air,

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2,$$

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe.$$

After the iron carbide or iron has settled, the fused potassium cyanide is run off. In the first process the separation is incomplete, and the product must be purified by dissolving it in alcohol or acetone and evaporating the filtered solution; in the second process the product contains a considerable quantity of cyanate, part of which may be reduced to cyanide by adding powdered charcoal to the fused mixture.

Sometimes a mixture of sodium and potassium cyanides is manufactured by fusing potassium ferrocyanide with sodium,

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The pure salt may be prepared by passing hydrogen cyanide into alcoholic potash, and separating the crystals which are precipitated.

Potassium cyanide crystallises in colourless plates, and is very readily soluble in water, but nearly insoluble in absolute alcohol; it is extremely poisonous.

Fused potassium cyanide is a powerful reducing agent; it liberates the metals from many metallic oxides, being itself converted into potassium cyanate,

$$KCN + PbO = KCNO + Pb,$$

hence its use in analytical chemistry and in some metallurgical operations; it is also used in large quantities in extracting gold from poor ores and 'tailings' by the MacArthur-Forrest cyanide process.*

* *Inorganic Chemistry*, Kipping and Perkin.

An aqueous solution of potassium cyanide gives, with silver nitrate, a curdy white precipitate of *silver cyanide*, AgCN, which is insoluble in dilute acids, but which is converted into soluble compounds by ammonium hydroxide and by potassium cyanide; silver cyanide is thus very similar in its properties to silver chloride, from which, however, it differs in this, that when heated it is decomposed completely into silver and cyanogen,

$$2AgCN = 2Ag + C_2N_2.$$

Mercuric cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in hydrocyanic acid,

$$HgO + 2HCN = Hg(CN)_2 + H_2O.$$

The solution, on evaporation, deposits the salt in colourless crystals, which are moderately soluble in water; when strongly heated, the salt is decomposed into mercury and cyanogen.

Mercuric cyanide does not show the ordinary reactions of a mercuric salt or those of a cyanide; in aqueous solution it is not ionised to an appreciable extent.

The detection of hydrocyanic acid or of a cyanide is usually based on the following tests:—(*a*) The aqueous solution is made strongly alkaline with potassium hydroxide, a few drops of ferrous sulphate solution are added, and the liquid is warmed; potassium ferrocyanide is thus formed (p. 320), and on the addition of ferric chloride to the acidified solution, a blue colouration or precipitate of 'Prussian blue' is produced. (*b*) The solution is mixed with a few drops of very dilute ammonium sulphide, and evaporated on a water-bath until all the unchanged ammonium sulphide is expelled; the residue contains ammonium thiocyanate, and on the addition of ferric chloride an intense blood-red colouration is produced.

The cyanides of many of the metals, like many of the metallic chlorides, form complex salts with one another. Silver cyanide, for instance, gives with potassium cyanide a complex soluble salt of the composition, $KAg(CN)_2$, which is used in electroplating; the compound, $KAu(CN)_4$, may be

obtained in a similar manner by treating auric cyanide, $Au(CN)_3$, with potassium cyanide. These complex salts crystallise unchanged from water, but are decomposed by mineral acids in the cold, with evolution of hydrogen cyanide. Like the soluble simple cyanides, they are extremely poisonous.

In addition to the above, complex metallic cyanides of a different class are known, the more important of which are potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. These salts are not poisonous, and are more stable than the double salts just referred to. On treatment with mineral acids, in the cold, they do not yield hydrogen cyanide, but hydrogen is substituted for the alkali metal only, and an acid, such as hydroferrocyanic acid, is liberated,

$$K_4Fe(CN)_6 + 4HCl = H_4Fe(CN)_6 + 4KCl.$$

Potassium ferrocyanide, $K_4Fe(CN)_6$ (yellow prussiate of potash), is formed when ferrous hydrate is treated with an aqueous solution of potassium cyanide,

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH.$$

It is manufactured by fusing together in an iron vessel nitrogenous animal refuse (horn-shavings, hair, blood, &c.), crude potashes (containing potassium carbonate), and iron borings. The cold product is extracted with hot water, and the filtered solution is evaporated to crystallisation.

Potassium ferrocyanide cannot be present in the melted mass, because it is decomposed at a high temperature (p. 318); it must, therefore, be formed when the product is extracted with water.

Probably the melt contains iron, potassium cyanide, and ferrous sulphide (the latter having been produced by the action of the sulphur in the animal refuse on the iron); these substances would interact in the presence of water, yielding potassium ferrocyanide,

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S$$
$$2KCN + Fe + 2H_2O = Fe(CN)_2 + 2KOH + H_2$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Potassium ferrocyanide crystallises in lemon-yellow, hydrated ($3H_2O$) prisms; it is soluble in about 4 parts of water.

When warmed with concentrated (90 per cent.) sulphuric acid it gives carbon monoxide,

$$K_4Fe(CN)_6 + 6H_2O\,{}^* + 6H_2SO_4 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4,$$

but when boiled with dilute sulphuric acid it gives hydrogen cyanide.

Solutions of ferric salts in excess give with potassium ferrocyanide a precipitate of 'Prussian blue,' or ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$.

Potassium ferricyanide, $K_3Fe(CN)_6$, (red prussiate of potash), is prepared by passing chlorine into a solution of potassium ferrocyanide, until the liquid ceases to give a blue precipitate with ferric salts; on evaporation, potassium ferricyanide separates out in dark-red crystals.

The transformation of potassium ferrocyanide into ferricyanide is a process of oxidation, and other oxidising agents, such as nitric acid and lead peroxide, produce the same result. Potassium ferrocyanide may be regarded as a compound of potassium cyanide and *ferrous* cyanide, $4KCN + Fe(CN)_2$. On oxidation, the ferrous is converted into ferric cyanide, and potassium ferricyanide, which may be regarded as a compound of potassium cyanide and *ferric* cyanide, $3KCN + Fe(CN)_3$, is formed.

Potassium ferricyanide gives, with ferrous salts, a precipitate of 'Turnbull's blue,' which is probably the same as 'Prussian blue;' it is employed as a mild oxidising agent, because in alkaline solution, in presence of an oxidisable substance, it is converted into potassium ferrocyanide,

$$2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + O.$$

The **nitriles,** or **alkyl cyanides,** as the esters of *hydrogen cyanide* are termed, may be prepared by heating the alkyl halogen compounds, or the salts of the alkyl sulphuric acids, with *potassium* cyanide,

$$KCN + C_2H_5I = C_2H_5{\cdot}CN + KI,$$
$$KCN + K(C_2H_5)SO_4 = C_2H_5{\cdot}CN + K_2SO_4,$$

* The water necessary for this decomposition is partly derived from the crystals of the salt, partly from the acid, which is not anhydrous.

or by distilling the ammonium salts, or the amides, of the fatty acids with some dehydrating agent, such as phosphorus pentoxide,

$$CH_3{\cdot}COONH_4 = CH_3{\cdot}CN + 2H_2O,$$
$$C_2H_5{\cdot}CO{\cdot}NH_2 = C_2H_5{\cdot}CN + H_2O.$$

They are also formed when *ald*oximes are treated with acetyl chloride or acetic anhydride,

$$CH_3{\cdot}CH:NOH = CH_3{\cdot}CN + H_2O.$$

The lower members of the series, such as *methyl cyanide* (b.p. 82°) and *ethyl cyanide* (b.p. 97°), are colourless liquids, possessing a strong but not disagreeable smell, and are readily soluble in water; the higher members, as, for example, octyl cyanide, $C_8H_{17}{\cdot}CN$, are almost insoluble in water.

When boiled with acids or alkalis they are decomposed, with formation of fatty acids, the –CN group being converted into the –COOH group,

$$CH_3{\cdot}CN + KOH + H_2O = CH_3{\cdot}COOK + NH_3,$$
$$C_2H_5{\cdot}CN + HCl + 2H_2O = C_2H_5{\cdot}COOH + NH_4Cl.$$

For this reason, and also because they may be obtained from the ammonium salts of the fatty acids, the nitriles are named after the acids which they yield on hydrolysis; methyl cyanide, $CH_3{\cdot}CN$, for example, is called *acetonitrile;* ethyl cyanide, $C_2H_5{\cdot}CN$, *propionitrile*, and so on.

On reduction with zinc and sulphuric acid, or, better, with sodium and alcohol, the alkyl cyanides are converted into primary amines, a fact which shows that the alkyl-group is directly united with carbon,

$$CH_3{\cdot}CN + 4H = CH_3{\cdot}CH_2{\cdot}NH_2.$$

The *isonitriles*, *carbylamines* or *isocyanides*, are isomeric with the corresponding nitriles. They may be prepared by heating the alkyl halogen compounds with *silver* cyanide,

$$C_2H_5I + AgCN = C_2H_5{\cdot}N{\equiv}C + AgI,$$

and by treating primary amines with chloroform and alcoholic potash (p. 212),

$$CH_3{\cdot}NH_2 + 3KOH + CHCl_3 = CH_3{\cdot}N{\equiv}C + 3KCl + 3H_2O.$$

The isonitriles or carbylamines are colourless liquids, sparingly soluble in water; they have an almost unbearable odour and poisonous properties.

They boil at lower temperatures than the isomeric cyanides; *methyl isonitrile*, $CH_3 \cdot NC$, for example, boils at 58°; *ethyl isonitrile*, $C_2H_5 \cdot NC$, at 78°. They differ from the nitriles, inasmuch as they are not decomposed by boiling alkalis; they are, however, readily decomposed by dilute mineral acids, yielding formic acid and an amine,

$$C_2H_5 \cdot NC + 2H_2O = H \cdot COOH + C_2H_5 \cdot NH_2.$$

This behaviour is also totally different from that of the nitriles, and shows that the alkyl-group in the isonitriles is united with nitrogen and not with carbon—that is to say, the nitriles are esters of hydrogen cyanide, H·C⋮N, whereas the isonitriles may be regarded as derivatives of an isomeride of the constitution, H·N≡C (see below).

In order to account for the formation of these different products by the action of alkyl halogen compounds on potassium and silver cyanide respectively, it may be assumed that in the one case a simple double decomposition occurs, whereas in the other the alkyl halogen compound unites with the cyanide to form an additive product, which is then decomposed, yielding the isonitrile,

$$Ag \cdot C \vdots N + C_2H_5I = Ag \cdot C \vdots N < \begin{matrix} C_2H_5 \\ I \end{matrix} = C \vdots N \cdot C_2H_5 + AgI.$$

Similar assumptions may be made in order to account for the production of alkyl nitrites and nitro-paraffins from potassium nitrite and silver nitrite respectively (p. 190).

According to another view, the metallic cyanides are not derived from H·C≡N, but from *hydrogen isocyanide*, H·N≡C, and both the nitriles (alkyl cyanides) and the carbylamines (alkyl isocyanides) are produced by reactions which involve the formation of intermediate additive products.

Cyanic acid, HO·CN, is produced when cyanuric acid (p. 315) is heated, and the vapours are condensed in a receiver, cooled in a freezing mixture,

$$C_3N_3(OH)_3 = 3HO \cdot CN.$$

It is a strongly acid, unstable liquid, and at temperatures

above 0° it rapidly undergoes polymerisation into an opaque, porcelain-like mass which consists of cyanuric acid (p. 315), and a small proportion of another polymeride, called cyamelide. It decomposes very rapidly in aqueous solution, giving carbon dioxide and ammonia,

$$HO{\cdot}CN + H_2O = CO_2 + NH_3,$$

and therefore the acid cannot be prepared by the decomposition of its salts with mineral acids.

Potassium cyanate, KO·CN (or KN: CO), is produced when potassium cyanide slowly oxidises in the air, and also when cyanogen chloride is dissolved in a solution of potassium hydroxide; it is usually prepared by heating potassium cyanide (or ferrocyanide) with some readily reducible metallic oxide, such as litharge or red-lead, and then extracting the product with dilute alcohol,

$$KCN + PbO = KO{\cdot}CN + Pb.$$

It is a colourless, crystalline substance, readily soluble in water and dilute alcohol, but insoluble in absolute alcohol; it rapidly decomposes in aqueous solution with formation of ammonium and potassium carbonates,

$$2KO{\cdot}CN + 4H_2O = (NH_4)_2CO_3 + K_2CO_3.$$

When a solution of this cyanate is mixed with ammonium sulphate and evaporated, *urea* is formed, ammonium cyanate, $NH_4O{\cdot}CN$, being the intermediate product (p. 331).

Cyanamide, $NC{\cdot}NH_2$, is formed by the action of ammonia on cyanogen chloride, and its important derivative, **calcium cyanamide**, NC·NCa, is prepared on the large scale by heating calcium carbide with nitrogen under pressure,

$$CaC_2 + N_2 = NC{\cdot}NCa + C;$$

the crude product (*Nitrolim* or *Kalkstickstoff*), which is used as a manure, undergoes decomposition in the soil,

$$NC{\cdot}NCa + CO_2 + H_2O = NC{\cdot}NH_2 + CaCO_3,$$
$$NC{\cdot}NH_2 + H_2O = CO(NH_2)_2,$$

and the urea thus produced is hydrolysed to ammonium

carbonate by certain organisms in the soil. Crude calcium cyanamide is also used for the manufacture of cyanides,

$$NC{\cdot}NCa + C = Ca(CN)_2.$$

Constitution of Cyanic Acid.—Although cyanic acid is a comparatively simple substance, there is some doubt as to whether its constitution should be expressed by the formula HO·C:N or H·N:CO. The fact that it contains a hydrogen atom displaceable by metals seems to point to the first formula; the following facts, however, point to the alternative constitution.

When potassium cyanate is distilled with potassium ethyl sulphate, and when silver cyanate is heated with ethyl iodide, *ethyl isocyanate* (b.p. 60°) is formed; the ethyl group in this compound is directly united to nitrogen because when ethyl isocyanate is heated with potash it yields ethylamine (p. 210),

$$C_2H_5{\cdot}N:CO + 2KOH = C_2H_5{\cdot}NH_2 + K_2CO_3.$$

Now, if the metallic cyanates are derivatives of HO·CN, since ethyl isocyanate is derived from an isomeric *iso-cyanic acid*, HN:CO, the formation of this alkyl compound may be explained by assuming that an additive product is first formed,

$$C_2H_5I + AgO{\cdot}C:N = AgO{\cdot}C:N\begin{matrix}<^{C_2H_5}\\ _{I}\end{matrix} = O:C:N{\cdot}C_2H_5 + AgI.$$

It may be, however, that the metallic salts of cyanic acid are also derived from an acid, HN:CO, and that this formula represents the structure of free cyanic acid. The *alkyl isocyanates*, of which ethyl isocyanate is an example, are unpleasant-smelling, volatile liquids, and were discovered by Würtz. They combine with alcohols to form *urethanes* (p. 330),

$$C_2H_5{\cdot}N:CO + CH_3{\cdot}OH = C_2H_5{\cdot}NH{\cdot}CO{\cdot}OCH_3,$$

and with primary or secondary amines to form substituted ureas,

$$C_2H_5{\cdot}N:CO + NH_2{\cdot}C_2H_5 = C_2H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_2H_5.$$

Phenyl isocyanate, $C_6H_5{\cdot}N:CO$, is employed for the detection of –OH, $-NH_2$, or >NH groups, as it reacts readily at ordinary temperatures with compounds which contain such groups, and gives a phenylurethane or a substituted urea.

Alkyl-derivatives of cyanic acid, HO·CN, are not known.

Thiocyanic acid, or sulphocyanic acid, HS·CN, is obtained in the form of its salts when the alkali cyanides are heated with sulphur,

$$KCN + S = KS{\cdot}CN,$$

the change being analogous to the formation of cyanates by the oxidation of cyanides.

Thiocyanic acid is liberated when potassium thiocyanate is treated with dilute sulphuric acid, but it is very unstable. It has a very penetrating odour, and is decomposed by moderately concentrated sulphuric acid, giving carbon oxysulphide and ammonia,

$$HS{\cdot}CN + H_2O = COS + NH_3.$$

Potassium thiocyanate, KS·CN, is prepared by fusing potassium cyanide (or ferrocyanide) with sulphur, extracting the mass with alcohol, and concentrating the alcoholic solution; it forms colourless, very deliquescent needles. The *ammonium salt*, $NH_4S{\cdot}CN$, is most conveniently prepared by warming alcoholic ammonia with carbon disulphide,

$$4NH_3 + CS_2 = NH_4S{\cdot}CN + (NH_4)_2S.$$

When heated at 170° it gradually undergoes isomeric change into *thiourea* or *thiocarbamide*, $NH_2{\cdot}CS{\cdot}NH_2$, a crystalline substance, which melts at 169°.

The thiocyanates are used in inorganic analysis, as reagents for ferric salts, with which they give an intense blood-red colouration, caused by the formation of complex salts, such as $Fe(CNS)_3,9KCNS$. Thiocyanates are also employed in dyeing and calico-printing as mordants, and are known commercially as 'rhodanates.'

Potassium ferrocyanide and various sulphocyanides are now manufactured from '*spent oxide*,' the substance obtained in purifying coal-gas from hydrogen sulphide, by passing the coal-gas through layers of ferric hydrate. Spent oxide contains 'Prussian blue' (ferric ferrocyanide), ammonium sulphocyanide, and other ammonium salts, together with a large quantity of sulphur. It is first extracted with water, and the ammonium sulphocyanide is separated from the solution by fractional crystallisation, or the solution is treated with copper sulphate and sulphur dioxide, when cuprous sulphocyanide, CuS·CN, is precipitated; this salt is then reconverted into the ammonium salt by decomposing it with ammonium sulphide. Ammonium sulphocyanide is also obtained from 'gas-liquor' by precipitating the cuprous salt and then proceeding as before.

The damp spent oxide, which has been extracted with water, is heated with quicklime in closed vessels by means of steam, in order to convert the ferric ferrocyanide into ferric hydrate and soluble *calcium ferrocyanide*,

$$Fe_4[Fe(CN)_6]_3 + 6Ca(OH)_2 = 4Fe(OH)_3 + 3Ca_2Fe(CN)_6,$$

and the latter is then extracted with water, the residue being used as a source of sulphur in the manufacture of sulphuric acid. The solution of the calcium salt is next treated with the proper quantity of potassium chloride, to form the very sparingly soluble *potassium calcium ferrocyanide*, $K_2CaFe(CN)_6$, which is separated, and heated with a solution of potassium carbonate in order to convert it into potassium ferrocyanide; the solution is filtered from calcium carbonate and evaporated.

Alkyl thiocyanates are produced by distilling the alkyl iodides with potassium thiocyanate, or by treating the mercaptides (especially lead mercaptide) with cyanogen chloride,

$$(C_2H_5S)_2Pb + 2ClCN = 2C_2H_5S{\cdot}CN + PbCl_2.$$

They are volatile liquids possessing a slight smell of garlic; when oxidised with nitric acid they are converted into alkyl sulphonic acids, $C_2H_5S{\cdot}CN$, for example, yielding $C_2H_5{\cdot}SO_3H$, a reaction which shows that the alkyl-group is united with sulphur, and that the esters are derived from an acid of the constitution, HS·C:N.

The *alkyl isothiocyanates*, or *mustard-oils*, are produced by heating the normal thiocyanates at 180°, or by repeatedly distilling them, intramolecular change (p. 331) taking place,

$$C_2H_5{\cdot}S{\cdot}C{:}N \longrightarrow S{:}C{:}N{\cdot}C_2H_5;$$

the alkyl-group in these compounds is combined with nitrogen, as shown by the fact that when heated with hydrochloric acid they are decomposed into primary amines, carbon dioxide, and hydrogen sulphide,

$$C_2H_5N{:}CS + 2H_2O = C_2H_5{\cdot}NH_2 + CO_2 + SH_2.$$

The isothiocyanates, therefore, are analogous to the alkyl isocyanates, and are derived from an unknown isothiocyanic acid of the constitution, HN:C:S.

Allyl isothiocyanate, or **'mustard-oil,'** $CH_2{:}CH{\cdot}CH_2{\cdot}N{:}CS$, is prepared by distilling macerated black mustard-seeds with steam. Mustard-seeds contain a glucoside,* 'potassium myronate,' $C_{10}H_{18}NS_2O_{10}K$, which is soluble in water; its solution gradually undergoes fermentation (owing to the

* Compare footnote, p. 316.

presence of an enzyme, '*myrosin*'), mustard-oil, glucose, and potassium hydrogen sulphate being produced,

$$C_{10}H_{18}NS_2O_{10}K = C_3H_5{\cdot}N{:}CS + C_6H_{12}O_6 + KHSO_4.$$

Allyl isothiocyanate may be obtained synthetically by heating allyl iodide with potassium thiocyanate (see above); it is a colourless, pungent-smelling liquid, boiling at 151°; when dropped on the skin it produces blisters.

CHAPTER XVIII.

Amino-Acids and their Derivatives.

Two classes of compounds containing the $-NH_2$ group have already been described—namely, the amides, such as acetamide, $CH_3{\cdot}CO{\cdot}NH_2$ (p. 168), and the primary amines, such as ethylamine, $C_2H_5{\cdot}NH_2$ (p. 210). In the former, the $-NH_2$ group is easily separated from the rest of the molecule, inasmuch as all amides are hydrolysed more or less rapidly by boiling aqueous alkalis, giving ammonia and an alkali salt of the acid; in the latter, however, the amino-group resists the action of alkalis, and can only be removed by the action of nitrous acid (p. 212). Another important difference between these two classes of compounds is that, whereas the amines are strongly basic and form very stable salts, the amides are only very weak bases, and, although they form salts with strong acids, their salts are very unstable; for this reason and because they show a neutral reaction to litmus, amides are not generally regarded as bases.

These facts afford a good illustration of the manner in which the properties of a given group may be modified by the other atoms or groups in the molecule.

Now, just as the halogen atom in an alkyl-halogen compound, or in an acid chloride, may be displaced by the $-NH_2$ group, so may the halogen atom of a substituted acid,

such as chloracetic acid; when, for example, chloracetic acid (p. 170) is dissolved in concentrated ammonia at ordinary temperatures, it is converted into the ammonium salt of *amino-acetic acid*,

$$CH_2Cl\cdot COOH + 3NH_4\cdot OH = NH_2\cdot CH_2\cdot COONH_4 + NH_4Cl + 3H_2O.$$

Glycine, $CH_2(NH_2)\cdot COOH$ (*amino-acetic acid*), can be prepared from this ammonium salt as described below; it is found in certain animal secretions, usually in combination. As *hippuric acid* or *benzoylglycine*, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH$ (Part II. p. 470), it occurs in considerable quantities in the urine of the horse, and it may be prepared by heating hippuric acid with hydrochloric acid,

$$C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot COOH + H_2O + HCl = \underset{\text{Benzoic Acid.}}{C_6H_5\cdot COOH} + \underset{\text{Glycine Hydrochloride.}}{NH_2\cdot CH_2\cdot COOH, HCl}.$$

Glycine crystallises from water in colourless prisms, and melts at about 235°; it has a sweet taste, is readily soluble in water, and its aqueous solution gives with ferric chloride a deep-red colouration.

Glycine contains a *carboxyl*-group, and, therefore, has the properties of an acid; but it also contains an amino-group, which, like that in methylamine, $H\cdot CH_2\cdot NH_2$, confers basic properties. The result is that glycine is *neutral* to litmus, but is capable of forming salts with bases or with acids.

The most characteristic metallic salt is the *copper salt*, which is obtained by boiling cupric hydrate with a hot, strong, aqueous solution of the acid or of its *ammonium salt*,

$$2NH_2\cdot CH_2\cdot COONH_4 + Cu(OH)_2 = (NH_2\cdot CH_2\cdot COO)_2Cu + 2NH_3 + 2H_2O;$$

the copper salt crystallises in deep-blue needles. The acid is obtained from this salt by passing hydrogen sulphide into its aqueous solution, filtering from copper sulphide, and evaporating.

Glycine hydrochloride, $C_2H_5NO_2, HCl$, is produced by dissolving glycine in hydrochloric acid, or by decomposing

hippuric acid with hydrochloric acid; it crystallises in colourless needles, and is readily soluble in water.

Towards nitrous acid glycine behaves like a primary amine; its amino-group is displaced by hydroxyl (p. 212), and glycollic acid (p. 237) is formed,

$$CH_2(NH_2)\cdot COOH + NO_2H = CH_2(OH)\cdot COOH + N_2 + H_2O.$$

Other *amino-acids*, such as *alanine* or α-aminopropionic acid, $CH_3\cdot CH(NH_2)\cdot COOH$, may be prepared from the corresponding halogen acids by the action of ammonia; they are very similar to glycine in chemical properties, and when treated with nitrous acid they yield the corresponding hydroxy-acids (p. 237). Some important amino-acids are described later (Part II. p. 552).

Amino-formic acid or *carbamic acid*, $NH_2\cdot COOH$, is known only in the form of its ammonium and alkyl salts. Its ammonium salt, *ammonium carbamate*, $NH_2\cdot COONH_4$, is produced by the direct combination of carbon dioxide and ammonia, and is one of the components of commercial ammonium carbonate.

The esters of amino-formic acid are termed *urethanes* (because of their relation to urea) or *alkyl carbamates*.

Urethane or *ethyl carbamate*, $NH_2\cdot COOC_2H_5$, may be prepared by treating ethyl carbonate (compare footnote, p. 182) or ethyl chloroformate with ammonia at ordinary temperatures,

$$CO\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + NH_3 = CO\langle\begin{matrix}NH_2\\OC_2H_5\end{matrix} + C_2H_5\cdot OH$$

$$CO\langle\begin{matrix}Cl\\OC_2H_5\end{matrix} + 2NH_3 = CO\langle\begin{matrix}NH_2\\OC_2H_5\end{matrix} + NH_4Cl.$$

It is a volatile crystalline compound melting at 50°, and when heated with ammonia it is converted into urea,

$$CO\langle\begin{matrix}NH_2\\OC_2H_5\end{matrix} + NH_3 = CO\langle\begin{matrix}NH_2\\NH_2\end{matrix} + C_2H_5\cdot OH.$$

Methylurethane, $CH_3\cdot NH\cdot COOEt$, obtained by treating ethyl carbonate, or ethyl chloroformate (footnote, p. 331), with methylamine, is a liquid, boiling at 170°.

Urea, or carbamide, $CO(NH_2)_2$, is a compound of very great physiological importance. It occurs in the urine of mammals and of carnivorous birds and reptiles, and is one

of the principal nitrogenous components of human urine, of which it forms about 3 per cent.

It was discovered in urine in 1773, and was first artificially produced in 1828 by Wöhler, who found that when an aqueous solution of ammonium cyanate was evaporated the salt was converted into urea; this discovery led to the first synthetical production of an animal product (compare p. 2).

Ammonium cyanate and urea are *isomeric*, and the conversion of the one into the other is called an *intra-molecular* or *isomeric change* because it merely involves a rearrangement of the atoms within the molecule, the structure, $NH_4 \cdot O \cdot C : N$, being transformed into $NH_2 \cdot CO \cdot NH_2$.*

Urea may be prepared by evaporating urine to a small bulk and adding strong nitric acid. The precipitate of crude *urea nitrate* (see below) is recrystallised from nitric acid, dissolved in boiling water, and decomposed with barium carbonate; the solution is then evaporated to dryness, and the urea extracted with alcohol, in which barium nitrate is insoluble.

It is more commonly prepared by mixing a solution of potassium cyanate (2 mols.) with an equivalent quantity of ammonium sulphate (1 mol.), evaporating to dryness, and extracting with alcohol. In both cases the crude urea is purified by recrystallisation from water or alcohol.

Urea may also be obtained synthetically by treating ethyl carbonate, or carbonyl chloride † (phosgene gas), with ammonia,

$$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2C_2H_5 \cdot OH,$$
$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

It crystallises in colourless needles, melts at 132°, and is readily soluble in water and alcohol, but almost insoluble in ether; when heated with water at 120°, or boiled with

* The conversion of ammonium cyanate into urea in aqueous solution is a reversible reaction, but at the equilibrium point the solution contains a relatively very small proportion (5 per cent.) of the ammonium salt.

† *Carbonyl chloride* is obtained by the direct combination of carbon monoxide and chlorine in sunlight; it is a gas which decomposes rapidly in contact with water into carbon dioxide and hydrochloric acid, and when treated with alcohol it gives *ethyl chloroformate*, $Cl \cdot CO \cdot OC_2H_5$, and ethyl carbonate (compare footnote, p. 182).

dilute acids, it is decomposed into carbon dioxide and ammonia (or one of its salts),

$$CO(NH_2)_2 + H_2O + 2HCl = CO_2 + 2NH_4Cl,$$

but when heated alone it yields ammonia, cyanuric acid, *biuret*, and other compounds.

Biuret is obtained when urea is heated at about 155°,

$$2NH_2{\cdot}CO{\cdot}NH_2 = NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_3;$$

an aqueous solution of the residue gives with a drop of copper sulphate solution, and excess of potash, a violet or red colouration (*biuret reaction*).

Urea is decomposed by nitrous acid, giving nitrogen, carbon dioxide, and water, the amino-groups being displaced by hydroxyl-groups,

$$CO(NH_2)_2 + 2HNO_2 = CO(OH)_2\{CO_2 + H_2O\} + 2N_2 + 2H_2O;$$

a similar change takes place when urea is treated with solutions of hypochlorites or hypobromites,

$$CO(NH_2)_2 + 3NaOCl = CO_2 + N_2 + 2H_2O + 3NaCl,$$

and by measuring the volume of nitrogen obtained in the latter reaction, the quantity of urea can be readily estimated.

Urea is also attacked by certain organisms (which are present in most soils), and is thereby converted into ammonium carbonate.

Urea possesses basic properties, and combines with *one* equivalent of an acid to form salts, most of which are soluble in water. A characteristic salt is *urea nitrate*, $CO(NH_2)_2,HNO_3$, which crystallises in glistening plates, and is sparingly soluble in nitric acid.

Constitution.—The formation of urea from ethyl carbonate and from the chloride of carbonic acid (carbonyl chloride) are reactions analogous to those which take place in the formation of acetamide from ethyl acetate and from acetyl chloride; urea, therefore, may be represented by the formula, $CO<\begin{matrix}NH_2\\NH_2\end{matrix}$, and regarded as the di-amide of carbonic acid—hence the name *carbamide*.

Carbonyl chloride, Cl·COCl, may also be regarded as the acid chloride of chloroformic acid, Cl·COOH, and urea as the *amide* of *aminoformic acid.*

Uric acid, $C_5H_4N_4O_3$, occurs in small quantities in human urine, from which it separates on exposure to the air in the form of a light yellow powder; sometimes it gradually accumulates in the bladder, forming large masses (stones), or is deposited in the tissues of the body (gout and rheumatism). It occurs in large quantities in the excrements of birds (*guano*) and reptiles.

The excrements of serpents consist principally of ammonium urate, and uric acid is conveniently prepared by boiling the excrement with caustic soda until all the ammonia has been expelled, and then pouring the hot filtered liquid into hydrochloric acid; the uric acid gradually separates as a fine crystalline powder.

Uric acid is insoluble in alcohol and ether, and very sparingly soluble in water (1 part dissolves in 1800 parts of water at 100°). If uric acid is moistened with nitric acid in a porcelain basin, and the mixture is then evaporated to dryness on a water-bath, a yellow stain is left, which, on the addition of ammonia, becomes intensely violet (murexide reaction).

Uric acid is a weak dibasic acid; when dissolved in sodium carbonate it yields an acid sodium salt, $C_5H_3N_4O_3Na,\frac{1}{2}H_2O$; the normal sodium salt, $C_5H_2N_4O_3Na_2,H_2O$, is formed when uric acid is dissolved in caustic soda. The metallic salts, like the acid itself, are all very sparingly soluble in water.

Uric acid has been prepared synthetically by heating glycine with urea, and by other methods (Part II. p. 566).

Organic Chemistry

ENTIRELY NEW EDITION

(November 1911)

PART II

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ORGANIC CHEMISTRY.

PART II.

CHAPTER XIX.

Production, Purification, and Properties of Benzene.

Distillation of Coal-tar.—When coal is strongly heated, out of contact with air, it undergoes very complex changes, and yields a great variety of gaseous, liquid, and solid, volatile products, together with a non-volatile residue of coke. This process of dry or destructive distillation is carried out on the large scale in the manufacture of **coal-gas**, for which purpose the coal is heated in clay or iron retorts, provided with air-tight doors; the gas and other volatile products escape from the retort through a pipe, and when distillation is at an end, the **coke**, a porous mass of impure carbon, containing the ash or mineral matter of the coal, is withdrawn.

The hot coal-gas passes first through a series of pipes or *condensers*, kept cool by immersion in water, or simply by exposure to the air, and, as its temperature falls, it deposits a considerable quantity of **tar** and **gas-liquor**, which are run together into a large tank; the gas is then forced through, or sprayed with, water, in *washers* and *scrubbers*, and, after having been further freed from tar, ammonia, carbon dioxide, and hydrogen sulphide by suitable processes of purification, it is led into the gas-holder and used for illuminating

and heating purposes. The average volume percentage composition of purified coal-gas is $H_2 = 47$, $CH_4 = 36$, $CO = 8$, $CO_2 = 1$, $N_2 = 4$, and hydrocarbons (acetylene, ethylene, benzene, &c.), other than marsh-gas, = 4, but its composition is very variable.

The coal-tar and the gas-liquor in the tank separate into two layers; the upper one consists of gas-liquor or ammoniacal-liquor (a yellow, unpleasant-smelling, aqueous solution of ammonium hydrogen carbonate, ammonium hydrosulphide, and numerous other compounds), from which practically the whole of the ammonia and ammonium salts of commerce are obtained. The lower layer in the tank is a dark, thick, oily liquid of sp. gr. 1·1 to 1·2, known as coal-tar. It is a mixture of a great number of organic compounds, and, although not long ago it was considered to be an obnoxious by-product, it is now the sole source of very many substances of great industrial importance.

In order to effect the separation of its components, the tar is submitted to fractional distillation; it is heated in large wrought-iron stills or retorts, the vapours which pass off are condensed in long iron or lead worms immersed in water, and the liquid distillate is collected in *fractions*. The point at which the receiver should be changed is ascertained by means of a thermometer, which dips into the tar, as well as by the character of the distillate.

In this way the tar is roughly separated into the following fractions:—

I. Light oil or crude naphtha.....Collected up to 170°.
II. Middle oil or carbolic oil..... " between 170° and 230°.
III. Heavy oil or creosote oil..... " " 230° " 270°.
IV. Anthracene oil..... " above 270°.
V. Pitch.....Residue in the still.

I. The first crude fraction separates into two layers—namely, gas-liquor (which the tar always retains mechanically to some extent) and an oil which is lighter than water, its sp. gr. being about 0·975, hence the name *light oil*. This oil is

first redistilled from a smaller iron retort and the distillate is collected in three principal portions—namely, from 82–110°, 110–140°, and 140–170° respectively. All these fractions consist principally of **hydrocarbons**, but contain basic substances, such as **pyridine**, acid substances, such as **phenol** or **carbolic acid**, and various other impurities; they are, therefore, separately agitated, first with concentrated sulphuric acid, which dissolves out the basic substances, and then with caustic soda, which removes the phenols (p. 433), and are washed with water after each treatment; afterwards they are again distilled. The oil obtained in this way from the fraction collected between 82° and 110° consists principally of the hydrocarbons **benzene** and **toluene**, and is sold as '90 per cent. benzol;' that obtained from the fraction 110–140° consists essentially of the same two hydrocarbons (but in different proportions), together with **xylene**, and is sold as '50 per cent. benzol.'* These two products are not usually further treated by the tar-distiller, but are worked up in the manner described later. The oil from the fraction collected between 140° and 170° consists of xylene, pseudocumene, mesitylene, &c., and is employed principally as '**solvent naphtha**,' also as 'burning naphtha.'

II. The second crude fraction, or middle oil, collected between 170° and 230°, has a sp. gr. of about 1·02, and consists principally of **naphthalene** and **carbolic acid**. On being cooled, the naphthalene separates in crystals, which are drained and pressed to squeeze out adhering carbolic acid and other substances; the crude crystalline product is further purified by treatment with caustic soda and sulphuric acid successively, and is finally sublimed or distilled. The oil from which the crystals have been separated is agitated with warm caustic soda, which dissolves the carbolic acid; the alkaline solution

* Commercial '90 per cent. benzol' contains about 70 per cent., and '50 per cent. benzol,' about 46 per cent. of pure benzene; the terms refer to the proportion of the mixture which passes over below 100° when the commercial product is distilled. Benzene, toluene, and xylene are known commercially as benzol, toluol, and xylol respectively.

is then drawn off from the insoluble portions of the oil and treated with sulphuric acid, whereon crude carbolic acid separates as an oil, which is washed with water and again distilled; it is thus separated into crystalline carbolic acid and liquid (impure) carbolic acid.

III. The third crude fraction, collected between 230° and 270°, is a greenish-yellow, fluorescent oil, specifically heavier than water; it contains **carbolic acid, cresol, naphthalene, anthracene,** and other substances, and is chiefly employed under the name of '**creosote oil**' for the preservation of timber.

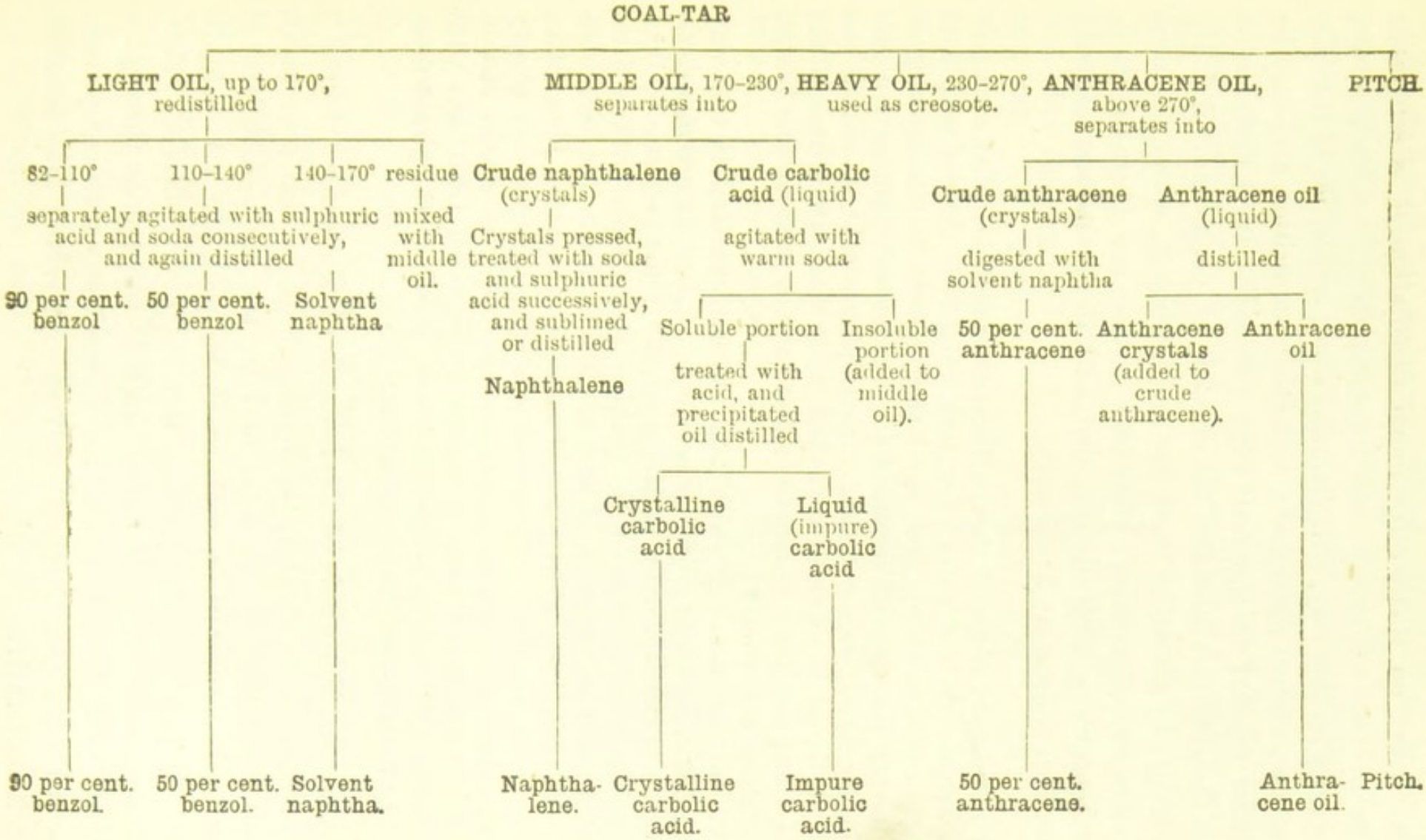
IV. The fourth crude fraction, collected at 270° and upwards, consists of **anthracene, phenanthrene,** and other hydrocarbons which are solid at ordinary temperatures and which are deposited in crystals as the fraction cools; after having been freed from oil by pressure, and further purified by digestion with solvent naphtha (which dissolves the other hydrocarbons more readily than it does the anthracene), the product is sold as '50 per cent. anthracene,' and is employed in the manufacture of alizarin dyes. The oil drained from the anthracene is redistilled, to obtain a further quantity of the crystalline product, the non-crystallisable portions being known as '**anthracene oil.**'

V. The **pitch** in the still is run out while it is hot, and is employed for the preparation of varnishes, for the protection of wood and metal work, and for the production of asphalt.

The table (p. 339), taken partly from Ost's *Lehrbuch der technischen Chemie*, summarises the results of tar distillation and shows the more important commercial products which are obtained.*

Benzene, C_6H_6.—The crude '90 per cent. benzol' of the tar-distiller consists essentially of a mixture of benzene and toluene, but contains small quantities of xylene and other

* In some works the first distillation is carried out under reduced pressure; there is then less decomposition of the valuable components of the tar.


COAL-TAR
LIGHT OIL, up to 170°, redistilled
MIDDLE OIL, 170–230°, separates into
HEAVY OIL, 230–270°, used as creosote.
ANTHRACENE OIL, above 270°, separates into
PITCH
82–110°
110–140°
140–170°
residue
separately agitated with sulphuric acid and soda consecutively, and again distilled
mixed with middle oil.
90 per cent. benzol
50 per cent. benzol
Solvent naphtha
Crude naphthalene (crystals)
Crude carbolic acid (liquid)
Crystals pressed, treated with soda and sulphuric acid successively, and sublimed or distilled
agitated with warm soda
Naphthalene
Soluble portion
Insoluble portion (added to middle oil).
treated with acid, and precipitated oil distilled
Crystalline carbolic acid
Liquid (impure) carbolic acid
Crude anthracene (crystals)
Anthracene oil (liquid)
digested with solvent naphtha
distilled
50 per cent. anthracene
Anthracene crystals (added to crude anthracene).
Anthracene oil
90 per cent. benzol.
50 per cent. benzol.
Solvent naphtha.
Naphtha-lene.
Crystalline carbolic acid.
Impure carbolic acid.
50 per cent. anthracene.
Anthra-cene oil.
Pitch.

substances; on further fractional distillation it is separated more or less efficiently into its components. The benzene, prepared in this way, still contains small quantities of toluene, paraffins, carbon disulphide, and other impurities, and may be further treated in the following manner:—It is first cooled in a freezing mixture and the crystals of benzene are quickly separated by filtration from the mother-liquor, which contains most of the impurities; after this process has been repeated, the benzene is carefully distilled, and the preparation should then boil constantly at 80–81°.

For ordinary purposes this purification is sufficient, but even now the benzene is not quite pure, and when it is shaken with cold concentrated sulphuric acid, the latter darkens in colour owing to its having charred and dissolved the impurities; pure benzene, on the other hand, does not char with sulphuric acid, so that if the impure liquid is repeatedly shaken with small quantities of the acid, until the latter ceases to be discoloured, most of the foreign substances are removed.

All coal-tar benzene which has not been purified in this way contains an interesting sulphur compound, C_4H_4S, named *thiophene*, which was discovered by V. Meyer (p. 633); the presence of thiophene is readily detected by shaking the sample with a little concentrated sulphuric acid and a trace of isatin (an oxidation product of indigo), when the acid assumes a beautiful blue colour (indophenin reaction). Thiophene resembles benzene very closely in chemical and physical properties, and for this reason cannot be easily separated from it except by repeated treatment with sulphuric acid, which sulphonates and dissolves thiophene more readily than it does the hydrocarbon.

Although the whole of the benzene of commerce ('benzol') is prepared from coal-tar, the hydrocarbon is also present in small quantities in wood-tar and in the tarry distillate of many other substances, such as shale, peat, &c.; it may, in fact, be produced by passing the vapour of alcohol, ether, petroleum, or of many other organic substances through a red-hot tube, because under these conditions such compounds lose hydrogen (and oxygen), and are converted into benzene and its derivatives.

Benzene may be produced *synthetically* by simply heating acetylene at a dull-red heat, when 3 mols. (or 3 vols.) of the latter are converted into 1 mol. (or 1 vol.) of benzene,

$$3C_2H_2 = C_6H_6.$$

Acetylene is collected over mercury in a piece of hard glass-tubing, closed at one end and bent at an angle of about 120°; when the tube is about half-full of gas, a piece of copper gauze is wrapped round a portion of the horizontal limb, as shown (fig. 26). This portion of the tube is then carefully heated with a Bunsen burner; after a short time fumes appear, and minute drops of benzene condense on the colder parts of the tube. When it has been heated for about fifteen minutes, the tube is allowed to cool; the mercury then rises above its original level.

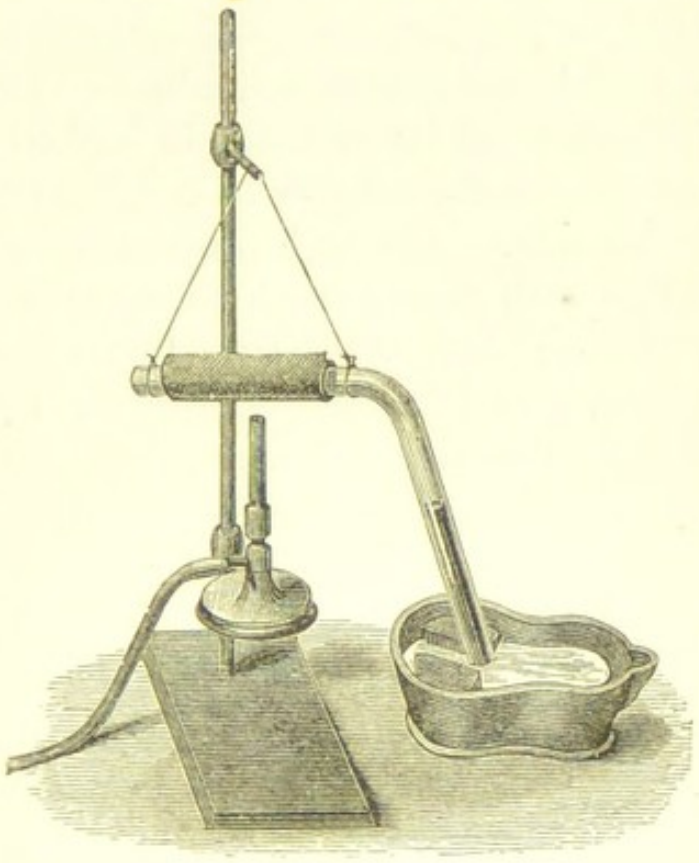


Fig. 26.

This conversion of acetylene into benzene is a process of polymerisation, and was first accomplished by Berthelot. It is, at the same time, an exceedingly important synthesis of benzene from its elements, because acetylene may be obtained by the direct combination of carbon and hydrogen (p. 83).

Benzene may also be obtained by heating pure benzoic acid or sodium benzoate with soda-lime, a reaction which recalls the formation of marsh-gas from sodium acetate,

$$C_6H_5\cdot COONa + NaOH = C_6H_6 + Na_2CO_3,$$
$$(C_6H_5\cdot COO)_2Ca + Ca(OH)_2 = 2C_6H_6 + 2CaCO_3.$$

The analysis of benzene shows that it consists of 92·31 per cent. of carbon and 7·69 per cent. of hydrogen, a result

which gives the empirical formula, CH; the vapour density of benzene, however, is 39, so that its molecular weight is 78, which corresponds with the *molecular formula*, C_6H_6.

At ordinary temperatures benzene is a colourless, highly refractive, mobile liquid of sp. gr. 0·8799 at 20°, but when cooled in a freezing mixture it solidifies to a crystalline mass, which melts at 5·4°, and boils at 80·5°. It has a burning taste, a peculiar, not unpleasant smell, and is highly inflammable, burning with a luminous, very smoky flame, which is indicative of its richness in carbon; the luminosity of an ordinary coal-gas flame, in fact, is largely due to the presence of benzene. Although practically insoluble in water, benzene mixes with liquids such as ether and petroleum in all proportions; like the latter, it readily dissolves fats, resins, iodine, and other substances which are insoluble in water, and for this reason is extensively used as a solvent and for cleaning purposes; its principal use, however, is for the manufacture of nitrobenzene (p. 393) and other benzene derivatives.

Benzene is a very stable compound, and is resolved into simpler substances only with great difficulty; when boiled with concentrated alkalis, for example, it undergoes no change, and even when heated with solutions of such powerful oxidising agents as chromic acid or potassium permanganate, it is only very slowly attacked and decomposed, carbon dioxide, water, and traces of other substances being formed. Under certain conditions, however, benzene readily yields *substitution* products; concentrated nitric acid, even at ordinary temperatures, converts the hydrocarbon into *nitrobenzene* by the substitution of the univalent nitro-group, $-NO_2$, for an atom of hydrogen,

$$C_6H_6 + HNO_3 = C_6H_5 \cdot NO_2 + H_2O;$$

and concentrated sulphuric acid, slowly at ordinary, more rapidly at higher, temperatures, transforms it into *benzenesulphonic acid*,

$$C_6H_6 + H_2SO_4 = C_6H_5 \cdot SO_3H + H_2O.$$

Chlorine and bromine, in absence of direct sunlight and at ordinary temperatures, react with benzene only very slowly, yielding *substitution* products, such as *chlorobenzene*, C_6H_5Cl, *bromobenzene*, C_6H_5Br, *dichlorobenzene*, $C_6H_4Cl_2$, &c.; when, however, some halogen carrier (p. 381), such as iron or iodine, is present, action takes place readily at ordinary temperatures, even in the dark, substitution products again being formed.

In presence of direct sunlight, the hydrocarbon is rapidly converted into *additive* products, such as *benzene hexachloride*, $C_6H_6Cl_6$, and *benzene hexabromide*, $C_6H_6Br_6$, by direct combination with six (but never more than six) atoms of the halogen.

CHAPTER XX.

Constitution of Benzene, and Isomerism of Benzene Derivatives.

It will be seen from the facts just stated that although benzene, like the paraffins, is an extremely stable substance, it differs from these hydrocarbons very considerably in chemical behaviour, more especially in being comparatively readily acted on by nitric acid and by sulphuric acid; further, when its properties are compared with those of the unsaturated hydrocarbons of the ethylene or acetylene series, the contrast is even more striking, because the proportion of carbon to hydrogen in the molecule of benzene, C_6H_6, would seem to indicate a relation to these unsaturated hydrocarbons.

In order, then, to obtain some clue to the constitution of benzene, it is clearly of importance to consider carefully the properties of other unsaturated hydrocarbons of known constitution, and to ascertain in what respects they differ from those of benzene; for this purpose the compound *dipropargyl*, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$ (p. 90), may be chosen, as it has the same molecular formula as benzene.

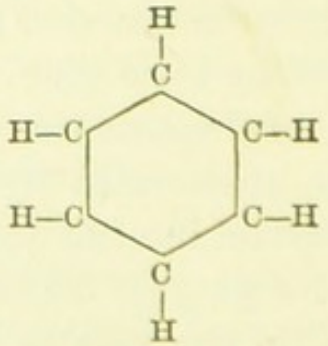
Now, although dipropargyl and benzene are isomeric, they

are absolutely different in chemical behaviour; the former is very unstable, readily undergoes polymerisation, combines energetically with bromine, giving *additive* compounds, and is immediately oxidised even by weak agents; it shows, in fact, all the properties of an unsaturated hydrocarbon of the acetylene series. Benzene, on the other hand, is extremely stable, is comparatively slowly acted on by bromine, giving (usually) *substitution* products, and is oxidised only with difficulty even by the most powerful agents. Since, therefore, dipropargyl must be represented by the above formula, in order to account for its method of formation and chemical properties, the constitution of benzene could not possibly be expressed by any similar formula, such as,

$$CH_3{\cdot}C{:}C{\cdot}C{:}C{\cdot}CH_3 \quad \text{or} \quad CH_2{:}C{:}CH{\cdot}CH{:}C{:}CH_2,$$

because compounds similar in constitution are always more or less similar in properties, and any such formula would not afford the slightest indication of the enormous differences between benzene and ordinary unsaturated hydrocarbons of the ethylene or acetylene series.

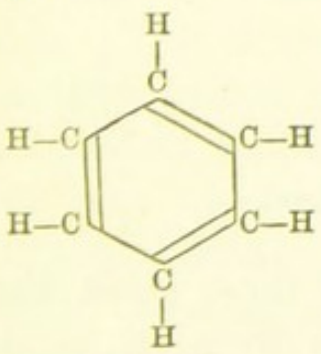
These and many other facts, which were established during the investigation of benzene and its derivatives, led Kekulé (1865) to conclude that *the six carbon atoms in benzene form a closed-chain or nucleus*, that *the molecule of benzene is symmetrical*, and that *each carbon atom is directly united with one* (and only one) *atom of hydrogen*, as may be represented by the formula,



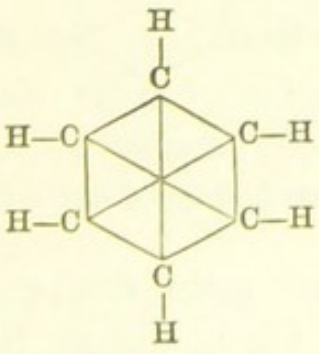
These views are now universally accepted, and the evidence on which they are based is given later; there is, however, at

least one important point which has still to be settled—namely, what is the best way of representing the state of combination of the carbon atoms?

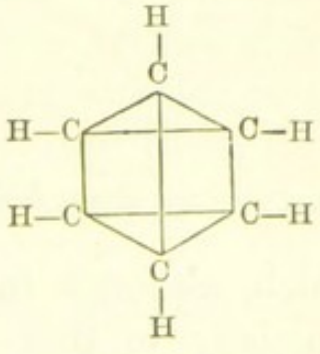
The whole theory of the constitution of organic compounds is based on the assumption that carbon is always quadrivalent, and this assumption, as already explained (p. 50), is expressed in graphic formulæ by drawing four lines from the symbol of each carbon atom, in such a way as to show what other atoms or groups the particular carbon atom in question is directly united with. Now, in the case of benzene, it is clear that two of the four lines or bonds, which represent the valencies of each carbon atom, must be drawn to meet two other carbon atoms, because unless each carbon atom is directly united with two others, the six could not together form a closed-chain; a third line or bond is easily accounted for, because each carbon atom is directly united with hydrogen. In this way, however, only three of the four units of valency of each carbon atom are disposed of, and the question remains, how may the fourth be represented so as to give the clearest indication of the behaviour of benzene? Many chemists have attempted to answer this question, and several constitutional formulæ for benzene have been put forward; that suggested by Kekulé in 1865, and given below, was for a long time considered to be the most satisfactory, but others, such as those of Claus and Ladenburg, also received support.



Kekulé.



Claus.
(Diagonal formula.)

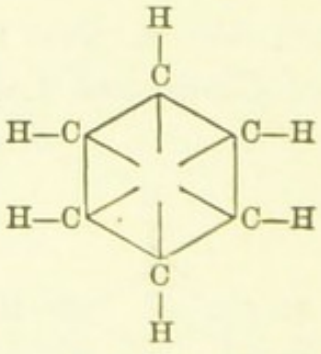


Ladenburg.
(Prism formula.)

It will be seen that these three formulæ all represent the

molecule of benzene as a symmetrical closed-chain of six carbon atoms, and that they differ, in fact, only as regards the representation of the way in which the carbon atoms are united with one another; this difference, moreover, only concerns the state or condition of the fourth unit of valency of each carbon atom. In Kekulé's formula, for example, two lines (or a double bond) are drawn between alternate carbon atoms, a method of representation which is analogous to that adopted in the case of ethylene and other olefines; in the formulæ of Claus and Ladenburg, on the other hand, each carbon atom is represented as directly united with three others (but with a different three in the two cases).

As it would be impossible to enter here into a discussion of the relative merits of the above three formulæ, it may at once be stated that they are all to some extent unsatisfactory, as they do not account for certain facts which have been established by Baeyer and others during various investigations of benzene derivatives. In order to meet these objections, it was suggested by Armstrong, and shortly afterwards by Baeyer, that the constitution of benzene should be represented by the formula,



Armstrong, Baeyer (Centric formula),

which, although in the main similar to those given above, especially to that of Claus, differs from them all in this: The fourth unit of valency of each of the six carbon atoms is represented as being *directed* towards a centre (as shown by the short lines) in order to indicate that the six carbon

atoms have a general attraction for one another, but are not directly united in the ordinary way by this particular unit of valency. This formula, named by Baeyer the *centric formula*, summarises all the facts relating to benzene and its derivatives better than any which has yet been advanced; unlike Kekulé's formula, it does not represent benzene as containing 'double bindings' similar to those in the olefines, and thus it recalls the great difference between benzene and the olefines in chemical behaviour.

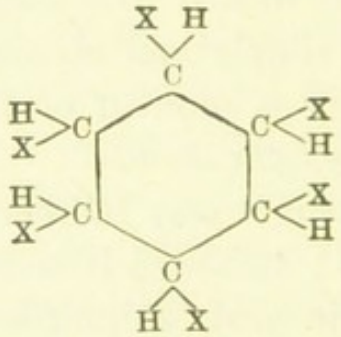
It now becomes necessary to give a few of the more important arguments which, in addition to those already considered, have led to the conclusion that the molecule of benzene consists of a symmetrical closed-chain of six carbon atoms, each of which is united with one atom of hydrogen; also to point out how simply and accurately this view of its constitution accounts for a number of facts which otherwise would be incapable of explanation.

In the first place, then, it may be repeated that benzene is a very stable substance; although it is acted on by powerful reagents, such as nitric acid, sulphuric acid, chlorine, and bromine, and thereby converted into new compounds, all these products or derivatives of benzene contain *six* carbon atoms; the hydrogen atoms may be displaced by certain atoms or groups, which in their turn may be displaced by others; but, in spite of all these changes, the six atoms of carbon remain, forming, as it were, a stable and permanent *nucleus*. This is expressed in the formula by the closed-chain of six carbon atoms, all of which are represented in the same state of combination, which implies that there is no reason why one should be attacked and taken away more readily than another.

Again, a great many compounds which are known to be derivatives of benzene contain more than six atoms of carbon; when, however, such compounds are treated in a suitable manner they are easily converted into substances containing six, but not *less* than six, atoms of carbon. This

fact shows that in these benzene derivatives there are six atoms of carbon which are in a different state of combination from the others, and thus emphasises the existence of the stable nucleus; the additional carbon atoms, not forming part of, but being simply united with, this nucleus, are more easily attacked and removed.

Further, it must be remembered that although benzene usually gives substitution products, it is capable, under certain conditions, of forming additive products; this behaviour is also accounted for. In the formula, only three of the four units of valency of each carbon atom are represented as actively engaged; each carbon atom, therefore, is capable of combining directly with one univalent atom or group, so as to form finally a fully saturated compound of the type,



Isomerism of Benzene Derivatives.

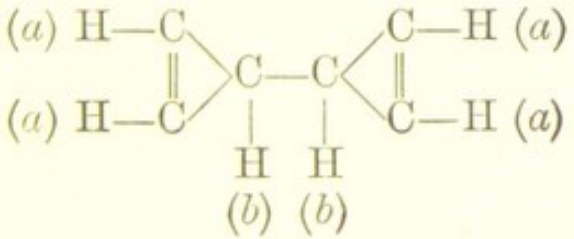
The most convincing evidence that the molecule of benzene is *symmetrical* is derived from a study of the isomerism of benzene derivatives. It has been proved, in the first place, that it is possible to substitute 1, 2, 3, 4, 5, or 6 univalent atoms or groups for a corresponding number of the hydrogen atoms in benzene, compounds such as *bromobenzene*, C_6H_5Br, *dinitrobenzene*, $C_6H_4(NO_2)_2$, *trimethylbenzene*, $C_6H_3(CH_3)_3$, *tetrachlorobenzene*, $C_6H_2Cl_4$, *pentamethylbenzene*, $C_6H(CH_3)_5$, and *hexacarboxybenzene*, $C_6(COOH)_6$, being produced; the substituting atoms or groups, moreover, may be identical or dissimilar.

The examination of such substitution products of benzene has shown that when only *one* atom of hydrogen is displaced

by any given atom or group, the same compound is always produced—that is to say, *the mono-substitution products of benzene exist in one form only;* when, for example, *nitro-benzene*, $C_6H_5 \cdot NO_2$, is prepared, no matter in what way this change may be brought about, the same substance is always produced.

This might be explained, of course, by the assumption that one particular hydrogen atom was always displaced by the nitro-group; when, for example, acetic acid is treated with sodium hydroxide, since only one of the four hydrogen atoms is displaceable, the same salt is invariably produced. In the case of benzene, however, it has been shown that although every one of the six hydrogen atoms may be displaced in turn, the same substance is always formed.

The only possible conclusion to be drawn from this fact is, that *all* the hydrogen atoms are in exactly similar positions relatively to the rest of the molecule; if this were not so, and the constitution of benzene were represented by a formula such as the following,



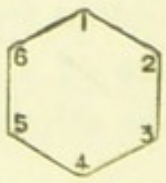
it would be possible to obtain (*two*) isomeric mono-substitution products, because some of the hydrogen atoms (*a*) are differently situated from the others (*b*).

As an example of the way in which it has been proved that the six hydrogen atoms in benzene are all similarly situated, the following may serve (Ladenburg):—Phenol, $C_6H_5 \cdot OH$, or hydroxy-benzene, with the aid of phosphorus pentabromide, may be directly converted into bromobenzene, C_6H_5Br, and the latter may be transformed into benzoic acid (or carboxybenzene), $C_6H_5 \cdot COOH$, with the aid of sodium and carbon dioxide; as these three substances are produced from one another by simple reactions, there is every

reason to suppose that the carboxyl-group in benzoic acid is united with the same carbon atom as the bromine atom in bromobenzene and the hydroxyl-group in phenol; that is to say, that the same hydrogen atom (A) has been displaced in all three cases. Now three different hydroxybenzoic acids of the composition, $C_6H_4(OH)\cdot COOH$, are known, and these three compounds may be either converted into, or obtained from, benzoic acid, $C_6H_5\cdot COOH$ (A), the difference between them being due to the fact that the hydroxyl-group has displaced a different hydrogen atom (B.C.D.) in each case. Each of these hydroxybenzoic acids forms a calcium salt which yields phenol when it is heated (the carboxyl-group being displaced by hydrogen), and the three specimens of phenol thus produced are identical with the original phenol; it is evident, therefore, that at least four (A.B.C.D.) hydrogen atoms in benzene occupy the same relative positions in the molecule. In a somewhat similar manner it can be shown that this is true of all six hydrogen atoms.

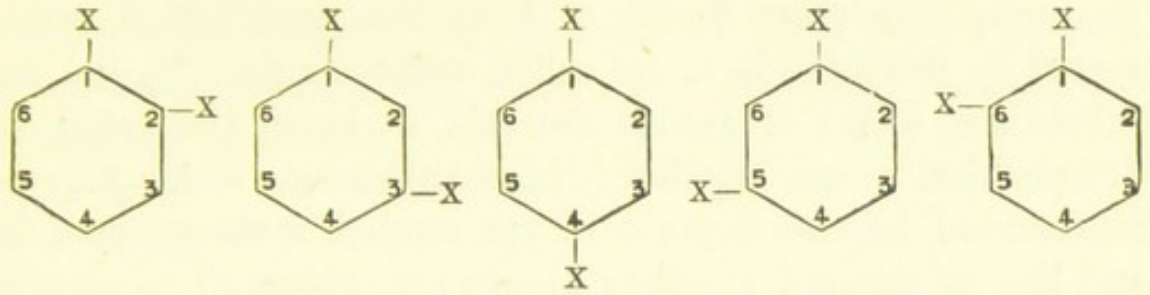
By the substitution of *two* univalent atoms or groups for two of the atoms of hydrogen in benzene, *three*, but not more than three, isomerides are obtained; there are, for example, three *dinitrobenzenes*, $C_6H_4(NO_2)_2$, three *dibromobenzenes*, $C_6H_4Br_2$, three *dihydroxybenzenes*, $C_6H_4(OH)_2$, three *nitrohydroxybenzenes*, $C_6H_4(NO_2)\cdot OH$, and so on.

Now the existence of the three isomerides can be easily accounted for with the aid of the formula already given, which, for this purpose, may conveniently be represented by a hexagon, numbered as shown, the symbols C and H being omitted, for the sake of simplicity.



Suppose that any mono-substitution product, C_6H_5X, which, as already stated, exists in one form only, is converted into a di-substitution product, $C_6H_4X_2$; then if the position occupied by the atom or group (X), which is first introduced, is numbered 1, the second atom or group may have substituted any one of the hydrogen atoms at 2, 3, 4, 5, or 6, giving a

substance the constitution of which might be represented by one of the following five formulæ :—

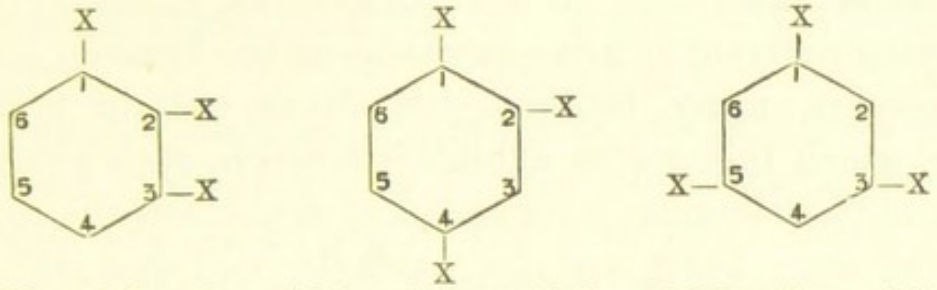

X
X
X

isomeric forms, it is convenient to have some way of distinguishing them by name; for this reason all di-substitution products, which are found to have the constitution represented by the formula I., are called **ortho**-compounds, and the substituent atoms or groups are said to be in the ortho- or 1:2-position to one another; those substances which may be represented by the formula II. are termed **meta**-compounds, and the substituent atoms or groups are spoken of as occupying the meta- or 1:3-position; the term **para** is applied to compounds represented by the formula III., in which the atoms or groups are situated in the para- or 1:4-position.

Ortho-compounds, then, are those in which it is concluded, for reasons given below, that the two substituent atoms or groups are combined with carbon atoms which are themselves *directly united*. Instead of the constitution of any ortho-compound being expressed by the formula I., which represents the substituent atoms or groups as combined with the carbon atoms 1 and 2, the result would be just the same if the substituents were shown to be united with the carbon atoms 2 and 3, 3 and 4, 4 and 5, 5 and 6, or 6 and 1; all such arrangements would be identical, because the benzene molecule is symmetrical, and the numbering of the carbon atoms simply a matter of convenience. In a similar manner the substituent atoms or groups in meta-compounds may be represented as combined with any two carbon atoms which are themselves not directly united, but linked together by one carbon atom; it is quite immaterial which two carbon atoms are chosen, since atoms or groups occupying the 1:3-, 2:4-, 3:5-, 4:6-, or 5:1-position are identically situated with regard to all the other atoms of the molecule. For the same reason para-compounds may be represented by placing the substituent atoms or groups in the 1:4-, 2:5-, or 3:6-position.

When more than two atoms of hydrogen in benzene are displaced, it has been found that the number of isomerides varies according as the substituent atoms or groups are identical or not. By displacing *three* atoms of hydrogen

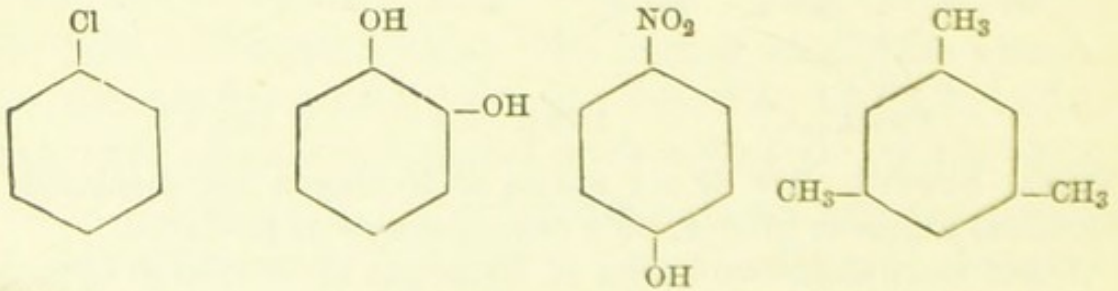
by three *identical* atoms or groups, *three* isomerides can be obtained, three *trimethylbenzenes*, $C_6H_3(CH_3)_3$, for example, being known. Again, the existence of these isomerides can be easily accounted for, since their constitutions may be represented as follows :—


X
X
X

1:3:4, or 1:3:5, all of which would be different. In a similar manner the number of isomerides theoretically obtainable in the case of all benzene derivatives, however complex, may be deduced with the aid of the hexagon formula.

All the cases of isomerism considered up to the present have been those due to the substituent atoms or groups occupying different relative positions in the benzene nucleus ; as, however, many benzene derivatives contain groups of atoms, which themselves exhibit isomerism, such groups may give rise to isomerides comparable with those of the paraffins, alcohols, &c. There are, for example, two isomeric hydrocarbons of the composition, $C_6H_5 \cdot C_3H_7$, namely, *propylbenzene*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$, and *isopropylbenzene*, $C_6H_5 \cdot CH(CH_3)_2$, just as there are two isomeric compounds of the composition, C_3H_7I. As, moreover, propyl- and isopropyl-benzene, $C_6H_5 \cdot C_3H_7$, are isomeric with the three (ortho-, meta-, and para-) *ethylmethylbenzenes*, $C_6H_4(C_2H_5) \cdot CH_3$, and also with the three (adjacent, symmetrical, and asymmetrical) *trimethylbenzenes*, $C_6H_3(CH_3)_3$, there are in all eight hydrocarbons of the molecular formula, C_9H_{12}, derived from benzene.

In studying the isomerism of benzene derivatives, the clearest impressions will be gained by making use of a simple, unnumbered hexagon to represent C_6H_6, and by expressing the constitutions of simple substitution products by formulæ such as,



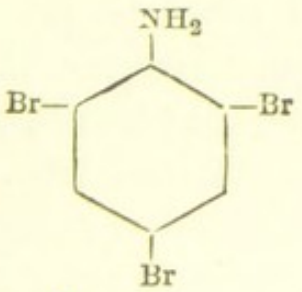
Chlorobenzene. Catechol. Nitrophenol. Trimethylbenzene.

The omission of the symbols C and H is attended by little, if any, disadvantage, because, in order to convert the above into the ordinary molecular formulæ, it is only necessary to write C_6 instead of the hexagon, and then to count

the unoccupied corners of the hexagon to find the number of hydrogen atoms in the nucleus, the substituent atoms or groups being added afterwards. In the case of *chlorobenzene*, for example, there are five unoccupied corners, so that the molecular formula is C_6H_5Cl; whereas in the case of *trimethylbenzene* there are three, and the formula, therefore, is $C_6H_3(CH_3)_3$.

As, however, such graphic formulæ occupy a great deal of space, their constant use in a text-book is inconvenient, and other methods are adopted. The most usual course in the case of the di-derivatives is to employ the terms ortho-, meta-, and para-, or simply the letters **o**, **m**, and **p**, as, for example, ortho-*dinitrobenzene* or **o**-*dinitrobenzene*, meta-*nitraniline* or **m**-*nitraniline*, para-*nitrophenol* or **p**-*nitrophenol*. The relative positions of the atoms or groups may also be expressed by numbers; **o**-*chloronitrobenzene*, for example, may be described as 1:2-*chloronitrobenzene*, as $C_6H_4{<}^{Cl\ (1)}_{NO_2(2)}$, or as $C_6H_4\overset{1}{Cl}{\cdot}\overset{2}{NO_2}$, the corresponding para-compound as 1:4-*chloronitrobenzene*, as $C_6H_4{<}^{Cl\ (1)}_{NO_2(4)}$, or as $C_6H_4\overset{1}{Cl}{\cdot}\overset{4}{NO_2}$.

In the case of the tri-derivatives the terms symmetrical, asymmetrical, and adjacent (compare p. 353) may be employed when all the atoms or groups are the same, but when they are different the constitution of the compound is usually expressed with the aid of numbers; the *tribromaniline* of the constitution,



for example, is described as $C_6H_2Br_3{\cdot}\overset{1}{NH_2}[\overset{1}{NH_2}{:}\overset{2}{Br}{:}\overset{4}{Br}{:}\overset{6}{Br}]$, or as $C_6H_2Br_3{\cdot}NH_2[NH_2{:}3Br = 1{:}2{:}4{:}6]$, but it is of course quite immaterial from which corner of the imaginary hexagon the numbering is commenced.

Determination of the Constitutions of Benzene Derivatives.

Since the di-substitution products of benzene, such as *dibromobenzene*, $C_6H_4Br_2$, *dihydroxybenzene*, $C_6H_4(OH)_2$, and *nitraniline*, $C_6H_4(NO_2)\cdot NH_2$, exist in three isomeric forms, it is now necessary to consider how the constitution of any such derivative is established; that is to say, how it is ascertained whether the given substance is an ortho-, meta-, or para-compound.*

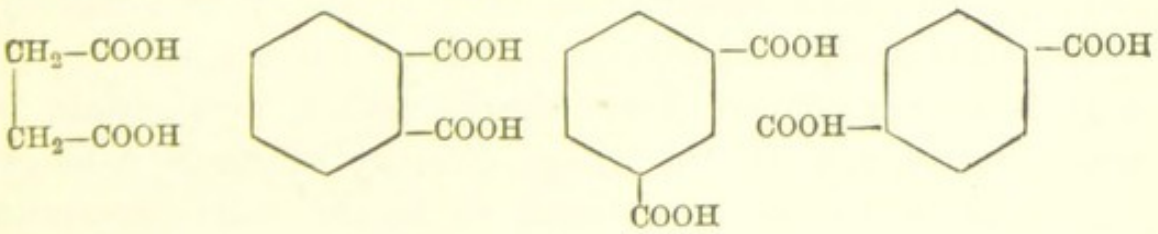
Now the methods which are adopted in deciding questions of this kind at the present time are comparatively simple, but they are based on the results of work which has extended over many years. One of the more important results of such work has been to prove that a given di-substitution product of benzene may be converted by more or less direct methods into many of the other di-substitution products of the *same type*. **Ortho**-*dinitrobenzene*, $C_6H_4(NO_2)_2$, for example, may be transformed into o-*diaminobenzene*, $C_6H_4(NH_2)_2$, o-*dihydroxybenzene*, $C_6H_4(OH)_2$, o-*dibromobenzene*, $C_6H_4Br_2$, o-*dimethylbenzene*, $C_6H_4(CH_3)_2$, and so on; corresponding changes are also possible in the case of meta- and para-compounds. If, therefore, it can be found to which type a given di-substitution product belongs, the constitutions of other di-substitution products, which may be derived from or converted into this compound, are thereby determined. There are, for example, three *dinitrobenzenes*, melting at 90°, 116°, and 173° respectively; now if it could be proved that the compound melting at 90° is a meta-derivative, then it would necessarily follow that the diamino-, dihydroxy-, dibromo-, and other di-derivatives of benzene, obtained from this particular dinitro-compound by substituting other atoms or groups for the two nitro-groups, must also be meta-compounds; it would also be known that the di-derivatives of benzene obtained from the

*The determination of the relative positions in the nucleus of the substituent atoms or groups is often referred to as the *orientation* of these substituents or of benzene derivatives.

other two dinitrobenzenes, melting at 116° and 173° respectively, in a similar manner, must be either ortho- or para-compounds as the case may be.

Obviously, then, it is necessary, in the first place, to determine the constitutions of those di-derivatives which are afterwards to be used as standards.

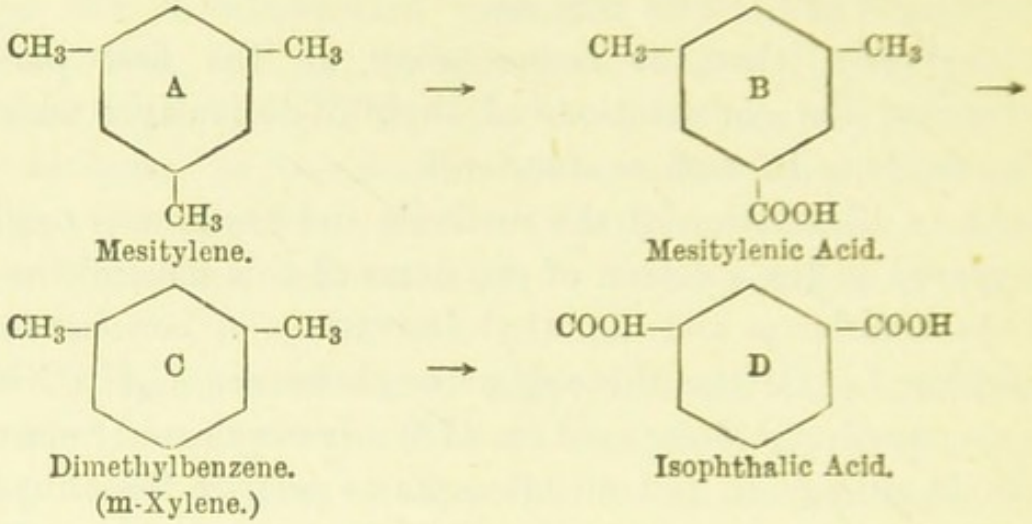
As an illustration of the methods and arguments originally employed in the solution of problems of this nature, the cases of the dicarboxy- and dimethyl-derivatives of benzene may be considered. Of the three dicarboxybenzenes, $C_6H_4(COOH)_2$, one—namely, *phthalic acid* (p. 478)—is very readily converted into its anhydride, but all attempts to prepare the anhydrides of the other two acids (*isophthalic acid* and *terephthalic acid*, p. 480) have been unsuccessful. It is assumed, therefore, that the acid which gives the anhydride is the **o**-compound, because, from a study of the behaviour of many other dicarboxylic acids, it has been found that anhydride formation takes place most readily when the two carboxyl-groups are severally combined with two carbon atoms, which are themselves directly united, as, for example, in the case of succinic acid. In other words, if the graphic formulæ of succinic acid and of the three dicarboxy-derivatives of benzene are compared, it will be evident that the relative positions of the two carboxyl-groups in the **o**-compound are practically the same as in succinic acid, but this is quite otherwise in the case of the **m**- and **p**-compounds.



For this reason, phthalic acid may be provisionally regarded as an *ortho*-dicarboxybenzene.

Again, the hydrocarbon *mesitylene* or *trimethylbenzene*, $C_6H_3(CH_3)_3$, may be produced synthetically from acetone (p. 377), and its formation in this way can be explained in

a simple manner, only on the assumption that mesitylene is a *symmetrical* trimethylbenzene of the constitution, (A).



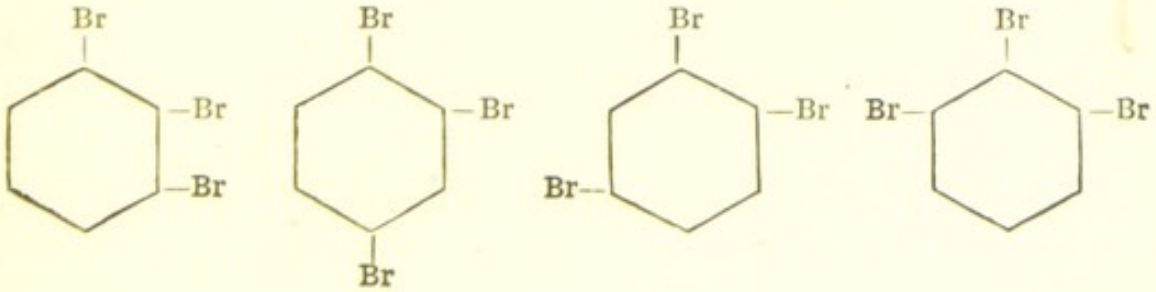
When this hydrocarbon is carefully oxidised, it yields an acid, (B), of the composition, $C_6H_3(CH_3)_2 \cdot COOH$ (by the conversion of one of the methyl-groups into carboxyl), from which a *dimethylbenzene*, $C_6H_4(CH_3)_2$, (C), is easily obtained by heating the acid with soda-lime. This dimethylbenzene, therefore, is a *meta*-compound, because no matter which of the original three methyl-groups in mesitylene has been finally displaced by hydrogen, the remaining two must occupy the **m**-position. Now when this **m**-dimethylbenzene is oxidised with chromic acid, it is converted into a dicarboxylic acid, (D) —namely, *isophthalic acid*, $C_6H_4(COOH)_2$—which, therefore, must also be regarded as a meta-compound. The constitutions of two of the three isomeric dicarboxy-derivatives of benzene having been thus determined, that of the third—namely, *terephthalic acid*, the *para*-compound—is also settled.

It is now a comparatively simple matter to ascertain to which series any of the three dimethylbenzenes belongs; one of them having been found to be the meta-compound, all that is necessary is to submit each of the other two to oxidation, and that which gives phthalic acid will be the ortho-compound, whilst that which yields terephthalic acid will be the para-derivative. Moreover, the constitution of any other di-substitution product of benzene may now be

determined, provided that it is possible to convert this product into one of these standards by simple reactions.

As the methods which have just been indicated are based entirely on arguments drawn from analogy, or deductions as to the probable course of a given reaction, the conclusions to which they lead cannot be accepted without reserve; there are, however, other ways in which it is possible to distinguish between ortho-, meta-, and para-compounds with much less uncertainty, and, of these, that employed by Körner may be given as an example.

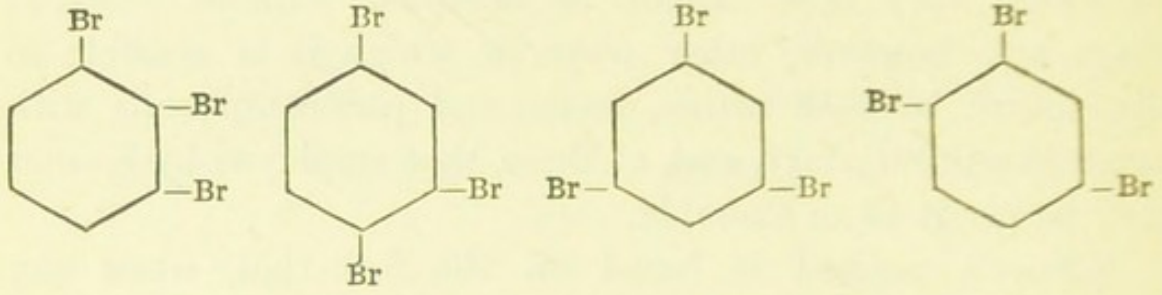
Körner's method is based on the fact that, when any di-substitution product of benzene is converted into a tri-derivative by further displacement of hydrogen of the nucleus, the number of isomerides which may be obtained from an ortho-, meta-, or para-compound is different in all three cases; if, therefore, the number of these products can be ascertained, the constitution of the original di-derivative is established. In the investigation of the *dibromobenzenes*, $C_6H_4Br_2$, for example, three isomerides melting at $-1°$, $+1°$, and 89°, respectively, were discovered, and the question arose, which of these is the ortho-, which the meta-, and which the para-compound? Suppose now that each of these isomerides is separately converted into a *tribromobenzene*, $C_6H_3Br_2 \cdot \mathbf{Br}$; then, if it is the *ortho*-dibromo-compound, it is possible to obtain from it *two*, but only two, tribromobenzenes, because, although there are four hydrogen atoms, any one of which



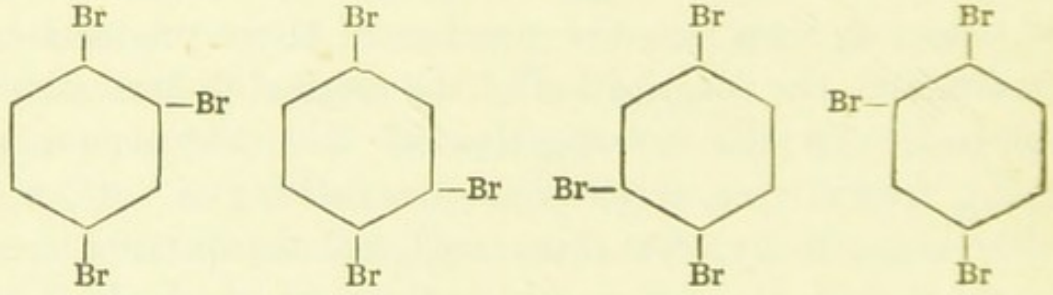
I. II. III. IV.

may be displaced, the compound of the constitution III. is identical with II., and IV. with I., the relative positions of all the atoms being the same in the two cases respectively.

If, on the other hand, the dibromobenzene is the *meta*-compound, it might yield *three*, but only three, isomeric tri-derivatives, which would be represented by the first three of the following formulæ, the fourth being identical with the second,



Finally, if the substance in question is *para*-dibromobenzene, it could give *one* tri-derivative only, the following four formulæ being identical,



Experiments showed that the compound melting at $-1°$ gave *two* tribromobenzenes; it is, therefore, the *ortho*-compound. The dibromobenzene melting at $+1°$ gave *three* such derivatives, and is thus proved to be the *meta*-compound; the isomeride melting at 89° gave only *one*, and, therefore, is the *para*-compound. Obviously this method may be applied in the case of *any* di-substitution product; it may also be employed for the *orientation* of the tri-derivatives in a similar manner.

At the present time the constitution of any new benzene derivative, as a rule, is very easily ascertained, because the new derivative is simply converted into one of the many compounds of known constitution.

CHAPTER XXI.

General Properties of Aromatic Compounds.

Classification of Organic Compounds.—The examples given in the foregoing pages will have afforded some indication of the large number of compounds which it is possible to prepare from benzene, by the substitution of various elements or groups for atoms of hydrogen. As the substances formed in this way, and many other benzene derivatives, which occur in nature, or may be prepared synthetically, retain to a greater or less extent the characteristic chemical behaviour of benzene, and differ in many respects from the paraffins, alcohols, acids, and all other compounds previously considered (Part I.), it is convenient to class benzene and its derivatives as a separate group.

Organic compounds, therefore, are classed in two principal divisions, the **fatty** or **aliphatic** (from ἄλειφαρ, fat) and the **aromatic.** The word 'fatty,' originally applied to some of the higher acids of the $C_nH_{2n}O_2$ series (p. 149), is now used to denote all compounds which may be considered as derivatives of methane; all the compounds described in Part I. belong to the fatty group or division. Benzene and its derivatives, on the other hand, are classed in the 'aromatic' group, this term having been first applied to certain naturally occurring compounds (which were afterwards proved to be benzene derivatives) on account of their peculiar aromatic odour.

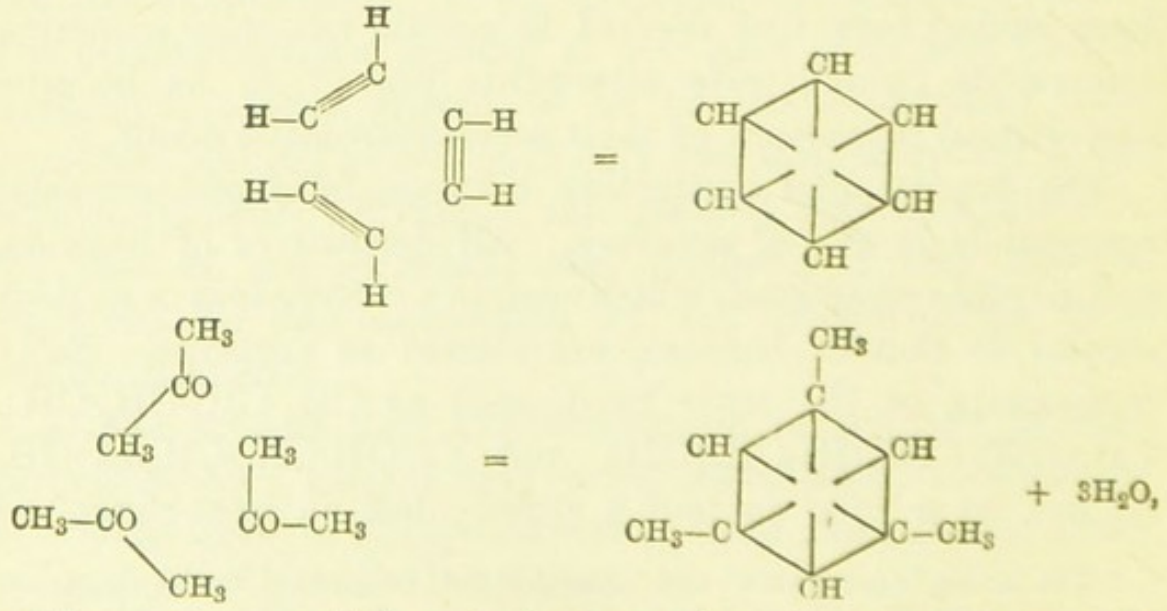
The fundamental distinction between fatty and aromatic compounds is one of *structure.* All derivatives of benzene, and all other compounds which contain a *closed-chain* or nucleus *similar to* that of benzene, are classed as aromatic. Fatty compounds, on the other hand, such as $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, $CH_2(OH){\cdot}CH(OH){\cdot}CH_2(OH)$, and $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, do not, as a rule, contain a closed-, but an *open-chain* * of

* The terms 'open-chain' and 'closed-chain' originated in the chain-like appearance of the structural formulæ as usually written, and are not intended to convey any idea of the arrangement of the atoms in space (compare p. 261).

carbon atoms; such compounds, moreover, may be regarded as derived from methane by a series of simple steps.

It must not be supposed, however, that all aromatic compounds are sharply distinguished from all aliphatic or fatty substances, or that either class can be defined in very exact terms. The mere fact that the constitution of a substance must be represented by a closed-chain formula does not make it an aromatic compound; succinimide (p. 215), for example, although it is a closed-chain compound, is clearly a member of the fatty series, because of its relationship to succinic acid. Although, again, the members of the aromatic group may all be regarded as derivatives of benzene, they might also be considered as derived from methane, since not only benzene itself, but many other aromatic compounds, may be directly obtained from members of the fatty series by simple reactions; conversely, many aromatic compounds may be converted into those of the fatty series.

Some examples of the production of aromatic, from fatty, compounds have already been given—namely, the formation of benzene by the polymerisation of acetylene, and that of mesitylene by the condensation of acetone; these two changes may be expressed graphically in the following manner,



and may be regarded as typical reactions, because many other substances, similar in constitution to acetylene and acetone

respectively, may be caused to undergo analogous transformations.

Bromacetylene, CBr:CH, for example, is converted into (symmetrical) tribromobenzene when it is left exposed to direct sunlight,

$$3C_2HBr = C_6H_3Br_3;$$

and methylethyl ketone (a homologue of acetone) is transformed into symmetrical triethylbenzene (a homologue of mesitylene or trimethylbenzene) when it is distilled with sulphuric acid,

$$3CH_3\cdot CO\cdot C_2H_5 = C_6H_3(C_2H_5)_3 + 3H_2O.$$

General Character of Aromatic Compounds.—Although, then, it is impossible to draw any sharp line between fatty and aromatic compounds, and many substances are known which form connecting links between the two groups, those which are classed as aromatic substances differ materially from those of the fatty division in constitution, and consequently also in properties.

Speaking generally, aromatic compounds contain a larger percentage of carbon than those of the fatty division; they have also a higher molecular weight, and for this reason they are more frequently crystalline at ordinary temperatures. They are, as a rule, less readily resolved into simple substances than are the members of the fatty series (except the very stable paraffins), although in most cases they are more easily converted into substitution products. Their behaviour with nitric acid and with sulphuric acid is very characteristic, and distinguishes them from nearly all fatty compounds; with concentrated nitric acid, as a rule, they readily give *nitro*-derivatives, and with concentrated sulphuric acid they give *sulphonic acids*, hydrogen atoms of the nucleus being displaced,

$$C_6H_5\cdot COOH + HNO_3 = C_6H_4{<}^{COOH}_{NO_2} + H_2O,$$

$$C_6H_5\cdot OH + 3HNO_3 = C_6H_2(OH)(NO_2)_3 + 3H_2O,$$

$$C_6H_5\cdot NH_2 + H_2SO_4 = C_6H_4{<}^{NH_2}_{SO_3H} + H_2O,$$

Fatty compounds rarely give nitro- or sulphonic-derivatives under such conditions, but are oxidised and resolved into two or more simpler substances.

When aromatic nitro-compounds are reduced, they are converted into *amino*-compounds,

$$C_6H_5{\cdot}NO_2 + 6H = C_6H_5{\cdot}NH_2 + 2H_2O,$$
$$C_6H_4(NO_2)_2 + 12H = C_6H_4(NH_2)_2 + 4H_2O.$$

These amino-compounds differ from the fatty amines in at least one very important respect, inasmuch as they are converted into diazonium-compounds (p. 412) on treatment with nitrous acid in the cold; this behaviour is highly characteristic, and the diazonium-compounds form one of the more interesting and important classes of aromatic substances.

It has already been pointed out that benzene does not show the ordinary behaviour of unsaturated fatty compounds, although, under certain conditions, both the hydrocarbon and its derivatives are capable of forming additive compounds by direct combination with two, four, or six (but not with one, three, or five) univalent atoms. This fact proves that benzene is not really a saturated compound like methane or ethane, for example, both of which are quite incapable of yielding derivatives except by substitution. Nevertheless, as a rule, the conversion of benzene and its derivatives into additive products is much less readily accomplished than in the case of fatty, unsaturated compounds; the halogen acids, for example, which unite directly with so many unsaturated fatty compounds, have no such action on benzene and its derivatives, and even in the case of the halogens and nascent hydrogen, direct combination occurs only under particular conditions. The additive compounds obtained from benzene and its derivatives form a connecting link between the members of the aromatic and fatty divisions.

Benzene itself is reduced only with great difficulty, and when strongly heated with hydriodic acid it yields *normal hexane*, C_6H_{14}, as principal product, the closed-chain suffering disruption.

Hexahydrobenzene, C_6H_{12} (*hexamethylene, cyclohexane**), is formed,

* The name *hexamethylene* serves to recall the fact that the compound is composed of six methylene ($-CH_2-$) groups; the name *cyclohexane* indicates a *ring* or closed-chain of six saturated carbon atoms.

but only in small quantities, when benzene is reduced with hydriodic acid ; it occurs in Russian petroleum, from which it can be isolated by repeated fractional distillation, but it is best prepared by reducing benzene with hydrogen, in presence of nickel (p. 623). It melts at 4·7°, boils at 81°, and when treated with bromine it gives *bromohexahydrobenzene* or *bromohexamethylene* (b.p. 162°),

$$C_6H_{12} + Br_2 = C_6H_{11}Br + HBr ;$$

when this bromo-derivative is warmed with alcoholic potash, it is converted into tetrahydrobenzene, just as ethyl bromide is converted into ethylene under similar conditions.

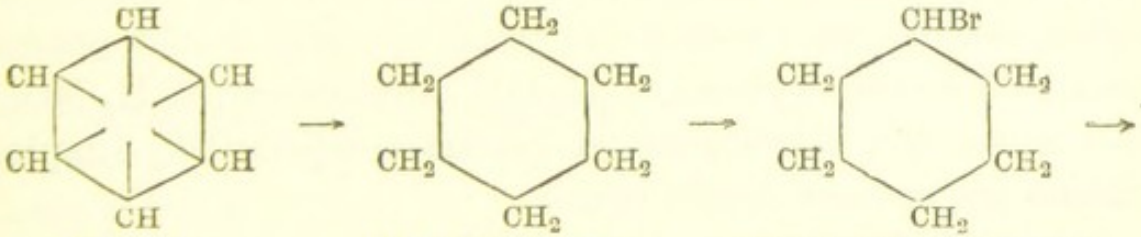
Tetrahydrobenzene, C_6H_{10} (*cyclohexene* *), boils at 83–84°, and combines directly with bromine at ordinary temperatures, yielding *dibromohexahydrobenzene* or *dibromohexamethylene*, $C_6H_{10}Br_2$.

Dihydrobenzene, C_6H_8 (*cyclohexadi-ene* *), is obtained by heating dibromohexahydrobenzene with alcoholic potash or with quinoline (which acts like alcoholic potash and removes hydrogen bromide),

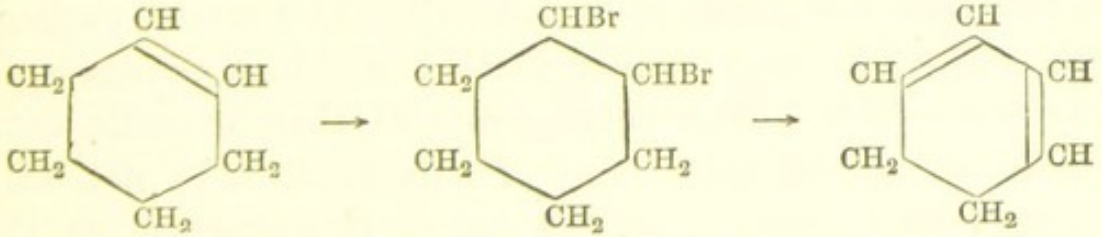
$$C_6H_{10}Br_2 = C_6H_8 + 2HBr ;$$

it boils at 84–86°, combines directly with bromine, giving a crystalline *tetrabromide*, $C_6H_8Br_4$, and rapidly oxidises on exposure to the air, being converted into a resin.

The following formulæ show the relationships of the above series of compounds :—



Benzene. Hexahydrobenzene. (Hexamethylene.) Bromohexahydrobenzene. (Bromohexamethylene.)



Tetrahydrobenzene. (Cyclohexene.*) Dibromohexahydrobenzene. (Dibromohexamethylene.) Dihydrobenzene. (Cyclohexadi-ene.*)

* The termination *ene* indicates the presence of an ethylenic or olefinic binding in the molecule, and *di-ene* the presence of two such 'double bindings.'

It is very important to note that *dihydro-* and *tetrahydro-*benzene, which must be regarded as incompletely or partially reduced benzene, differ very much from the original hydrocarbon, the difference, in fact, being much the same as that which exists between unsaturated and saturated fatty compounds. In other words, when benzene unites with two or four atoms of hydrogen, the product is no longer characterised by great stability, but shows the ordinary behaviour of *unsaturated* compounds, inasmuch as it is readily oxidised and readily combines with bromine; this is also true in the case of all *partially reduced* benzene derivatives (p. 628).

As expressed by the above formulæ, the conversion of benzene or of a benzene derivative into a *di-* or *tetra*-additive product is accompanied by a change in the mode of combination of all the carbon atoms; two, or four, of the six units of valency (represented in the centric formula by the short lines directed towards the centre) being required to take up the additive atoms, the remaining ones are released from their original state, and the carbon atoms become united in the same way as in ethylene (compare p. 466).

When the hydrogen atoms in benzene are displaced by groups or radicles which are composed of several atoms, these groups are spoken of as **side-chains**; the aliphatic groups in *ethylbenzene*, $C_6H_5 \cdot CH_2 \cdot CH_3$, *benzyl alcohol*, $C_6H_5 \cdot CH_2 \cdot OH$, and *methylaniline*, $C_6H_5 \cdot NH \cdot CH_3$, for example, would be called side-chains, whereas the term, as a rule, would not be used in the case of *phenol*, $C_6H_5 \cdot OH$, *nitrobenzene*, $C_6H_5 \cdot NO_2$, &c., where the substituent groups are comparatively simple, and do not contain carbon atoms.

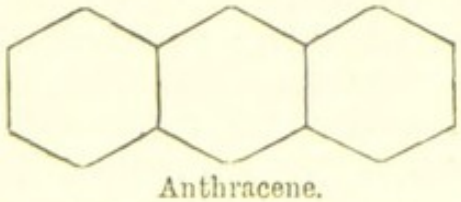
Now the character of any particular atom or group in an aliphatic side-chain, although influenced to some extent by the fact that the group is united with the benzene nucleus, is on the whole very similar to that which it possesses in fatty compounds. The consequence is that aromatic compounds, containing side-chains of this kind, have not only the properties already referred to, as characteristic of the derivatives of benzene, but show also, to a certain extent, the behaviour of fatty compounds. *Benzyl chloride*, $C_6H_5 \cdot CH_2Cl$, for example, may be directly converted into the nitro-derivative, $C_6H_4(NO_2) \cdot CH_2Cl$, and the sulphonic acid, $C_6H_4(SO_3H) \cdot CH_2Cl$,

reactions characteristic of aromatic compounds. On the other hand, the $-CH_2Cl$ group may be transformed into $-CH_2\cdot OH$, $-CHO$, $-COOH$, and so on, just as may the $-CH_2Cl$ group in ethyl chloride, $CH_3\cdot CH_2Cl$; and in all cases the products retain, to some extent, the properties of fatty substances so long as the side-chain remains. The carbon atoms contained in the side-chains, moreover, are generally more easily attacked and separated from the rest of the molecule than are those of the closed-chain or nucleus; when *ethylbenzene*, $C_6H_5\cdot CH_2\cdot CH_3$, or *propylbenzene*, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH_3$, for example, is boiled with chromic acid, the side-chain undergoes oxidation, carbon dioxide is evolved, and benzoic acid, $C_6H_5\cdot COOH$, is produced in both cases, the benzene nucleus remaining unchanged (p. 469).

Although the compounds derived from benzene by direct substitution are very numerous, the aromatic group also includes a great many other substances, which are more distantly related to benzene, and which can only be regarded as derived from it indirectly. The hydrocarbon *diphenyl*, $C_6H_5-C_6H_5$, for example, which, theoretically, is formed by the union of two *phenyl-* or C_6H_5- groups, just as dimethyl or ethane, CH_3-CH_3, is produced by the combination of two methyl-groups, is an important member of the aromatic division, and, like benzene, is capable of yielding a very large number of derivatives. Other hydrocarbons are known in which the presence of two or more closed carbon chains, combined in different ways, must be assumed, as, for example, in the cases of naphthalene (p. 496) and anthracene (p. 512),



Naphthalene.

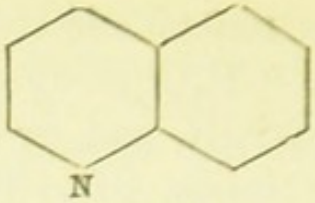


Anthracene.

and there are also substances, such as pyridine (p. 526) and quinoline (p. 535), in which a nitrogen atom occupies the position of one of the $CH\equiv$ groups in the closed-chain,



Pyridine.



Quinoline.

All these, and many other different types of compounds, are classed as aromatic, because they show the general behaviour already referred to, and resemble benzene more or less closely in constitution.

CHAPTER XXII.

Homologues of Benzene and other Hydrocarbons.

Benzene, the simplest hydrocarbon of the aromatic group, is also the first member of a homologous series of the general formula, C_nH_{2n-6}; the hydrocarbons of this series are derived from benzene by the substitution of alkyl-groups for hydrogen atoms, just as the homologous series of paraffins is derived from methane. *Toluene* or *methylbenzene*, $C_6H_5 \cdot CH_3$, is the only homologue of the molecular formula, C_7H_8, but the next higher member, which has the molecular formula, C_8H_{10}, occurs in four isomeric forms—namely, as *ethylbenzene*, $C_6H_5 \cdot C_2H_5$, and as ortho-, meta-, and para-*dimethylbenzene*, $C_6H_4(CH_3)_2$; higher up the series, the number of theoretically possible isomerides rapidly increases.

By the substitution of a methyl-group for one atom of hydrogen in the hydrocarbon, C_8H_{10}, for example, eight isomerides of the composition, C_9H_{12}, may theoretically be obtained, and are, in fact, known. Of these isomerides, five—namely, *propylbenzene* and *isopropylbenzene*, $C_6H_5 \cdot C_3H_7$, and o-, m-, and p-*methylethylbenzene*, $C_6H_4(CH_3) \cdot C_2H_5$, are derived from ethylbenzene; the other three —namely, symmetrical, adjacent, and asymmetrical *trimethylbenzene*, $C_6H_3(CH_3)_3$, are derived from the dimethylbenzenes.

Many of the hydrocarbons of this series, and others which will be mentioned later, occur in coal-tar, from which they

are extracted in much the same way as is benzene; it is, however, very difficult to obtain any of them in a pure state directly from this source, by fractional distillation, as the boiling-points of some of the compounds lie very close together; nevertheless, the process is now carried out on the large scale with such care, and with such efficient apparatus, that the purified compounds contain, in some cases, only traces of foreign substances.

The homologues of benzene may be obtained by the following general methods :—

(1) Benzene (or one of its homologues) is treated with alkyl halogen compounds in presence of anhydrous aluminium chloride (*Friedel and Crafts' reaction*); under these conditions the hydrogen atoms of the nucleus are displaced by alkyl-groups, *benzene* and methyl chloride, for example, giving *toluene*, $C_6H_5{\cdot}CH_3$, *xylene*, $C_6H_4(CH_3)_2$, *trimethylbenzene*, $C_6H_3(CH_3)_3$, &c.; whereas *ethylbenzene*, with the same alkyl compounds, yields *methylethylbenzene*, $C_6H_4(CH_3){\cdot}C_2H_5$; *dimethylethylbenzene*, $C_6H_3(CH_3)_2{\cdot}C_2H_5$; and so on,

$$C_6H_6 + CH_3Cl = C_6H_5{\cdot}CH_3 + HCl,$$
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl,$$
$$C_6H_5{\cdot}C_2H_5 + CH_3Cl = C_6H_4(CH_3){\cdot}C_2H_5 + HCl.$$

Anhydrous benzene, or one of its homologues, is placed in a flask connected with a reflux condenser, and about one-third of its weight of anhydrous aluminium chloride is added; the alkyl chloride or bromide is then passed into the liquid, if a gas, or dropped in, if a liquid, and the mixture is afterwards heated on a water-bath until the evolution of hydrogen chloride or bromide is at an end; the apparatus and materials must be dry. In some cases, ether, carbon disulphide, or petroleum is mixed with the original hydrocarbon in order to dilute it, experience having shown this to be advantageous. When the product is quite cold, water is gradually added to it in order to dissolve the aluminium compounds, and after having been separated, and dried with calcium chloride, the mixture of hydrocarbons is submitted to fractional distillation; in some cases a preliminary distillation in steam is advisable.

It is probable that an aluminium compound, such as $C_6H_5{\cdot}Al_2Cl_5$, is first formed, with evolution of hydrogen chloride; this substance

then reacts with the alkyl halogen compound to form the new hydrocarbon, aluminium chloride being regenerated,

$$C_6H_5\cdot Al_2Cl_5 + CH_3Cl = C_6H_5\cdot CH_3 + Al_2Cl_6.$$

Anhydrous ferric or zinc chloride may be employed in the place of aluminium chloride, but, as a rule, not so successfully.

(2) A mixture, consisting of a halogen derivative of benzene or of one of its homologues, and an alkyl halogen compound, is heated with sodium or potassium (*Fittig's reaction*); this method of formation is similar to that by which the higher paraffins may be synthetically produced from methane (p. 69), and has the great advantage over Friedel and Crafts' method that the constitution of the product is known. *Bromobenzene* and methyl iodide, for example, give *toluene*, whereas **o**-, **m**-, and **p**-*bromotoluene* and ethyl iodide yield **o**-, **m**-, and **p**-*ethylmethylbenzene* respectively,

$$C_6H_5Br + CH_3I + 2Na = C_6H_5\cdot CH_3 + NaI + NaBr,$$

$$C_6H_4Br\cdot CH_3 + C_2H_5I + 2K = C_6H_4{<}\begin{matrix}CH_3\\C_2H_5\end{matrix} + KBr + KI.$$

The bromo-derivatives of the aromatic hydrocarbons are usually employed in such cases because the chloro-derivatives are not so readily acted on, and the iodo-compounds are not so easily prepared; the alkyl iodides are also used in preference to the chlorides or bromides because they interact more readily. Dry ether is usually employed as a diluent.

(3) The carboxy-derivatives of benzene, or of its homologues, are heated with soda-lime, a method analogous to that employed for the conversion of the fatty acids into paraffins (p. 69),

$$C_6H_4(CH_3)\cdot COOH = C_6H_5\cdot CH_3 + CO_2,$$

$$C_6H_4(COOH)_2 = C_6H_6 + 2CO_2.$$

(4) The vapour of a hydroxy-derivative of benzene, or of one of its homologues, is passed over strongly heated zinc-dust,

$$C_6H_5\cdot OH + Zn = C_6H_6 + ZnO,$$

$$C_6H_4(CH_3)\cdot OH + Zn = C_6H_5\cdot CH_3 + ZnO.$$

(5) Coal, wood, peat, &c. are submitted to destructive dis-

tillation, or the vapour of some fatty compound is passed through a red-hot tube (compare p. 340).

General Properties.—Most of the homologues of benzene are colourless, mobile liquids; one or two, however, are crystalline at ordinary temperatures. They all distil without decomposing, are volatile in steam, and burn with a smoky flame; they are insoluble in water, but miscible with (absolute) alcohol, ether, petroleum, &c., in all proportions; they dissolve fats and many other substances which are insoluble in water.

Just as in other homologous series, the homologues of benzene show a gradual variation in physical properties with increasing molecular weight, but owing to the large number of isomerides, this is only obvious when *corresponding* compounds are compared; as an example of this, the following *mono*-substitution products of benzene may be considered:—

Benzene, C_6H_6	Sp. gr. at 0°, 0·899	B.p., 80·5°
Toluene, C_7H_8	" 0·882	" 110·3°
Ethylbenzene, C_8H_{10}	" 0·883	" 134°
Propylbenzene, C_9H_{12}	" 0·881	" 158°

There are, however, three hydrocarbons isomeric with ethylbenzene (p. 368), whilst propylbenzene has seven isomerides (p. 368), so that the original homologous series given above branches into a number of series, in which the homology becomes rather confused. In the case of isomeric *di*-substitution products there is usually some difference in physical properties, but the extent of this difference is rather variable; the three xylenes, $C_6H_4(CH_3)_2$, for example, show the following differences:—

	Orthoxylene.	Metaxylene.	Paraxylene.
Sp. gr. at 0°	0·893	0·881	0·880
B.p.	142°	139°	138° (M.p. 15°)

As a general rule, to which, however, there are some exceptions, para-compounds melt at a higher temperature than the corresponding meta-compounds; the latter usually melt at a higher temperature than the corresponding ortho-compounds.

The boiling-points also vary, but with less regularity. This applies to all benzene derivatives, not to hydrocarbons only.

The homologues of benzene show the characteristic chemical behaviour of the simplest hydrocarbon, inasmuch as they readily yield nitro- and sulphonic-derivatives; toluene, for example, gives *nitrotoluene*, $C_6H_4(CH_3)\cdot NO_2$, and *toluenesulphonic* acid, $C_6H_4(CH_3)\cdot SO_3H$; xylene yields *nitroxylene*, $C_6H_3(CH_3)_2\cdot NO_2$, and *xylenesulphonic acid*,

$$C_6H_3(CH_3)_2\cdot SO_3H.$$

In these, and in all similar reactions, the product invariably consists of a mixture of isomerides, and the course of the reaction depends both on the nature of the interacting compounds and on the conditions of the experiment (compare p. 392); as a rule, the greater the number of alkyl-groups in the hydrocarbon, the more readily does it yield nitro- and sulphonic-derivatives.

The fact that benzene and its homologues gradually dissolve in concentrated sulphuric acid is sometimes made use of for the separation of these aromatic hydrocarbons from the paraffins, as, for example, in the analysis of coal-gas; their separation from unsaturated fatty hydrocarbons could not of course be accomplished in this way, as the latter are also dissolved by concentrated sulphuric acid.

All the homologues of benzene are very stable, and are with difficulty resolved into compounds containing a smaller number of carbon atoms; powerful oxidising agents, however, such as chromic acid, potassium permanganate, and *dilute* nitric acid, act on them slowly, the alkyl-groups or side-chains being attacked, and, as a rule, converted into carboxyl-groups; toluene and ethylbenzene, for example, give benzoic acid, whereas the xylenes yield dicarboxylic acids (p. 476),

$$C_6H_5\cdot CH_3 + 3O = C_6H_5\cdot COOH + H_2O,$$
$$C_6H_5\cdot CH_2\cdot CH_3 + 6O = C_6H_5\cdot COOH + CO_2 + 2H_2O,$$
$$C_6H_4(CH_3)_2 + 6O = C_6H_4(COOH)_2 + 2H_2O.$$

Although in most cases oxidation leads to the formation of a carboxy-derivative of benzene, the stable benzene nucleus remain-

ing unchanged, some of the homologues are completely oxidised to carbon dioxide and water (compare p. 376), and benzene itself undergoes a similar change on prolonged and vigorous treatment.

In the case of aromatic, as in that of aliphatic compounds, it is convenient to give names to certain groups of atoms or *radicles;* the mono- and di-substitution products of benzene, for example, may be regarded as compounds of the univalent radicle, *phenyl*, C_6H_5-,* and of the bivalent radicle, *phenylene*, $C_6H_4<$, respectively, as in *phenylamine* (aniline), $C_6H_5\cdot NH_2$, and in o-, m-, and p-*phenylenediamine*, $C_6H_4(NH_2)_2$. Toluene derivatives, again, may be named as if they were derived from the radicle, *tolyl*, $CH_3\cdot C_6H_4-$, or from the radicle, *benzyl*, $C_6H_5\cdot CH_2-$, according as hydrogen of the nucleus, or of the side-chain, has been displaced. The compound, $C_6H_5\cdot CH_2\cdot OH$, for example, is called *benzyl alcohol;* the isomeric hydroxy-toluenes, $C_6H_4(CH_3)\cdot OH$, however, are usually known as the (o.m.p.) cresols (p. 444).

Radicles derived from aromatic hydrocarbons are termed **aryl** radicles.

Toluene, $C_6H_5\cdot CH_3$ (methylbenzene, phenylmethane), although always prepared from the '90 per cent. benzol' separated from coal-tar (p. 337), can be obtained by any of the general reactions given above, and also by the dry distillation of balsam of Tolu (hence the name toluene) and other resins.

Commercial toluene is invariably impure, and when shaken with concentrated sulphuric acid it colours the acid brown or black. It may be purified by repeated fractional distillation, but even then it contains *thiotolene*, C_5H_6S, a homologue of thiophene (p. 633), and shows the indophenin reaction (with isatin and concentrated sulphuric acid).

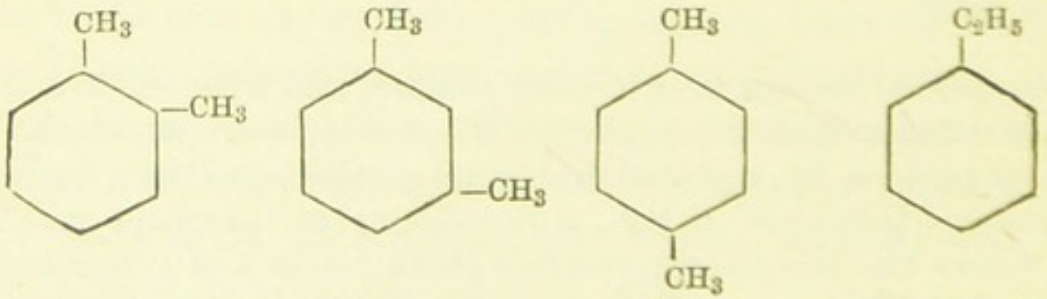
Pure toluene is most conveniently prepared from balsam of Tolu, or by distilling pure toluic acid with soda-lime,

$$C_6H_4(CH_3)\cdot COOH = C_6H_5\cdot CH_3 + CO_2.$$

* This radicle is often represented by Ph.

It is a mobile liquid of sp. gr. 0·882 at 0°, and boils at 110°; it does not solidify even at −28°, and cannot, therefore, like benzene, be purified by crystallisation. It resembles benzene very closely in most respects, and differs from it principally in those properties which are due to the presence of the methyl-group. Its behaviour with nitric acid and with sulphuric acid, for example, is similar to that of benzene, inasmuch as it yields nitro- and sulphonic-derivatives; these compounds, moreover, exist in three isomeric (**o.m.p.**) forms, since they are di-substitution products of benzene. The presence of the methyl-group, on the other hand, causes toluene to show in some respects the properties of a paraffin. The hydrogen of this methyl-group may be displaced by chlorine, for example, and the latter by a hydroxyl- or amino-group, by methods exactly similar to those employed in bringing about corresponding changes in fatty compounds; substances such as $C_6H_5 \cdot CH_2Cl$, $C_6H_5 \cdot CH_2 \cdot OH$, and $C_6H_5 \cdot CH_2 \cdot NH_2$, are thus obtained. This behaviour, perhaps, was to be expected, since toluene or phenylmethane is a mono-substitution product of methane just as much as a derivative of benzene.

The next homologue of toluene—namely, the hydrocarbon of the molecular formula, C_8H_{10}—exists in the following four isomeric forms, of which the three *xylenes* or dimethylbenzenes are the more important:—



The three **xylenes** occur in coal-tar, and may be partially separated from the other components of '50 per cent. benzol' (p. 337) by fractional distillation. The portion which, after repeated distillation, boils at 136–141°, contains a large quantity (up to 85 per cent.) of **m**-xylene and smaller quan-

tities of the o- and p-compounds; the three isomerides cannot be separated from one another (or from all impurities) by further distillation, or by any simple means, although it is possible to obtain a complete separation by taking advantage of differences in their chemical behaviour.

m-Xylene is readily separated from the other isomerides with the aid of boiling dilute nitric acid, which oxidises o- and p-xylene to the corresponding toluic acids, $C_6H_4(CH_3)\cdot COOH$, but does not readily attack m-xylene; the product is rendered alkaline by the addition of potash, and the unchanged hydrocarbon is purified by distillation in steam and fractionation. The isolation of o- and p-xylene depends on the following facts :—(1) When crude xylene is agitated with concentrated sulphuric acid, o- and m-xylene are converted into sulphonic acids, $C_6H_3(CH_3)_2\cdot SO_3H$; p-xylene remains unchanged, as it is only slowly acted on even by anhydrosulphuric acid. (2) The sodium salt of o-xylenesulphonic acid is less soluble in water than the sodium salt of m-xylenesulphonic acid; it is purified by recrystallisation and heated with hydrochloric acid under pressure, whereby it is converted into o-xylene (p. 428).

The three xylenes may all be prepared by one or other of the general methods; when, for example, methyl chloride is passed into benzene in presence of aluminium chloride, o-xylene and a small quantity of the p-compound are obtained,

$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl;$$

toluene, under the same conditions, yields the same two compounds,

$$C_6H_5\cdot CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl.$$

The non-formation of m-xylene in these two cases shows that the methyl-group first introduced into the benzene molecule exerts some *directing influence* on the position taken up by the second one (p. 392).

o-*Xylene* is obtained in a state of purity by treating o-bromotoluene with methyl iodide and sodium,

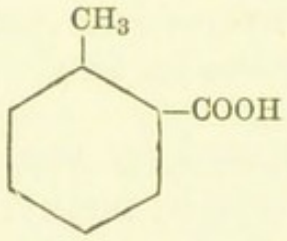
$$C_6H_4{<}\begin{matrix}CH_3\\Br\end{matrix} + CH_3I + 2Na = C_6H_4{<}\begin{matrix}CH_3\\CH_3\end{matrix} + NaBr + NaI;$$

pure p-*xylene* is produced in a similar manner from

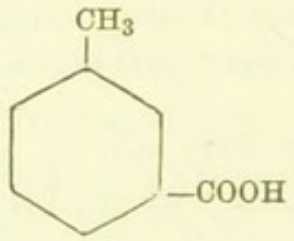
p-bromotoluene; m-*xylene* might be obtained by treating m-bromotoluene with methyl iodide and sodium, but is more easily prepared in a pure condition by distilling mesitylenic acid (p. 358) with soda-lime,

$$C_6H_3(CH_3)_2\cdot COOH = C_6H_4(CH_3)_2 + CO_2.$$

The three xylenes are very similar in physical properties (compare p. 371), and are all mobile, rather pleasant-smelling, inflammable liquids (p-xylene melts at 15°), which distil without decomposing, and are readily volatile in steam. They also resemble one another in chemical properties, although in some respects they show important differences, which must be ascribed to their difference in constitution. On oxidation, under suitable conditions, they are all converted in the first place into monocarboxylic acids, which are respectively represented by the formulæ,



o-Toluic Acid.



m-Toluic Acid.



p-Toluic Acid.

On further oxidation the second methyl-group undergoes a like change, and the three corresponding dicarboxylic acids, $C_6H_4(COOH)_2$, are formed (p. 476).

The three hydrocarbons show slight differences in behaviour on oxidation, one being more easily acted on than another by a particular oxidising agent. With chromic acid, for example, o-xylene is completely oxidised to carbon dioxide and water, whereas m-xylene and p-xylene yield the dicarboxylic acids (see above); with dilute nitric acid, o-xylene gives o-toluic acid, and p-xylene, p-toluic acid, but m-xylene is not readily acted on. Their behaviour with sulphuric acid is also different (p. 375).

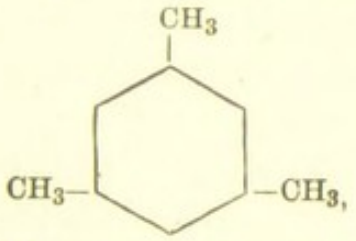
Ethylbenzene, $C_6H_5\cdot C_2H_5$ (phenylethane), an isomeride of the xylenes, is not of much importance; it occurs in coal-tar, and may be obtained by the general methods,

It is a colourless liquid, boiling at 134°, and on oxidation with dilute nitric acid or chromic acid it is converted into benzoic acid,

$$C_6H_5\cdot CH_2\cdot CH_3 + 6O = C_6H_5\cdot COOH + CO_2 + 2H_2O.$$

The next member of the series has the molecular formula, C_9H_{12}, and exists, as already pointed out (p. 368), in eight isomeric forms, of which the three trimethylbenzenes and isopropylbenzene are the more important.

Mesitylene, 1:3:5- or symmetrical trimethylbenzene,



occurs in small quantities in coal-tar, but is most conveniently prepared by distilling a mixture of acetone (2 vols.), concentrated sulphuric acid (2 vols.), and water (1 vol.), sand being added to prevent frothing,

$$3(CH_3)_2CO = C_6H_3(CH_3)_3 + 3H_2O.$$

The formation of mesitylene in this way is of interest, not only because it affords a means of synthesising the hydrocarbon from its elements, but also because it throws light on the constitution of the compound. Although the change is a process of condensation, and is most simply expressed by the graphic equation already given (p. 362), it might be assumed that the acetone is first converted into $CH_3\cdot C(OH):CH_2$ (by intramolecular change), or into $CH_3\cdot C:CH$, and that mesitylene is then produced by a secondary reaction. Whatever view, however, is adopted, as to the various stages of the reaction (unless, indeed, highly improbable assumptions are made), it would seem that the constitution of the product must be expressed by a *symmetrical* formula; for this and other reasons, mesitylene is regarded as *symmetrical* or 1:3:5-trimethylbenzene.

Mesitylene is a colourless, mobile, pleasant-smelling liquid, boiling at 164·5°, and volatile in steam; when treated with concentrated nitric acid, it yields *mononitro-* and *dinitromesitylene*, whereas with a mixture of nitric and sulphuric acids it is converted into *trinitromesitylene*, $C_6(NO_2)_3(CH_3)_3$.

On oxidation with dilute nitric acid, it yields *mesitylenic acid*, $C_6H_3(CH_3)_2 \cdot COOH$, *uvitic acid*, $C_6H_3(CH_3)(COOH)_2$, and *trimesic acid*, $C_6H_3(COOH)_3$, by the successive transformation of methyl- into carboxyl-groups.

Pseudocumene, or 1:2:4-trimethylbenzene, and **hemimellitene**, or 1:2:3-trimethylbenzene, also occur in small quantities in coal-tar, and are very similar to mesitylene in properties; on oxidation, they yield various acids by the conversion of one or more methyl- into carboxyl-groups.

Cumene, $C_6H_5 \cdot CH(CH_3)_2$ (isopropylbenzene), is usually obtained from coal-tar; it may be prepared in a pure condition by distilling *cumic acid* (*isopropylbenzoic acid*) with soda-lime,

$$C_6H_4 < \begin{matrix} C_3H_7 \\ COOH \end{matrix} = C_6H_5 \cdot C_3H_7 + CO_2,$$

by treating a mixture of isopropyl bromide and benzene with aluminium chloride,

$$C_6H_6 + C_3H_7Br = C_6H_5 \cdot C_3H_7 + HBr,$$

and by the action of sodium on a mixture of bromobenzene and isopropyl bromide,

$$C_6H_5Br + C_3H_7Br + 2Na = C_6H_5 \cdot C_3H_7 + 2NaBr.$$

It is a colourless liquid, boiling at 153°, and on oxidation with dilute nitric acid, it is converted into benzoic acid.

Cymene, $C_6H_4(CH_3) \cdot C_3H_7$ (**p**-methylisopropylbenzene), is a hydrocarbon of considerable importance, as it occurs in the ethereal oils or essences of many plants; it is easily prepared in many ways, as, for example, by heating camphor with phosphorus pentoxide,

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O,$$

by heating turpentine with concentrated sulphuric acid or with iodine (both of which, in this case, act as oxidising agents),

$$C_{10}H_{16} + O = C_{10}H_{14} + H_2O,$$

and by heating thymol (p. 445), or carvacrol (p. 445), with phosphorus pentasulphide (which acts as a reducing agent),

$$C_6H_3(OH) < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix} + 2H = C_6H_4 < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix} + H_2O.$$

Cymene is a pleasant-smelling liquid of sp. gr. 0·8722 at 0°, and boils at 175–176°; on oxidation with dilute nitric acid, it yields **p**-*toluic acid*, $C_6H_4(CH_3)\cdot COOH$, and *terephthalic acid*, $C_6H_4(COOH)_2$.

Diphenyl, Diphenylmethane, and Triphenylmethane.

All the hydrocarbons hitherto described contain only *one* benzene nucleus, and may be regarded as derived from benzene by the substitution of alkyl-groups for atoms of hydrogen; there are, however, several other series of aromatic hydrocarbons, which include compounds of considerable importance.

Diphenyl, $C_6H_5–C_6H_5$, is not a homologue of benzene, and its molecule contains *two* benzene nuclei. It is formed by treating bromobenzene with sodium in ethereal solution,

$$2C_6H_5Br + 2Na = C_6H_5\cdot C_6H_5 + 2NaBr,$$

a reaction which is analogous to the formation of ethane (dimethyl) from methyl iodide (p. 60); it is also produced in the preparation of magnesium phenyl bromide (p. 390).

Diphenyl may be prepared by passing benzene vapour through a red-hot tube filled with pieces of pumice,

$$2C_6H_6 = C_6H_5\cdot C_6H_5 + H_2.$$

The dark-coloured distillate is fractionated, and the diphenyl is purified by recrystallisation from alcohol.

Diphenyl is colourless, melts at 71°, and boils at 254°; when oxidised with chromic acid it yields benzoic acid, one of the benzene nuclei being destroyed. Its behaviour with halogens, nitric acid, and sulphuric acid is similar to that of benzene, substitution products being formed.

Diphenylmethane, $C_6H_5\cdot CH_2\cdot C_6H_5$, also contains *two* benzene nuclei; it may be regarded as derived from methane by the substitution of two phenyl-groups for two atoms of hydrogen, just as toluene or phenylmethane may be considered as a mono-substitution product of methane.

Diphenylmethane may be prepared by treating benzene

with benzyl chloride (p. 389) in presence of aluminium chloride,

$$C_6H_6 + C_6H_5{\cdot}CH_2Cl = C_6H_5{\cdot}CH_2{\cdot}C_6H_5 + HCl.$$

It is crystalline, and melts at 26·5°; when treated with nitric acid, it yields nitro-derivatives in the usual way, and on oxidation with chromic acid, it is converted into diphenyl ketone or *benzophenone*, $C_6H_5{\cdot}CO{\cdot}C_6H_5$ (p. 462).

Triphenylmethane, $(C_6H_5)_3CH$, is the parent substance of an important group of compounds, all of which contain *three* benzene nuclei. It is formed when benzal chloride (p. 390) is treated with benzene in presence of aluminium chloride,

$$C_6H_5{\cdot}CHCl_2 + 2C_6H_6 = (C_6H_5)_3CH + 2HCl,$$

but it is usually prepared by warming a mixture of chloroform and benzene with aluminium chloride,

$$CHCl_3 + 3C_6H_6 = (C_6H_5)_3CH + 3HCl.$$

Aluminium chloride (5 parts) is gradually added to a mixture of chloroform (1 part) and benzene (5 parts), which is then heated at about 60° (with reflux condenser) until the evolution of hydrogen chloride ceases, an operation which occupies about thirty hours; when cold, the product is carefully treated with water, and the oil is separated and submitted to fractional distillation. Those portions of the distillate which solidify on being cooled consist of crude triphenylmethane, which is further purified by recrystallisation from benzene and then from ether.

Triphenylmethane is colourless, melts at 92°, and boils at 358°; it is readily soluble in ether and benzene, but only sparingly so in cold alcohol. When treated with fuming nitric acid, it is converted into a yellow, crystalline *trinitro*-derivative, $CH(C_6H_4{\cdot}NO_2)_3$, which, like other nitro-compounds, is readily reduced to the corresponding *triamino*-compound, $CH(C_6H_4{\cdot}NH_2)_3$; the last-named substance is of considerable importance, as many of its derivatives are largely employed as dyes (p. 642).

On oxidation with chromic acid, triphenylmethane is converted into *triphenyl carbinol*, $(C_6H_5)_3C{\cdot}OH$.

CHAPTER XXIII.

Halogen Derivatives of Benzene and of its Homologues.

The action of chlorine and bromine on benzene has already been referred to (p. 343). At ordinary temperatures, in absence of direct sunlight, *substitution* products are slowly formed; this action is greatly hastened by the presence of a halogen carrier, such as iodine, iron, aluminium, &c.* In presence of direct sunlight, however, the hydrocarbon yields *additive* compounds by direct combination with six atoms of the halogen.

The homologues of benzene also show a curious behaviour; when treated with chlorine or bromine at ordinary temperatures in absence of direct sunlight, they are converted into *substitution* products by the displacement of hydrogen of the *nucleus*, and, as in the case of benzene itself, the reaction is greatly promoted by the presence of a halogen carrier; under these conditions toluene, for example, gives a mixture of o- and p-*chlorotoluenes* or *bromotoluenes*,

$$C_6H_5\cdot CH_3 + Cl_2 = C_6H_4{<}^{Cl}_{CH_3} + HCl.$$

When, on the other hand, no halogen carrier is present, and the hydrocarbons are treated with chlorine or bromine at their boiling-points, or in direct sunlight, they yield derivatives by the displacement of hydrogen of the *side-chain*; when, for example, chlorine is passed into *boiling* toluene, the three hydrogen atoms of the methyl-group are succes-

* The action of iodine has already been explained (p. 170); iron, aluminium, antimony, and certain other metals act as halogen carriers, possibly because their chlorides ($FeCl_3$, $AlCl_3$ $SbCl_5$) react with the hydrocarbons and give products, which are then decomposed by the free halogen, with formation of the metallic chloride and a halogen substitution product of the hydrocarbon.

sively displaced, *benzyl chloride*, $C_6H_5 \cdot CH_2Cl$, *benzal chloride*, $C_6H_5 \cdot CHCl_2$, and *benzotrichloride*, $C_6H_5 \cdot CCl_3$, being formed; xylene, again, when heated at its boiling-point and treated with bromine, gives the compounds,

$$C_6H_4 < \begin{matrix} CH_2Br \\ CH_3 \end{matrix} \quad \text{and} \quad C_6H_4 < \begin{matrix} CH_2Br \\ CH_2Br \end{matrix}.$$

Although these statements are true in the main, it must not be supposed that under any conditions substitution takes place *only* in the nucleus *or* in the side-chain, as the case may be, because this is not so; in presence of a halogen carrier, relatively small quantities of halogen derivatives are formed by displacement of hydrogen of the side-chain, and at the boiling-point of the hydrocarbon, or in direct sunlight, hydrogen of the nucleus is displaced to some extent.

Iodine, as a rule, does not act on aromatic hydrocarbons, and if at high temperatures substitution occurred, the product would be reduced again to the hydrocarbon,

$$C_6H_6 + I_2 = C_6H_5I + HI,$$
$$C_6H_5I + HI = C_6H_6 + I_2.$$

When, however, iodic acid, or some other substance which decomposes hydrogen iodide, is present, iodo-derivatives may sometimes be prepared by direct treatment with the halogen at high temperatures.*

Preparation.—Chloro- and bromo-derivatives of benzene and of its homologues may be prepared by direct '*chlorination*' or '*bromination*;' † the conditions employed depend on whether hydrogen of the nucleus or of the side-chain is to be displaced. If, for example, toluene is to be converted into **p**-*chlorobenzyl chloride*, $C_6H_4Cl \cdot CH_2Cl$, the hydrocarbon

* $HIO_3 + 5HI = 3I_2 + 3H_2O$. Iodo-substitution products are also frequently formed when ferric chloride or aluminium chloride is employed as a carrier, because the iodine monochloride which is produced has a much more energetic substituting action than iodine, owing to the simultaneous formation of hydrogen chloride (a strongly exothermic compound),

$$C_6H_6 + ICl = C_6H_5I + HCl.$$

† These terms are applied to processes in which hydrogen is displaced by the use of the *free halogens* themselves.

might be first treated with chlorine at ordinary temperatures in presence of iodine; the **p**-*chlorotoluene*, $C_6H_4Cl{\cdot}CH_3$, thus formed (after having been separated from the accompanying ortho-compound), would then be boiled in a flask connected with a reflux condenser, and a stream of dry chlorine led into it.

In all operations of this kind the theoretical quantity, or a slight excess of halogen, is employed. Bromine is weighed directly, but in the case of chlorine the process of chlorination is continued until the theoretical gain in weight has taken place; the halogen should be dry, as, in presence of water, oxidation products of the hydrocarbon may be formed. The fumes of hydrogen chloride or bromide evolved during such operations are conveniently absorbed with the aid of a vessel containing damp coke.

A very important general method for the preparation of aromatic halogen derivatives, *containing the halogen in the nucleus*, consists in the decomposition of the diazonium-salts. As the properties and decompositions of the last-named substances are described later (p. 412), it is only necessary to state here that this method is used in the preparation of nearly all iodo-compounds, and that it affords a means of indirectly substituting any of the halogens, not only for hydrogen, but also for nitro- or amino-groups.

The conversion of benzene or toluene, for example, into a mono-halogen derivative by this method involves the following steps:—

$$\underset{\text{Benzene.}}{C_6H_6} \longrightarrow \underset{\text{Nitrobenzene.}}{C_6H_5{\cdot}NO_2} \longrightarrow \underset{\text{Aminobenzene.}}{C_6H_5{\cdot}NH_2} \longrightarrow \underset{\text{Phenyldiazonium Chloride.}}{C_6H_5{\cdot}N_2Cl} \longrightarrow \underset{\text{Chlorobenzene.}}{C_6H_5Cl}$$

$$\underset{\text{Toluene.}}{C_6H_5{\cdot}CH_3} \longrightarrow \underset{\text{Nitrotoluene.}}{C_6H_4\langle^{CH_3}_{NO_2}} \longrightarrow \underset{\text{Aminotoluene.}}{C_6H_4\langle^{CH_3}_{NH_2}} \longrightarrow \underset{\text{Tolyldiazonium Bromide.}}{C_6H_4\langle^{CH_3}_{N_2Br}} \longrightarrow \underset{\text{Bromotoluene.}}{C_6H_4\langle^{CH_3}_{Br}}.$$

The preparation of a *di*-halogen derivative may sometimes be carried out in a similar manner, the hydrocarbon being first converted into the *di*-nitro-derivative; in most cases, however, it is necessary to prepare the *mono*-halogen derivative

by the reactions given above, to convert the latter into the nitro-compound, and then to displace the nitro-group by a halogen atom in the usual way,

$$C_6H_5Br \rightarrow C_6H_4\langle{}^{Br}_{NO_2} \rightarrow C_6H_4\langle{}^{Br}_{NH_2} \rightarrow C_6H_4\langle{}^{Br}_{N_2Cl} \rightarrow C_6H_4\langle{}^{Br}_{Cl}.$$

Bromo-benzene. Nitrobromo-benzene. Aminobromo-benzene. Bromophenyl-diazonium Chloride. Bromochloro-benzene.

Halogen derivatives of benzene and its homologues are sometimes prepared by treating hydroxy-compounds with the tri- or penta-halogen derivatives of phosphorus, the changes being similar to those which occur in the case of fatty hydroxy-compounds;* when the hydroxyl-group is present in the nucleus, the halogen naturally takes up the same position, phenol, for example, giving *chlorobenzene*, and cresol, *chlorotoluene*,

$$C_6H_5\cdot OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl,$$

$$C_6H_4\langle{}^{CH_3}_{OH} + PCl_5 = C_6H_4\langle{}^{CH_3}_{Cl} + POCl_3 + HCl.$$

An aromatic alcohol (p. 450), such as benzyl alcohol, also yields the corresponding halogen derivative (*benzyl chloride*), containing the halogen in the side-chain,

$$C_6H_5\cdot CH_2\cdot OH + PCl_5 = C_6H_5\cdot CH_2Cl + POCl_3 + HCl.$$

Halogen derivatives may also be obtained by distilling halogen acids with lime,

$$C_6H_4Br\cdot COOH = C_6H_5Br + CO_2,$$

and by heating sulphonic chlorides (p. 429) with phosphorus pentachloride,

$$C_6H_5\cdot SO_2Cl + PCl_5 = C_6H_5Cl + POCl_3 + SOCl_2.$$

Properties.—At ordinary temperatures, most of the *mono*-halogen derivatives of benzene and its simpler homologues are colourless liquids; the *di*-halogen derivatives, however, are generally crystalline solids. They are all insoluble, or nearly so, in water, but soluble in alcohol, ether, &c. Many are readily volatile in steam, and distil without decomposing, the boiling-point being higher, and the specific gravity greater, than that of the parent hydrocarbon, and rising also as bromine is substituted for chlorine, or iodine for bromine.

* The tri-halogen derivatives generally give the better results (compare footnote, p. 94).

	Benzene.	Chlorobenzene.	Bromobenzene.	Iodobenzene.
B.p.....	80·5°	132°	155°	188°.
Sp. gr. at 0°	0·899	1·128	1·521	1·857.

They are not so inflammable as the hydrocarbons, and the vapours of many of them have a very irritating action on the eyes and respiratory organs.

When the halogen is united with carbon of the benzene nucleus, it is, as a rule, very firmly combined, and *cannot be displaced by the hydroxyl- or amino-group, with the aid of aqueous alkalis, silver hydroxide, or alcoholic ammonia.* Such halogen derivatives, moreover, are *not acted on by alcoholic potash*, and cannot be converted into less saturated compounds in the same way as ethyl bromide, for example, may be converted into ethylene; in fact, no derivative of benzene containing less than six univalent atoms, or their valency equivalent, is known. If, however, hydrogen of the nucleus has been displaced by one or more nitro-groups, as well as by a halogen, the latter often becomes much more open to attack; **o**- and **p**-*chloronitrobenzene*, $C_6H_4Cl{\cdot}NO_2$, for example, are moderately easily acted on by alcoholic potash and by alcoholic ammonia at high temperatures, yielding the corresponding nitro-phenols, $C_6H_4(OH){\cdot}NO_2$, and nitranilines, $C_6H_4(NH_2){\cdot}NO_2$; **m**-*chloronitrobenzene*, however, is not acted on under these conditions, a fact which shows that such isomerides sometimes differ very considerably in chemical properties.

Halogen atoms in the side-chains are very much less firmly combined than are those in the nucleus, and may be displaced by hydroxyl- or amino-groups just as in fatty compounds; *benzyl chloride*, $C_6H_5{\cdot}CH_2Cl$, for example, is converted into *benzyl alcohol*, $C_6H_5{\cdot}CH_2{\cdot}OH$, by boiling sodium carbonate solution, and when heated with alcoholic ammonia, it yields *benzylamine*, $C_6H_5{\cdot}CH_2{\cdot}NH_2$ (p. 411).

Halogen atoms in the nucleus, as well as those in the side-chain, are displaced by hydrogen with the aid of hydriodic acid and red phosphorus at high temperatures, or with

sodium amalgam in alcoholic solution; the former, however, are much less readily displaced than the latter.

Chlorobenzene, C_6H_5Cl (phenyl chloride), may be described as a typical example of those halogen derivatives in which the halogen is combined with carbon of the nucleus. It may be obtained (together with dichlorobenzenes, $C_6H_4Cl_2$, trichlorobenzenes, $C_6H_3Cl_3$, &c.), by *chlorinating* benzene; also by treating phenol (p. 439) with phosphorus pentachloride, just as ethyl chloride may be produced from ethyl alcohol,

$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl.$$

It is usually prepared by Sandmeyer's reaction—that is to say, by warming an aqueous solution of phenyldiazonium chloride with cuprous chloride (p. 414); this method, therefore, affords a means of preparing chlorobenzene, not only from the diazonium-salt, but also indirectly from aminobenzene (aniline), nitrobenzene, and benzene, in the manner already indicated (p. 383).

Aniline (20 g.) is *diazotised* in the manner described on p. 415. The solution of the diazonium chloride is then dropped from a stoppered funnel into a boiling solution of cuprous chloride (10 g.) in concentrated hydrochloric acid (about 100 c.c.), which is contained in a flask provided with a reflux condenser. When the evolution of nitrogen is at an end, the chlorobenzene is distilled in steam, and isolated in the usual manner.

Chlorobenzene is a colourless, mobile, pleasant-smelling liquid, specifically heavier than water; it boils at 132°, and is readily volatile in steam. Like benzene, it is capable of yielding nitro-, amino-, and other derivatives; it differs from ethyl chloride and from other alkyl halogen compounds in being unacted on by water and alkalis, or by metallic salts; it is impossible, for example, to prepare phenyl acetate, $CH_3{\cdot}COOC_6H_5$, by treating silver acetate with chlorobenzene, although ethyl acetate is easily obtained from ethyl chloride in this way.

Bromobenzene, C_6H_5Br (phenyl bromide), may be prepared from phenyldiazonium sulphate by Sandmeyer's reaction,

using cuprous bromide (p. 414); also by *brominating* benzene in presence of iron.

Benzene (1 part), together with a little iron wire, is placed in a flask provided with a reflux condenser, and the bromine (2 parts) is added gradually from a stoppered funnel, the bent stem of which passes through the cork of the flask; the hydrogen bromide which is evolved is absorbed in a tower containing moist coke. The product is washed well with dilute caustic soda and water successively, dried, and separated from any unchanged benzene by fractional distillation. The p-*dibromobenzene* (m.p. 89°; b.p. 219°), which is also formed in the above reaction, remains as a residue if the distillation is stopped when the thermometer rises to about 170°; it solidifies when cold, and may be recrystallised from aqueous alcohol.

Bromobenzene is a colourless liquid, which boils at 155°, and closely resembles chlorobenzene in all respects. As a rule, the bromo-derivatives crystallise more readily, and have higher melting-points than the corresponding chloro-compounds.

Iodobenzene, C_6H_5I (phenyl iodide), cannot be obtained by the action of iodine alone on benzene;* it is most conveniently prepared by decomposing phenyldiazonium sulphate with potassium iodide in aqueous solution,

$$C_6H_5{\cdot}N_2{\cdot}SO_4H + KI = C_6H_5I + KHSO_4 + N_2.$$

Aniline (1 part) is *diazotised* with sodium nitrite and sulphuric acid (compare p. 415), the cold solution of the diazonium sulphate is poured into a concentrated solution of potassium iodide (2½ parts), and the mixture is gradually heated until nitrogen is no longer evolved; the iodobenzene is then separated by steam distillation, washed with dilute caustic soda, dried, and distilled.

It is a heavy, colourless, mobile liquid, boiling at 188°.

Iodobenzene dichloride, $C_6H_5{\cdot}ICl_2$, separates in crystals when iodobenzene is dissolved in chloroform and dry chlorine is passed into the *well-cooled* solution. It is slowly decomposed by dilute caustic soda (4–5 per cent.), and in the course of 6–8 hours at ordinary temperatures, it is converted into *iodosobenzene*,

$$C_6H_5ICl_2 + 2NaOH = C_6H_5IO + 2NaCl + H_2O,$$

* It is formed when the hydrocarbon is heated with iodine in presence of iodic acid at about 220° (p. 382).

which can be separated by filtration, washed with water, and dried on porous earthenware.

Iodosobenzene, C_6H_5IO, is a colourless solid, moderately easily soluble in warm water and alcohol; it explodes at about 210°. It has *basic* properties, and reacts with acids, forming a salt and water,

$$C_6H_5IO + 2C_2H_4O_2 = C_6H_5I(C_2H_3O_2)_2 + H_2O;$$

it is also an oxidising agent, and liberates iodine from potassium iodide in acid solution,

$$C_6H_5IO + 2HI = C_6H_5I + I_2 + H_2O.$$

When iodosobenzene is submitted to distillation in steam, it undergoes a most interesting decomposition, giving iodobenzene, which distils over with the water, and *iodoxybenzene*, which is non-volatile,

$$2C_6H_5IO = C_6H_5I + C_6H_5IO_2.$$

Iodoxybenzene, $C_6H_5IO_2$, separates in colourless needles when the aqueous solution is evaporated to a small volume and then allowed to cool; it explodes at about 230°. Unlike iodosobenzene, it does not show basic properties, but it is an oxidising agent and liberates iodine (4 atoms) from hydrogen iodide.

When a mixture of iodosobenzene and iodoxybenzene is shaken with water and freshly precipitated silver hydroxide, interaction takes place and **diphenyliodonium iodate** is formed,

$$C_6H_5IO + C_6H_5IO_2 = (C_6H_5)_2I{\cdot}IO_3.$$

This product is the salt of a strongly basic hydroxide, $(C_6H_5)_2I{\cdot}OH$, **diphenyliodonium hydroxide**, which has only been isolated in the form of its salts; it is an interesting fact that such derivatives of tervalent iodine should show basic properties.

These remarkable compounds were discovered and investigated by Willgerodt and by V. Meyer; analogous compounds have been obtained from other iodo-derivatives containing the iodine atom directly united with the benzene (or naphthalene) nucleus.

Chlorotoluene, $C_6H_4Cl{\cdot}CH_3$ (tolyl chloride), being a di-substitution product of benzene, exists in three isomeric modifications, only two of which—namely, the **o**- and **p**-compounds—are formed when *cold* toluene is treated with chlorine in presence of iodine or iron; the three isomerides may be separately prepared by treating the corresponding cresols (p. 444) with phosphorus pentachloride,

$$C_6H_4{<}\begin{matrix}OH\\CH_3\end{matrix} + PCl_5 = C_6H_4{<}\begin{matrix}Cl\\CH_3\end{matrix} + POCl_3 + HCl,$$

but they are best prepared from the corresponding toluidines by Sandmeyer's method,

$$C_6H_4\begin{cases}NH_2\\CH_3\end{cases} \rightarrow C_6H_4\begin{cases}N_2Cl\\CH_3\end{cases} \rightarrow C_6H_4\begin{cases}Cl\\CH_3\end{cases}.$$

Toluidine. Tolyldiazonium Chloride. Chlorotoluene.

o-*Chlorotoluene* boils at 156°, m-*chlorotoluene* at 150°, and p-*chlorotoluene* at 160°; they resemble chlorobenzene in most respects, but, since they contain a methyl-group, they have also some of the properties of fatty compounds; on oxidation, they are converted into the corresponding *chlorobenzoic acids*, $C_6H_4Cl{\cdot}COOH$, just as toluene is transformed into benzoic acid.

Benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, although isomeric with the three chlorotoluenes, differs from them very widely, and may be taken as an example of the class of halogen compounds in which the halogen is present in the *side-chain*. It can be obtained by treating benzyl alcohol (p. 451) with phosphorus pentachloride,

$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl,$$

but is always prepared by passing chlorine into boiling toluene,

$$C_6H_5{\cdot}CH_3 + Cl_2 = C_6H_5{\cdot}CH_2Cl + HCl.$$

The toluene is contained in a flask which is heated on a sand-bath and connected with a reflux condenser; a stream of dry chlorine is then passed into the boiling liquid, until the theoretical gain in weight has taken place, and the product is purified by fractional distillation; the action takes place most rapidly in strong sunlight.

Benzyl chloride is a colourless, unpleasant-smelling liquid, boiling at 176°; it is insoluble in water, but miscible with alcohol, ether, benzene, &c. It behaves like other aromatic compounds towards nitric acid, by which it is converted into a mixture of isomeric nitro-compounds, $C_6H_4(NO_2){\cdot}CH_2Cl$. At the same time, however, it has many properties in common with the alkyl halogen compounds; like ethyl chloride,

it is slowly decomposed by boiling water, yielding the corresponding hydroxy-compound, *benzyl alcohol* (p. 451),

$$C_6H_5\cdot CH_2Cl + H_2O = C_6H_5\cdot CH_2\cdot OH + HCl,$$

and just as ethyl chloride interacts with silver acetate, giving ethyl acetate, so benzyl chloride, under the same conditions, yields the ester, *benzyl acetate* (b.p. 206°),

$$C_6H_5\cdot CH_2Cl + CH_3\cdot COOAg = CH_3\cdot COO\cdot CH_2\cdot C_6H_5 + AgCl.$$

Benzyl chloride is a substance of considerable commercial importance, inasmuch as it is used for the preparation of benzaldehyde (p. 453).

Benzal chloride, $C_6H_5\cdot CHCl_2$, may be obtained by treating benzaldehyde with phosphorus pentachloride,

$$C_6H_5\cdot CHO + PCl_5 = C_6H_5\cdot CHCl_2 + POCl_3,$$

but it is prepared by chlorinating toluene, just as described in the case of benzyl chloride, except that the process is continued until twice as much chlorine has been absorbed. It is a colourless liquid, boiling at 206°, and is used for the preparation of benzaldehyde.

Benzotrichloride, $C_6H_5\cdot CCl_3$ (phenylchloroform), is also prepared by chlorinating boiling toluene; it boils at 213°, and when heated with water, it is converted into benzoic acid,

$$C_6H_5\cdot CCl_3 + 2H_2O = C_6H_5\cdot COOH + 3HCl.$$

The aromatic halogen derivatives, like the alkyl halogen compounds, react readily with magnesium in presence of pure ether, and the *Grignard reagents* which are thus formed show the behaviour of those of the aliphatic series (pp. 227, 228).

Magnesium phenyl bromide, $C_6H_5\cdot MgBr$, and **magnesium benzyl chloride,** $C_6H_5\cdot CH_2\cdot MgCl$, are common reagents of this type. As these compounds are decomposed by water, giving benzene and toluene respectively, the aromatic monohalogen derivatives may be easily transformed into the parent hydrocarbons.

CHAPTER XXIV.

Nitro-Compounds.

It has already been stated that one of the more characteristic properties of aromatic compounds is the readiness with which they may be converted into nitro-derivatives, by the substitution of nitro-groups for hydrogen of the *nucleus;* the compounds formed in this way are of the greatest importance, more especially because it is from them that the amino- and diazonium-compounds are prepared.

Preparation.—Many aromatic compounds are '*nitrated*'—that is to say, converted into their nitro-derivatives—when they are treated with concentrated nitric acid (sp. gr. 1·3 to 1·5), in the cold or at ordinary temperatures, and under such conditions a mononitro-compound is usually produced; benzene, for example, yields *nitrobenzene*, and toluene, a mixture of o- and p-*nitrotoluenes*,

$$C_6H_6 + HNO_3 = C_6H_5{\cdot}NO_2 + H_2O,$$
$$C_6H_5{\cdot}CH_3 + HNO_3 = C_6H_4(CH_3){\cdot}NO_2 + H_2O.$$

Some aromatic compounds, however, are only very slowly acted on by nitric acid alone; in such cases a mixture of concentrated nitric and sulphuric acids is used. This mixture is also employed in many cases, even when nitric acid alone might be used, because nitration then takes place more readily. When a large excess of such a mixture is used, and especially when heat is applied, the aromatic compound is usually converted into (a mixture of isomeric) dinitro- or trinitro-derivatives; benzene, for instance, yields a mixture of three *dinitro-benzenes*, the principal product, however, being the meta-compound,

$$C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O.$$

As soon as nitration is complete (portions of the product may be tested from time to time), the solution or mixture, having been

cooled if necessary, is poured on to ice or into a large volume of water, and the product, which is usually precipitated in crystals, is separated by filtration, or if an oil, by extraction with ether.

Generally speaking, the number of hydrogen atoms displaced by nitro-groups is greater the higher the temperature and the more concentrated the acid, or mixture of acids, employed, but depends to an even greater extent on the nature of the substance undergoing nitration; as a rule, the introduction of nitro-groups is facilitated when other atoms or groups, especially hydroxy- or alkyl-groups, have already been substituted for hydrogen of the nucleus. The *nature* of these atoms or groups, moreover, determines the position taken up by the entering nitro-group; if the former are strongly negative or acid in character, as, for example, $-NO_2$, $-COOH$, and $-SO_3H$, the **m**-nitro-derivative is formed, whereas, when the atom or group in question is a halogen, or an alkyl-, amino-, or hydroxyl-group, a mixture of the **o**- and **p**-nitro-derivatives is produced.

This *directing* influence of an atom or group, already combined with the nucleus, on the position which is taken up by a second substituent, is by no means restricted to the case of nitro-compounds, but is observed in the formation of all benzene substitution products, except, of course, in that of the mono-derivatives; so regularly, in fact, is this influence exercised that it is possible to summarise the course of those reactions, which take place in the formation of the best-known di-derivatives, in the following statements:—

The relative position taken up by one of the following atoms or groups, Cl, Br, NO_2, SO_3H, which are capable of directly displacing hydrogen of the nucleus, depends on the nature of the atom or group, A, already united with the nucleus.

When A = Cl, Br, I, NH_2, OH, CH_3 (or other alkyl-groups), a *para*-compound is the principal product, but it is usually accompanied by smaller and varying quantities of the *ortho*-compound.

When, on the other hand,

$$A = NO_2, COOH, SO_3H, CHO, CO{\cdot}CH_3, CN,$$

a *meta*-derivative is the principal product, and only very small quantities of the ortho- and para-compounds are formed.

This general behaviour may also be summarised as follows (*Crum Brown's rule*):—When the atom or group, A, in a mono-substitution product is such that its hydrogen compound, HA, cannot be *directly* oxidised to HO·A, the di-substitution product is a mixture of the *ortho-* and *para*-compounds; if, on the other hand, HA can be directly oxidised to HO·A, the di-substitution product is the meta-compound.

These statements also hold good when two identical atoms or groups are introduced in one operation, since the change really takes place in *two stages;* when benzene, for example, is treated with nitric acid, *meta*-dinitrobenzene is the principal product, whereas with bromine, it yields *para*-dibromobenzene.

Properties.—As a rule, aromatic nitro-compounds are yellow, well-defined, crystalline substances, and, therefore, they often serve for the identification of hydrocarbons and other liquids. Many of them are volatile in steam, but, with the exception of certain mono-nitro-derivatives, they cannot be distilled under ordinary pressure, as when heated strongly they decompose, sometimes with explosive violence; they are generally sparingly soluble in water, but readily soluble in benzene, ether, alcohol, &c.* As in the case of the nitro-paraffins (p. 189), the nitro-group is very firmly combined, and, as a rule, is not displaced by the hydroxyl-group on treatment with aqueous or alcoholic potash, even at high temperatures.

The most important reaction of the nitro-compounds—namely, their behaviour on reduction—is described later (p. 397).

Nitrobenzene, $C_6H_5{\cdot}NO_2$, is usually prepared in the labora-

* The solubility in water is closely connected with the structure of the compound, and, as a rule, the displacement of hydrogen atoms in a compound by -OH, $-NH_2$, or -COOH groups is accompanied by an increase in solubility.

tory by slowly adding to benzene (10 parts) a mixture of nitric acid of sp. gr. 1·45 (12 parts) and concentrated sulphuric acid (16 parts), the temperature being kept below about 40°.

The benzene is placed in a flask (which must *not* be corked), and the acid mixture is slowly added from a dropping funnel. The flask is cooled in water. The nitrobenzene separates at the surface as a yellow oil, which takes up the benzene, so that it is necessary to bring the latter into contact with the acid mixture by giving the vessel a rotatory motion. As soon as all the benzene has been added, the mixture is heated at about 80° for half-an-hour, then cooled, and poured into a large volume of water; the nitrobenzene, which collects at the bottom of the vessel, is separated with the aid of a funnel, washed with a little water or dilute alkali until free from acid, and dried with anhydrous calcium chloride.* It is then fractionated, in order to separate it from unchanged benzene and from small quantities of dinitrobenzene, which may have been produced; this is very easily accomplished, as the boiling-points of the three compounds are widely different. The fraction which passes over from about 200–215° is sufficiently free from impurity for ordinary purposes.

On the large scale, nitrobenzene is prepared in a similar manner, but the operation is carried out in iron vessels provided with stirrers; the product is separated from the acid mixture and distilled in a current of steam.

Nitrobenzene is a pale-yellow oil of sp. gr. 1·2 at 20°, and has a strong smell, which is very like that of benzaldehyde (p. 394); it boils at 205°, is volatile in steam, and is miscible with organic liquids, but is practically insoluble in water. In spite of the fact that it is poisonous, it is sometimes employed, instead of oil of bitter almonds, for flavouring and perfuming purposes, under the name of 'essence of mirbane;' its principal use, however, is for the manufacture of aniline (p. 402).

* The nitrobenzene is shaken with a few small lumps of the calcium chloride in the separating-funnel; as these dissolve, more are added, and so on, until the nitrobenzene becomes clear. It is then filtered into a distillation flask. If incompletely dried, the contents of the flask crackle and splutter when heat is applied.

Meta-dinitrobenzene, $C_6H_4(NO_2)_2$, is obtained, together with small quantities of the **o**- and **p**-dinitro-compounds, when nitrobenzene (1 part) is gradually added to a mixture of nitric acid (sp. gr. 1·5; $1\frac{1}{2}$ parts) and concentrated sulphuric acid ($1\frac{1}{2}$ parts), which is then heated on a sand-bath, until a drop of the oil, which floats at the surface, solidifies completely when it is stirred with cold water.

When cold, the mixture is poured into a large volume of water, and the solid product is separated by filtration, washed with water, and recrystallised from hot alcohol until its melting-point is constant; the **o**- and **p**-compounds, formed only in relatively small quantities, remain dissolved in the mother-liquors.

m-Dinitrobenzene crystallises in pale-yellow needles, melts at 90°, and is volatile in steam; it is only sparingly soluble in boiling water, but dissolves freely in most organic liquids. On reduction with alcoholic ammonium sulphide (p. 398), it is first converted into **m**-*nitraniline* (p. 395), and then into **m**-*phenylenediamine* (**m**-*diaminobenzene*), $C_6H_4(NH_2)_2$ (p. 407).

o-*Dinitrobenzene* and **p**-*dinitrobenzene* are colourless, crystalline compounds, melting at 118° and 173° respectively; they resemble the corresponding **m**-compound in their behaviour on reduction, and in most other respects. **o**-Dinitrobenzene, however, differs notably from the other two isomerides, inasmuch as it reacts with boiling caustic soda, yielding **o**-*nitrophenol* (p. 441), and with alcoholic ammonia, at moderately high temperatures, giving **o**-*nitraniline* (p. 405). A similar behaviour is observed in the case of other **o**-dinitro-compounds, the presence of the one nitro-group rendering the other more easily displaceable.

Symmetrical *trinitrobenzene*, $C_6H_3(NO_2)_3$, is formed when the **m**-dinitro-compound is heated with a mixture of nitric and anhydrosulphuric acids; it forms colourless crystals, and melts at 121–122°.

The halogen derivatives of benzene are readily nitrated, yielding, however, the **o**- and **p**-mononitro-derivatives only,

according to the general rule; the **m**-nitro-halogen compounds, therefore, are prepared by chlorinating or brominating nitrobenzene. All these nitro-halogen derivatives are crystalline, and, as will be seen from the following table, their melting-points exhibit the regularlity already mentioned (p. 371), except in the case of **m**-*iodonitrobenzene.*

		Ortho.	Meta.	Para.
Chloronitrobenzene,	$C_6H_4Cl{\cdot}NO_2$,	32·5°	44·4°	83°
Bromonitrobenzene,	$C_6H_4Br{\cdot}NO_2$,	41·5	56	126
Iodonitrobenzene,	$C_6H_4I{\cdot}NO_2$,	49	33	171

They are, on the whole, very similar in chemical properties, except that, as already pointed out (p. 385), the **o**- and **p**-compounds differ from the **m**-compounds in their behaviour with alcoholic potash and ammonia, a difference which recalls that shown by the three dinitrobenzenes.

The **nitrotoluenes**, $C_6H_4(CH_3){\cdot}NO_2$, are important, because they serve for the preparation of the toluidines (p. 406). The **o**- and **p**-compounds are prepared by nitrating toluene, and may be partially separated by fractional distillation; **o**-*nitrotoluene* melts at 10·5°, and boils at 218°, whereas **p**-*nitrotoluene* melts at 54°, and boils at 230°. **m**-*Nitrotoluene* is not easily prepared; it melts at 16°, and boils at 230°.

Many other nitro-compounds are mentioned later.

Phenylnitromethane, $C_6H_5{\cdot}CH_2{\cdot}NO_2$, is an example of a compound which contains a nitro-group in the side-chain. It is obtained by the interaction of *benzyl iodide*, $C_6H_5{\cdot}CH_2I$, and silver nitrite, and is a colourless liquid, boiling at 141° under 35 mm. pressure. Like the primary and secondary nitroparaffins, it is a *pseudo-acid* (p. 191), and gives, with sodium hydroxide, a salt, $C_6H_5{\cdot}CH{:}NO{\cdot}ONa$, which is derived from the acid, $C_6H_5{\cdot}CH{:}NO{\cdot}OH$; this acid is obtained as a crystalline precipitate (m.p. 84°) when the sodium salt is treated with a mineral acid in aqueous solution, but it soon undergoes isomeric change into phenylnitromethane, even at ordinary temperatures.

CHAPTER XXV.

Amino-Compounds and Amines.

The hydrogen atoms in aromatic compounds may be indirectly displaced by amino-groups, and in this way bases, such as *aniline*, $C_6H_5 \cdot NH_2$, *benzylamine*, $C_6H_5 \cdot CH_2 \cdot NH_2$, and *diaminobenzene*, $C_6H_4(NH_2)_2$, which are analogous to, and have many properties in common with, the fatty amines, are produced; as, however, those compounds which contain the amino-group directly united with carbon of the nucleus differ in several respects from those in which this group is present in the side-chain, and, moreover, are of much greater importance than the latter, they may be considered as forming a separate group, the members of which will be referred to as *amino-compounds*.

Amino-Compounds.

The amino-compounds, therefore, are derived from benzene and other aromatic substances, by the substitution of one or more amino-groups for hydrogen atoms of the *nucleus;* they may be classed as mono-, di-, tri-, &c., amino-compounds, according to the number of such groups which they contain,

$C_6H_5 \cdot NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$.
Aminobenzene (Aniline).	Diaminobenzene.	Triaminobenzene.

With the exception of aniline, all amino-compounds exist in three or more isomeric modifications; there are, for example, three isomeric (o.m.p.) *diaminobenzenes*, and three isomeric (o.m.p.) *aminotoluenes*, or *toluidines*, $C_6H_4(CH_3) \cdot NH_2$, a fourth isomeride of the toluidines—namely, *benzylamine*, $C_6H_5 \cdot CH_2 \cdot NH_2$ (p. 411)—being also known.

Preparation.—The amino-compounds are generally prepared by the reduction of the nitro-compounds; various reducing agents, such as tin, zinc, or iron, and hydrochloric or acetic

acid, are employed, but perhaps the most common one is a solution of stannous chloride in hydrochloric acid,

$$C_6H_5\cdot NO_2 + 6H = C_6H_5\cdot NH_2 + 2H_2O,$$
$$C_6H_4(CH_3)\cdot NO_2 + 6H = C_6H_4(CH_3)\cdot NH_2 + 2H_2O,$$
$$C_6H_5\cdot NO_2 + 3SnCl_2 + 6HCl = C_6H_5\cdot NH_2 + 3SnCl_4 + 2H_2O.$$

Reduction is usually effected by simply treating the nitro-compound with the reducing agent, when a vigorous reaction often ensues, and the application of heat is seldom necessary except towards the end of the operation. The solution then contains the amino-compound, combined as a salt with the acid which has been employed; when, however, tin, or stannous chloride, and hydrochloric acid have been used, a complex salt may be produced from the hydrochloride of the base and the stannic chloride which has been formed; in the preparation of aniline (p. 403), for example, the complex salt, *aniline stannichloride*, $(C_6H_5\cdot NH_2, HCl)_2, SnCl_4$, is formed. The amino-compound is liberated by adding excess of caustic soda or lime, and is distilled in steam, extracted with ether, or isolated in some other manner suitable to the special case.

The reduction of nitro-compounds takes place in two stages: in the first there is produced an unstable derivative of hydroxylamine,

$$R\cdot NO_2 + 4H = R\cdot NH\cdot OH + H_2O,$$

which, by the further action of the reducing agent, is converted into the amino-compound.

β-Phenylhydroxylamine is obtained when nitrobenzene, dissolved in ether, is cautiously reduced with aluminium amalgam and water. It is a crystalline substance, melting at 81°, and, like hydroxylamine, it is a base and forms salts, such as the hydrochloride, $C_6H_5\cdot NH\cdot OH, HCl$. When oxidised with potassium dichromate and dilute sulphuric acid, it yields *nitrosobenzene*, $C_6H_5\cdot NO$, a crystalline, very volatile substance, melting at 68°, which, on oxidation, is converted into nitrobenzene, and on reduction, into aniline.

Nitro-compounds may also be reduced to amino-compounds with hydrogen sulphide in alkaline solution, or, more conveniently, with an alcoholic solution of ammonium sulphide,

$$C_6H_5\cdot NO_2 + 3SH_2 = C_6H_5\cdot NH_2 + 2H_2O + 3S.$$

The nitro-compound is dissolved in alcohol, a concentrated solution of ammonium hydroxide is added, and hydrogen sulphide

is passed into the solution until reduction is complete, heat being applied if necessary. The solution is then filtered from precipitated sulphur, the alcohol is distilled off, and the residue is acidified with hydrochloric acid; the filtered solution of the hydrochloride of the base is now evaporated to a small bulk and treated with caustic soda, when the base separates as an oil or a solid, and may then be purified by distillation, recrystallisation, &c.

When a compound contains two or more nitro-groups, its partial reduction may be accomplished by treating its alcoholic solution either with the calculated quantity of stannous chloride and hydrochloric acid, or with ammonia and hydrogen sulphide; in the latter, as in the former case, one nitro-group is reduced before a second is attacked, so that if the current of gas is stopped at the right time (which must be ascertained by experiment), partial reduction only takes place. Dinitrobenzene, for example, can be converted into nitraniline by either of these methods, the latter being the more convenient,

$$C_6H_4{<}^{NO_2}_{NO_2} + 3SH_2 = C_6H_4{<}^{NO_2}_{NH_2} + 2H_2O + 3S.$$

The amino-derivatives of toluene, xylene, &c. are prepared commercially by heating the hydrochlorides of the isomeric alkylanilines, such as *methylaniline* and *dimethylaniline* (p. 408), at 280–300°, when the alkyl-group leaves the nitrogen atom and displaces hydrogen from the nucleus,

$$C_6H_5{\cdot}NH{\cdot}CH_3,\ HCl \rightarrow C_6H_4{<}^{CH_3}_{NH_2},\ HCl.$$

Methylaniline Hydrochloride. *p*-Toluidine Hydrochloride.

In the case of dimethylaniline the change takes place in two stages, which may be represented as follows:—

$$C_6H_5{\cdot}N(CH_3)_2 \rightarrow C_6H_4{<}^{CH_3}_{NH{\cdot}CH_3} \rightarrow C_6H_3{<}^{CH_3}_{CH_3}_{NH_2}.$$

Dimethylaniline. Methyl-*p*-toluidine. Xylidine.

In this remarkable *isomeric change* the alkyl-group displaces hydrogen from the ortho- and from the para-position to the amino-group, but principally the latter; meta-derivatives cannot be prepared in this way.

The diamino-compounds, such as the **o**-, **m**-, and **p**-*diamino-benzenes* or *phenylenediamines*, $C_6H_4(NH_2)_2$, are prepared by reducing either the corresponding *dinitrobenzenes*, $C_6H_4(NO_2)_2$, or the *nitranilines*, $C_6H_4(NO_2)\cdot NH_2$, generally with tin and hydrochloric acid.

Properties.—The *monamino*-compounds are mostly colourless liquids, which distil without decomposing, and are specifically heavier than water; they have a faint but characteristic odour, and dissolve freely in alcohol, ether, and other organic solvents, but they are only sparingly soluble or insoluble in water; on exposure to air and light they darken, and ultimately become brown or black.

They are comparatively weak bases, and are *neutral* to litmus, in which respect they differ from the strongly basic fatty amines and from the aromatic amines, such as benzylamine (p. 411), which contain the amino-group in the *side-chain;* nevertheless, they combine with acids to form salts, such as aniline hydrochloride, $C_6H_5\cdot NH_2$, HCl. The simple salts of the amino-compounds are usually soluble in water, by which they are hydrolysed to a greater or less extent; they are completely decomposed by weak alkalis or alkali carbonates, with liberation of the base.

From a comparison of the properties of the amino-compounds with those of ammonia, it is found that the substitution of the phenyl radicle, C_6H_5–, for one of the hydrogen atoms in ammonia diminishes the basic character of the latter; the opposite result is attained when the hydrogen atoms of ammonia are displaced by an alkyl- (or positive) group, since the amines are stronger bases than ammonia; for this and other reasons (p. 438), the phenyl-group may be regarded as a negative or acid radicle.

When two hydrogen atoms in ammonia are displaced by phenyl-groups, as in *diphenylamine*, $(C_6H_5)_2NH$ (p. 410), the product is so feebly basic that its salts are decomposed by water. *Triphenylamine*, $(C_6H_5)_3N$ (p. 410), moreover, does not form salts at all.

For the same reason, the hydroxy-, nitro-, and halogen-derivatives of the amino-compounds, such as *amino-phenol*, $C_6H_4(OH)\cdot NH_2$, *nitraniline*, $C_6H_4(NO_2)\cdot NH_2$, *chloraniline*, $C_6H_4Cl\cdot NH_2$, &c., are even weaker bases than the amino-compounds themselves, because the presence of the negative group or atom, HO–, NO_2–, Cl–, &c., enhances the acid character of the phenyl-radicle.

The amino-compounds differ from the fatty primary amines, and from those aromatic primary amines which contain the amino-group in the side-chain, in their remarkable behaviour with nitrous acid. Although, when their salts are *warmed* with nitrous acid in aqueous solution, they yield phenols by the substitution of the hydroxy- for the amino-group, just as the fatty amines under similar treatment give alcohols (p. 212),

$$C_6H_5\cdot NH_2 + NO_2H = C_6H_5\cdot OH + N_2 + H_2O,$$
$$C_2H_5\cdot NH_2 + NO_2H = C_2H_5\cdot OH + N_2 + H_2O,$$

yet when treated with nitrous acid in *cold* aqueous solution, they are converted into *diazonium-salts* (p. 412), substances which are not produced from the primary amines.

It will be evident from the above statements that there are several important differences between the amino-compounds and the aliphatic primary amines, the character of an amino-group in the nucleus being influenced by its state of combination; nevertheless, except as regards those points already mentioned, amino-compounds have, on the whole, properties very similar to those of the fatty primary amines.

The amino-compounds, like the fatty primary amines, react readily with alkyl halogen compounds, yielding alkyl-derivatives, such as *methylaniline*, $C_6H_5\cdot NH\cdot CH_3$, *dimethylaniline*, $C_6H_5\cdot N(CH_3)_2$, &c., and also compounds such as *phenyl-trimethylammonium iodide*, $C_6H_5\cdot N(CH_3)_3I$, which correspond with the quaternary ammonium salts (p. 215).

They are also readily acted on by acid chlorides and anhydrides, yielding substances such as *acetanilide* and *aceto-toluide*, which are closely allied to, and may be regarded as derived from, the fatty amides,

$$C_6H_5\cdot NH_2 + CH_3\cdot COCl = C_6H_5\cdot NH\cdot CO\cdot CH_3 + HCl,$$

$$C_6H_4(CH_3)\cdot NH_2 + (CH_3\cdot CO)_2O =$$

p-Toluidine.

$$C_6H_4(CH_3)\cdot NH\cdot CO\cdot CH_3 + CH_3\cdot COOH.$$

Aceto-p-toluide.

These *substituted amides* are crystalline, and serve for the identification of the (liquid) amino-compounds; like the amides, they are hydrolysed by boiling acids or alkalis, but sometimes hydrolysis is accomplished only with very great difficulty,*

$$C_6H_4{<}\begin{matrix}CH_3\\NH\cdot CO\cdot CH_3\end{matrix} + H_2O = C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix} + CH_3\cdot COOH.$$

The amino-compounds, like the fatty primary amines, give the carbylamine reaction; when a trace of aniline, for example, is heated with alcoholic potash and chloroform, an intensely nauseous smell is observed, due to the formation of phenyl-carbylamine (pp. 182, 212, 403),

$$C_6H_5\cdot NH_2 + CHCl_3 + 3KOH = C_6H_5\cdot N{\vdots}C + 3KCl + 3H_2O.$$

Diamino- and *triamino-compounds*, such as the three (**o.m.p.**) *phenylenediamines* or *diaminobenzenes*, $C_6H_4(NH_2)_2$, and the *triaminobenzenes*, $C_6H_3(NH_2)_3$, are very similar to the mon-amino-compounds in chemical properties, but differ from them usually in being solid, more readily soluble in water, and less volatile; the triamino-compounds generally form salts, such as $C_6H_3(NH_2)_3$, 2HCl, with only *two* equivalents of an acid.

Aniline and its Derivatives.

Aniline, $C_6H_5\cdot NH_2$ (aminobenzene, phenylamine), was first prepared by Unverdorben in 1826 by the distillation of indigo.† Runge in 1834 showed that aniline is contained in small quantities in coal-tar, but its preparation from nitro-benzene was first accomplished by Zinin in 1841.

* Sulphuric acid, diluted with about an equal volume of water, is generally the most suitable hydrolysing agent in such cases, but it may be necessary to heat the substituted amide with the acid on a reflux condenser during many hours.

† The name aniline is derived from *an-nil* (*al-nil*), the Arabic for the indigo-plant.

Aniline is manufactured on a very large scale by the reduction of nitrobenzene with scrap iron and crude hydrochloric acid; but in preparing small quantities in the laboratory, the most convenient reducing agent is tin and hydrochloric acid,

$$C_6H_5\cdot NO_2 + 6H = C_6H_5\cdot NH_2 + 2H_2O,$$
$$2C_6H_5\cdot NO_2 + 3Sn + 12HCl = 2C_6H_5\cdot NH_2 + 3SnCl_4 + 4H_2O.$$

Nitrobenzene (50 grams) and granulated tin (80 grams) are placed in a flask, and concentrated hydrochloric acid (290 grams) is added in small quantities at a time; at first the mixture must be cooled, otherwise the reaction becomes violent, but when all the acid has been added, the flask is gently heated on a water-bath until drops of nitro-benzene are no longer visible. The solution of *aniline stannichloride* (p. 398) is now cautiously treated with sodium hydroxide (solid) in *excess*, and the liberated aniline is distilled in steam. The distillate is saturated with salt, and the base is extracted with ether. The extract is dried over solid potash, decanted into a dry flask, and the ether is then distilled from a water-bath; the aniline is finally purified by distillation.

Aniline is a poisonous oil, boiling at 184°, and having a faint odour, which is common to many amino-compounds; it is sparingly soluble in water, and gradually turns yellow when exposed to light and air, becoming ultimately almost black. Although neutral to litmus, aniline has very decided basic properties, and, with acids, it forms soluble salts, such as aniline *hydrochloride*, $C_6H_5\cdot NH_2$, HCl, and the rather sparingly soluble *sulphate*, $(C_6H_5\cdot NH_2)_2$, H_2SO_4. The former, like the hydrochlorides of the fatty amines, forms complex salts with platinic and auric chlorides; a moderately concentrated solution of the hydrochloride gives with platinic chloride, for example, the *platinichloride*, $(C_6H_5\cdot NH_2)_2$, H_2PtCl_6, which is precipitated in yellow plates, and is only moderately soluble in water.

When aniline (*one drop* *) is heated with chloroform and alcoholic potash, it yields phenylcarbylamine, $C_6H_5\cdot N{:}C$, a substance readily recognised by its extremely disagreeable odour; aniline may also be detected by treating its aqueous

* Compare footnote, p. 182.

solution with bleaching-powder or sodium hypochlorite, when an intense purple colouration is produced.

These reactions, combined with a determination of the boiling-point, are sufficient for the identification of aniline; if the boiling-point cannot be ascertained, the base may be identified with the aid of its *benzoyl*-derivative (compare pp. 472, 473).

When solutions of the salts of aniline are treated with nitrous acid in the cold, diazonium-salts (p. 412) are formed, but at higher temperatures, the latter are decomposed, with formation of phenol (p. 439).

Aniline is very largely employed in the manufacture of dyes, and in the preparation of a great number of benzene derivatives.

Acetanilide, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$, is formed when aniline is treated with acetyl chloride or acetic anhydride.* It is prepared by boiling aniline (5 g.) with glacial acetic acid (6 g.) on a reflux apparatus for several hours, when the aniline acetate which is first formed is slowly converted into acetanilide, with elimination of water,†

$$C_6H_5{\cdot}NH_2,\ CH_3{\cdot}COOH = C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + H_2O.$$

The product is purified by distillation or by recrystallisation from boiling water.

It crystallises in glistening plates, melts at 112°, and is sparingly soluble in cold, but readily in hot, water; when heated with acids or alkalis, it is hydrolysed, giving aniline and acetic acid. It is used in medicine, under the name of *antifebrin*, for reducing the temperature of the body in cases of fever, &c.

* The product of the (vigorous) reaction is treated with cold water, in order to dissolve the aniline hydrochloride or acetate, which is also formed, and the undissolved acetanilide is then recrystallised from boiling water.

† The conversion is complete when a test portion of the product gives, with water, a solution from which oily drops of aniline are *not* precipitated on the addition of caustic soda. Aniline acetate is very readily soluble in cold water, and the solution gives a precipitate of aniline immediately when an alkali hydroxide or carbonate is added to it.

Formanilide, $C_6H_5 \cdot NH \cdot CHO$ (m.p. 46°), the anilide of formic acid, and *oxanilide*, $C_6H_5 \cdot NH \cdot CO \cdot CO \cdot NH \cdot C_6H_5$ (m.p. 245°), the anilide of oxalic acid, may be prepared by heating the corresponding aniline salts; *benzanilide*, $C_6H_5 \cdot NH \cdot CO \cdot C_6H_5$ (m.p. 160°), is easily prepared by the Schotten-Baumann method (p. 473).

Halogen Substitution Products of Aniline.—Aniline and, in fact, all amino-compounds are much more readily attacked by halogens than are the hydrocarbons. When aniline, for example, is treated with chlorine or bromine in aqueous solution, it is at once converted into *trichloraniline*, $C_6H_2Cl_3 \cdot NH_2$, or *tribromaniline*, $C_6H_2Br_3 \cdot NH_2$, so that in order to obtain mono- and di-substitution products indirect methods must be employed.

The o- and p-*chloranilines*, $C_6H_4Cl \cdot NH_2$, may be prepared by passing chlorine into acetanilide, the p-derivative being obtained in the larger quantity. The two isomerides are first separated by crystallisation, and are then decomposed by boiling alkalis or acids,

$$\underset{\text{Chloracetanilide.}}{C_6H_4Cl \cdot NH \cdot CO \cdot CH_3} + KOH = \underset{\text{Chloraniline.}}{C_6H_4Cl \cdot NH_2} + CH_3 \cdot COOK.$$

The effect of introducing an acetyl radicle into the amino-group, therefore, is to render aniline less readily attacked; acetanilide, in fact, behaves towards chlorine and bromine more like benzene than like aniline. m-Chloraniline is most conveniently prepared by the reduction of m-chloronitrobenzene, $C_6H_4Cl \cdot NO_2$ (a substance formed by chlorinating nitrobenzene in the presence of antimony). o-Chloraniline and m-chloraniline are oils, boiling at 207° and 230° respectively, but p-chloraniline is a solid, which melts at 70° and boils at 230°.

The **nitranilines**, $C_6H_4(NO_2) \cdot NH_2$, cannot be prepared by nitrating aniline, because the base undergoes oxidation and complex changes occur; if, however, the amino-group is '*protected*' or '*blocked*' by the introduction of an acetyl radicle, nitration takes place in a normal manner, and the acetyl derivatives of o- and p-nitraniline are formed.

The o- and p-nitracetanilides, thus obtained, are separated by fractional crystallisation, and are then converted into the corresponding nitranilines by hydrolysis. m-Nitraniline is prepared by the partial reduction of m-dinitrobenzene, $C_6H_4(NO_2)_2$, with ammonium sulphide (p. 398).

m-Dinitrobenzene (2 parts), alcohol (6 parts), and concentrated ammonium hydroxide solution (1 part) are placed in a flask, and hydrogen sulphide is passed into the liquid, which, later on, is warmed from time to time. The dinitrobenzene gradually disappears and sulphur is deposited. The contents of the flask are tested at intervals, in order to ascertain when the stream of hydrogen sulphide should be stopped. For this purpose a small quantity of the solution and a portion of the deposit are evaporated together in a basin on the water-bath, and the residue is treated with cold dilute hydrochloric acid, which dissolves m-nitraniline (in the form of its hydrochloride), but not dinitrobenzene or sulphur; the residue insoluble in dilute acid is then extracted with a little boiling alcohol, and the filtered solution is treated with water (or evaporated), in order to prove the presence or absence of m-dinitrobenzene (sulphur is only very sparingly soluble in alcohol). When the test portion gives a satisfactory result, the m-nitraniline is extracted from the whole of the product in the manner described above, the acid solution is treated with excess of caustic soda, and the precipitated base is purified by recrystallisation from boiling water or very dilute aqueous alcohol.

o-Nitraniline melts at 71°, m- at 114°, and p- at 147°; they are all sparingly soluble in cold water, readily in alcohol, and on reduction they yield the corresponding o-, m-, and p-*phenylenediamines* (p. 407),

$$C_6H_4{<}^{NO_2}_{NH_2} + 6H = C_6H_4{<}^{NH_2}_{NH_2} + 2H_2O.$$

Homologues of Aniline.—The **toluidines** or amino-toluenes, $C_6H_4(CH_3)\cdot NH_2$, are prepared by reducing the corresponding o-, m-, and p-nitrotoluenes (p. 396), with tin and hydrochloric acid, as described in the case of the preparation of aniline from nitrobenzene,

$$C_6H_4{<}^{CH_3}_{NO_2} + 6H = C_6H_4{<}^{CH_3}_{NH_2} + 2H_2O;$$

the o- and p-compounds may also be prepared from methylaniline (p. 399). Both o- and m-toluidine are oils, boiling at 197° and 199° respectively, but p-toluidine is crystalline, and melts at 45°, boiling at 198°.

The **o**-, **m**-, and **p**-*acetotoluides*, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$, melt at 110°, 65°, and 153° respectively, the corresponding *benzotoluides*, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$, at 131°, 125°, and 158° respectively. These compounds may serve for the identification of the bases (compare p. 473).

When treated with nitrous acid, the toluidines yield diazonium-salts, from which the corresponding cresols, $C_6H_4(CH_3) \cdot OH$, are obtained, and in all other reactions they show the greatest similarity to aniline; **o**- and **p**-toluidine are employed in the manufacture of dyes.

Diaminobenzenes.—The *phenylenediamines*, $C_6H_4(NH_2)_2$, are obtained by the reduction of the corresponding dinitrobenzenes, or the nitranilines, and a general description of their properties has already been given (p. 402); **o**-phenylenediamine melts at 102°, the **m**- and **p**-compounds at 63° and 147° respectively. **m**-Phenylenediamine gives an intense yellow colouration with a trace of nitrous acid, and is employed in water-analysis for the detection and estimation of nitrites; both the **m**- and **p**-compounds are employed in the manufacture of dyes.

Alkylanilines.

Those derivatives of the amino-compounds, obtained by displacing one or both of the hydrogen atoms of the amino-group by alkyl radicles, are substances of considerable importance, and are usually known as **alkylanilines.** They are obtained by heating the amino-compounds with the alkyl halogen compounds, the reaction being analogous to that which occurs in the formation of secondary, and tertiary, from primary, fatty amines (p. 218),

$$C_6H_5 \cdot NH_2 + RCl = C_6H_5 \cdot NHR, HCl,$$
$$C_6H_5 \cdot NH_2 + 2RCl = C_6H_5 \cdot NR_2, HCl + HCl.$$

Instead of the alkyl halogen compounds, a mixture of the corresponding alcohol and halogen acid may be used; *methyl-* and *dimethyl-aniline*, for example, are prepared, on the large

scale, by heating aniline with methyl alcohol and hydrochloric acid at 200–250°,

$$C_6H_5\cdot NH_2,\ HCl + CH_3\cdot OH = C_6H_5\cdot NH(CH_3),\ HCl + H_2O,$$
$$C_6H_5\cdot NH_2,\ HCl + 2CH_3\cdot OH = C_6H_5\cdot N(CH_3)_2,\ HCl + 2H_2O.$$

These mono- and di-alkyl derivatives are stronger bases than the amino-compounds from which they are derived; the presence of the positive alkyl-group counteracts to some extent the action of the negative phenyl-group (compare p. 400). They are, in fact, very similar in properties to the secondary and tertiary fatty amines respectively, and may be regarded as derived from the primary fatty amines by the substitution of a phenyl-group for a hydrogen atom, just as the secondary and tertiary fatty amines are obtained by the displacement of hydrogen atoms by alkyl-groups. Methylaniline, for example, is also *phenylmethylamine*, and its properties are those of a substitution product of methylamine.

The mono-alkylanilines, like the secondary amines, are converted into pale yellow *nitroso-amines* on treatment with nitrous acid,

$$\underset{\text{Methylaniline.}}{C_6H_5\cdot NH\cdot CH_3} + HO\cdot NO = \underset{\text{Methylphenylnitrosamine.}}{C_6H_5\cdot N(NO)\cdot CH_3} + H_2O,$$

$$\underset{\text{Dimethylamine.}}{(CH_3)_2NH} + HO\cdot NO = \underset{\text{Dimethylnitrosamine.}}{(CH_3)_2\cdot N\cdot NO} + H_2O.$$

These nitroso-amines give Liebermann's nitroso-reaction (p. 214), and on reduction they yield ammonia and the original alkylaniline,

$$C_6H_5\cdot N(NO)\cdot CH_3 + 6H = C_6H_5\cdot NH\cdot CH_3 + NH_3 + H_2O.$$

Methylaniline, $C_6H_5\cdot NH\cdot CH_3$, prepared as just described, is a colourless liquid, which boils at 192°, and, compared with aniline, has strongly basic properties. On the addition of sodium nitrite to its solution in hydrochloric acid, *methylphenylnitrosamine*, $C_6H_5\cdot N(NO)\cdot CH_3$, separates as a light-yellow *oil*.

Methylacetanilide, $C_6H_5\cdot N(CH_3)\cdot CO\cdot CH_3$ (the acetyl derivative of methylaniline), melts at 101°.

Dimethylaniline, $C_6H_5 \cdot N(CH_3)_2$, the preparation of which has just been given, is a colourless, strongly basic oil, which boils at 192°; it is largely used in the manufacture of dyes.

The *di*-alkylanilines, such as dimethylaniline, $C_6H_5 \cdot N(CH_3)_2$, also react readily with nitrous acid (a behaviour which is *not* shown by tertiary fatty amines), intensely green nitroso-compounds (*not* nitro*samines*) being formed, the NO– group displacing hydrogen of the *nucleus* from the p-position to the nitrogen atom,

$$C_6H_5 \cdot N(CH_3)_2 + HO \cdot NO = C_6H_4 \begin{cases} NO \\ N(CH_3)_2 \end{cases} + H_2O.$$

p-Nitrosodimethylaniline.

These substances do *not* give Liebermann's nitroso-reaction, and when reduced they yield derivatives of p-phenylenediamine,

$$C_6H_4 \begin{cases} NO \\ N(CH_3)_2 \end{cases} + 4H = C_6H_4 \begin{cases} NH_2 \\ N(CH_3)_2 \end{cases} + H_2O.$$

Dimethyl-p-phenylenediamine.

p-*Nitrosodimethylaniline*, $C_6H_4 \begin{cases} NO \\ N(CH_3)_2 \end{cases}$, is prepared by dissolving dimethylaniline (1 part) in water (5 parts) and concentrated hydrochloric acid (2·5 parts), and gradually adding to the well-cooled solution the theoretical quantity of sodium nitrite, dissolved in a little water. The yellow crystalline precipitate of *nitrosodimethylaniline hydrochloride* is separated by filtration, dissolved in water, and decomposed by potassium carbonate; the free base is extracted with ether. Nitrosodimethylaniline crystallises from ether in dark-green plates, and melts at 85°; it is not a nitrosamine, because the NO– group is not united to nitrogen, and it does not give Liebermann's nitroso-reaction. When reduced with zinc and hydrochloric acid it is converted into *dimethyl-p-phenylenediamine* (see above), and when boiled with caustic soda it is decomposed into dimethylamine and p-*nitrosophenol* or *quinone monoxime* (compare p. 465),

$$C_6H_4 \begin{cases} NO \\ N(CH_3)_2 \end{cases} + H_2O = NH(CH_3)_2 + C_6H_4 \begin{cases} NO \\ OH \end{cases} \text{ or } C_6H_4 \begin{cases} N \cdot OH \\ O \end{cases}.$$

Diphenylamine and Triphenylamine.

The hydrogen atoms of the amino-group in aniline may also be displaced by phenyl radicles, the compounds, *diphenylamine*, $(C_6H_5)_2NH$, and *triphenylamine*, $(C_6H_5)_3N$, being pro-

duced. These substances, however, cannot be obtained by treating aniline with chlorobenzene, C_6H_5Cl, a method which would be analogous to that which is employed in the preparation of diethylamine and triethylamine, because the halogen in chlorobenzene is so firmly held that no action takes place, even when the substances are heated together.

Diphenylamine, $(C_6H_5)_2NH$, is most conveniently prepared by heating aniline hydrochloride with aniline at about 240°, in closed vessels,

$$C_6H_5\cdot NH_2,\ HCl + C_6H_5\cdot NH_2 = (C_6H_5)_2\cdot NH + NH_4Cl.$$

It is a crystalline substance, melts at 54°, boils at 310°, and is insoluble in water. It is only a feeble base, and its salts are decomposed by water; hence diphenylamine, unlike the great majority of bases, is practically insoluble in dilute mineral acids. Its solution in concentrated sulphuric acid gives, with a trace of nitric acid, an intense blue colouration, and, therefore, serves as a very delicate test for nitric acid or nitrates. Diphenylamine is used in the manufacture of dyes; also for experiments in which a constant high temperature is required, as, for example, in the determination of the vapour density of substances of high boiling-point by V. Meyer's method.

When treated with potassium, diphenylamine yields a solid potassium derivative, $(C_6H_5)_2NK$, the presence of the two phenyl-groups being sufficient to impart to the $>NH$ group a feeble acid character.

Triphenylamine, $(C_6H_5)_3N$, may be prepared by heating potassium diphenylamine with bromobenzene at 300°,

$$(C_6H_5)_2NK + C_6H_5Br = (C_6H_5)_3N + KBr.$$

It is a colourless, crystalline substance, melts at 127°, and does not combine with acids.

Aromatic Amines.

The aromatic amino-compounds, in which the amino-group is united with carbon of the *side-chain*, are of far less importance than those in which the amino-group is united with

carbon of the nucleus, and, as will be seen from the following example, they closely resemble the fatty amines in chemical properties.

Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$, may be obtained by reducing phenyl cyanide (benzonitrile, p. 473) or benzaldoxime (p. 456),

$$C_6H_5 \cdot CN + 4H = C_6H_5 \cdot CH_2 \cdot NH_2,$$
$$C_6H_5 \cdot CH : NOH + 4H = C_6H_5 \cdot CH_2 \cdot NH_2 + H_2O,$$

by treating the amide of phenylacetic acid (p. 482) with bromine and potash,

$$C_6H_5 \cdot CH_2 \cdot CO \cdot NH_2 + Br_2 + 4KOH = C_6H_5 \cdot CH_2 \cdot NH_2 + 2KBr + K_2CO_3 + 2H_2O,$$

and by heating benzyl chloride with alcoholic ammonia,

$$C_6H_5 \cdot CH_2Cl + NH_3 = C_6H_5 \cdot CH_2 \cdot NH_2, HCl.$$

All these methods are similar to those employed in the preparation of primary fatty amines (pp. 210, 217).

Benzylamine is a colourless, pungent-smelling liquid, boiling at 187°; it closely resembles the fatty amines in nearly all respects, and differs from the amino-compounds (aniline, toluidine, &c.) in being strongly basic, alkaline to litmus, and readily soluble in water. Like aniline and other primary amines, it gives the carbylamine reaction, but when solutions of its salts are treated with nitrous acid, it is converted into the corresponding alcohol (benzyl alcohol, p. 451), and *not* into a diazonium-salt.

Secondary and tertiary aromatic amines are formed when a primary amine is heated with an aromatic halogen compound, containing the halogen in the *side-chain;* when, for example, benzylamine is heated with benzyl chloride, both *dibenzylamine* and *tribenzylamine* are produced, just as diethylamine and triethylamine are obtained when ethylamine is heated with ethyl bromide,

$$C_6H_5 \cdot CH_2 \cdot NH_2 + C_6H_5 \cdot CH_2Cl = (C_6H_5 \cdot CH_2)_2NH, HCl,$$
$$C_6H_5 \cdot CH_2 \cdot NH_2 + 2C_6H_5 \cdot CH_2Cl = (C_6H_5 \cdot CH_2)_3N, HCl + HCl.$$

When, therefore, benzyl chloride is heated with ammonia, the product consists of a mixture of the salts of all three amines.

CHAPTER XXVI.

Diazonium-Salts and Related Compounds.

It has already been stated that when the amino-compounds, in the form of their salts, are treated with nitrous acid in *warm* aqueous solution, they yield phenols; when, however, a *well-cooled*, dilute solution of aniline hydrochloride is treated with nitrous acid, phenol is *not* produced, and the solution contains an unstable substance called *phenyldiazonium chloride* (*diazobenzene chloride*), the formation of which may be expressed by the equation,

$$C_6H_5\cdot NH_2,HCl + NO_2H = C_6H_5\cdot N_2Cl + 2H_2O.$$

In this respect, then, aniline, and all those amino-compounds which contain the amino-group directly united with carbon of the *nucleus*, differ from other primary amines; the latter are at once converted into alcohols by nitrous acid in the cold, whereas the former are first transformed into diazonium-salts, which, usually only at higher temperatures, decompose more or less readily, with formation of phenols (p. 434).

The *diazo-* or *diazonium*-salts were discovered in 1858 by P. Griess, and may be regarded as salts of *phenyldiazonium hydroxide*, $C_6H_5\cdot N_2\cdot OH$, and its derivatives.

The bases or hydroxides from which these salts are derived are only known in aqueous solution; they cannot be isolated, because they immediately change into highly explosive, very unstable products which seem to be their anhydrides.

The diazonium- (or diazo-) salts may be isolated without much difficulty, and are colourless, crystalline compounds, very readily soluble in water; in the dry state, most of them are *highly explosive*, and should be handled only with the greatest caution.

Diazonium-salts may be obtained *in crystals* by treating a well-cooled solution of an amino-compound in absolute alcohol with

amyl nitrite and a mineral acid, as far as possible in absence of water,*

$$C_6H_5\cdot NH_2,HCl + C_5H_{11}\cdot O\cdot NO = C_6H_5\cdot N_2Cl + C_5H_{11}\cdot OH + H_2O.$$

Phenyldiazonium sulphate, $C_6H_5\cdot N_2\cdot SO_4H$, for example, is prepared as follows:—Aniline (15 parts) is dissolved in absolute alcohol (10 parts), concentrated sulphuric acid (20 parts) is added, the solution is cooled in a freezing mixture, and pure amyl nitrite (20 grams) is cautiously dropped into the liquid; after 10–15 minutes phenyldiazonium sulphate separates in crystals, which are washed with alcohol and ether, and dried in the air at ordinary temperatures.

Phenyldiazonium chloride and *phenyldiazonium nitrate* may be obtained in a similar manner, hydrogen chloride or nitric acid being employed in the place of sulphuric acid; but particular precautions must be taken in the case of the nitrate.

Phenyldiazonium nitrate, $C_6H_5\cdot N_2\cdot NO_3$, may be more conveniently isolated as follows:—Aniline nitrate is suspended in a small quantity of water, and the liquid is saturated with nitrous acid (generated from arsenious anhydride and nitric acid), whereon the crystals gradually dissolve, with formation of diazobenzene nitrate; on the addition of alcohol and ether, this salt separates in colourless needles. Special precautions are to be observed in preparing this substance, as when dry it is highly explosive, although it may be handled with comparative safety if kept moist.

The diazonium-salts are of great importance in synthetical chemistry and in the preparation of dyes, because they undergo a number of remarkable reactions; for nearly all purposes for which they are required, however, it is quite unnecessary to isolate the salts, and their aqueous solutions are directly employed.

The *preparation of a solution of a diazonium-salt*, therefore, is a very common and a very important operation, and is carried out as follows:—The amino-compound is dissolved in an excess of the theoretical quantity (2 mols.) of a dilute mineral acid, the solution is cooled in ice, and an aqueous solution of sodium or potassium nitrite (1 mol.) is very slowly added to it; this process is known as *diazotisation*, and further details are given later (pp. 415, 474).

* Amyl nitrite and a mineral acid give nitrous acid; the ester is used instead of sodium nitrite because it is soluble in alcohol.

The more important *reactions* of the diazonium-salts may now be described.

When heated with (absolute) alcohol they yield hydrocarbons, part of the alcohol being oxidised to aldehyde,*

$$C_6H_5\cdot N_2Cl + C_2H_5\cdot OH = C_6H_6 + N_2 + HCl + CH_3\cdot CHO.$$

When warmed, in aqueous solution, they decompose rapidly, with evolution of nitrogen and formation of phenols (p. 434),

$$C_6H_5\cdot N_2\cdot SO_4H + H_2O = C_6H_5\cdot OH + N_2 + H_2SO_4,$$

$$\underset{\text{Tolyldiazonium Chloride.}}{C_6H_4(CH_3)\cdot N_2Cl} + H_2O = \underset{\text{Cresol.}}{C_6H_4(CH_3)\cdot OH} + N_2 + HCl,$$

but if warmed with concentrated halogen acids they give halogen derivatives,

$$C_6H_5\cdot N_2\cdot SO_4H + HI = C_6H_5I + N_2 + H_2SO_4;$$

the latter reaction is made use of principally for the preparation of iodo-derivatives (p. 387), because when the other halogen acids are used, the product contains the corresponding phenol.

The diazonium-salts behave in a very remarkable way when they are treated with cuprous salts; when, for example, a solution of phenyldiazonium chloride is warmed with a solution of cuprous chloride in hydrochloric acid, nitrogen is evolved, but instead of phenol, *chlorobenzene* is produced. In this reaction the diazonium-salt combines with the cuprous chloride to form a brownish additive compound, which is decomposed at higher temperatures,

$$C_6H_5\cdot N_2Cl,\ 2CuCl = C_6H_5Cl + N_2 + 2CuCl.$$

If, instead of the chloride, cuprous bromide is employed, bromobenzene is produced,

$$\underset{\text{Additive Compound.}}{C_6H_5\cdot N_2Cl,\ 2CuBr} = \underset{\text{Bromobenzene.}}{C_6H_5Br} + N_2 + CuCl + CuBr,$$

* This is one of the few cases in which the salt, as distinct from its aqueous solution, must be employed. A much better method for the conversion of a diazonium-salt into a hydrocarbon is given later (p. 422).

whereas by using a solution of potassium cuprous cyanide, a cyanide or nitrile is formed (compare p. 474),

$$\underset{\text{Additive Compound.}}{C_6H_5\cdot N_2Cl},\ 2CuCN = \underset{\text{Phenyl Cyanide.}}{C_6H_5\cdot CN} + N_2 + CuCl + CuCN.$$

By means of these very important reactions, which were discovered by Sandmeyer in 1884, it is possible to displace the *diazonium*-group (and therefore indirectly also the NH_2–group) by Cl, Br, I,* CN, and indirectly by COOH (since the CN– group may be hydrolysed to –COOH), and indeed by other atoms or groups; as, moreover, the yield is generally good, Sandmeyer's reaction is of great practical value. As the amino-compounds are readily obtainable from the nitro-compounds, and the latter from the hydrocarbons, this series of reactions affords a means of preparing halogen, cyanogen, and other derivatives indirectly from the hydrocarbons.

It will be seen from the above statements that the preparation of a halogen, cyanogen, or other derivative from the amino-compound involves two distinct reactions: firstly, the preparation of a *solution* of the diazonium-salt; and, secondly, the decomposition of this salt in a suitable manner.

As an example of the method employed in preparing a solution of the diazonium-salt, the following may serve:—Aniline (1 part) is dissolved in a mixture of ordinary concentrated hydrochloric acid (about 2½ parts) and water (about 2½ parts), and the solution is cooled by the addition of coarsely powdered ice; when the temperature has fallen to about 5°, an aqueous solution of the theoretical quantity of sodium nitrite † is slowly run in from a tap-funnel, the solution being stirred constantly and the temperature kept as low as possible. The solution now contains *phenyldiazonium chloride*; if sulphuric had been used instead of hydrochloric acid, *phenyldiazonium sulphate* would have been formed. The aniline is said to be *diazotised.*

* The use of a cuprous salt is unnecessary in the displacement of the diazonium-group by iodine (compare p. 387).

† When the quantity of nitrite to be used cannot be directly weighed out, a probable excess is dissolved, and the solution is run in until the solution of the diazonium-salt contains free nitrous acid (as shown by starch-potassium-iodide paper) after it has been stirred well and *left for a short time.*

If, now, the solution of the diazonium-salt is warmed *alone*, nitrogen is evolved and phenol is produced; if, however, it is slowly added to a hot solution of cuprous chloride in hydrochloric acid, *chlorobenzene* is produced (p. 386), whereas with an aqueous solution of potassium cuprous cyanide, *cyanobenzene* is formed (p. 474). In all these cases the final product is usually separated by distillation in steam.

Gattermann has shown that in many cases the decomposition of the diazonium-salts is best brought about by adding copper powder (prepared by the action of zinc-dust on a solution of copper sulphate) to the *cold* acid solution of the salt; when, for example, a solution of phenyldiazonium chloride is treated in this way, nitrogen is evolved and *chlorobenzene* is produced, the reaction being complete in about half-an-hour.

The diazonium-salts also serve for the preparation of an important class of compounds known as the *hydrazines;* these substances are obtained by reducing the diazonium-salts, usually with stannous chloride and hydrochloric acid (p. 421),

$$R{\cdot}N_2Cl + 4H = R{\cdot}NH{\cdot}NH_2,HCl.$$

Diazonium Chloride. Hydrazine Hydrochloride.

Constitution of Diazonium-Salts.—The state of combination of the two nitrogen atoms and of the acid radicle in diazonium-salts has formed the subject of much discussion, and for a long time the view first expressed by Kekulé (1866), that such salts have the constitution, $C_6H_5{\cdot}N{:}NX$ (where X = Cl, Br, I, NO_3, HSO_4, &c.), was generally adopted. That only *one* of the two nitrogen atoms is directly united to the nucleus is clearly shown by many facts—as, for example, by the conversion of the diazonium-salts into *mono*-halogen derivatives, *mono*hydric phenols, &c., and by their conversion into hydrazines, such as $C_6H_5{\cdot}NH{\cdot}NH_2$, on reduction (p. 421).

That the acid radicle is combined with that nitrogen atom which is *not* directly united to the nucleus *seems* to be proved by many reactions of diazonium-salts—as, for example, the following:—Phenyldiazonium chloride reacts readily with dimethylaniline, giving dimethylaminoazobenzene (p. 421),

$$\underset{a\ b}{C_6H_5{\cdot}N{:}NCl} + C_6H_5{\cdot}NMe_2 = \underset{a\ b}{C_6H_5{\cdot}N{:}N}{\cdot}C_6H_4{\cdot}NMe_2 + HCl,$$

and this substance, on reduction, yields aniline and dimethyl-p-phenylenediamine (p. 421),

$$C_6H_5\cdot\underset{a}{N}{:}\underset{b}{N}\cdot C_6H_4\cdot NMe_2 + 4H = C_6H_5\cdot\underset{a}{NH_2} + \underset{b}{NH_2}\cdot C_6H_4\cdot NMe_2.$$

These changes are easily explained on the assumption that the acid radicle is attached to the *b*-nitrogen atom, as in the above formula, but *apparently* they could not very well take place if the acid radicle were united to the *a*-nitrogen atom.

There are, however, other facts which seem to point to the formula, $C_6H_5\cdot NX{:}N$, suggested by Blomstrand. The physical properties of dilute solutions of the diazonium-salts are similar to those of solutions of quaternary ammonium-salts, such as $C_6H_5\cdot NX{\equiv}(CH_3)_3$, in which the acid radicle (X) is directly united to *quinquevalent* nitrogen. In other words, the salts derived from the diazonium-hydroxides behave like those derived from strongly basic hydroxides; they are not hydrolysed in aqueous solution, but are ionised to an extent comparable with that to which potassium chloride is ionised. Now a hydroxide of the constitution, $C_6H_5\cdot N{:}N\cdot OH$, judging from analogy, would be only feebly basic (as are the oximes, for example), whereas a hydroxide, $C_6H_5\cdot N(OH){:}N$, like other hydroxy-derivatives of quinquevalent nitrogen, should be a strong base. Probably, therefore, the two formulæ, $C_6H_5\cdot NX{:}N$ and $C_6H_5\cdot N{:}NX$, represent *tautomeric* forms (p. 205), and the compounds react in one or the other form according to the conditions of the experiment; for these reasons the diazonium- (or diazo-) group may be conveniently represented by $-N_2X$, as in most of the formulæ used above, without indicating further the actual state of combination of the atoms.

The nomenclature adopted above is not universally used, and the diazonium-salts are often called diazo-salts, while phenyldiazonium chloride is termed *diazobenzene* chloride, and so on.

Diazo-Derivatives of Aliphatic Compounds.—Although aliphatic amino-compounds cannot be transformed into diazonium-salts,

corresponding with those of the aromatic series, the esters of fatty amino-acids may be converted into highly reactive diazo-derivatives with the aid of nitrous acid (Curtius). When, for example, ethyl amino-acetate, in the form of its hydrochloride, is treated with sodium nitrite in aqueous solution, *ethyl diazo-acetate* is precipitated as a yellow oil (b.p. 143°), which is sparingly soluble in water,

$$NH_2{\cdot}CH_2{\cdot}COOEt,HCl + NaNO_2 = \overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH{\cdot}COOEt + NaCl + 2H_2O.$$

Similar diazo-compounds may be obtained from the esters of other aliphatic amino-acids; most of them have a penetrating odour, and explode when they are heated.

Ethyl diazoacetate, $\overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH{\cdot}COOEt$, and its analogues differ entirely from the diazonium-salts in constitution, but like the latter they are readily decomposed, with elimination of nitrogen. The following are some of the more important reactions of the compounds of this type:—

They are transformed into esters of hydroxy-fatty acids when they are boiled with water or dilute acids,

$$\overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH{\cdot}COOEt + H_2O = HO{\cdot}CH_2{\cdot}COOEt + N_2,$$

and they give alkyl or acidyl derivatives of the hydroxy-fatty acids when they are heated with alcohols and organic acids respectively,

$$\overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH_2{\cdot}COOEt + CH_3{\cdot}OH = CH_3O{\cdot}CH_2{\cdot}COOEt + N_2,$$

$$\overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH{\cdot}COOEt + CH_3{\cdot}COOH = CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}COOEt + N_2.$$

They yield dihalogen substituted fatty acids when they are treated with halogens (even with iodine), and the corresponding monohalogen substitution products with concentrated halogen acids,

$$\overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH{\cdot}COOEt + I_2 = CHI_2{\cdot}COOEt + N_2,$$

$$\overset{N}{\underset{N}{\overset{\cdot\cdot}{>}}}CH{\cdot}COOEt + HBr = CH_2Br{\cdot}COOEt + N_2.$$

Ethyl diazoacetate is reduced to aminoacetic acid (glycine) and ammonia when it is treated with zinc-dust and acetic acid, but when reduced with ferrous sulphate and caustic soda, or with

sodium amalgam and water, it is converted into a salt of **hydrazi-acetic acid,**

$$\begin{matrix}N\\ \vdots\\ N\end{matrix}\!\!>\!CH\cdot COOEt + 2H + H_2O = \begin{matrix}NH\\ |\\ NH\end{matrix}\!\!>\!CH\cdot COOH + C_2H_5\cdot OH;$$

this acid is only stable in the form of its salts, and when the latter are treated with a mineral acid, hydrazine and glyoxylic acid are formed,

$$\begin{matrix}NH\\ |\\ NH\end{matrix}\!\!>\!CH\cdot COOH + H_2O = NH_2\cdot NH_2 + CHO\cdot COOH.$$

Ethyl diazoacetate is hydrolysed by concentrated caustic soda, but the sodium diazoacetate undergoes polymerisation, giving the sodium salt of *bis-diazoacetic acid*,

$$\begin{matrix}N\\ \vdots\\ N\end{matrix}\!\!>\!CH\cdot COONa = COONa\cdot CH\!<\!\begin{matrix}N{:}N\\ N{:}N\end{matrix}\!\!>\!CH\cdot COONa;$$

the acid, liberated from this salt, is decomposed by boiling water, giving hydrazine and oxalic acid,

$$C_2H_2N_4(COOH)_2 + 4H_2O = 2NH_2\cdot NH_2 + 2C_2H_2O_4.$$

It was in this way that hydrazine was first obtained (Curtius and Jay).

Diazomethane, $\begin{matrix}N\\ \vdots\\ N\end{matrix}\!\!>\!CH_2$, is related to the aliphatic diazo-esters, and is the simplest compound of this type. It may be obtained by treating *methylurethane* (p. 330) with nitrous acid in ethereal solution, and then warming the product (*nitrosomethylurethane*) with caustic potash (Pechmann),

$$CH_3\cdot N(NO)\cdot COOEt + 2KOH = CH_2\!<\!\begin{matrix}N\\ \vdots\\ N\end{matrix} + C_2H_5\cdot OH + K_2CO_3 + H_2O.$$

It is a yellow, odourless, very poisonous gas, and like the aliphatic diazo-esters it is very reactive; it is decomposed by water, iodine, hydrochloric acid, and hydrogen cyanide, with evolution of nitrogen, giving methyl alcohol, methylene di-iodide, methyl chloride, and methyl cyanide respectively, and reducing agents convert it into *methylhydrazine*, $NH_2\cdot NH\cdot CH_3$.

Diazoamino- and Aminoazo-Compounds.

Although some of the more characteristic reactions of the diazonium-salts have already been mentioned, there are numerous other changes of great interest and of great commercial importance which these substances undergo.

When, for example, phenyldiazonium chloride is treated with aniline, a reaction takes place very readily, and diazoaminobenzene is formed,

$$C_6H_5\cdot N_2Cl + NH_2\cdot C_6H_5 = C_6H_5\cdot N_2\cdot NH\cdot C_6H_5 + HCl.$$

Diazoaminobenzene.

As, moreover, other diazonium-salts and other amino-compounds interact in a similar manner, numerous diazoamino-compounds may be obtained.

Diazoaminobenzene, $C_6H_5\cdot N_2\cdot NH\cdot C_6H_5$, may be described as a typical compound of this class; it is conveniently prepared by treating aniline with nitrous acid in alcoholic solution,*

$$2C_6H_5\cdot NH_2 + HO\cdot NO = C_6H_5\cdot N_2\cdot NH\cdot C_6H_5 + H_2O.$$

Diazoaminobenzene crystallises in brilliant yellow needles, and is sparingly soluble in water, but readily in alcohol and ether; it is only very feebly basic, and does not form stable salts with acids.

Aminoazobenzene, $C_6H_5\cdot N_2\cdot C_6H_4\cdot NH_2$, is formed when diazoaminobenzene is warmed with a small quantity of aniline hydrochloride at 40°, intramolecular change taking place,

$$C_6H_5\cdot N_2\cdot NH\cdot C_6H_5 = C_6H_5\cdot N_2\cdot C_6H_4\cdot NH_2.$$

This remarkable reaction, which is a general one, may be compared with that which occurs in the transformation of methylaniline into paratoluidine (p. 399); the group, $-N_2\cdot C_6H_5$, leaves the nitrogen atom and migrates to the *para*-position in the nucleus,

$$\underset{\text{Diazoaminobenzene.}}{C_6H_5\cdot NH{-}N_2\cdot C_6H_5} \longrightarrow \underset{\text{p-Aminoazobenzene.}}{C_6H_4\!<\!\begin{matrix}NH_2\\N_2\cdot C_6H_5\end{matrix}},$$

$$\underset{\text{Methylaniline.}}{C_6H_5\cdot NH{-}CH_3} \longrightarrow \underset{\text{p-Toluidine.}}{C_6H_4\!<\!\begin{matrix}NH_2\\CH_3\end{matrix}}.$$

That the group, $-N_2\cdot C_6H_5$, displaces hydrogen from the p-position to the $-NH_2$ group is proved by the fact that the aminoazobenzene

* Nitrous anhydride, prepared from a nitrite and dilute sulphuric acid, or by warming arsenious anhydride with nitric acid, is passed into the alcoholic solution.

thus produced is converted into *para*-phenylenediamine and aniline, on reduction with tin and hydrochloric acid,

$$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_5 + 4H = {}^{(1)}NH_2 \cdot C_6H_4 \cdot NH_2{}^{(4)} + NH_2 \cdot C_6H_5.$$

Aminoazobenzene may also be prepared by nitrating azobenzene (p. 424), and then reducing with ammonium sulphide the p-nitroazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NO_2$, which is thus produced; these changes are analogous to those which occur in the formation of aniline from benzene—and the formation of aminoazobenzene in this way proves that it is an amino-derivative of azobenzene.

Aminoazobenzene crystallises from alcohol in brilliant orange-red plates, and melts at 123°. Its salts are intensely coloured; the hydrochloride, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NH_2$, HCl, for example, forms beautiful steel-blue needles, and used to come on the market under the name of 'aniline yellow' as a silk dye.

Other aminoazo-compounds may be obtained *directly* by treating tertiary alkylanilines (p. 407) with diazonium-salts; dimethylaniline, for example, reacts with phenyldiazonium chloride, yielding dimethylaminoazobenzene hydrochloride,

$$C_6H_5 \cdot N_2Cl + C_6H_5 \cdot N(CH_3)_2 = C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N(CH_3)_2, HCl,$$

and a diazoamino-compound is not formed as an intermediate product, because dimethylaniline does not contain an NH< or NH_2– group.

In this case also, the diazo-group, $C_6H_5 \cdot N_2$–, takes up the p-position to the $N(CH_3)_2$– group, as is shown by the fact that, on reduction, dimethylaminoazobenzene is converted into aniline and dimethyl-p-phenylenediamine, the latter being identical with the base which is produced by reducing p-nitrosodimethylaniline (p. 409).

Phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, a compound of great importance, is easily prepared by the reduction of phenyldiazonium chloride (E. Fischer),

$$C_6H_5 \cdot N_2Cl + 4H = C_6H_5 \cdot NH \cdot NH_2, HCl.$$

Aniline (9 g.) is dissolved in concentrated hydrochloric acid (170 c.c.), and diazotised in the usual way (p. 415); to the well-cooled solution of phenyldiazonium chloride a solution of stan-

nous chloride ($SnCl_2,2H_2O$, 45 g.) in concentrated hydrochloric acid (100 c.c.) is then slowly added. The precipitate of phenylhydrazine hydrochloride, which rapidly forms, is separated on a suction filter, washed with a little concentrated hydrochloric acid, and decomposed with excess of concentrated potash; the oily base is extracted with ether, the extract is dried over potassium hydroxide, and the ether is distilled. The product may then be purified by distillation under reduced pressure.

Phenylhydrazine crystallises in colourless prisms, melts at 23°, and boils at 241°, decomposing slightly. It is sparingly soluble in cold water, readily in alcohol and ether; it is a strong base, and forms well-characterised salts, such as the hydrochloride, $C_6H_5{\cdot}NH{\cdot}NH_2$, HCl, which crystallises in colourless needles, and is readily soluble in hot water; solutions of the free base and of its salts reduce Fehling's solution in the cold.

Phenylhydrazine is converted into benzene, with evolution of nitrogen, when it is heated with a solution of copper sulphate or ferric chloride. This important reaction may be used in order to convert nitrobenzene, aniline, or a diazonium-salt into benzene, since all these compounds may be transformed into phenylhydrazine by the methods already given,

$$C_6H_5{\cdot}NO_2 \rightarrow C_6H_5{\cdot}NH_2 \rightarrow C_6H_5{\cdot}N_2X \rightarrow C_6H_5{\cdot}NH{\cdot}NH_2 \rightarrow C_6H_6.$$

Similar transformations may be brought about in the case of corresponding aromatic compounds; bromonitrobenzene, for example, may be thus converted into bromobenzene. Further, since the evolution of nitrogen takes place quantitatively when a hydrazine is decomposed with a solution of copper sulphate, this reaction may be employed for the estimation of hydrazines.

The *constitution* of phenylhydrazine is established by the fact that, when heated with zinc-dust and hydrochloric acid, it is converted into aniline and ammonia.

Phenylhydrazine reacts readily with aldehydes and ketones, with formation of water and a *phenylhydrazone* (hydrazone); as these compounds are usually sparingly soluble and often

crystallise well, they are frequently employed for the identification and isolation of aldehydes and ketones (p. 140),

$$\underset{\text{Benzaldehyde.}}{C_6H_5\cdot CHO} + C_6H_5\cdot NH\cdot NH_2 = \underset{\text{Benzaldehyde Hydrazone.}}{C_6H_5\cdot CH{:}N\cdot NH\cdot C_6H_5} + H_2O,$$

$$\underset{\text{Acetophenone.}}{C_6H_5\cdot CO\cdot CH_3} + C_6H_5\cdot NH\cdot NH_2 = \underset{\text{Acetophenone Hydrazone.}}{\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C{:}N\cdot NH\cdot C_6H_5} + H_2O.$$

Many hydrazones are decomposed by strong mineral acids, with regeneration of the aldehyde or ketone, and formation of a salt of phenylhydrazine,

$$C_6H_5\cdot CH{:}N\cdot NH\cdot C_6H_5 + H_2O + HCl = C_6H_5\cdot CHO + C_6H_5\cdot NH\cdot NH_2,\ HCl\ ;$$

on reduction with zinc-dust and acetic acid, they yield primary amines,

$$\underset{\text{Benzylidenehydrazone.}}{C_6H_5\cdot CH{:}N\cdot NH\cdot C_6H_5} + 4H = \underset{\text{Benzylamine.}}{C_6H_5\cdot CH_2\cdot NH_2} + C_6H_5\cdot NH_2.$$

The value of phenylhydrazine for the detection and separation of the sugars has already been mentioned (p. 301).

In the preparation of a hydrazone a slight excess of phenylhydrazine is directly added to the aldehyde or ketone, or the two substances are separately dissolved in *dilute* acetic acid, and the solutions are mixed. Very often a reaction takes place spontaneously, and its occurrence is recognised by the development of heat and separation of water, or, in the case of the dissolved substances, by the separation of an oily, or solid, sparingly soluble precipitate. Sometimes the application of heat is necessary. The hydrazone is separated, washed with dilute acetic acid, and, if a solid, purified by recrystallisation.

The occurrence of a reaction, when a neutral substance is treated with phenylhydrazine in the above-described manner, is a very important qualitative test for aldehydes and ketones.

Osazones (p. 301) are prepared by boiling a dilute aqueous solution of the sugar with excess of phenylhydrazine acetate; after some time the osazone begins to separate in yellow crystals, and the heating is continued until no further separation occurs.

Azo- and Azoxy-Compounds.

It has already been stated that when nitro-compounds are treated with *acid* reducing agents, they are converted

into amino-compounds; a similar change takes place when alcoholic ammonium sulphide is employed. When, however, nitro-compounds are treated with other *alkaline* reducing agents, such as alcoholic potash, sodium amalgam and water, stannous oxide and potash, or zinc-dust and potash, they yield *azo-compounds*, such as azobenzene—*azoxy-compounds*, such as azoxybenzene, being formed as intermediate products; in these reactions two molecules of the nitro-compound give one molecule of the azoxy- or of the azo-compound,

$$2C_6H_5\cdot NO_2 + 6H = C_6H_5\cdot N<\overset{O}{\underset{}{}}>N\cdot C_6H_5 + 3H_2O,$$

Azoxybenzene.

$$2C_6H_5\cdot NO_2 + 8H = C_6H_5\cdot N{:}N\cdot C_6H_5 + 4H_2O.$$

Azobenzene.

Azoxybenzene, $C_6H_5\cdot N<\overset{O}{\underset{}{}}>N\cdot C_6H_5$, is generally prepared by heating nitrobenzene ($1\frac{1}{2}$ parts) with a solution of sodium (1 part) in methyl alcohol,

$$4C_6H_5\cdot NO_2 + 3CH_3\cdot ONa = 2C_{12}H_{10}N_2O + 3H\cdot COONa + 3H_2O.$$

The solution is heated (with reflux condenser) for about four hours; the alcohol is then distilled off and water is added; when sufficiently hard the pasty product is pressed on porous earthenware, left to dry, and crystallised from light petroleum.

It forms yellow needles, melting at 36°, and is insoluble in water, but readily soluble in most organic liquids.

Azobenzene, $C_6H_5\cdot N{:}N\cdot C_6H_5$, may be prepared by heating an intimate mixture of azoxybenzene (1 part) and iron filings (3 parts).

The mixture is carefully heated in a small retort, and the solid distillate is purified as described in the case of the azoxy-compound.

Azobenzene crystallises in brilliant red plates, melts at 68°, and distils at 293°; it is readily soluble in ether and alcohol, but insoluble in water. Alkaline reducing agents, such as ammonium sulphide, zinc-dust and potash, &c., convert

azobenzene into *hydrazobenzene*, a colourless, crystalline substance, which melts at 131°,

$$C_6H_5\cdot N{:}N\cdot C_6H_5 + 2H = C_6H_5\cdot NH\cdot NH\cdot C_6H_5,$$

whereas a mixture of zinc-dust and acetic acid decomposes it, with formation of aniline,

$$C_6H_5\cdot N{:}N\cdot C_6H_5 + 4H = 2C_6H_5\cdot NH_2.$$

Other azo-compounds behave in a similar manner.

Hydrazobenzene, $C_6H_5\cdot NH\cdot NH\cdot C_6H_5$, is readily converted into azobenzene by mild oxidising agents such as mercuric oxide, and slowly even when air is passed through its alcoholic solution. When treated with strong acids, it undergoes a very remarkable intramolecular change, and is converted into p-diaminodiphenyl or *benzidine* (m.p. 122°), a base which is largely used in the preparation of azo-dyes (p. 660),

$$\underset{\text{Hydrazobenzene.}}{C_6H_5\cdot NH\cdot NH\cdot C_6H_5} \longrightarrow \underset{\text{Benzidine.}}{NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2}.$$

Benzidine may be produced in one operation by reducing azobenzene with tin and strong hydrochloric acid; its *sulphate* forms lustrous scales, and is very sparingly soluble in water.

Other azo-compounds behave like azobenzene; o-*azotoluene*, $CH_3\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CH_3$, for example, is first converted into the corresponding hydrazo-compound, which then undergoes isomeric or intramolecular change into *dimethylbenzidine* (tolidine),

$$\begin{matrix}{}^{(4)}NH_2 \\ {}^{(2)}CH_3\end{matrix}\!\!>\!{}^{(1)}C_6H_3\cdot{}^{(1)}C_6H_3\!<\!\begin{matrix}NH_{2(4)} \\ CH_{3\,(2)}\end{matrix}.$$

These changes, like that of diazoaminobenzene into p-aminoazobenzene (p. 420), involve the *migration* of a complex group of atoms from an amino-group to the *para*-position in the nucleus,

$$C_6H_5\cdot NH{-}NH\cdot C_6H_5 \longrightarrow C_6H_4\!<\!\begin{matrix}{}^{(1)}NH_2 \\ {}_{(4)}C_6H_4\cdot NH_2\end{matrix};$$

if the p-position is already occupied, isomeric change takes place far *less readily*, and the group migrates to the o-position.

Azimido-Compounds or Azides.—Organic derivatives of azoimide (hydrazoic acid) may be obtained from organic derivatives of hydrazine, just as azoimide itself may be prepared from hydrazine—namely, with the aid of nitrous acid.

Phenyl azide, $C_6H_5\cdot N\!<\!\begin{matrix}N \\ \vdots \\ N\end{matrix}$ (phenylazoimide), for example, is

formed when sodium nitrite is added to an aqueous solution of phenylhydrazine hydrochloride,

$$C_6H_5\cdot NH\cdot NH_2 + HO\cdot NO = C_6H_5\cdot N\begin{matrix}<^{NH_2}_{NO}\end{matrix} + H_2O = C_6H_5\cdot N_3 + 2H_2O.$$

It is also produced by the interaction of phenylhydrazine and phenyldiazonium sulphate,

$$C_6H_5\cdot NH\cdot NH_2 + C_6H_5\cdot N_2\cdot SO_4H = C_6H_5\cdot N_3 + C_6H_5\cdot NH_2, H_2SO_4,$$

or of phenyldiazonium sulphate and hydroxylamine,

$$C_6H_5\cdot N_2\cdot SO_4H + NH_2\cdot OH = C_6H_5\cdot N_3 + H_2SO_4 + H_2O.$$

Other azides may be prepared by these general reactions.

Phenyl azide is a yellow oil, having a very disagreeable and penetrating odour; it may be distilled under greatly reduced pressure, but it explodes when it is heated under the ordinary pressure. It is a very reactive substance; when boiled with dilute sulphuric acid it gives **p-*aminophenol***, and with hydrochloric acid it gives *chloraniline*, nitrogen being evolved in both cases. It combines with the Grignard reagents to give products which are readily converted into diazoamino-compounds,

$$C_6H_5\cdot N_3 + Ph\cdot MgBr = \begin{matrix}C_6H_5\\BrMg\end{matrix}>N\cdot N{:}NPh,$$

$$\begin{matrix}C_6H_5\\BrMg\end{matrix}>N\cdot N{:}NPh + H_2O = C_6H_5\cdot N_2\cdot NH\cdot C_6H_5 + MgBr\cdot OH.$$

Methyl azide, $CH_3\cdot N_3$, the simplest compound of this type, may be obtained by treating sodium azide (sodium azoimide) with dimethyl sulphate; it boils at 20–21°, and explodes when it is strongly heated. When treated with magnesium methyl iodide it gives **diazoaminomethane**, $CH_3\cdot N{:}N\cdot NH\cdot CH_3$, a very reactive liquid (b.p. 92°), which is decomposed by acids, giving methylamine, methyl alcohol, and nitrogen.

Ethyl azidoacetate, $N_3\cdot CH_2\cdot COOEt$, prepared from ethyl chloracetate and sodium azide, **azidoacetic acid**, $N_3\cdot CH_2\cdot COOH$, and many other aliphatic derivatives of azoimide, are known.

CHAPTER XXVII.

Sulphonic Acids and their Derivatives.

When benzene is heated with concentrated sulphuric acid it gradually dissolves, and *benzenesulphonic acid* is formed by the substitution of the *sulphonic*-group, $-SO_3H$ or $-SO_2\cdot OH$, for an atom of hydrogen,

$$C_6H_6 + H_2SO_4 = C_6H_5\cdot SO_3H + H_2O.$$

The homologues of benzene and aromatic compounds in general behave in a similar manner, and this property of yielding sulphonic derivatives, by the displacement of hydrogen of the *nucleus*, is one of the important characteristics of aromatic, as distinct from fatty, compounds.

The sulphonic acids are *not* analogous to the alkylsulphuric acids (p. 191), which are acid esters, but they are related to the carboxylic acids, since they may be regarded as derived from sulphuric acid, $SO_2(OH)_2$, just as the carboxylic acids are derived from carbonic acid, $CO(OH)_2$—namely, by the substitution of an aromatic radicle for one of the hydroxyl-groups of the acid.

Sulphuric acid, $SO_2<^{OH}_{OH}$. Carbonic acid, $CO<^{OH}_{OH}$.

Sulphonic acid, $SO_2<^{R}_{OH}$. Carboxylic acid, $CO<^{R}_{OH}$.

Preparation.—Sulphonic acids are prepared by treating an aromatic compound with sulphuric acid, or with anhydrosulphuric acid,

$$C_6H_5\cdot CH_3 + H_2SO_4 = C_6H_4<^{CH_3}_{SO_3H} + H_2O,$$

$$C_6H_5\cdot NH_2 + H_2SO_4 = C_6H_4<^{NH_2}_{SO_3H} + H_2O,$$

$$C_6H_6 + 2H_2SO_4 = C_6H_4(SO_3H)_2 + 2H_2O.$$

The number of hydrogen atoms displaced by sulphonic

groups depends (as in the case of nitro-groups) on the temperature, on the concentration of the acid, and on the nature of the substance undergoing *sulphonation*.

The substance to be sulphonated is mixed with, or dissolved in, excess of the acid, and, if necessary, the mixture or solution is then heated on a water- or sand-bath until the desired change is complete. After being cooled, the product is carefully poured into water, and the acid is isolated as described later (p. 429). In the case of a substance which is insoluble in water or dilute sulphuric acid, it is easy to ascertain when its sulphonation is complete by taking out a small portion of the mixture and adding water; unless the whole is soluble, unchanged substance is still present.

Sometimes chlorosulphonic acid, $Cl{\cdot}SO_3H$, is employed as a sulphonating agent, and in such cases chloroform or carbon disulphide may be used as a solvent to moderate the action,

$$C_6H_6 + Cl{\cdot}SO_3H = C_6H_5{\cdot}SO_3H + HCl.$$

Properties.—Sulphonic acids, as a rule, are crystalline, readily soluble in water, and often very hygroscopic; they have seldom a definite melting-point, and gradually decompose when heated, so they cannot be distilled. They have a sour taste, a strongly acid reaction, and show, in fact, all the properties of strong acids, their basicity depending on the number of sulphonic-groups in the molecule. They decompose carbonates, and dissolve certain metals with evolution of hydrogen; their metallic salts (including the barium salts), as a rule, are readily soluble in water.

Although, generally speaking, the sulphonic acids are very stable, and are not decomposed by boiling aqueous alkalis or mineral acids, they undergo certain changes of great importance. When fused with potash they yield *phenols* (p. 435), and when strongly heated with potassium cyanide, or with potassium ferrocyanide, they are converted into *cyanides* (or nitriles, p. 321), which distil, leaving a residue of potassium sulphite,

$$C_6H_5{\cdot}SO_3K + KCN = C_6H_5{\cdot}CN + K_2SO_3.$$

The sulphonic-group may also be displaced by hydrogen. This may be done by strongly heating the acids alone, or with

hydrochloric acid, in sealed tubes, or by passing superheated steam into the acids, or into their solutions in concentrated sulphuric acid.

Sulphonic acids yield numerous derivatives, which may generally be prepared by methods similar to those used in the case of the corresponding derivatives of carboxylic acids. When, for example, a sulphonic acid (or its alkali salt) is treated with phosphorus pentachloride, the hydroxyl-group is displaced by chlorine, and a *sulphonic chloride* is obtained,

$$C_6H_5\cdot SO_2\cdot OH + PCl_5 = C_6H_5\cdot SO_2Cl + POCl_3 + HCl.$$

All sulphonic acids behave in this way, and the sulphonic chlorides are of great value, not only because they are often useful for the isolation and identification of the ill-characterised acids, but also because, like the chlorides of the carboxylic acids, they react readily with many other compounds.

The sulphonic chlorides are decomposed by water and by alkalis, giving the sulphonic acids or their salts; they react with alcohols at high temperatures, yielding esters such as *ethyl benzenesulphonate*,

$$C_6H_5\cdot SO_2Cl + C_2H_5\cdot OH = C_6H_5\cdot SO_2\cdot OC_2H_5 + HCl,$$

and when shaken with concentrated ammonia they are usually converted into well-defined crystalline *sulphonamides*, which often serve for the identification of the acids,

$$\underset{\text{Benzenesulphonic Chloride.}}{C_6H_5\cdot SO_2Cl} + NH_3 = \underset{\text{Benzenesulphonamide.}}{C_6H_5\cdot SO_2\cdot NH_2} + HCl.$$

The isolation of sulphonic acids is very often a matter of some difficulty, because they are readily soluble in water and non-volatile, and cannot be extracted from their aqueous solutions with ether, &c., or separated from other substances by steam distillation. The first step usually consists in their separation from the excess of sulphuric acid employed in their preparation; this may be done in the following manner:—The aqueous solution of the product of sulphonation (see above) is boiled with excess of barium (or calcium) carbonate, filtered from the precipitated barium (or calcium) sulphate, and the filtrate—which contains the barium

(or calcium) salt of the sulphonic acid—is treated with sulphuric acid drop by drop so long as a precipitate is produced; an aqueous solution of the sulphonic acid is thus obtained, and when the filtered solution is evaporated to dryness, the acid remains as a syrup or in a crystalline form. If calcium carbonate has been used, the acid will contain a little calcium sulphate, which may be got rid of by adding a little alcohol, filtering, and again evaporating.

Lead carbonate is sometimes employed instead of barium or calcium carbonate; in such cases the filtrate from the lead sulphate is treated with hydrogen sulphide, filtered from lead sulphide, and then evaporated. These methods, of course, are only applicable provided that the barium, calcium, or lead salt of the acid is soluble in water; in other cases the separation is much more troublesome.

The alkali salts are easily prepared from the barium, calcium, or lead salts by treating the solution of the latter with the alkali carbonate as long as a precipitate is produced, filtering from the insoluble carbonate, and then evaporating.

When two or more sulphonic acids are present in the product, they are usually separated by the fractional crystallisation of their salts. Sometimes a complete separation cannot be accomplished with the aid of any of the salts, and in such cases the sulphonic chlorides are prepared by treating the alkali salts with phosphorus pentachloride; these compounds are soluble in ether, chloroform, &c., and generally crystallise well, so that they are easily separated and obtained in a state of purity.

Benzenesulphonic acid, $C_6H_5 \cdot SO_3H$, is prepared by gently boiling a mixture of equal volumes of benzene and concentrated sulphuric acid on a sand-bath (using a reflux condenser) during twenty to thirty hours.

The reaction is at an end when all the benzene has disappeared. The *calcium* (or barium) salt is first isolated, and from the latter the *potassium* salt or the free acid may be prepared; the details of these processes are given above.

The acid crystallises with $1\frac{1}{2}H_2O$ in colourless, hygroscopic plates, and dissolves freely in alcohol; when fused with potash it yields phenol (p. 439). *Benzenesulphonic chloride*, $C_6H_5 \cdot SO_2Cl$, is an oil, but the *sulphonamide*, $C_6H_5 \cdot SO_2 \cdot NH_2$, is crystalline, and melts at 150°.

Benzene-*m*-disulphonic acid, $C_6H_4(SO_3H)_2$, is also prepared by heating the hydrocarbon with concentrated sulphuric acid, but a larger proportion (two volumes) of the acid is employed, and the solution is heated more strongly (or anhydrosulphuric acid is used); when fused with potash, it yields resorcinol (p. 447).

The three (**o.m.p.**) *toluenesulphonic acids*, $C_6H_4(CH_3)\cdot SO_3H$, are crystalline, and their barium salts are soluble in water; the **o**- and **p**-acids are the principal products when toluene is sulphonated.

Sulphanilic acid, $C_6H_4(NH_2)\cdot SO_3H$ (aminobenzene-**p**-sulphonic acid, or aniline-**p**-sulphonic acid), is easily prepared by heating aniline sulphate at about 200° for some time.

Aniline is slowly added to a slight excess of the theoretical quantity of sulphuric acid, contained in a porcelain dish, and the mixture is constantly stirred as it becomes solid; the dish is then *cautiously* heated on a sand-bath, the contents being stirred, and care being taken to prevent charring. The process is at an end as soon as a small portion of the product, dissolved in water, gives no oily precipitate of aniline on the addition of excess of alkali. When it has cooled, a little water is added to the product, and the sparingly soluble sulphonic acid is separated by filtration, and purified by recrystallisation from boiling water, with addition of animal charcoal if necessary.

Sulphanilic acid crystallises with $2H_2O$, and is readily soluble in hot, but only sparingly so in cold, water. It forms salts with bases, but it does not combine with acids, the basic character of the amino-group being neutralised by the acid character of the sulphonic-group; in this respect, therefore, it differs from glycine (p. 329), which forms salts both with acids and bases.

When sulphanilic acid is dissolved in dilute soda, and the solution is mixed with a slight excess of sodium nitrite and poured into well-cooled, dilute sulphuric acid, a **p**-*sulphonic acid* of phenyldiazonium hydroxide is formed,

$$C_6H_4<\begin{matrix}NH_2\\SO_3H\end{matrix} + HO\cdot NO = C_6H_4<\begin{matrix}N_2\cdot OH\\SO_3H\end{matrix} + H_2O;$$

this compound, however, immediately loses water, and is converted into its anhydride,* $C_6H_4<\begin{matrix}N_2\\SO_3\end{matrix}>$, which separates from the solution in colourless crystals.

This anhydride shows the characteristic properties of diazonium-salts; when boiled with water it is converted into *phenol*-**p**-*sulphonic acid* (p. 443),

$$C_6H_4<\begin{matrix}N_2\\SO_3\end{matrix}> + H_2O = C_6H_4<\begin{matrix}OH\\SO_3H\end{matrix} + N_2,$$

whereas when heated with concentrated hydrochloric or hydrobromic acid, it gives *chlorobenzene-* or *bromobenzene*-**p**-*sulphonic acid*,

$$C_6H_4<\begin{matrix}N_2\\SO_3\end{matrix}> + HCl = C_6H_4<\begin{matrix}Cl\\SO_3H\end{matrix} + N_2;$$

it reacts readily with dimethylaniline, giving *helianthin* (p. 659).

Aminobenzene-**o**-*sulphonic acid* and the **m**-acid (*metanilic acid*) may be obtained by reducing the corresponding *nitrobenzene-sulphonic acids*, $C_6H_4(NO_2)\cdot SO_3H$, both of which are formed, together with the **p**-acid, when benzenesulphonic acid is nitrated; they resemble sulphanilic acid in properties, and are readily converted into the anhydrides of the corresponding diazoniumsulphonic acids.

Arsanilic acid, $C_6H_4(NH_2)\cdot AsO(OH)_2$ (**p**-*aminophenylarsenic acid*), prepared by heating aniline arsenate, corresponds with sulphanilic acid; its sodium salt is known as *atoxyl*, and is employed as a drug in cases of sleeping sickness. Even more efficient is the sodium salt of the acetyl-derivative of arsanilic acid, which is known as *arsacetin;* this compound has the composition, $C_6H_4(NHAc)\text{-}AsO(OH)\cdot ONa$, and when injected into the system, it has such a remarkably poisonous action on the trypanosomes of sleeping sickness that the parasites' disappear from the blood in the course of 5–6 hours, after an injection of 0·5 g.

Many other sulphonic acids are described later.

* The existence of this anhydride (and of that of *aminobenzene*-**m**-*sulphonic acid*) is a very interesting fact, because, as a rule, anhydride formation takes place only between groups in the o-position to one another (compare p. 627).

CHAPTER XXVIII.

Phenols.

The hydroxy-compounds of the aromatic series, such as *phenol* or *hydroxy-benzene*, $C_6H_5 \cdot OH$, the isomeric *hydroxy-toluenes*, $C_6H_4(CH_3) \cdot OH$, and *benzyl alcohol*, $C_6H_5 \cdot CH_2 \cdot OH$, are derived from the aromatic hydrocarbons by the substitution of hydroxyl-groups for atoms of hydrogen, just as the fatty alcohols are derived from the paraffins. It will be seen, however, from the examples just given, that, whereas in the case of benzene hydrogen atoms of the nucleus must necessarily be displaced, in that of toluene and all the higher homologues this is not so, since the hydroxyl-groups may displace hydrogen either of the *nucleus* or of the *side-chain*. Now the hydroxy-derivatives of benzene, and all those aromatic hydroxy-compounds formed by the substitution of hydroxyl-groups for hydrogen atoms of the *nucleus*, differ in many respects, not only from the fatty alcohols, but also from those aromatic compounds which contain the hydroxyl-group in the side-chain; it is convenient, therefore, to make some distinction between the two kinds of aromatic hydroxy-compounds, and for this reason they are classed in two groups, (*a*) the **phenols**, and (*b*) the **aromatic alcohols** (p 450).

The **phenols** are those hydroxy-compounds in which the hydroxyl-groups are united directly with carbon of the *nucleus*; they may be subdivided into monohydric, dihydric, trihydric phenols, &c., according to the number of hydroxyl-groups which they contain. *Phenol*, or *carbolic acid*, $C_6H_5 \cdot OH$, for example, is a monohydric phenol, as are also the three isomeric *cresols* or *hydroxytoluenes*, $C_6H_4(CH_3) \cdot OH$; the three isomeric *dihydroxybenzenes*, $C_6H_4(OH)_2$, on the other hand, are dihydric phenols, whereas *phloroglucinol*, $C_6H_3(OH)_3$, is an example of a trihydric compound.

Many of the phenols are easily obtainable, well-known compounds; carbolic acid, for instance, is prepared from coal-tar in large quantities; *carvacrol* and *thymol* occur in various plants; and *catechol*, *pyrogallol*, &c. may be obtained by the dry distillation of certain vegetable products.

Preparation.—Phenols may be prepared by treating salts of amino-compounds with nitrous acid in aqueous solution, and then heating the solution until nitrogen ceases to be evolved,

$$C_6H_5\cdot NH_2,HCl + HO\cdot NO = C_6H_5\cdot OH + N_2 + H_2O + HCl,$$

$$C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix},HCl + HO\cdot NO = C_6H_4{<}\begin{matrix}CH_3\\OH\end{matrix} + N_2 + H_2O + HCl.$$

It is possible, therefore, to prepare phenols, not only from the amino-compounds themselves, but also indirectly from the corresponding nitro-derivatives and from the hydrocarbons, since these substances may be converted into amino-compounds,

$$\underset{\text{Benzene.}}{C_6H_6} \rightarrow \underset{\text{Nitrobenzene.}}{C_6H_5\cdot NO_2} \rightarrow \underset{\text{Aminobenzene.}}{C_6H_5\cdot NH_2} \rightarrow \underset{\text{Phenol.}}{C_6H_5\cdot OH}.$$

The conversion of an amino-compound into a phenol really takes place in two stages, as already explained (p. 412); at low temperatures the salt of the amino-compound is transformed into a diazonium-salt, but the latter decomposes when its aqueous solution is heated, yielding a phenol,

$$C_6H_5\cdot NH_2,\ HCl + HCl + KNO_2 = C_6H_5\cdot N_2Cl + KCl + 2H_2O,$$
$$C_6H_5\cdot N_2Cl + H_2O = C_6H_5\cdot OH + HCl + N_2.$$

The amino-compound, aniline, for example, is dissolved in dilute hydrochloric acid or sulphuric acid, and *diazotised* in the manner already described (p. 415). The solution of the diazonium-salt is then gradually heated to boiling (reflux condenser) until the evolution of nitrogen (which at first causes a brisk effervescence) is at an end; the phenol is afterwards separated from the tarry matter, which is almost invariably produced, by distillation in steam, or by crystallisation from hot water. In some cases the phenol is extracted with ether, and the ethereal solution is shaken with

dilute caustic soda, which dissolves out the phenol, leaving most of the impurities in the ether.

Dihydric phenols may sometimes be prepared from the corresponding di-substitution products of the hydrocarbon by a series of changes indicated by the following formulæ,

$$C_6H_6 \quad C_6H_4\!<\!\begin{matrix}NO_2\\NO_2\end{matrix} \quad C_6H_4\!<\!\begin{matrix}NH_2\\NH_2\end{matrix} \quad C_6H_4\!<\!\begin{matrix}N_2Cl\\N_2Cl\end{matrix} \quad C_6H_4\!<\!\begin{matrix}OH\\OH\end{matrix}$$

Benzene. Dinitrobenzene. Diaminobenzene. Diazonium-Salt. Dihydric Phenol.

They may also be obtained from the monohydric compounds in a corresponding manner,

$$C_6H_5\cdot OH \quad C_6H_4\!<\!\begin{matrix}NO_2\\OH\end{matrix} \quad C_6H_4\!<\!\begin{matrix}NH_2\\OH\end{matrix} \quad C_6H_4\!<\!\begin{matrix}N_2Cl\\OH\end{matrix} \quad C_6H_4\!<\!\begin{matrix}OH\\OH\end{matrix}$$

Phenol. Nitrophenol. Aminophenol. Diazonium-Salt. Dihydric Phenol.

These two methods, however, are limited in their application, because o- and m-diamino-compounds cannot always be converted into the corresponding diazonium-salts, but more often yield products of quite a different nature; o- and p-amino-hydroxy-compounds also show an abnormal behaviour with nitrous acid, as the former are not acted on at all, the latter only with difficulty. For these reasons dihydric phenols are usually most conveniently prepared by the methods given below.

Another important general method for the preparation of phenols consists in fusing sulphonic acids or their salts with caustic alkalis; in this case, also, their preparation from the hydrocarbons is often easily accomplished, since the latter are usually converted into sulphonic acids without difficulty,

$$C_6H_5\cdot SO_3K + KOH = C_6H_5\cdot OH^* + K_2SO_3,$$

$$C_6H_4\!<\!\begin{matrix}CH_3\\SO_3Na\end{matrix} + NaOH = C_6H_4\!<\!\begin{matrix}CH_3\\OH\end{matrix} + Na_2SO_3.$$

The sulphonic acid or its alkali salt is placed in an iron—or, better, nickel or silver—dish,† together with excess of solid potash (or soda) and a little water, and the dish is heated over a free flame, while the mixture is constantly stirred with a nickel or silver spatula,

* In all cases the phenols are present in the product as alkali salts.

† Caustic alkalis readily attack platinum and porcelain at high temperatures, but have little action on nickel and none on silver.

or with a thermometer, the bulb of which is encased in a glass tube, or covered with a film of silver.* After the potash and the salt have dissolved, the temperature is slowly raised, during which process the mixture sometimes undergoes a variety of changes in colour, by which an experienced operator can tell when the decomposition of the sulphonic acid is complete; as a rule, a temperature considerably above 200° is required, so that if the sulphonic acid is simply boiled with concentrated potash, the desired change does not occur. When the operation is finished, the fused mass is allowed to cool, dissolved in water, and treated with *excess* of dilute sulphuric acid; the liberated phenol is then isolated in some suitable manner (p. 434).

Dihydric phenols may often be obtained in a similar manner from the disulphonic acids,

$$C_6H_4(SO_3K)_2 + 2KOH = C_6H_4(OH)_2 + 2K_2SO_3.$$

Owing to the high temperature at which these reactions must be carried out, secondary changes very often occur. When the sulphonic acid contains halogens, the latter are usually displaced by hydroxyl-groups, especially if certain other acid radicles, such as $-NO_2$, are also present in the molecule; when, for example, *chlorobenzenesulphonic acid*, $C_6H_4Cl\cdot SO_3H$, is fused with potash, a dihydric phenol, $C_6H_4(OH)_2$, is produced, the halogen as well as the sulphonic-group being displaced. For this reason, also, compounds such as **o**- and **p**-chloronitrobenzene may be converted into the corresponding nitrophenols (p. 441) even by a boiling solution of caustic potash, the presence of the nitro-group facilitating the displacement of the halogen atom; **m**-*chloronitrobenzene*, on the other hand, is not acted on under these conditions. Sometimes, also, the process is not one of direct substitution only—that is to say, the hydroxyl-groups in the product are not united with the same carbon atoms as those with which the displaced atoms or groups were united; the three (**o.m.p.**) *bromobenzenesulphonic acids*, for example, all yield *one and the same* dihydric phenol—namely, the **m**-compound, *resor-*

* As the mixture is very liable to spirt, the eyes of the operator must be protected by spectacles or by a sheet of glass suitably placed.

cinol, $C_6H_4(OH)_2$, because the o- and p-dihydric compounds, which are first produced from the corresponding bromo-sulphonic acids, are converted into the more stable m-derivative by intramolecular change.

Phenols may be obtained by distilling hydroxy-acids, such as salicylic acid, with lime,

$$C_6H_4(OH)\cdot COOH = C_6H_5\cdot OH + CO_2,$$

a reaction which is similar to that which occurs in the preparation of the hydrocarbons from the acids.

They may also be formed by treating the aryl Grignard reagents (p. 390) with oxygen,

$$2C_6H_5\cdot MgBr + O_2 = 2C_6H_5\cdot O\cdot MgBr,$$

and then decomposing the products with mineral acids.

When phenols are heated with fatty alcohols in presence of zinc chloride, the alkyl-group displaces hydrogen of the nucleus, just as in the production of toluidine, &c., from aniline (pp. 399, 408),

$$C_6H_5\cdot OH + C_2H_5\cdot OH = C_6H_4\begin{matrix}<^{C_2H_5}\\ _{OH}\end{matrix} + H_2O.$$

A phenol may thus be transformed into its higher homologues.

Properties.—Most phenols are colourless, crystalline substances, readily soluble in alcohol and ether; their solubility in water usually increases with the number of hydroxyl-groups in the molecule, while their volatility diminishes; phenol and cresol, for example, are sparingly soluble, distil without decomposing, and are readily volatile in steam, whereas the three dihydric phenols are readily soluble and volatilise very slowly in steam. Alcoholic and aqueous solutions of phenols (and of some of their derivatives) give a green, violet, or yellow colouration with ferric salts.

In the case of the di- and poly-hydric compounds, the particular colouration depends on the relative positions of the hydroxyl-groups. o-Dihydroxy-compounds give an *intense green* colouration, which first becomes deep violet, and then bright red, on the addition of sodium bicarbonate; m-dihydroxy-compounds give a deep *violet* colouration; p-dihydroxy-compounds give a faint green colouration, which immediately changes to yellow owing to the formation of a quinone (p. 464).

Most phenols give Liebermann's reaction—that is to say, when dissolved in concentrated sulphuric acid and treated with a nitrosamine or a nitrite, they yield (red, brown, &c.) solutions which, on the addition of water and excess of alkali, assume an intense blue or green colour. This reaction, therefore, affords a convenient test for phenols as well as for nitrosamines (p. 214).

Although the phenols resemble the fatty alcohols and the alcohols of the aromatic series in some respects, they have, on the whole, very little in common with these substances. The reason of this is that the character of the hydroxyl-group (like that of the amino-group, p.400) is greatly modified by its union with carbon of the benzene nucleus, just as that of the hydroxyl-group in water is altered by combination with acid-forming atoms or radicles, such as Cl–, NO_2–, &c., as, for example, in HOCl and $HO{\cdot}NO_2$; in other words, the phenolic hydroxyl-group has a much more pronounced acid character than that in alcohols, and for this reason the radicles *phenyl*, C_6H_5–, *phenylene*, $C_6H_4<$, &c., may be regarded as acid-forming (p. 400).

The acid character of the hydroxyl-group in phenols is shown by their behaviour towards solutions of the alkali hydroxides, in which they dissolve freely, owing to the formation of metallic derivatives or salts, such as *sodium phenate*, $C_6H_5{\cdot}ONa$, and *potassium cresate*, $C_6H_4(CH_3){\cdot}OK$; these compounds, unlike the alkali derivatives of the alcohols, are stable in presence of water, but are decomposed by carbonic acid and by all other acids, with regeneration of the phenols. For this reason phenols which are insoluble in water are also *insoluble* in solutions of the alkali carbonates, unless they contain other acid-forming groups or atoms; *nitrophenol*, $C_6H_4(NO_2){\cdot}OH$, and *picric acid*, $C_6H_2(NO_2)_3{\cdot}OH$, for example, are so acidic in character that they decompose the alkali carbonates and dissolve in their aqueous solutions.

The metallic derivatives of the phenols, like those of the alcohols, react with alkyl halogen compounds, with dimethyl

sulphate (p. 193), and with acid chlorides, yielding substances analogous to the ethers and esters respectively,

$$C_6H_5\cdot OK + CH_3I = C_6H_5\cdot O\cdot CH_3 + KI,$$

$$C_6H_4\begin{<}{}^{CH_3}_{ONa} + C_2H_5Br = C_6H_4\begin{<}{}^{CH_3}_{OC_2H_5} + NaBr,$$

$$C_6H_4\begin{<}{}^{CH_3}_{OK} + CH_3\cdot COCl = C_6H_4\begin{<}{}^{CH_3}_{O\cdot CO\cdot CH_3} + KCl;$$

the former, like the ethers, are *not* decomposed by boiling alkalis, but the latter undergo hydrolysis, just as do the esters,

$$C_6H_4\begin{<}{}^{CH_3}_{O\cdot CO\cdot CH_3} + KOH = C_6H_4\begin{<}{}^{CH_3}_{OH} + C_2H_3O_2K.$$

Towards pentachloride and pentabromide of phosphorus, and towards acetic anhydride and acetyl chloride, phenols behave in the same way as the alcohols,

$$C_6H_5\cdot OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl,^*$$

$$C_6H_5\cdot OH + (CH_3\cdot CO)_2O = C_6H_5\cdot O\cdot CO\cdot CH_3 + C_2H_4O_2.$$

When heated with acids, however, the phenols are not changed to any appreciable extent, because, being less basic in character than the alcohols, they do not so readily form esters.

In constitution the phenols may be regarded as somewhat similar to the *tertiary* alcohols, and, like the latter, many of them undergo complex changes on oxidation.

Monohydric Phenols.

Phenol, $C_6H_5\cdot OH$ (*carbolic acid*, or hydroxybenzene), occurs in very small quantities in human urine and also in that of the ox; it may be obtained from benzene, nitrobenzene, aniline, phenyldiazonium chloride, benzenesulphonic acid, and salicylic acid (p. 491) by the methods already given; but the whole of the phenol of commerce is prepared from coal-tar

* Compare footnote, p. 94.

(compare p. 337), in which it was discovered by Runge in 1834.

Phenol crystallises in colourless, deliquescent prisms, which melt at 42°, and turn pink on exposure to air and light; it boils at 183°, and is volatile in steam. It has a very characteristic smell, is highly poisonous, and has a strong caustic action on the skin, quickly causing blisters. It dissolves freely in most organic liquids, but is only sparingly soluble (1 part in about 15) in cold water; its aqueous solution gives a violet colouration with ferric chloride, and a pale-yellow precipitate of *tribromophenol*, $C_6H_2Br_3 \cdot OH$ (m.p. 92°), with bromine water; both these reactions may serve for the detection of phenol. Owing to its poisonous and antiseptic properties, phenol is extensively used as a disinfectant; it is also employed for the manufacture of picric acid. *Potassium phenate*, $C_6H_5 \cdot OK$, is obtained when phenol is dissolved in potash and the solution is evaporated; it is a crystalline substance, readily soluble in water, and is decomposed by carbon dioxide, with separation of phenol.

Phenyl methyl ether, $C_6H_5 \cdot O \cdot CH_3$ (*anisole*), may be prepared by heating potassium phenate with methyl iodide or with dimethyl sulphate; it boils at 155°, and is similar to the ethers of the fatty series in chemical properties, although it also shows the usual behaviour of aromatic compounds, and readily yields nitro-derivatives, &c. When warmed with concentrated hydriodic acid, it yields phenol and methyl iodide,

$$C_6H_5 \cdot O \cdot CH_3 + HI = C_6H_5 \cdot OH + CH_3I.$$

Phenyl ethyl ether, $C_6H_5 \cdot O \cdot C_2H_5$ (*phenetole*), can be obtained in a similar manner; it boils at 172°.

Phenyl acetate, $CH_3 \cdot CO \cdot OC_6H_5$, prepared by heating phenol with acetic anhydride, boils at 195°, and is readily hydrolysed even by boiling water.

Nitrophenols, $C_6H_4(NO_2) \cdot OH$, are formed very readily when phenol is treated even with dilute nitric acid; the presence of the hydroxyl-group not only facilitates the intro-

duction of the nitro-group, but also determines the position taken up by the latter (p. 392). When phenol (1 part) is gradually added to nitric acid of sp. gr. 1·11 (6 parts), the mixture being kept cold and frequently shaken, it is converted into *ortho*- and *para*-nitrophenol, which separate as a dark-brown oil or resinous mass.

This product is left to settle, washed with water by decantation, and then submitted to distillation in steam, whereon *ortho*-nitrophenol passes over as a yellow oil, which crystallises as it cools. The receiver is changed when the distillate ceases to give crystals (or oil), but distillation is continued until the whole of the ortho-compound has passed over. The boiling solution of the residue is filtered from tarry matter, and the *para*-nitrophenol, which separates when the solution cools, is purified by recrystallisation from boiling water, with addition of animal charcoal.

m-*Nitrophenol* is prepared by reducing **m**-dinitrobenzene to **m**-nitraniline (p. 406), and then treating a solution of the latter in excess of dilute sulphuric acid with nitrous acid; the solution of the diazonium-salt is slowly heated to boiling, and the **m**-nitrophenol, which is thus produced, is purified by recrystallisation from water.

The melting-points of the three compounds are :—

Ortho-nitrophenol,	Meta-nitrophenol,	Para-nitrophenol,
45°.	96°.	114°.

The **o**- and the **m**-compounds are yellow, but the **p**-derivative is colourless; only the **o**-compound is volatile in steam. The three nitrophenols are all sparingly soluble in cold water, but dissolve freely in alkalis and also in alkali carbonates, forming dark-yellow or red salts, which are not decomposed by carbonic acid; they have, therefore, a more marked acid character than phenol itself, the presence of the nitro-group having an effect comparable to that of the nitro-group in nitric acid, $HO \cdot NO_2$.

The *ethoxy*-derivative of **p**-nitrophenol gives on reduction **p**-*aminophenetole*, $C_6H_4 < \begin{matrix} OC_2H_5 \\ NH_2 \end{matrix}$ (*phenetidine*), which is converted

into its acetyl-derivative when it is heated with acetic acid (compare acetanilide, p. 404). This *acetyl*-p-*phenetidine*, $C_6H_4<^{OC_2H_5}_{NHAc}$ (acetyl-p-aminophenetole), melts at 135°, is only very sparingly soluble in water, and is used in medicine, under the name *phenacetin*, in cases of neuralgia, and as an antipyretic.

Picric acid, $C_6H_2(NO_2)_3 \cdot OH$ (trinitrophenol), is formed when materials such as wool, silk, leather, and resins are heated with concentrated nitric acid, very complex reactions taking place; it may be obtained by heating phenol, or the o- and p-nitrophenols, with nitric acid, but the product is not very easily purified from resinous substances which are formed at the same time.

Picric acid is best prepared by dissolving phenol (1 part) in an equal weight of concentrated sulphuric acid, and adding this solution to nitric acid of sp. gr. 1·4 (3 parts) in small quantities at a time; after the first energetic action has subsided, the mixture is carefully heated on a water-bath for about two hours, and then allowed to cool. The product solidifies to a mass of crystals; it is mixed with a little water, separated by filtration, washed, and recrystallised from hot water.

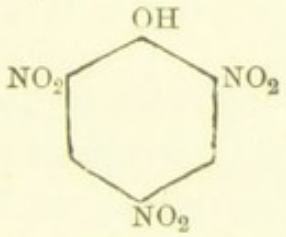
When phenol is dissolved in sulphuric acid, it is converted into a mixture of o- and p-*phenolsulphonic acids*, $C_6H_4(OH)\cdot SO_3H$ (see below); on subsequent treatment with nitric acid, the sulphonic-group, as well as two atoms of hydrogen, are displaced by nitro-groups,

$$C_6H_4<^{OH}_{SO_3H} + 3HO\cdot NO_2 = C_6H_2(NO_2)_3\cdot OH + H_2SO_4 + 2H_2O.$$

Picric acid is a yellow crystalline compound, melting at 122·5°. It is only very sparingly soluble in cold, but is moderately easily soluble in hot, water, and its solutions dye silk and wool (not cotton, p. 637) a beautiful yellow colour; it is, in fact, one of the earlier known artificial organic dyes. It has very marked acid properties, and readily decomposes carbonates. The *potassium* derivative, $C_6H_2(NO_2)_3\cdot OK$, and the *sodium* derivative, $C_6H_2(NO_2)_3\cdot ONa$, are yellow crystalline compounds, the former being sparingly, the latter readily;

soluble in cold water. These compounds, and also the ammonium derivative, *explode* violently on percussion or when heated, and are employed in the preparation of explosives; picric acid itself burns quietly when it is ignited, but can be caused to explode violently with a detonator.

Picric acid may be produced by oxidising 1:3:5-*trinitrobenzene*, $C_6H_3(NO_2)_3$, with potassium ferricyanide, the presence of the nitro-groups facilitating the substitution of hydroxyl for hydrogen; as, moreover, it is quite immaterial which of the three hydrogen atoms is displaced, since they all occupy similar positions relatively to the rest of the molecule, the constitution of picric acid must be represented by the formula,



Picric acid has the curious property of forming crystalline compounds with benzene, naphthalene, anthracene, and many other hydrocarbons, so that it is sometimes used for the detection, and also for the purification, of small quantities of the substances in question; the compound which it forms with benzene, for example, crystallises in yellow needles, is decomposed by water, and has the composition, $C_6H_2(NO_2)_3 \cdot OH, C_6H_6$.

Phenol-o-*sulphonic acid*, $C_6H_4(OH) \cdot SO_3H$, is formed, together with a comparatively small quantity of the p-acid, when a solution of phenol in concentrated sulphuric acid is kept for some time at ordinary temperatures; when, however, the solution is heated at 100–110°, the o-acid, which is the primary product, is gradually converted into *phenol*-p-*sulphonic acid*.

Phenol-m-*sulphonic acid* is prepared by carefully heating benzene-m-disulphonic acid with potash at 170–180°; under these conditions only one of the sulphonic-groups is displaced,

$$C_6H_4\begin{matrix}SO_3K\\SO_3K\end{matrix} + 2KOH = C_6H_4\begin{matrix}OK\\SO_3K\end{matrix} + K_2SO_3 + H_2O.$$

The o-acid is interesting on account of the fact that it is converted into the p-acid when it is boiled with water, and also because it is used as an antiseptic under the name *aseptol*.

The three (o.m.p.) **cresols**, $C_6H_4(CH_3)\cdot OH$ (hydroxytoluenes), the next homologues of phenol, occur in coal-tar, but cannot be conveniently isolated from this source, owing to the difficulty of separating them from one another. They are prepared from the corresponding *toluidines* (aminotoluenes), $C_6H_4(CH_3)\cdot NH_2$, by the general reaction, or by fusing the corresponding *toluenesulphonic acids* with potash,

$$C_6H_4\begin{matrix}CH_3\\SO_3K\end{matrix} + KOH = C_6H_4\begin{matrix}CH_3\\OH\end{matrix} + K_2SO_3.$$

They resemble phenol in most ordinary properties, as, for example, in being sparingly soluble in water, and in forming potassium and sodium derivatives, which are decomposed by carbonic acid; they also yield alkyl-derivatives, &c., by the displacement of the hydrogen of the hydroxyl-group. On distillation with zinc-dust, they are all converted into toluene,

$$C_6H_4\begin{matrix}CH_3\\OH\end{matrix} + Zn = C_6H_5\cdot CH_3 + ZnO,$$

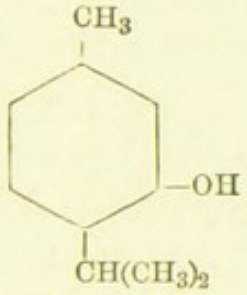
and they all give a bluish colouration with ferric chloride.

One very curious fact regarding the three cresols is that they are not oxidised by chromic acid, although toluene, as already stated, is slowly converted into benzoic acid; the presence of the hydroxyl-group, therefore, protects the methyl-group from the attack of acid oxidising agents, and this is true also in the case of other phenols of similar constitution. If, however, the hydrogen of the hydroxyl-group is displaced by an alkyl, or by an acid group such as acetyl, then the protection is withdrawn, and the methyl-group is converted into the carboxyl-group in the usual manner; the *methylcresols*, $C_6H_4(OCH_3)\cdot CH_3$, for example, are oxidised by chromic acid, and are converted into the corresponding *methoxybenzoic acids*, $C_6H_4(OCH_3)\cdot COOH$.

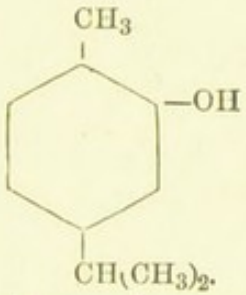
The melting- and boiling-points of the three cresols are given below.

	Ortho-cresol.	Meta-cresol.	Para-cresol.
M.p.	31°	5°	36°
B.p.	188°	201°	198°

Of the higher monohydric phenols, **thymol** and **carvacrol** may be mentioned; these two compounds are isomeric monohydroxy-derivatives of *cymene*, $C_6H_4(CH_3)\cdot C_3H_7$ (p. 378), and their constitutions are respectively represented by the following formulæ:—



Thymol.



Carvacrol.

Thymol occurs in oil of thyme, together with cymene; it crystallises in large plates, melts at 51·5°, and has a characteristic smell, like that of thyme. It is only very sparingly soluble in water, and does not give a colouration with ferric chloride; when heated with phosphoric anhydride, it yields propylene and **m**-cresol,

$$C_6H_3(OH)\begin{cases}CH_3\\C_3H_7\end{cases} = C_6H_4(OH)\cdot CH_3 + C_3H_6.$$

Carvacrol occurs in the oil of *Origanum hirtum*, and may be prepared by heating camphor with iodine,

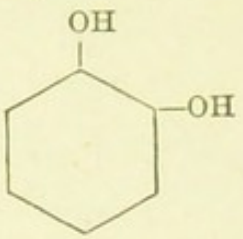
$$C_{10}H_{16}O + I_2 = C_{10}H_{14}O + 2HI;$$

it is an oil boiling at 237°, and its alcoholic solution gives a green colouration with ferric chloride. When heated with phosphoric anhydride, it is decomposed into propylene and **o**-cresol.

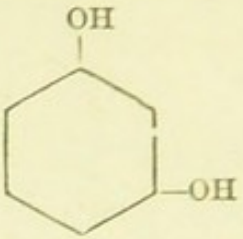
Dihydric Phenols.

The isomeric dihydric phenols—*catechol*, *resorcinol*, and *quinol* (hydroquinone)—are well-known compounds of con-

siderable importance, and are respectively represented by the formulæ,



Catechol
(*Ortho*-dihydroxybenzene).



Resorcinol
(*Meta*-dihydroxybenzene).



Quinol (Hydroquinone)
(*Para*-dihydroxybenzene).

Catechol, $C_6H_4(OH)_2$, occurs in *catechu*, a substance obtained in India from *Acacia catechu* and other trees, and was first obtained by the dry distillation of this vegetable product. It may be obtained by fusing *phenol*-o-*sulphonic acid* with potash, but is most conveniently prepared by heating *guaiacol* or *methylcatechol*, a solid (m.p. 28°) contained in the tar of beechwood, with concentrated hydriodic acid,

$$C_6H_4{<}\begin{matrix}OCH_3\\OH\end{matrix} + HI = C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} + CH_3I.$$

It is a colourless, crystalline substance, melting at 104°, and is readily soluble in water; its aqueous solution gives, with ferric chloride, a *green* colouration, which, on the addition of sodium bicarbonate, changes first to violet and then to red, a reaction which is common to many *ortho*-dihydric phenols (p. 437).

Guaiacol shows a similar behaviour with ferric chloride, but when the hydrogen atoms of both the hydroxyl-groups are displaced, as, for example, in *dimethylcatechol* or *veratrol*, $C_6H_4(OCH_3)_2$, there is no colouration.

Adrenaline $\begin{matrix}(1)HO\\(2)HO\end{matrix}{>}C_6H_3\cdot\overset{(4)}{C}H(OH)\cdot CH_2\cdot NHMe$ (*epinephrine*), may be regarded as a derivative of catechol, and is a substance of great physiological importance. It occurs in the suprarenal glands, and has the remarkable property of causing the contraction of the small arteries, on account of which it is used as a styptic. It melts at 212°, is insoluble in water, and forms crystalline salts with acids. It is usually obtained from the suprarenal glands of the horse, but it may also be produced synthetically.

Resorcinol, $C_6H_4(OH)_2$, is prepared on a large scale by fusing benzene-**m**-disulphonic acid with potash,

$$C_6H_4<\begin{matrix}SO_3K\\SO_3K\end{matrix}+2KOH=C_6H_4<\begin{matrix}OH\\OH\end{matrix}+2K_2SO_3,$$

but it is also obtained when the **p**-disulphonic acid and many other **o**- and **p**-derivatives of benzene are treated in the same way, because the primary product undergoes intramolecular change (p. 437). It melts at 110°, and dissolves freely in water, alcohol, and ether; its aqueous solution gives a dark-violet colouration with ferric chloride, and a crystalline precipitate of *tribromoresorcinol*, $C_6HBr_3(OH)_2$, with bromine water. When resorcinol is strongly heated for a few minutes with phthalic anhydride (p. 477), and the brown or red mass is then dissolved in caustic soda, there results a brownish-red solution, which, when poured into a large volume of water, shows a beautiful green fluorescence; this phenomenon is due to the formation of *fluoresceïn* (p. 654). Other **m**-dihydric phenols give this *fluoresceïn reaction*, which, therefore, affords a convenient and very delicate test for such compounds; the fluoresceïn reaction may also be employed as a test for *inner* anhydrides of *dicarboxylic acids* (p. 478).

Resorcinol is used in large quantities in preparing *fluoresceïn*, *eosin*, and various azo-dyes.

Quinol, $C_6H_4(OH)_2$ (hydroquinone), is formed, together with glucose, when the glucoside, *arbutin*—a substance which occurs in the leaves of the bear-berry—is boiled with water,

$$C_{12}H_{16}O_7+H_2O=C_6H_4(OH)_2+C_6H_{12}O_6.$$

It is usually prepared by reducing quinone (p. 465) with sulphurous acid in aqueous solution,*

$$C_6H_4O_2+H_2SO_3+H_2O=C_6H_4(OH)_2+H_2SO_4.$$

It melts at 169°, is readily soluble in water, and when treated

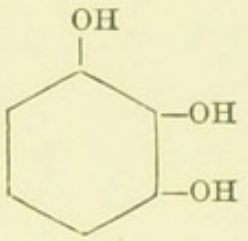
* The name *hydroquinone*, by which this dihydroxybenzene was for long known, recalls its relation to quinone; it was changed to quinol, in conformity with the rule that the name of a hydroxy-compound should end in ol.

with ferric chloride or other mild oxidising agents it is converted into quinone,

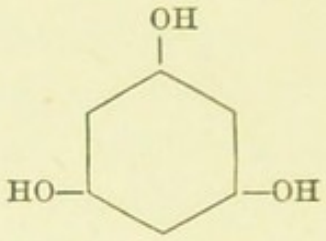
$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

Trihydric Phenols.

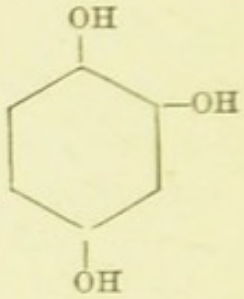
The three trihydric phenols, $C_6H_3(OH)_3$, which exist (in accordance with theory), are respectively represented by the following formulæ :—



Pyrogallol.
1:2:3-Trihydroxybenzene.



Phloroglucinol.
1:3:5-Trihydroxybenzene.



Hydroxyquinol.
1:2:4-Trihydroxybenzene.

Pyrogallol, $C_6H_3(OH)_3$, sometimes called pyrogallic acid, is prepared by heating gallic acid (p. 494) alone or with glycerol, at about 210°, until the evolution of carbon dioxide ceases,

$$C_6H_2(OH)_3 \cdot COOH = C_6H_3(OH)_3 + CO_2.$$

It is a colourless, crystalline substance, melting at 115°, and is readily soluble in water, but more sparingly soluble in alcohol and ether (the effect of hydroxyl-groups); its aqueous solution gives, with ferric chloride, a red, and with ferrous sulphate containing a trace of ferric chloride, a deep, dark-blue, colouration. It dissolves freely in alkalis, giving solutions which rapidly absorb oxygen and turn black on exposure to the air, a fact which is made use of in gas analysis, for the estimation of oxygen. Pyrogallol has powerful reducing properties, and precipitates gold, silver, and mercury from solutions of their salts, being itself oxidised to oxalic and acetic acids; many other phenols, such as *catechol*, *resorcinol*, and *quinol*, show a corresponding behaviour, especially in alkaline solution, but the monohydric-compounds are much less readily oxidised, and consequently

do not exhibit reducing properties. Pyrogallol and quinol are used in photography as developers.

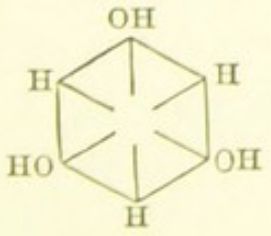
Like glycerol and other trihydric-compounds, pyrogallol forms mono-, di-, and tri-alkyl-derivatives, as, for example, $C_6H_3(OH)_2 \cdot OC_2H_5$, $C_6H_3(OH)(OC_2H_5)_2$, and $C_6H_3(OC_2H_5)_3$; the *dimethyl*-derivative, $C_6H_3(OCH_3)_2 \cdot OH$, occurs in beech-wood tar.

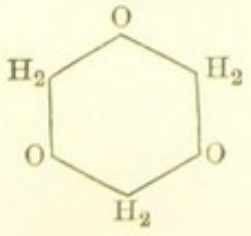
Phloroglucinol, $C_6H_3(OH)_3$ (1:3:5- or symmetrical trihydroxybenzene), is produced when phenol, resorcinol, and many resinous substances, such as gamboge, dragon's-blood, &c., are fused with potash.

It is best prepared by fusing resorcinol (1 part) with caustic soda (6 parts) for about twenty-five minutes, or until the vigorous evolution of hydrogen has ceased. The chocolate-coloured melt is dissolved in water, and the solution is treated with excess of dilute sulphuric acid, and extracted with ether; the ethereal extract is evaporated, and the residue recrystallised from water.

It crystallises with $2H_2O$ in colourless prisms, melts at about 218°, and is very soluble in water; the solution, which has a sweet taste, gives, with ferric chloride, a bluish-violet colouration, and when mixed with potash, it rapidly turns brown in contact with air, owing to absorption of oxygen. When warmed with acetyl chloride, phloroglucinol yields a *triacetate*, $C_6H_3(C_2H_3O_2)_3$, melting at 106°, and in many other reactions its behaviour points to the conclusion that it contains three *hydroxyl*-groups; on the other hand, when treated with hydroxylamine, it gives a *trioxime*, $C_6H_6(N \cdot OH)_3$, and in this and certain other respects it behaves as though it were a *triketone*.

For these reasons phloroglucinol may be represented by one of the following formulæ,





and it may be assumed that the *trihydroxy*-compound is readily convertible into the *triketone* and *vice versâ* by tautomeric change (compare p. 205).

Hydroxyquinol, or 1:2:4-trihydroxybenzene, is formed when quinol is fused with potash. It melts at 140°, is very soluble in water, and its aqueous solution is coloured greenish-brown by ferric chloride, but on the addition of sodium bicarbonate the colour changes to blue and then to red (p. 437).

CHAPTER XXIX.

Alcohols, Aldehydes, Ketones, and Quinones.

Alcohols.

The aromatic alcohols are derived from the hydrocarbons by the substitution of hydroxyl-groups for hydrogen atoms of the *side-chain: benzyl alcohol*, $C_6H_5 \cdot CH_2 \cdot OH$, for example, is derived from *toluene; tolyl carbinol*, $C_6H_4(CH_3) \cdot CH_2 \cdot OH$, from *xylene;* and so on. The compounds of this type are very closely related to the alcohols of the fatty series, although, of course, they show at the same time the general behaviour of aromatic substances.

They may be prepared by methods exactly analogous to those employed in the case of the aliphatic alcohols—namely, by heating the corresponding halogen derivatives with water, weak alkalis, or silver hydroxide,

$$C_6H_5 \cdot CH_2Cl + H_2O = C_6H_5 \cdot CH_2 \cdot OH + HCl,$$

and by reducing the corresponding aldehydes and ketones,

$$C_6H_5 \cdot CHO + 2H = C_6H_5 \cdot CH_2 \cdot OH,$$
$$C_6H_5 \cdot CO \cdot CH_3 + 2H = C_6H_5 \cdot CH(OH) \cdot CH_3.$$

Those compounds which, like benzyl alcohol, contain the carbinol-group, $-CH_2 \cdot OH$, directly united with the benzene nucleus, may also be prepared by treating the corresponding aldehydes with caustic potash (compare p. 456),

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CH_2 \cdot OH + C_6H_5 \cdot COOK.$$

The aromatic alcohols are usually colourless liquids or solids, sparingly soluble in water; their behaviour with alkali metals, phosphorus pentachloride, and acids is similar to that of the fatty compounds, as will be seen from a consideration of the properties of benzyl alcohol, one of the better-known aromatic alcohols.

Benzyl alcohol, $C_6H_5 \cdot CH_2 \cdot OH$ (phenylcarbinol), an isomeride of the three *cresols* (p. 444), occurs in storax (a resin obtained from the tree, *Styrax officinalis*), and also in balsam of Peru and balsam of Tolu, either in the free state or as an ester in combination with cinnamic or benzoic acid.

It may be obtained by reducing benzaldehyde (p. 453) with sodium amalgam and water,

$$C_6H_5 \cdot CHO + 2H = C_6H_5 \cdot CH_2 \cdot OH,$$

and by boiling benzyl chloride with a solution of sodium carbonate,

$$C_6H_5 \cdot CH_2Cl + H_2O = C_6H_5 \cdot CH_2 \cdot OH + HCl;$$

but it is most conveniently prepared by treating benzaldehyde with cold caustic potash,

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CH_2 \cdot OH + C_6H_5 \cdot COOK.$$

The aldehyde (10 parts) is shaken with a solution of potash (9 parts) in water (10 parts) until the whole forms an emulsion, which is allowed to stand for twenty-four hours; water is then added to dissolve the potassium benzoate, the solution is extracted with ether, the dried ethereal extract is evaporated, and the benzyl alcohol is purified by distillation.

Benzyl alcohol is a colourless liquid, boiling at 206°; it is only sparingly soluble in water, but is miscible with alcohol, ether, &c., in all proportions. It is readily acted on by sodium and potassium, with evolution of hydrogen, yielding metallic derivatives, which are decomposed by water, and when treated with phosphorus pentachloride, it is converted into *benzyl chloride*,

$$C_6H_5 \cdot CH_2 \cdot OH + PCl_5 = C_6H_5 \cdot CH_2Cl + POCl_3 + HCl.$$

When heated with concentrated acids, or treated with anhydrides or acid chlorides, it gives esters; with hydrobromic acid, for example, it yields *benzyl bromide*, $C_6H_5 \cdot CH_2Br$ (b.p. 199°), and with acetyl chloride or acetic anhydride it gives *benzyl acetate*, $C_6H_5 \cdot CH_2 \cdot O \cdot CO \cdot CH_3$ (b.p. 206°). On oxidation with dilute nitric acid, it is first converted into benzaldehyde and then into benzoic acid,

$$C_6H_5 \cdot CH_2 \cdot OH + O = C_6H_5 \cdot CHO + H_2O,$$
$$C_6H_5 \cdot CH_2 \cdot OH + 2O = C_6H_5 \cdot COOH + H_2O.$$

All these changes are strictly analogous to those undergone by the fatty alcohols.

A great many alcohols containing both aliphatic (alkyl) and aromatic (aryl) hydrocarbon radicles have been prepared with the aid of the Grignard reagents. *Phenyldimethyl carbinol*, $C_6H_5 \cdot C(CH_3)_2OH$, for example, is easily obtained from acetone and magnesium phenyl bromide (p. 390); *phenylethyl carbinol*, $C_6H_5 \cdot CH(C_2H_5) \cdot OH$, from benzaldehyde and magnesium ethyl bromide, and so on.

Saligenin, $C_6H_4(OH) \cdot CH_2 \cdot OH$ (o-*hydroxybenzyl alcohol*, *salicyl alcohol*), is an example of a substance which is both a phenol and an alcohol. It is produced, together with glucose, by the action of dilute acids or enzymes on *salicin*, a glucoside occurring in the bark of the willow-tree,

$$C_{13}H_{18}O_7 + H_2O = C_6H_4\begin{<}{OH}{CH_2 \cdot OH} + C_6H_{12}O_6.$$

It may be prepared synthetically by reducing salicylaldehyde (p. 459) with sodium amalgam and aqueous alcohol,

$$C_6H_4\begin{<}{OH}{CHO} + 2H = C_6H_4\begin{<}{OH}{CH_2 \cdot OH}.$$

Saligenin melts at 82°, and is readily soluble in water; the solution becomes deep blue on the addition of ferric chloride. Owing to its phenolic nature, it forms alkali salts, which, when heated with alkyl halogen compounds, give the corresponding ethers (the *methyl ether*, $C_6H_4(OCH_3) \cdot CH_2 \cdot OH$, is a colourless oil, boiling at 247°); on the other hand, it shows the properties of an alcohol, and yields salicylaldehyde and salicylic acid on oxidation.

The m- and p-*hydroxybenzyl alcohols* may be prepared by the

reduction of the m- and p-*hydroxybenzaldehydes* (p. 459); they melt at 67° and 110° respectively.

Anisyl alcohol, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$ (p-methoxybenzyl alcohol), is obtained by treating *anisaldehyde*, $C_6H_4(OCH_3)\cdot CHO$ (p. 460), with sodium amalgam and alcohol or with alcoholic potash. It has been prepared synthetically by heating p-hydroxybenzyl alcohol with caustic potash and methyl iodide in alcoholic solution,

$$C_6H_4\begin{matrix}OK\\CH_2\cdot OH\end{matrix} + CH_3I = C_6H_4\begin{matrix}OCH_3\\CH_2\cdot OH\end{matrix} + KI.$$

It is crystalline, melts at 25°, and boils at 258°; on oxidation, it yields *anisaldehyde* and *anisic acid*, $C_6H_4(OCH_3)\cdot COOH$.

Aldehydes.

The relation between the aromatic aldehydes and the aromatic alcohols is the same as that which exists between the corresponding classes of fatty compounds—that is to say, the aldehydes are formed from the primary alcohols by the oxidation of the $-CH_2\cdot OH$ group; *benzaldehyde*, $C_6H_5\cdot CHO$, for example, corresponds with *benzyl alcohol*, $C_6H_5\cdot CH_2\cdot OH$; *salicylaldehyde*, $C_6H_4(OH)\cdot CHO$, with *salicyl alcohol*, $C_6H_4(OH)\cdot CH_2\cdot OH$; *phenylacetaldehyde*, $C_6H_5\cdot CH_2\cdot CHO$, with *phenylethyl alcohol*, $C_6H_5\cdot CH_2\cdot CH_2\cdot OH$; and so on.

Now those compounds which contain an aldehyde-group directly united with carbon of the *nucleus* are of far greater importance than those in which the aldehyde-group is combined with a carbon atom of the *side-chain;* whereas, moreover, the latter resemble the fatty aldehydes very closely in general character, and do not therefore require a detailed description, the former differ from the fatty compounds in several important particulars, as will be seen from the following account of *benzaldehyde* and *salicylaldehyde*, two of the better-known aromatic compounds which contain the aldehyde-group directly united with the benzene *nucleus*.

Benzaldehyde, $C_6H_5\cdot CHO$, sometimes called 'oil of bitter almonds,' was formerly obtained from the glucoside, *amygdalin* (footnote, p. 316), which occurs in bitter almonds, and

which, in contact with water, is gradually decomposed by the enzyme, *emulsin*, into benzaldehyde, hydrogen cyanide, and glucose.

Benzaldehyde may be obtained by oxidising benzyl alcohol with nitric acid, and also by heating a mixture of calcium benzoate and calcium formate,

$$(C_6H_5\cdot COO)_2Ca + (H\cdot COO)_2Ca = 2C_6H_5\cdot CHO + 2CaCO_3,$$

reactions analogous to those employed in the fatty series.

It is prepared both in the laboratory and on the large scale either by heating benzal chloride (p. 390) with moderately dilute sulphuric acid, or calcium hydroxide, under pressure, or by boiling benzyl chloride with an aqueous solution of lead nitrate, or copper nitrate. In the first method, the benzal chloride is probably first converted into the corresponding dihydroxy-derivative of toluene,

$$C_6H_5\cdot CHCl_2 + 2H_2O = C_6H_5\cdot CH(OH)_2 + 2HCl\,;$$

but as this compound contains two hydroxyl-groups which are united with one and the same carbon atom, it is very unstable (footnote, p. 133), and undergoes decomposition into benzaldehyde and water. In the second method, the benzyl chloride is probably transformed into benzyl alcohol, which is then oxidised to the aldehyde by the metallic nitrate, with evolution of oxides of nitrogen and formation of copper or lead chloride, as indicated by the equation,

$$2C_6H_5\cdot CH_2\cdot OH + Cu(NO_3)_2 + 2HCl = 2C_6H_5\cdot CHO + CuCl_2 + N_2O_3 + 3H_2O.$$

Benzyl chloride (5 parts), water (25 parts), and copper nitrate (4 parts) are placed in a flask connected with a reflux condenser, and the mixture is boiled for six to eight hours, a stream of carbon dioxide being passed into the liquid all the time, in order to expel the oxides of nitrogen, which would otherwise oxidise the benzaldehyde to benzoic acid. The process is at an end when the oil contains only traces of chlorine, which is ascertained by washing a small portion with water, and boiling it with silver nitrate and nitric acid. The benzaldehyde is then extracted with ether, the ethereal extract is shaken with a concentrated solution of

sodium bisulphite, and the crystals of the bisulphite compound, $C_6H_5 \cdot CHO$, $NaHSO_3$, are separated by filtration and washed with ether; the benzaldehyde is then regenerated, by decomposing the crystals with dilute sulphuric acid, extracted with ether, and distilled.

Benzaldehyde is also prepared on the large scale directly from benzene. For this purpose a mixture of carbonic oxide and hydrogen chloride is passed into the hydrocarbon in presence of anhydrous cuprous chloride and aluminium chloride (Gattermann). This reaction seems to depend on the formation of the very unstable chloride of formic acid, $H \cdot CO \cdot Cl$, which, in presence of the aluminium chloride, condenses with the benzene,

$$C_6H_6 + H \cdot CO \cdot Cl = C_6H_5 \cdot CHO + HCl.$$

Many other aromatic aldehydes may be prepared in a similar manner.

Benzaldehyde is a colourless, highly refractive liquid of sp. gr. 1·05 at 15°; it boils at 179°, and is volatile in steam. It has a pleasant smell, like that of bitter almonds, and is only sparingly soluble in water, but is miscible with alcohol, ether, &c., in all proportions. It is extensively used for flavouring purposes, and is employed, on the large scale, in the manufacture of various dyes.

Benzaldehyde, and aromatic aldehydes in general, *resemble* the fatty aldehydes in the following respects:—They readily undergo oxidation, sometimes merely on exposure to the air, yielding the corresponding acids,

$$C_6H_5 \cdot CHO + O = C_6H_5 \cdot COOH,$$

and consequently they reduce ammoniacal solutions of silver hydroxide. On reduction they are converted into the corresponding alcohols,

$$C_6H_5 \cdot CHO + 2H = C_6H_5 \cdot CH_2 \cdot OH.$$

When treated with phosphorus pentachloride, they give dihalogen derivatives, such as benzal chloride, $C_6H_5 \cdot CHCl_2$, two atoms of chlorine being substituted for one atom of

oxygen. They react with hydroxylamine, yielding aldoximes, and with phenylhydrazine, giving hydrazones,

$$C_6H_5\cdot CHO + NH_2\cdot OH = H_2O + C_6H_5\cdot CH{:}N\cdot OH,$$

Benzaldoxime (m.p. 35°).*

$$C_6H_5\cdot CHO + NH_2\cdot NH\cdot C_6H_5 = H_2O + C_6H_5\cdot CH{:}N_2H\cdot C_6H_5.$$

Benzylidenehydrazone (m.p. 152°).†

They also react with semicarbazide (p. 141). *Benzaldehyde semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N{:}CH\cdot C_6H_5$ (m.p. 214°), for example, separates at once in crystals when benzaldehyde is shaken with an aqueous solution of semicarbazide hydrochloride and sodium acetate. Like the hydrazones, the semicarbazones are decomposed by acids, yielding the aldehyde or ketone and a salt of semicarbazide.

They combine directly with sodium bisulphite, forming crystalline compounds, and with hydrogen cyanide they yield hydroxycyanides, such as *benzylidenehydroxycyanide*, $C_6H_5\cdot CH(OH)\cdot CN$.

Aromatic aldehydes readily undergo *condensation* with many other fatty and aromatic compounds. When, for example, a mixture of benzaldehyde and acetone is treated with a few drops of caustic soda at ordinary temperatures, *benzylideneacetone*, $C_6H_5\cdot CH{:}CH\cdot CO\cdot CH_3$ (m.p. 42°), is formed, and when benzaldehyde is warmed with aniline, condensation occurs, with formation of *benzylideneaniline*, $C_6H_5\cdot CH{:}N\cdot C_6H_5$ (m.p. 42°).

Benzaldehyde, and other aromatic aldehydes which contain the –CHO group directly united with the benzene nucleus, *differ* from the fatty aldehydes in the following respects:— They do not reduce Fehling's solution, and they do not undergo polymerisation; when shaken with concentrated potash (or soda), they yield a mixture of the corresponding alcohol and acid (compare p. 450),

$$2C_6H_5\cdot CHO + KOH = C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot COOK.$$

They do not readily form additive compounds with ammonia, but yield complex products, such as *hydrobenzamide*, $(C_6H_5\cdot CH)_3N_2$, which is obtained when benzaldehyde is treated with ammonia.

* There are two isomeric benzaldoximes (compare p. 462).

† The name *benzylidene* is given to the group of atoms, $C_6H_5\cdot CH<$, which is analogous to ethylidene, $CH_3\cdot CH<$ (footnote, p. 146); this compound is also called *benzalphenylhydrazone*.

When benzaldehyde (5 parts) is heated with a solution of potassium cyanide (1 part) in aqueous alcohol for about an hour, it is converted into *benzoïn*, which separates in colourless crystals when the solution is cooled. Benzoïn is a ketonic alcohol, formed in accordance with the equation,

$$2C_6H_5\cdot CHO = C_6H_5\cdot CO\cdot CH(OH)\cdot C_6H_5;$$

it melts at 137°, and is oxidised by boiling concentrated nitric acid, giving a diketone, *benzil*, $C_6H_5\cdot CO\cdot CO\cdot C_6H_5$, which is yellow and melts at 95°.

Many other aromatic (and certain aliphatic) aldehydes give products corresponding with benzoïn when they are treated with potassium cyanide; this transformation, which is known as the *benzoïn condensation*, depends on the intermediate formation of a hydroxy-cyanide,

$$C_6H_5\cdot CH(OH)\cdot CN + C_6H_5\cdot CHO = C_6H_5\cdot CH(OH)\cdot CO\cdot C_6H_5 + HCN.*$$

Nitrobenzaldehydes, $C_6H_4(NO_2)\cdot CHO$.—When treated with a mixture of nitric and sulphuric acids, benzaldehyde yields m-nitrobenzaldehyde (m.p. 58°) as principal product, small quantities of o-nitrobenzaldehyde (m.p. 46°) being formed at the same time.

p-Nitrobenzaldehyde (m.p. 107°), and also the o-compound, are most conveniently prepared by the oxidation of the corresponding nitrocinnamic acids (p. 485) with potassium permanganate,

$$C_6H_4\begin{<}{}^{NO_2}_{CH:CH\cdot COOH}\end{} + 4O = C_6H_4\begin{<}{}^{NO_2}_{CHO}\end{} + 2CO_2 + H_2O.$$

During the operation the mixture is shaken with benzene in order to extract the aldehyde as fast as it is formed, and thus prevent its further oxidation. The benzene solution is then evaporated, and the aldehyde is purified by recrystallisation.

The nitrobenzaldehydes are colourless, crystalline substances; when reduced with ferrous sulphate and ammonia, they are converted into the corresponding *aminobenzaldehydes*, $C_6H_4(NH_2)\cdot CHO$.

o-*Nitrobenzaldehyde* is a particularly interesting substance, as, when its solution in acetone is mixed with a few drops of dilute caustic soda, a precipitate of *indigo-blue* gradually forms (Baeyer). This synthesis of this important vegetable dye may be represented by the equation,

$$2C_6H_4\begin{<}{}^{NO_2}_{CHO}\end{} + 2CH_3\cdot CO\cdot CH_3 = C_6H_4\begin{<}{}^{NH}_{CO}\end{>}C{:}C\begin{<}{}^{NH}_{CO}\end{>}C_6H_4$$

Indigo-blue.

$$+ 2CH_3\cdot COOH + 2H_2O.$$

* The hydrogen cyanide required for the production of the hydroxy-cyanide is formed by the hydrolysis of the potassium cyanide.

Phenolic- or Hydroxy-Aldehydes.

The hydroxy-derivatives of the aldehydes, such as the *hydroxybenzaldehydes*, $C_6H_4(OH)\cdot CHO$, which contain the hydroxyl-group united with the *nucleus*, combine the properties of phenols and aldehydes.

They may be obtained by the oxidation of the corresponding hydroxy-alcohols; *saligenin* (p. 452), or *o-hydroxybenzyl alcohol*, for example, yields *salicylaldehyde* or *o-hydroxybenzaldehyde*,

$$C_6H_4<\begin{matrix}OH\\CH_2\cdot OH\end{matrix} + O = C_6H_4<\begin{matrix}OH\\CHO\end{matrix} + H_2O.$$

Such alcohols, however, are not easily obtained, and indeed in many cases have only been produced by the reduction of the hydroxy-aldehydes.

Many phenolic-aldehydes may be prepared by heating phenols with chloroform in alkaline solution (Reimer's reaction),

$$C_6H_5\cdot OH + CHCl_3 + 4KOH = C_6H_4<\begin{matrix}OK\\CHO\end{matrix} + 3KCl + 3H_2O.$$

The changes which occur in Reimer's reaction are not understood; possibly the phenol reacts with the chloroform, in the presence of the alkali, yielding an intermediate product containing halogen,

$$C_6H_5\cdot OH + CHCl_3 = C_6H_4<\begin{matrix}OH\\CHCl_2\end{matrix} + HCl,$$

which by the further action of the alkali is converted into a hydroxybenzaldehyde, just as *benzalchloride*, $C_6H_5\cdot CHCl_2$, is transformed into *benzaldehyde* (compare p. 454),

$$C_6H_4<\begin{matrix}OH\\CHCl_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}OH\\CH(OH)_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}OH\\CHO\end{matrix}.$$

As a rule, the principal product is the o-hydroxyaldehyde, small quantities of the corresponding p-compound being produced at the same time.

Many phenolic-aldehydes may also be prepared by treating phenols with hydrogen cyanide and hydrogen chloride in presence of anhydrous aluminium chloride and in absence of water (Gattermann; compare p. 455). In this reaction, the two acids unite and

form a compound of the constitution, CHCl:NH, which then gives with the phenol an *aldimine*,

$$C_6H_5\cdot OH + CHCl:NH = HO\cdot C_6H_4\cdot CH:NH + HCl;$$

this product is readily hydrolysed by acids or alkalis, with formation of the p-hydroxy-aldehyde and ammonia.

Salicylaldehyde, $C_6H_4(OH)\cdot CHO$ (o-hydroxybenzaldehyde), may be obtained by oxidising saligenin with chromic acid (p. 458), but it is usually prepared from phenol by Reimer's reaction.

Phenol (20 grams) is dissolved in caustic soda (60 grams) and water (120 grams), the solution is heated to 60° in a flask provided with a reflux condenser, and chloroform (30 grams) is added in small quantities at a time from a dropping funnel; the liquid is then heated until it boils. The unchanged chloroform is distilled off, and the alkaline solution is mixed with excess of dilute sulphuric acid and distilled in steam, when phenol and salicylaldehyde pass over. (The residue in the flask contains p-*hydroxybenzaldehyde*, which may be extracted from the filtered liquid with ether, and purified by recrystallisation.) The oily mixture is extracted from the distillate with ether, and the extract is shaken with a strong solution of sodium bisulphite, which dissolves the aldehyde in the form of its bisulphite compound. The aqueous solution is then separated, and treated with sodium carbonate in excess; the regenerated *salicylaldehyde* is extracted with ether and purified by distillation.

Salicylaldehyde is a colourless oil, which boils at 196°, and has a penetrating, aromatic odour; it is moderately soluble in water, and its solution gives a deep-violet colouration with ferric chloride. When reduced with sodium amalgam it yields *saligenin*, $C_6H_4(OH)\cdot CH_2\cdot OH$ (p. 452), whereas oxidising agents convert it into *salicylic acid*, $C_6H_4(OH)\cdot COOH$.

p-*Hydroxybenzaldehyde* (m.p. 116°) dissolves readily in hot water, and gives, with ferric chloride, a violet colouration.

m-*Hydroxybenzaldehyde* is obtained by converting m-nitrobenzaldehyde into m-aminobenzaldehyde, and then displacing the amino-group by hydroxyl, with the aid of nitrous acid. It crystallises from water in needles, and melts at 104°.

Anisaldehyde, $C_6H_4(OCH_3)\cdot CHO$ (**p**-methoxybenzaldehyde), is prepared from oil of aniseed. This essential oil contains *anethole*, $C_6H_4(OCH_3)\cdot CH{:}CH\cdot CH_3$, a crystalline substance (m.p. 21°), which on oxidation with potassium dichromate and sulphuric acid is converted into *anisaldehyde*. It may be prepared synthetically by warming **p**-*hydroxybenzaldehyde* with alcoholic potash and methyl iodide (or sulphate, p. 193),

$$C_6H_4{<}\begin{matrix}OK\\CHO\end{matrix} + CH_3I = C_6H_4{<}\begin{matrix}OCH_3\\CHO\end{matrix} + KI.$$

Anisaldehyde boils at 248°, and has a penetrating, aromatic odour; on reduction with sodium amalgam it yields *anisyl alcohol*, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$ (p. 453); on oxidation it gives *anisic acid*, $C_6H_4(OCH_3)\cdot COOH$ (p. 493).

Vanillin, $C_6H_3(OH)(OCH_3)\cdot CHO$ [$CHO{:}OCH_3{:}OH = 1{:}3{:}4$], the essential and sweet-smelling component of the vanilla-bean, was first obtained by oxidising *coniferyl alcohol* with chromic acid; it may be prepared synthetically from guaiacol (p. 446), with the aid of Reimer's reaction (p. 458), or by Gattermann's method (p. 458). It melts at 80°.

Coniferyl alcohol, $C_6H_3(OH)(OCH_3)\cdot CH{:}CH\cdot CH_2\cdot OH$, is formed, together with glucose, when the glucoside, *coniferin* (which occurs in the coniferæ), is hydrolysed with acids or with emulsin (p. 316).

Ketones.

The ketones of the aromatic, like those of the fatty, series have the general formula $R-CO-R'$, where R and R′ represent different or identical radicles, one of which, of course, must be aromatic.

Acetophenone, $C_6H_5\cdot CO\cdot CH_3$ (phenylmethyl ketone, acetylbenzene), may be described as a typical aromatic ketone. It is formed, and distils over, when a mixture of calcium benzoate and calcium acetate is heated, a reaction which is exactly analogous to that by which mixed ketones of the fatty series are obtained,

$$(C_6H_5\cdot COO)_2Ca + (CH_3\cdot COO)_2Ca = 2C_6H_5\cdot CO\cdot CH_3 + 2CaCO_3.$$

It is most conveniently prepared by dropping acetyl chloride

(1 mol.) into well-cooled benzene (1 mol.), in presence of anhydrous aluminium chloride ($AlCl_3$, 1 mol.),

$$C_6H_6 + CH_3 \cdot COCl = C_6H_5 \cdot CO \cdot CH_3 + HCl.$$

This method is a general one, as, by the use of other acid chlorides and other hydrocarbons, many other ketones may be prepared; it is an extension of Friedel and Crafts' method of preparing hydrocarbons (p. 369).

The benzene and aluminium chloride are placed in a flask (reflux condenser) and cooled in ice. The acetyl chloride is added from a dropping funnel. When the evolution of hydrogen chloride ceases, the flask is taken out of the ice, and after about an hour's time the product is *very cautiously* treated with ice-cold water, until no further development of heat occurs. The acetophenone is then extracted with ether and isolated from the dried ethereal solution in the ordinary way; it is finally purified by distillation. The portion collected from about 194–200° should solidify at ordinary temperatures.

In this, as in all other syntheses by Friedel and Crafts' reaction, the apparatus and materials must be dry, and it is essential that the aluminium chloride should be of good quality; samples which have absorbed atmospheric moisture, and which look white and powdery, are practically useless.

Acetophenone melts at 20·5°, and boils at 202°; it is used as a hypnotic in medicine, under the name of *hypnone*. Its chemical behaviour is so similar to that of the fatty ketones that most of its reactions, or at any rate those which are determined by the carbonyl-group, might be foretold from a consideration of those of acetone. On reduction with sodium amalgam and aqueous alcohol, acetophenone is converted into *phenylmethyl carbinol*, $C_6H_5 \cdot CH(OH) \cdot CH_3$, just as acetone is transformed into isopropyl alcohol; like acetone, and other fatty ketones, it reacts with hydroxylamine and with phenylhydrazine, giving the *oxime*, $C_6H_5 \cdot C(NOH) \cdot CH_3$ (m.p. 59°), and the *hydrazone*, $C_6H_5 \cdot C(N_2HC_6H_5) \cdot CH_3$ (m.p. 105°), respectively. On oxidation it is resolved into benzoic acid and carbon dioxide, just as acetone is oxidised to acetic acid and carbon dioxide,

$$C_6H_5 \cdot CO \cdot CH_3 + 4O = C_6H_5 \cdot COOH + CO_2 + H_2O.$$

Acetophenone shows also the general behaviour of aromatic compounds, inasmuch as it may be converted into nitro-, amino-, and halogen-derivatives by the displacement of hydrogen of the nucleus.

The homologues of acetophenone, such as *propiophenone*, $C_6H_5 \cdot CO \cdot C_2H_5$, *butyrophenone*, $C_6H_5 \cdot CO \cdot C_3H_7$, &c., are of little importance, but *benzophenone*, an aromatic ketone of a different series, may be briefly described.

Benzophenone, $C_6H_5 \cdot CO \cdot C_6H_5$ (diphenyl ketone, benzoylbenzene), may be obtained by heating calcium benzoate, and by treating benzene with benzoyl chloride, or with carbonyl chloride, in presence of aluminium chloride,

$$C_6H_6 + C_6H_5 \cdot COCl = C_6H_5 \cdot CO \cdot C_6H_5 + HCl,$$
$$2C_6H_6 + COCl_2 = C_6H_5 \cdot CO \cdot C_6H_5 + 2HCl.$$

It melts at 48–49°, and is very similar to acetophenone in most respects; when distilled over zinc-dust it is converted into *diphenylmethane*, $C_6H_5 \cdot CH_2 \cdot C_6H_5$ (p. 379).

Isomerism of Oximes.

The oxime (*α-benzaldoxime*), produced by the interaction of benzaldehyde and hydroxylamine (p. 456), melts at 35°; when it is treated with hydrogen chloride, at ordinary temperatures, it gives an unstable hydrochloride, from which an isomeric *β-benzaldoxime*, melting at about 128°, is obtained.

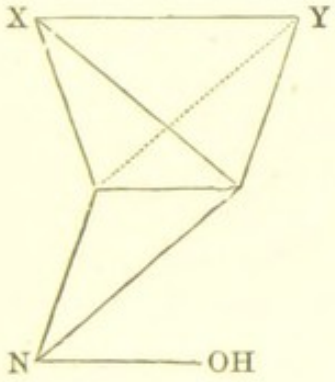
Many other aldehydes, both aliphatic and aromatic, give isomeric oximes, as do also many ketones, R·CO·R′, in which the radicles R and R′ are not identical.

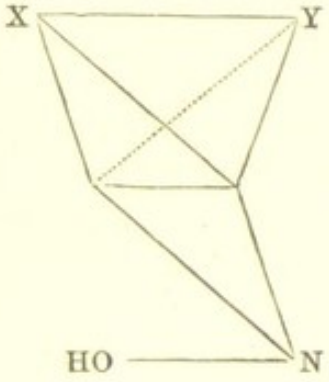
In some cases *both* the isomerides are produced by the interaction of the aldehyde, or ketone, and hydroxylamine; as a rule, the isomerides may be converted one into the other, more or less readily, with the aid of various solvents or reagents. The isomerides usually resemble one another very closely in many of their chemical properties, and, under particular conditions, yield corresponding *isomeric* derivatives; the two benzaldoximes, for example, may be converted into isomeric alkyl-, or aryl-benzaldoximes, with the aid of sodium ethoxide and an alkyl or aryl halogen compound, or by other methods.

The explanation of the existence of isomeric oximes has been

much discussed, and many investigations have been made on the subject. One possibility is that the isomeric compounds differ in *structure*, and that the one contains the group, >C:N·OH, the other, the group, $>C<^{NH}_{O}$; but so far there is no conclusive experimental evidence in favour of this assumption. Another explanation, suggested by Hantzsch and Werner, is, that the compounds in question are *stereoisomeric*, or different in *configuration*, and that their stereoisomerism is due to different relative arrangements in space of the hydroxy-groups, which are directly united to the nitrogen atoms in the molecules of the two compounds.

This view may be further explained with the help of the following figures :—





The upper regular tetrahedron, in each figure, represents the configuration of the carbon atom, which is united to the nitrogen atom (N) of the oximino- or >N·OH-group by two of its units of valency. When the atoms or groups, X and Y, with which this carbon atom is also combined, are not identical, the hydroxyl-radicle may occupy one of two different relative positions, as shown. The configurations of these two possible stereoisomeric forms may be represented by the following formulæ :—

$$\begin{array}{c} X-C-Y \\ \| \\ N-OH \end{array} \qquad \begin{array}{c} X-C-Y \\ \| \\ HO-N. \end{array}$$

According to this view, every aldoxime, R·CH:N·OH, and every ketoxime, $\begin{matrix} R' \\ R \end{matrix}>C:N\cdot OH$, in which R and R′ are different radicles, may exist in such stereoisomeric forms, which correspond, to some extent, with the cis- and trans-modifications of certain unsaturated compounds (p. 279).

Such stereoisomeric oximes are distinguished by the prefix, *syn-*

or *anti-*. In the case of the aldoximes, one of the isomerides is generally more readily converted into a cyanide (or nitrile) and water than is the other; this particular form is then called the *syn-*oxime, and is represented by the configuration, $\begin{matrix} R-C-H \\ \| \\ N\cdot OH \end{matrix}$, which indicates a closer spacial relationship between the hydrogen atom and the hydroxyl-group than does the alternative anti-configuration, and also postulates that this relationship facilitates the decomposition of the oxime into the cyanide and water.

In the case of ketoximes, it is assumed that the configuration of the compound may be determined from the structure of the *substituted amide* into which the oxime may be converted (p. 140). This change, generally known as the *Beckmann transformation*, may be brought about by treating the ketoxime with phosphorus pentachloride, concentrated sulphuric acid, acetyl chloride, &c.; but when the two isomerides are thus transformed they do not give identical products. Of the two oximes of p-*hydroxybenzophenone*, for example, one (m.p. 152°) is converted principally into the *anilide* of p-*hydroxybenzoic acid*, $HO\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_5$, whereas the other (m.p. 81°) gives *benzoyl*-p-*aminophenol* (the p-hydroxyanilide of benzoic acid), $HO\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_5$, as the main product. To the former (*anti*-p-*hydroxybenzophenone oxime*) the configuration, $\begin{matrix} HO\cdot C_6H_4\cdot C\cdot C_6H_5 \\ \| \\ N\cdot OH \end{matrix}$, and to the latter (*syn*-p-*hydroxybenzophenone oxime*) the configuration, $\begin{matrix} HO\cdot C_6H_4\cdot C\cdot C_6H_5 \\ \| \\ HO\cdot N \end{matrix}$, is assigned, the assumption being that in the one compound the phenyl-group, in the other the hydroxyphenyl-group, is the nearer to the hydroxyl-radicle of the oximino-group.

In distinguishing such isomerides, the name of the radicle to which the relative position of the hydroxyl-group is referred is put first; thus the compound represented by the configurational formula, $\begin{matrix} C_6H_5-C\cdot C_6H_4Me \\ \| \\ N-OH \end{matrix}$, is called *syn-tolylphenylketoxime* or *anti-phenyltolylketoxime*, while the isomeride is named either *syn-phenyltolylketoxime* or *anti-tolylphenylketoxime*.

Quinones.

When quinol (p. 447) is oxidised with excess of ferric chloride in aqueous solution, a yellowish colouration is pro-

duced; the solution acquires a very penetrating odour, and, if sufficiently concentrated, yellow crystals are deposited.

The substance formed in this way is named *quinone* (benzoquinone), and is the simplest member of a very interesting class of compounds; its formation may be expressed by the equation,

$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

Quinone, $C_6H_4O_2$, is usually prepared by oxidising aniline with potassium dichromate and sulphuric acid.

Aniline (1 part) is dissolved in water (25 parts) and sulphuric acid (8 parts), and finely powdered potassium dichromate (3·5 parts) is gradually added, the whole being well cooled and constantly stirred during the operation; the product, which is very dark-coloured owing to the presence of aniline black, may be extracted with ether, but is more conveniently isolated by submitting the liquid, in *small* portions at a time, to steam distillation, *as rapidly as possible*. The quinone is then separated by filtration, the filtrate being extracted with ether if necessary.

Quinone crystallises in golden-yellow prisms, melts at 116°, sublimes very readily, and is volatile in steam; it has a peculiar, irritating, and very characteristic smell, and is only sparingly soluble in water, but dissolves freely in alcohol and ether. It is readily reduced by sulphurous acid, zinc and hydrochloric acid, &c., being converted into quinol,

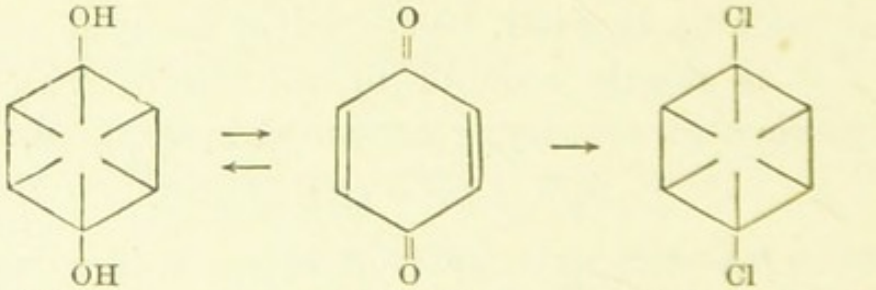
$$C_6H_4O_2 + 2H = C_6H_4(OH)_2.$$

In some respects quinone behaves as if it contained two carbonyl-groups, each having properties similar to those of the carbonyl-groups in compounds such as acetone, acetophenone, &c.; when treated with hydroxylamine hydrochloride, for example, quinone yields a *monoxime*, $C_6H_4\begin{matrix}O\\ \diagdown\!\!\diagup\\ N\cdot OH\end{matrix}$ (identical with p-*nitrosophenol*, p. 409), and also a *dioxime*, $C_6H_4\begin{matrix}N\cdot OH\\ \diagdown\!\!\diagup\\ N\cdot OH\end{matrix}$. The two carbonyl-groups, moreover, are in the *para*-position to one another, as is shown by the facts that, when quinone is reduced, it gives *quinol* (p-dihydroxybenzene), and when

quinone-dioxime is reduced with tin and hydrochloric acid, it yields **p**-*phenylenediamine* (p. 407).

In other respects, however, quinone undergoes changes which are quite different from those observed in the case of ordinary ketones; on reduction, for instance, each >CO group is transformed into >C·OH, and not into >CH·OH, as might have been expected from analogy; again, on treatment with phosphorus pentachloride, each oxygen atom is displaced by *one* atom of chlorine, **p**-*dichlorobenzene*, $C_6H_4Cl_2$, being formed, and not a tetrachloro-derivative, $C_6H_4Cl_4$, as might have been expected.

This curious behaviour, and the close relation between quinol and quinone, is explained by assuming that in the conversion of the former into the latter by oxidation, intramolecular change also takes place, and in such a way as to bring about a rearrangement of the carbon bindings. When quinone is reduced, or treated with phosphorus pentachloride, this change is reversed, and the condition represented by the centric formula is again established; the following formulæ indicate the nature of these changes:—



Quinol. Quinone. Dichlorobenzene.

According to this view, the structure of quinone is fundamentally different from that of any aromatic compound which, so far, has been described; the closed-chain of six carbon atoms in its molecule is not a centric or benzene nucleus, but contains two pairs of unsaturated carbon atoms which are united together in the same way as those in the molecules of ethylene and other olefines. Quinone, therefore, is regarded as a closed-chain olefine or *cyclo-olefine;* like the open-chain or aliphatic olefines, it combines *directly* with bromine,

giving a di- and a tetra-bromide, $C_6H_4Br_2O_2$ and $C_6H_4Br_4O_2$, and it readily undergoes oxidation.

Benzoquinone and many other *para*-quinones (that is to say, quinones in which the two carbonyl-groups are in the para-position to one another) may be produced by the oxidation, with chromic acid or ferric chloride, of many hydroxy- and amino-compounds, which contain the substituent groups in the *para*-position; quinone, for example, is formed by oxidising aniline, p-aminophenol, $C_6H_4(OH)\cdot NH_2$, and p-phenylene-diamine, $C_6H_4(NH_2)_2$, whereas o-toluidine and p-tolylene-diamine, $C_6H_4(NH_2)_2\cdot CH_3$, $[NH_2:NH_2:CH_3 = 1:4:2]$, yield *toluquinone* $[O:O:CH_3 = 1:4:2]$. All *para*-quinones resemble (benzo)quinone in smell, in having a yellow colour, and in being readily volatile.

o-*Benzoquinone*, $CH\langle\begin{matrix}CH{:}CH\\CH{\cdot}CO\end{matrix}\rangle CO$, is a dark-red, crystalline substance, which is obtained when catechol is oxidised with silver oxide in dry ethereal solution (in presence of anhydrous sodium sulphate). It has no smell, is not volatile in steam, and decomposes when it is heated at 60–70°; it is reduced to catechol by sulphurous acid in aqueous solution.*

When bleaching-powder is used in oxidising amino-compounds, such as the above, *quinone chlorimides* and *quinone dichloro-diimides* are formed in the place of quinones,

$$NH_2\cdot C_6H_4\cdot OH + 4Cl = NCl:C_6H_4:O + 3HCl,$$

Quinone Chlorimide.

$$NH_2\cdot C_6H_4\cdot NH_2 + 6Cl = NCl:C_6H_4:NCl + 4HCl.$$

Quinone Dichlorodiimide.

The quinone chlorimides and dichlorodiimides resemble quinone in many respects; they are crystalline, readily volatile in steam, and are respectively converted into p-aminophenol and p-phenylene diamine, or their derivatives, on reduction.

Chloranil, $O:C_6Cl_4:O$ (tetrachloroquinone), is produced when chlorine acts on quinone, but it is usually prepared by treating phenol with hydrochloric acid and potassium chlorate, oxidation and chlorination taking place,

$$C_6H_5\cdot OH + 10Cl + O = O:C_6Cl_4:O + 6HCl.$$

* Other 'quinones,' of a somewhat different class from the benzoquinones, are described later (p. 524).

It crystallises in yellow plates, sublimes without melting, and is sparingly soluble in alcohol, and insoluble in water.

It is readily reduced to *tetrachloroquinol*, $HO \cdot C_6Cl_4 \cdot OH$, and is, therefore, a powerful oxidising agent, for which reason it is much employed in the preparation of dyes, when the use of inorganic oxidising agents is undesirable.

CHAPTER XXX.

Carboxylic Acids.

The carboxylic acids of the aromatic series are derived from the aromatic hydrocarbons, just as those of the fatty series are derived from the paraffins—namely, by the substitution of one or more carboxyl-groups for a corresponding number of hydrogen atoms. In this, as in other cases, however, one of two classes of compounds may be obtained, according as substitution takes place in the *nucleus* or in the *side-chain;* benzene, of course, yields only acids of the first class, such as *benzoic acid*, $C_6H_5 \cdot COOH$, the three (o.m.p.) *phthalic acids*, $C_6H_4(COOH)_2$, the three tricarboxylic acids, $C_6H_3(COOH)_3$, &c., but toluene (and all the higher homologues) may give rise to derivatives of both kinds—as, for example, the three *toluic acids*, $C_6H_4(CH_3) \cdot COOH$, and *phenylacetic acid*, $C_6H_5 \cdot CH_2 \cdot COOH$.

Although there are no very important differences in the properties of these two classes of acids, it is more convenient to describe them separately, taking first those compounds in which the carboxyl-groups are directly united with carbon of the *nucleus*.

Preparation.—Such acids may be obtained by oxidising the alcohols or aldehydes,

$$C_6H_5 \cdot CH_2 \cdot OH + 2O = C_6H_5 \cdot COOH + H_2O,$$
$$C_6H_5 \cdot CHO + O = C_6H_5 \cdot COOH,$$

and by hydrolysing the nitriles (p. 474) with alkalis or mineral acids,

$$C_6H_5\cdot CN + 2H_2O = C_6H_5\cdot COOH + NH_3,$$
$$C_6H_5\cdot CH_2\cdot CN + 2H_2O = C_6H_5\cdot CH_2\cdot COOH + NH_3,$$

reactions which are exactly similar to those employed in the case of the fatty acids (p. 173).

Aromatic acids may also be obtained by treating aryl Grignard reagents (p. 390) with dry carbon dioxide, and then decomposing the products with a mineral acid (p. 228).

Perhaps, however, the most important method, and one which has no counterpart in the fatty series, consists in oxidising the homologues of benzene with dilute nitric acid or chromic acid,

$$C_6H_5\cdot CH_3 + 3O = C_6H_5\cdot COOH + H_2O,$$
$$C_6H_5\cdot CH_2\cdot CH_3 + 6O = C_6H_5\cdot COOH + CO_2 + 2H_2O.$$

As a rule, only those acids which contain the *carboxyl-group united with the nucleus* can be obtained in this way, because a saturated side-chain is oxidised to –COOH, no matter how many $-CH_2-$ groups it may contain; in other words, all homologues of benzene which contain only one side-chain yield *benzoic acid*, whereas those containing two give one of the *phthalic acids*.* In the latter case, however, one of the side-chains may be oxidised before the other is attacked, in which case an alkyl-derivative of benzoic acid may be obtained,

$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3)\cdot COOH + H_2O,$$
$$C_6H_4(CH_3)\cdot COOH + 3O = C_6H_4(COOH)_2 + H_2O.$$

Oxidation is frequently carried out by boiling the hydrocarbon with nitric acid (1 vol.), diluted with water (2–4 vols.), until brown fumes are no longer formed. The mixture is then made slightly alkaline with soda, and any unchanged hydrocarbon and traces of nitro-hydrocarbon are separated by distillation with steam,

* The reason of this is that when the side-chain contains more than one carbon atom, the $-CH_2-$ group, which is united to the nucleus, is attacked before the terminal $-CH_3$ group, and the intermediate product, a ketone, then undergoes further oxidation in the usual way.

or by extraction with ether; the solution is then strongly acidified, and the precipitated acid is purified by recrystallisation.

Most hydrocarbons are only very slowly attacked by oxidising agents, and therefore it is often advantageous to first substitute chlorine or some other group for hydrogen of the side-chain, as in this way oxidation is facilitated. *Benzyl chloride*, $C_6H_5 \cdot CH_2Cl$, and *benzyl acetate*, $C_6H_5 \cdot CH_2 \cdot O \cdot CO \cdot CH_3$ (p. 452), for example, are much more readily oxidised than toluene, because they first undergo hydrolysis, giving alcohols.

Properties.—The aromatic acids are crystalline, and generally distil without decomposing; they are sparingly soluble in cold water, but dissolve much more readily in hot water, alcohol, and ether. As regards all those properties which are determined by the carboxyl-group, the aromatic acids are closely analogous to the fatty compounds, and give corresponding derivatives, as the following examples show:—

Benzoic acid,	$C_6H_5 \cdot COOH$.	Benzoyl chloride,	$C_6H_5 \cdot COCl$.
Sodium benzoate,	$C_6H_5 \cdot COONa$.	Benzamide,	$C_6H_5 \cdot CO \cdot NH_2$.
Ethyl benzoate,	$C_6H_5 \cdot COOC_2H_5$.	Benzoic anhydride,	$(C_6H_5 \cdot CO)_2O$.

When distilled with soda-lime, they are decomposed with loss of carbon dioxide and formation of the corresponding hydrocarbons, just as acetic acid under similar circumstances yields methane,

$$C_6H_5 \cdot COOH = C_6H_6 + CO_2,$$
$$C_6H_4(CH_3) \cdot COOH = C_6H_5 \cdot CH_3 + CO_2.$$

Benzoic acid, $C_6H_5 \cdot COOH$, occurs in the free state in many resins, especially in gum benzoïn and Peru balsam; it is also found in the urine of the ox and the horse, as *hippuric acid* or *benzoylglycine*, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COOH$, to the extent of about 2 per cent.

It may be obtained by subliming gum benzoïn in iron vessels, the crude sublimate being purified by recrystallisation from water; or by boiling hippuric acid with hydrochloric acid (p. 329),

$$C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COOH + HCl + H_2O = C_6H_5 \cdot COOH + NH_2 \cdot CH_2 \cdot COOH, HCl.$$

Benzoic acid is manufactured by oxidising benzyl chloride (p. 389) with 60 per cent. nitric acid,

$$C_6H_5\cdot CH_2Cl + 2O = C_6H_5\cdot COOH + HCl,$$

or by heating calcium phthalate with lime at about 350°,

$$2C_6H_4(COO)_2Ca + Ca(OH)_2 = (C_6H_5\cdot COO)_2Ca + 2CaCO_3.$$

It may also be prepared by oxidising toluene, benzyl alcohol, or benzaldehyde, and by hydrolysing *benzonitrile* (p. 473) with caustic soda,

$$C_6H_5CN + 2H_2O = C_6H_5\cdot COOH + NH_3.$$

Benzoic acid separates from water in glistening crystals, melts at 121·5°, and boils at 249°, but it sublimes very readily even at 100°, and is volatile in steam; it dissolves in 400 parts of water at 15°, but is readily soluble in hot water, alcohol, and ether. Its vapour has a characteristic odour, and an irritating action on the throat, causing violent coughing. Most of the metallic salts of benzoic acid are soluble in water, and crystallise well; *calcium benzoate*, $(C_6H_5\cdot COO)_2Ca,3H_2O$, for example, prepared by neutralising benzoic acid with milk of lime, crystallises in needles, and is very soluble in water.

Ethyl benzoate, $C_6H_5\cdot COOC_2H_5$, is prepared by saturating a solution of benzoic acid (1 part) in alcohol (3 parts) with hydrogen chloride, and then boiling the solution (with reflux condenser) for about two hours (p. 196).

The alcohol is then distilled, and the oily residue is shaken with a dilute solution of sodium carbonate until free from acids;* the ester is next washed with water, dried with calcium chloride, and distilled. A little ether may be used to dissolve the ester, if it does not separate well from the aqueous solution.

It boils at 213°, has a pleasant aromatic odour, and is readily hydrolysed by boiling alcoholic potash.

* When this process is carried out in a separating-funnel, the funnel is held in an inverted position and *gently* agitated; the tap is then opened for a moment to allow the carbon dioxide to escape, otherwise the pressure of this gas may blow out the stopper or burst the separating-funnel. These operations are repeated until no further evolution of gas occurs.

Methyl benzoate boils at 199°.

Phenyl benzoate, $C_6H_5 \cdot CO \cdot OC_6H_5$, prepared from phenol by the Schotten-Baumann method (p. 473), melts at 71°, and is readily hydrolysed by aqueous alkalis.

Benzoyl chloride, $C_6H_5 \cdot COCl$, is easily obtained by treating benzoic acid with phosphorus pentachloride.

The dry acid is placed in a distillation flask, and about 5 per cent. more than one molecular proportion of the pentachloride is added; the fumes which are evolved are passed into water or dilute soda (care being taken that the water is not sucked into the flask). When the reaction is finished, the mixture of phosphorus oxychloride (b.p. 107°) and benzoyl chloride is submitted to fractional distillation. The whole operation is conducted in a fume cupboard.

It is a colourless oil, possessing a most irritating odour, and boils at 198°; it is gradually decomposed by water, yielding benzoic acid and hydrochloric acid. Benzoyl chloride is a very important laboratory reagent (see below).

Benzoic anhydride, $(C_6H_5 \cdot CO)_2O$, is produced when benzoyl chloride is treated with sodium benzoate, just as acetic anhydride is formed by the interaction of acetyl chloride and sodium acetate (p. 167); it is a crystalline substance, melting at 42°, and closely resembles acetic anhydride in ordinary chemical properties.

Benzoyl chloride and benzoic anhydride, more especially the former, are frequently used for the detection of hydroxy- and amino-compounds, as they react with all such substances (except acids), yielding *benzoyl-derivatives*, the univalent *benzoyl*-group, $C_6H_5 \cdot CO-$, taking the place of the hydrogen of the hydroxyl- or amino-group,

$$C_6H_5 \cdot COCl + C_2H_5 \cdot OH = C_6H_5 \cdot CO \cdot O \cdot C_2H_5 + HCl,$$
$$(C_6H_5 \cdot CO)_2O + C_2H_5 \cdot OH = C_6H_5 \cdot CO \cdot O \cdot C_2H_5 + C_6H_5 \cdot COOH,$$
$$C_6H_5 \cdot COCl + NH_2 \cdot C_6H_5 = C_6H_5 \cdot CO \cdot NH \cdot C_6H_5 + HCl.$$

As such benzoyl-derivatives usually crystallise much more readily than the corresponding acetyl-derivatives, they are generally prepared in preference to the latter when it is a question of the identification or isolation of a substance.

Benzoyl-derivatives may be prepared by heating the hydroxy- or amino-compound with benzoyl chloride or with benzoic anhydride. A more convenient method, however, is that of Baumann and Schotten :—Benzoyl chloride and 10 per cent. caustic potash are added alternately, in *small* quantities at a time, to the compound, which is either dissolved or suspended in water, and, after each addition, the mixture is well shaken and cooled. Potash alone is then added until the disagreeable smell of benzoyl chloride is no longer noticed, and the solution remains permanently *alkaline ;* * the product is finally separated by filtration or by extraction with ether, and, if a solid, is purified by recrystallisation. The alkali serves to neutralise the hydrochloric acid and benzoic acid which are formed, the interaction taking place much more readily in the neutral or slightly alkaline solution.

Benzamide, $C_6H_5 \cdot CO \cdot NH_2$, may be taken as an example of an aromatic amide; it may be obtained by reactions similar to those employed in the case of acetamide (p. 168), as, for example, by treating ethyl benzoate with ammonia,

$$C_6H_5 \cdot COOC_2H_5 + NH_3 = C_6H_5 \cdot CO \cdot NH_2 + C_2H_5 \cdot OH ;$$

but it is also conveniently prepared by treating benzoyl chloride with excess of dry 'ammonium carbonate,'

$$C_6H_5 \cdot COCl + 2(NH_4)HCO_3 = C_6H_5 \cdot CO \cdot NH_2 + 2CO_2 + 2H_2O + NH_4Cl.$$

The ammonium carbonate (about 10 g.) is placed in a mortar, the benzoyl chloride (4–5 g.) is added, and the two substances are well mixed with a pestle; if the smell of the chloride continues at the end of about ten minutes, a little more ammonium carbonate is stirred in. The solid is extracted with a little cold water, which removes the ammonium salts, and is then recrystallised from boiling water.

Benzamide is crystalline, melts at 130°, and is sparingly soluble in cold, but readily soluble in hot, water; like other amides, it is decomposed by boiling alkalis, yielding ammonia and an alkali salt,

$$C_6H_5 \cdot CO \cdot NH_2 + KOH = C_6H_5 \cdot COOK + NH_3.$$

Benzonitrile, $C_6H_5 \cdot CN$ (phenyl cyanide), may be obtained

* Unless the solution is kept alkaline, benzoic acid separates in crystals, and renders the product impure.

by heating benzamide with phosphorus pentoxide, a method similar to that employed in the preparation of fatty nitriles,

$$C_6H_5\cdot CO\cdot NH_2 = C_6H_5\cdot CN + H_2O.$$

Although it cannot be prepared by treating chloro- or bromobenzene with potassium cyanide (the halogen atom being so firmly held that no interaction occurs), it may be obtained by fusing potassium benzenesulphonate with potassium cyanide (or with potassium ferrocyanide, which yields the cyanide),

$$C_6H_5\cdot SO_3K + KCN = C_6H_5\cdot CN + K_2SO_3.$$

It is, however, most conveniently prepared from aniline by Sandmeyer's reaction—namely, by treating a solution of phenyldiazonium chloride with potassium cuprous cyanide,

$$C_6H_5\cdot N_2Cl, 2CuCN = C_6H_5\cdot CN + CuCl + CuCN + N_2.$$

Aniline (1 part) is *diazotised* exactly as already described (p. 415), and the solution of the diazonium chloride is then gradually added to a hot solution of potassium cuprous cyanide; the product is distilled in steam and extracted with ether. The extract is washed with a little dilute soda, and dried with calcium chloride; the ether is then distilled, and the cyanide is purified by distillation.

The solution of potassium cuprous cyanide is prepared by slowly adding a solution of potassium cyanide (3 parts) to a solution of hydrated cupric sulphate (2½ parts),

$$2CuSO_4 + 6KCN = 2CuCN, KCN + (CN)_2 + K_2SO_4.$$

This and the subsequent operations, including steam distillation, must be conducted in a good draught cupboard, on account of the evolution of cyanogen and hydrogen cyanide.

Benzonitrile is a colourless oil, boiling at 191°, and smells like nitrobenzene. Its reactions resemble those of the fatty nitriles; thus, it is converted into the corresponding acid on hydrolysis with alkalis or mineral acids,

$$C_6H_5\cdot CN + 2H_2O = C_6H_5\cdot COOH + NH_3,$$

and into a primary amine on reduction,

$$C_6H_5\cdot CN + 4H = C_6H_5\cdot CH_2\cdot NH_2.$$

Other aromatic nitriles, such as the three *tolunitriles*, $C_6H_4(CH_3)\cdot CN$, are known; also compounds such as *phenyl-*

acetonitrile (*benzyl cyanide*, p. 483), $C_6H_5 \cdot CH_2 \cdot CN$, which contain the cyanogen-group in the side-chain.

Substitution Products of Benzoic Acid.—Benzoic acid is attacked by halogens (although not so readily as the hydrocarbons), and the first product consists of the *meta*-derivative (p. 393); when, for example, benzoic acid is heated with bromine and water at 125°, **m**-*bromobenzoic acid*, $C_6H_4Br \cdot COOH$ (m.p. 155°), is formed. The **o**- and **p**-*bromobenzoic acids* are obtained by oxidising the corresponding *bromotoluenes* with dilute nitric or chromic acid; the former melts at 147°, the latter at 251°. Nitric acid, in the presence of sulphuric acid, acts readily on benzoic acid, **m**-*nitrobenzoic acid*, $C_6H_4(NO_2) \cdot COOH$ (m.p. 141°), being the principal product; **o**-*nitrobenzoic acid* (m.p. 147°) and **p**-*nitrobenzoic acid* (m.p. 238°) are obtained by the oxidation of **o**- and **p**-*nitrotoluene* respectively (p. 396); when these acids are reduced with tin and hydrochloric acid, they yield the corresponding *aminobenzoic acids*, $C_6H_4(NH_2) \cdot COOH$, which, like glycine (p. 329), form salts both with acids and bases.

Anthranilic acid, $C_6H_4(NH_2) \cdot COOH$ (**o**-aminobenzoic acid), was first obtained by the oxidation of indigo (p. 663); it melts at 144°, and decomposes at higher temperatures, giving aniline and carbon dioxide.

When heated with sulphuric acid, benzoic acid is converted into **m**-*sulphobenzoic acid*, $C_6H_4(SO_3H) \cdot COOH$, small quantities of the **p**-acid also being produced. The **o**-acid is obtained by oxidising *toluene*-**o**-*sulphonic acid*; when treated with ammonia, it yields an *imide* (p. 479),

$$C_6H_4 \begin{cases} SO_2 \cdot OH \\ COOH \end{cases} + NH_3 = C_6H_4 \begin{cases} SO_2 \\ CO \end{cases} > NH + 2H_2O,$$

which is remarkable for possessing an exceedingly sweet taste, and which is known as *saccharin*.

The sulphobenzoic acids are very soluble in water; when fused with potash they yield hydroxy-acids (p. 488), just as benzenesulphonic acid gives phenol,

$$C_6H_4(SO_3K) \cdot COOK + 2KOH = C_6H_4(OK) \cdot COOK + K_2SO_3 + H_2O.$$

The three (**o.m.p.**) **toluic acids**, $C_6H_4(CH_3) \cdot COOH$, may be

produced by oxidising the corresponding *xylenes* with dilute nitric acid,

$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3)\cdot COOH + H_2O,$$

but the o- and p-acids are best prepared by converting the corresponding *toluidines* (m-toluidine cannot easily be obtained) into the nitriles by Sandmeyer's reaction (p. 415), and then hydrolysing the latter with acids or alkalis,

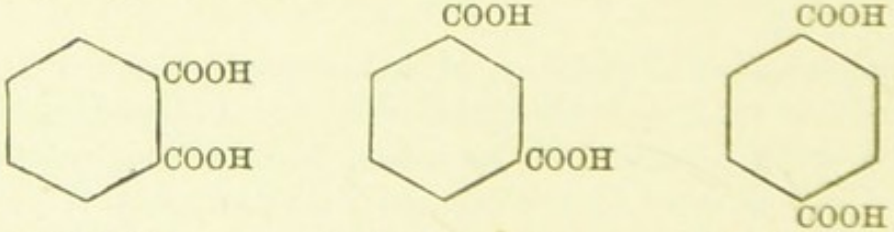
$$C_6H_4\begin{matrix}CH_3\\NH_2\end{matrix} \rightarrow C_6H_4\begin{matrix}CH_3\\CN\end{matrix} \rightarrow C_6H_4\begin{matrix}CH_3\\COOH.\end{matrix}$$

The o-, m-, and p-toluic acids melt at 103°, 110°, and 180° respectively, and resemble benzoic acid very closely, but since they contain a methyl-group, they have also properties which are not shown by benzoic acid; on oxidation, for example, they are converted into the corresponding *phthalic acids*, just as toluene is transformed into benzoic acid,

$$C_6H_4\begin{matrix}CH_3\\COOH\end{matrix} + 3O = C_6H_4\begin{matrix}COOH\\COOH\end{matrix} + H_2O.$$

Dicarboxylic Acids.

The important dicarboxylic acids are the three (o.m.p.) *phthalic acids*, or benzenedicarboxylic acids, which are respectively represented by the formulæ,



Phthalic Acid. Isophthalic Acid. Terephthalic Acid.

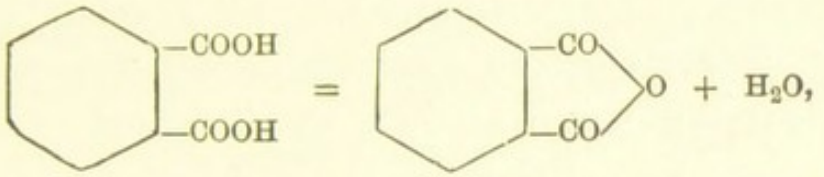
These compounds may be prepared by the oxidation of the corresponding *xylenes* (dimethylbenzenes) with dilute nitric acid, or by treating the *toluic acids* with potassium permanganate in alkaline solution,

$$C_6H_4\begin{matrix}CH_3\\CH_3\end{matrix} + 6O = C_6H_4\begin{matrix}COOH\\COOH\end{matrix} + 2H_2O,$$

$$C_6H_4\begin{matrix}CH_3\\COOH\end{matrix} + 3O = C_6H_4\begin{matrix}COOH\\COOH\end{matrix} + H_2O.$$

They are colourless, crystalline substances, and have all the ordinary properties of carboxylic acids. They yield normal and hydrogen metallic salts, esters, acid chlorides, amides, &c., which are formed by reactions similar to those employed in the preparation of corresponding derivatives of other dicarboxylic acids (p. 243).

Phthalic acid, like succinic acid (p. 249), is converted into its anhydride when it is strongly heated,



but an anhydride of *isophthalic acid* or of *terephthalic acid* cannot be produced; it is, in fact, a general rule that the formation of an anhydride from *one* molecule of an acid (an *inner* anhydride) takes place only when the two carboxyl-groups in the *benzene nucleus* are in the o-position, never when they occupy the m- or p-position.

When cautiously heated with lime, all these dicarboxylic acids yield benzoic acid,

$$C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} = C_6H_5\cdot COOH + CO_2,$$

but at high temperatures both carboxyl-groups are displaced by hydrogen, and benzene is formed,

$$C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} = C_6H_6 + 2CO_2;$$

this behaviour clearly shows that these acids are all dicarboxy-derivatives of benzene.

When a trace of phthalic acid is heated with resorcinol and a drop of sulphuric acid,* *fluoresceïn* (p. 447) is produced, and the reddish-brown product, when dissolved in caustic soda and poured into a large quantity of water, yields a magnificently fluorescent solution. This reaction is shown

* The sulphuric acid facilitates the formation of the anhydride; sometimes, as in the case of phthalic acid itself, the addition of sulphuric acid is unnecessary.

by all the o-dicarboxylic acids of the benzene series, but not by the m- and p-dicarboxylic acids; it is also shown by acids of the fatty series, such as succinic acid, which give *inner* anhydrides—that is to say, anhydrides formed from *one* molecule of the acid.

Phthalic acid, $C_6H_4(COOH)_2$ (benzene-o-dicarboxylic acid), may be obtained by oxidising o-*xylene* or o-*toluic acid*, but it is usually manufactured by oxidising *naphthalene* (p. 496) with sulphuric acid, in presence of a small quantity of mercury; for laboratory purposes *naphthalene tetrachloride*, $C_{10}H_8Cl_4$ (p. 504), is oxidised with nitric acid.

Concentrated nitric acid (sp. gr. 1·45, 10 parts) is gradually added to naphthalene tetrachloride (1 part), and the mixture is heated until a clear solution is produced; this is then evaporated to dryness, and the residue is distilled. The phthalic anhydride (see below), which passes over, is boiled with caustic soda, the solution of sodium phthalate is treated with excess of a mineral acid, and the crystalline precipitate of phthalic acid is purified by recrystallisation from boiling water.

Phthalic acid crystallises in colourless prisms, and melts at 184°, with formation of the anhydride, so that, when the melted substance has solidified, and the melting-point is again determined, it is found to be about 128°, the melting-point of phthalic anhydride.

Phthalic acid is readily soluble in hot water, alcohol, and ether, and gives with metallic hydroxides well-characterised salts; the *barium* salt, $C_6H_4<\begin{matrix}COO\\COO\end{matrix}>Ba$, obtained as a white precipitate on the addition of barium chloride to a neutral solution of the ammonium salt, is very sparingly soluble in water.

Ethyl phthalate, $C_6H_4(COOC_2H_5)_2$, is readily prepared by saturating an alcoholic solution of phthalic acid (or its anhydride) with hydrogen chloride. It is a colourless liquid, boiling at 295°.

Phthalyl chloride, $C_6H_4(COCl)_2$, is prepared by heating phthalic anhydride (1 mol.) with phosphorus pentachloride (1 mol.). It is a

colourless oil, boils at 275° (726 mm.), and is slowly decomposed by water, with regeneration of phthalic acid. In many of its reactions it behaves as if it had the constitution represented by the formula, $C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$ (compare succinyl chloride, p. 251).

Phthalic anhydride, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O$, is produced when phthalic acid is distilled. It sublimes readily in long needles, melts at 128°, boils at 284°, and is only very gradually decomposed by water, but is readily hydrolysed by alkalis, yielding salts of phthalic acid. When heated in a stream of ammonia it is converted into *phthalimide*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NH$, a substance (m.p. 229°) which yields a potassium derivative, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NK$, with alcoholic potash. There is thus a great similarity between phthalimide and succinimide (p. 252).

Potassium phthalimide reacts with various halogen derivatives, as, for example, with ethyl iodide and with ethylene dibromide, giving substituted phthalimides,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NK + C_2H_5I = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_2H_5 + KI,$$

Ethylphthalimide.

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NK + CH_2Br\cdot CH_2Br =$$

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2Br + KBr,$$

Bromethylphthalimide.

$$2C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NK + CH_2Br\cdot CH_2Br =$$

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4 + 2KBr.$$

Ethylenediphthalimide.

These products are hydrolysed by mineral acids and by alkalis yielding phthalic acid and an amine, or a bromo- or hydroxy-amine; *ethylphthalimide*, for example, gives ethylamine, whereas *bromethylphthalimide* gives *bromethylamine*, $NH_2\cdot CH_2\cdot CH_2Br$, or *aminoethyl alcohol*, $NH_2\cdot CH_2\cdot CH_2\cdot OH$, according to the hydrolysing agent used. *Ethylenediphthalimide* yields *ethylene diamine*, $NH_2\cdot CH_2\cdot CH_2\cdot NH_2$.

Isophthalic acid, $C_6H_4(COOH)_2$ (benzene-**m**-dicarboxylic acid), is produced by oxidising **m**-*xylene* with nitric acid or chromic acid; or from **m**-*toluic acid* (p. 476), by oxidation with potassium permanganate in alkaline solution.

It crystallises in needles, melts above 300°, and when strongly heated sublimes unchanged; it is very sparingly soluble in water. *Methyl isophthalate*, $C_6H_4(COOCH_3)_2$, melts at 65°.

Terephthalic acid, $C_6H_4(COOH)_2$ (benzene-**p**-dicarboxylic acid), is formed by the oxidation of **p**-*xylene*, **p**-*toluic acid*, and of all di-alkyl substitution derivatives of benzene, which, like *cymene*, $CH_3{\cdot}C_6H_4{\cdot}CH(CH_3)_2$, contain the alkyl-groups in the **p**-position. It is best prepared by oxidising **p**-toluic acid (p. 476) in alkaline solution with potassium permanganate.

Terephthalic acid is almost insoluble in water, and, when heated, sublimes without melting; the *methyl* ester, $C_6H_4(COOCH_3)_2$, melts at 140°.

Isophthalic acid, terephthalic acid, and other acids which have an indefinite melting-point, or which melt above 300°, are best identified with the aid of their methyl esters, which generally crystallise well, and melt at comparatively low temperatures.

For this purpose, the acid (0·1–0·5 g.) is warmed in a test tube with about three times its weight of phosphorus pentachloride, and the clear solution, which now contains the chloride of the acid, is poured into excess of methyl alcohol. As soon as the vigorous reaction has subsided, the liquid is diluted with water, and the crude methyl ester is collected and recrystallised; its melting-point is then determined.

Phenylacetic Acid, Phenylpropionic Acid, and their Derivatives.

Many cases have already been mentioned in which aromatic compounds have been found to have certain properties similar to those of members of the fatty series, and it has been pointed out that this is due to the presence, in the former, of groups of atoms (*side-chains*), which may be considered as fatty radicles; benzyl chloride, for example, has many pro-

perties in common with methyl chloride, benzyl alcohol with methyl alcohol, benzylamine with methylamine, and so on, because similar groups or radicles confer, as a rule, similar properties on the compounds in which they occur. Since, moreover, nearly all fatty compounds may theoretically be converted into aromatic compounds of corresponding types, by the substitution of a phenyl-group for hydrogen, it follows that any series of fatty compounds may have its counterpart in the aromatic group. This is well illustrated in the case of the carboxylic acids; corresponding with the fatty acids, there is a series of aromatic acids which may be regarded as derived from the former in the manner just mentioned.

Formic acid, $H{\cdot}COOH$,
Benzoic acid, $C_6H_5{\cdot}COOH$ (phenylformic acid).
Acetic acid, $CH_3{\cdot}COOH$,
Phenylacetic acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$.
Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$,
Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.
Butyric acid, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$,
Phenylbutyric acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

With the exception of benzoic acid, all the above aromatic acids are derived from the aromatic hydrocarbons by the substitution of carboxyl for hydrogen of the *side-chain*. They have not only the characteristic properties of aromatic compounds in general, but also those of fatty acids, and, like the latter, they may be converted into unsaturated compounds by loss of two or more atoms of hydrogen; the compounds thus produced correspond with the unsaturated aliphatic acids, as the following examples will show:—

Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$,
Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.
Acrylic acid, $CH_2{:}CH{\cdot}COOH$,
Phenylacrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$.
Propiolic acid, $CH{:}C{\cdot}COOH$,
Phenylpropiolic acid, $C_6H_5{\cdot}C{:}C{\cdot}COOH$.

Preparation.—Aromatic acids, containing the carboxyl-group in the *side-chain*, may be prepared by *carefully* oxi-

dising the corresponding alcohols and aldehydes, and by hydrolysing the nitriles with alkalis or mineral acids,

$$C_6H_5\cdot CH_2\cdot CN + 2H_2O = C_6H_5\cdot CH_2\cdot COOH + NH_3,$$

but these methods are limited in application, owing to the difficulty of obtaining the requisite substances.

The more important general methods are :—(*a*) By the reduction of the corresponding unsaturated acids, compounds which are prepared without much difficulty (p. 484),

$$C_6H_5\cdot CH{:}CH\cdot COOH + 2H = C_6H_5\cdot CH_2\cdot CH_2\cdot COOH.$$

(*b*) By the interaction of the sodium compound of ethyl malonate or of ethyl acetoacetate and a halogen derivative of an aromatic hydrocarbon. As in the latter case the procedure is exactly similar to that employed in preparing fatty acids (pp. 198–208), one example only need be given—namely, the synthesis of *phenylpropionic acid.*

The sodium compound of ethyl malonate is heated with benzyl chloride, and the *ethyl benzylmalonate* which is thus produced,

$$C_6H_5\cdot CH_2Cl + CHNa(COOC_2H_5)_2 = C_6H_5\cdot CH_2\cdot CH(COOC_2H_5)_2 + NaCl,$$

Ethyl Benzylmalonate.

is hydrolysed with alcoholic potash. The *benzylmalonic acid* is then isolated, and heated at 200°, when it is converted into *phenylpropionic acid*, with loss of carbon dioxide,

$$C_6H_5\cdot CH_2\cdot CH(COOH)_2 = C_6H_5\cdot CH_2\cdot CH_2\cdot COOH + CO_2.$$

It should be remembered that only those halogen derivatives in which the halogen is in the *side-chain* can be employed in such syntheses, because when the halogen is united with the nucleus, as in *monochlorotoluene*, $C_6H_4Cl\cdot CH_3$, for example, no action takes place (compare p. 385).

The properties of two typical acids of this class are described below.

Phenylacetic acid, $C_6H_5\cdot CH_2\cdot COOH$ (α-toluic acid), is prepared by boiling a solution of benzyl chloride (1 mol.) and

potassium cyanide (1 mol.) in dilute alcohol for about three hours; the *benzyl cyanide*, which is thus formed, is purified by fractional distillation, the fraction 220–235° (benzyl cyanide boils at 232°) is hydrolysed with boiling dilute sulphuric acid, and the product is purified by recrystallisation from water,

$$C_6H_5\cdot CH_2Cl \rightarrow C_6H_5\cdot CH_2\cdot CN \rightarrow C_6H_5\cdot CH_2\cdot COOH.$$

Phenylacetic acid melts at 76·5°, boils at 262°, and crystallises from water in glistening plates; it has a characteristic smell, and forms salts and other derivatives just as do benzoic and acetic acids.

When oxidised with chromic acid it yields benzoic acid, a change very different from that undergone by the isomeric toluic acids (p. 476),

$$C_6H_5\cdot CH_2\cdot COOH + 3O = C_6H_5\cdot COOH + CO_2 + H_2O.$$

Phenylacetaldehyde, $C_6H_5\cdot CH_2\cdot CHO$, is prepared by distilling a mixture of the calcium salts of phenylacetic and formic acids. It is a colourless oil, boiling at 206°, and resembles the aldehydes of the fatty series in properties.

Phenylpropionic acid, $C_6H_5\cdot CH_2\cdot CH_2\cdot COOH$ (hydrocinnamic acid), is conveniently prepared by reducing *cinnamic acid* (see below) with sodium amalgam and water,

$$C_6H_5\cdot CH{:}CH\cdot COOH + 2H = C_6H_5\cdot CH_2\cdot CH_2\cdot COOH,$$

but may also be obtained from the product of the action of benzyl chloride on the sodium compound of ethyl malonate (p. 482). It crystallises from water in needles, melts at 47°, and boils at 280°.

Cinnamic acid, $C_6H_5\cdot CH{:}CH\cdot COOH$ (phenylacrylic acid), is closely related to phenylpropionic acid, and is perhaps the best-known *unsaturated* acid of the aromatic series. It occurs in large quantities in storax (*Styrax officinalis*), and may be obtained by warming this resin with caustic soda; the filtered aqueous solution of *sodium cinnamate* is treated with hydrochloric acid, and the precipitated cinnamic acid is purified by recrystallisation from boiling water.

Cinnamic acid is usually prepared by heating benzaldehyde with acetic anhydride and anhydrous sodium acetate,

$$C_6H_5\cdot CHO + CH_3\cdot COONa = C_6H_5\cdot CH{:}CH\cdot COONa + H_2O.$$

A mixture of benzaldehyde (3 parts), acetic anhydride (10 parts), and anhydrous sodium acetate (3 parts) is heated to boiling in a flask placed in an oil-bath. After about eight hours' time, the mixture is poured into water, and distilled in steam to separate the unchanged benzaldehyde; the residue is then treated with caustic soda, and the hot alkaline solution is filtered from oily and tarry impurities, and strongly acidified with hydrochloric acid; the precipitated cinnamic acid is purified by recrystallisation from boiling water.

This method (*Perkin's reaction*) is a general one for the preparation of unsaturated aromatic acids, as, by employing the anhydrides and sodium salts of other fatty acids, homologues of cinnamic acid are obtained. When, for example, benzaldehyde is treated with sodium propionate and propionic anhydride, *phenylmethylacrylic acid* (*α-methylcinnamic acid*), $C_6H_5\cdot CH{:}C(CH_3)\cdot COOH$, is formed; *phenylisocrotonic acid*, $C_6H_5\cdot CH{:}CH\cdot CH_2\cdot COOH$, is not obtained by this reaction, because combination always takes place between the aldehyde oxygen atom and the hydrogen atoms of that $-CH_2-$ group which is directly united with the carboxyl-radicle of the *sodium salt*.

Phenylisocrotonic acid, however, may be prepared by heating benzaldehyde with a mixture of sodium succinate and succinic anhydride, carbon dioxide being eliminated,

$$C_6H_5\cdot CHO + COOH\cdot CH_2\cdot CH_2\cdot COOH = C_6H_5\cdot CH{:}CH\cdot CH_2\cdot COOH + CO_2 + H_2O.$$

It is a colourless, crystalline substance, melts at 86°, and boils at 302°; at its boiling-point, it is gradually converted into *α-naphthol* and water (p. 501).

Other aldehydes which contain the aldehyde-group directly united to the nucleus may be used in the Perkin reaction; the three *toluic aldehydes*, $CH_3\cdot C_6H_4\cdot CHO$, for example, give with sodium acetate and acetic anhydride the three *methylcinnamic acids*, $CH_3\cdot C_6H_4\cdot CH{:}CH\cdot COOH$.

Cinnamic acid crystallises from water in needles, and melts at 133°. Its chemical behaviour, in many respects, is similar to that of acrylic acid and other unsaturated fatty acids; it combines directly with bromine, for example, yielding

phenyl-αβ-dibromopropionic acid, $C_6H_5 \cdot CHBr \cdot CHBr \cdot COOH$, and with hydrogen bromide, giving *phenyl-β-bromopropionic acid*, $C_6H_5 \cdot CHBr \cdot CH_2 \cdot COOH$.

A solution of cinnamic acid in sodium carbonate immediately reduces (decolourises) a dilute solution of potassium permanganate at *ordinary* temperatures; all *unsaturated* acids show this behaviour, and are thus easily distinguished from saturated aromatic compounds (Baeyer). On reduction with sodium amalgam and water, cinnamic acid is converted into phenylpropionic acid (p. 483), just as acrylic acid is transformed into propionic acid.

When distilled with lime, cinnamic acid is decomposed into carbon dioxide, and *phenylethylene* or *styrolene*,*

$$C_6H_5 \cdot CH{:}CH \cdot COOH = C_6H_5 \cdot CH{:}CH_2 + CO_2.$$

Concentrated nitric acid converts cinnamic acid into a mixture of about equal quantities of o- and p-*nitrocinnamic acids*, $C_6H_4(NO_2) \cdot CH{:}CH \cdot COOH$. For their separation, these acids are converted into their ethyl esters, $C_6H_4(NO_2) \cdot CH{:}CH \cdot COOC_2H_5$ (by means of alcohol and hydrogen chloride), which are then dissolved in alcohol; the sparingly soluble ester of the p-acid separates from the solution, while the readily soluble *ethyl* o-*nitrocinnamate* remains in the mother-liquor. From the pure esters the acids are then regenerated, by hydrolysis with dilute sulphuric acid. They resemble cinnamic acid closely in properties, and combine directly with bromine, yielding the corresponding *nitrophenyldibromopropionic acids*, $C_6H_4(NO_2) \cdot CHBr \cdot CHBr \cdot COOH$.

Cinnamic aldehyde, $C_6H_5 \cdot CH{:}CH \cdot CHO$, is the principal component of oil of cinnamon, from which it may be extracted with the aid of a solution of sodium hydrogen sulphite. It may be obtained by heating a mixture of the calcium salts of cinnamic and formic acids, or by condensing benzaldehyde with acetaldehyde, in presence of sodium ethoxide.

It is a liquid, boiling at 247°, and has a characteristic aromatic

* *Styrolene*, $C_6H_5 \cdot CH{:}CH_2$, may be taken as a typical example of an aromatic hydrocarbon containing an *unsaturated* side-chain. It is a colourless liquid, which boils at 145°, and in chemical properties shows the closest resemblance to ethylene, of which it is the phenyl substitution product. With bromine, for example, it yields a dibromo-additive product, $C_6H_5 \cdot CHBr \cdot CH_2Br$ (*dibromethylbenzene*), and when heated with hydriodic acid, it is reduced to *ethylbenzene*, $C_6H_5 \cdot CH_2 \cdot CH_3$.

odour; on exposure to the air, it is oxidised to cinnamic acid. Its *hydrazone* melts at 168°. Cinnamic aldehyde, like benzaldehyde, condenses readily with many other compounds; thus, when heated with malonic acid, in presence of pyridine, it gives *cinnamylidene-malonic acid*, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}C(COOH)_2$, which decomposes into *cinnamylideneacetic acid*, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COOH$, and carbon dioxide.

Stereoisomerism of Aromatic Olefinic Acids.—Some of the unsaturated acids of the aromatic series may exist in stereoisomeric (*cis-* and *trans-*) forms corresponding respectively with maleïc and fumaric acids. *Allocinnamic acid*, $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$, for example, is a stereoisomeride of cinnamic acid, and occurs, together with the latter, in certain by-products from the preparation of cocaine. *Cinnamylideneacetic acid* (see above) also exists in stereoisomeric forms, both of which are produced in the reaction just described.

Many olefinic acids, not only of the aromatic, but also of the aliphatic series, undergo an interesting intramolecular change when they are heated with a concentrated aqueous solution of sodium hydroxide. Phenylisocrotonic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, for example, is converted into a *structural* isomeride, $C_6H_5{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$, owing to the migration or shifting of the double binding from the $\beta\gamma$- to the $\alpha\beta$-position. In such intramolecular changes the general rule is, that the double binding in the molecule of the product is nearer to the carboxyl-group than that in the molecule of the original subtance.

Phenylpropiolic acid, $C_6H_5{\cdot}C{:}C{\cdot}COOH$, is obtained by treating phenyl-$\alpha\beta$-dibromopropionic acid (p. 485), or its ethyl ester, with alcoholic potash,

$$C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH = C_6H_5{\cdot}C{:}C{\cdot}COOH + 2HBr,$$

a method which is exactly similar to that employed in preparing acetylene by the action of alcoholic potash on ethylene dibromide. It melts at 137°, and at higher temperatures, or when heated with water at 120°, it decomposes into carbon dioxide and *phenylacetylene*, a colourless liquid (b.p. 140°) which is closely related to acetylene in chemical properties,

$$C_6H_5{\cdot}C{:}C{\cdot}COOH = C_6H_5{\cdot}C{:}CH + CO_2.$$

o-Nitrophenylpropiolic acid, $C_6H_4(NO_2){\cdot}C{:}C{\cdot}COOH$, may be

similarly prepared from o-nitrophenyldibromopropionic acid; it is a substance of great interest, as when treated with reducing agents, such as hydrogen sulphide, or grape-sugar and potash, it is converted into indigo-blue (Baeyer),

$$2C_6H_4\begin{cases}C\!:\!C\cdot COOH\\NO_2\end{cases}+4H=C_{16}H_{10}N_2O_2+2CO_2+2H_2O.$$

This method of preparation, however, is not of technical value, (compare p. 664).

CHAPTER XXXI.

Phenolic- and Hydroxy-Carboxylic Acids.

The hydroxy-acids of the aromatic series are derived from benzoic acid and its homologues, by the substitution of hydroxyl-groups for hydrogen atoms, just as glycollic acid, for example, is derived from acetic acid (p. 237); like the simple hydroxy-derivatives of the aromatic hydrocarbons, they may be divided into two classes, according as the hydroxyl-group is united with carbon of the nucleus or of the side-chain. In the first case, the hydroxyl-group has the same character as in phenols, and consequently hydroxy-acids of this class, as, for example, the three (o.m.p.) *hydroxybenzoic acids*, $C_6H_4(OH)\cdot COOH$, are both phenols and carboxylic acids; in the second case, however, the hydroxyl-group has the same character as in alcohols, so that the compounds of this class, such as *mandelic acid*, $C_6H_5\cdot CH(OH)\cdot COOH$, have properties closely resembling those of the fatty hydroxy-acids; in other words, the differences between the two classes of aromatic hydroxy-acids are practically the same as those between phenols and alcohols.

As those acids which contain the hydroxyl-group united with carbon of the nucleus form by far the more important class, they will be described first, and the following statements refer to them only, except where stated to the contrary.

Preparation.—The phenolic-acids may be prepared from the simple carboxylic acids, by reactions exactly similar to those employed in the preparation of phenols from hydrocarbons; that is to say, the acids are converted into nitro-compounds, then into amino-compounds, and the latter are treated with nitrous acid in the usual manner,

$$C_6H_5\cdot COOH \rightarrow C_6H_4{<}^{COOH}_{NO_2} \rightarrow C_6H_4{<}^{COOH}_{NH_2} \rightarrow C_6H_4{<}^{COOH}_{OH},$$

or, the acids are heated with sulphuric acid, and the sulphonic acids obtained in this way are fused with a caustic alkali,

$$C_6H_5\cdot COOH \rightarrow C_6H_4{<}^{COOH}_{SO_3H} \rightarrow C_6H_4{<}^{COOH}_{OH}.$$

It must be borne in mind, however, that as the carboxyl-group of the acid determines the position taken up by the nitro- and sulphonic-groups (p. 393), only the m-hydroxy-compounds are formed in this manner.

The o-phenolic-acids, and in some cases the m- and p-compounds, are most conveniently prepared from the phenols by one of the following methods:—

The dry sodium compound of the phenol is heated at about 200° in a stream of carbon dioxide,

$$2C_6H_5\cdot ONa + CO_2 = C_6H_4{<}^{COONa}_{ONa} + C_6H_5\cdot OH.$$

Under these conditions half the phenol distils over and is recovered; but if the sodium compound is first saturated with carbon dioxide under pressure, it is converted into an aromatic derivative of carbonic acid, which, when heated at about 130° under pressure, is completely transformed into a salt of the phenolic-acid by intramolecular change,

$$C_6H_5\cdot ONa + CO_2 = C_6H_5\cdot O\cdot COONa = C_6H_4{<}^{COONa}_{OH}.$$

Sodium Phenylcarbonate.

Many dihydric and trihydric phenols may be converted into the corresponding phenolic-acids, simply by heating them

with ammonium (or potassium) hydrogen carbonate; when resorcinol, for example, is treated in this way, it yields a mixture of isomeric *resorcylic acids*, $C_6H_3(OH)_2 \cdot COOH$.

The second general method for the preparation of phenolic-acids from phenols consists in boiling a strongly alkaline solution of the phenol with carbon tetrachloride; the principal product is the o-acid, but varying proportions of the p-acid are also formed,

$$C_6H_5 \cdot ONa + CCl_4 + 5NaOH = C_6H_4 \begin{cases} COONa \\ ONa \end{cases} + 4NaCl + 3H_2O.$$

After the substances have been heated together during some hours, the unchanged carbon tetrachloride is distilled off, and the aqueous solution is acidified and extracted with ether; the ethereal extract is then shaken with a solution of sodium carbonate, which extracts the acid, leaving the phenol dissolved in the ether. The phenolic-acid is then precipitated with a mineral acid, and purified by recrystallisation.

The above method is clearly analogous to that of Reimer (p. 458), and it may be assumed that the changes which occur take place in various stages as indicated below,

$$C_6H_5 \cdot OH \rightarrow C_6H_4 \begin{cases} CCl_3 \\ OH \end{cases} \rightarrow C_6H_4 \begin{cases} C(OH)_3 \\ OH \end{cases} \rightarrow C_6H_4 \begin{cases} COOH \\ OH \end{cases}.$$

Properties.—The phenolic-acids are colourless, crystalline substances, more readily soluble in water, and less volatile, than the acids from which they are derived; many of them undergo decomposition when heated strongly, carbon dioxide being evolved; when heated with lime they are decomposed, with formation of phenols,

$$C_6H_4(OH) \cdot COOH = C_6H_5 \cdot OH + CO_2,$$
$$C_6H_3(OH)_2 \cdot COOH = C_6H_4(OH)_2 + CO_2.$$

The o-acids, as, for example, *salicylic acid*, give, in neutral solution, a violet colouration with ferric chloride, whereas the m- and p-acids, such as the m- and p-*hydroxybenzoic acids*, give no colouration.

The chemical properties of the phenolic-acids will be readily understood when it is remembered that they are both phenols and carboxylic acids. As carboxylic acids, they form salts by

the displacement of the hydrogen atom of the carboxyl-group, such salts being obtained when the acids are treated with *carbonates* or with one equivalent of a metallic hydroxide; when, however, excess of *alkali hydroxide* is employed, the hydrogen of the phenolic hydroxyl-group is also displaced, just as in the case of phenols. Phenolic-acids, therefore, form both mono- and di-metallic salts; *salicylic acid*, for example, yields the two sodium salts, $C_6H_4(OH)\cdot COONa$ and $C_6H_4(ONa)\cdot COONa$.

The di-metallic salts are decomposed by carbonic acid, with formation of mono-metallic salts, just as the phenates are decomposed, giving phenols; the metal in combination with the carboxyl-group, however, cannot be displaced in this way.

The *esters* of the phenolic-acids are prepared in the usual manner—namely, by saturating a solution of the acid in excess of the alcohol with hydrogen chloride (p. 196); by this treatment the hydrogen of the carboxyl-group only is displaced, ordinary esters, such as *methyl salicylate*, $C_6H_4(OH)\cdot COOCH_3$, being formed. These compounds have still phenolic properties, and dissolve in caustic alkalis, forming metallic derivatives, such as *methyl potassiosalicylate*, $C_6H_4(OK)\cdot COOCH_3$, which, when heated with alkyl halogen compounds, yield alkyl-derivatives, such as *methyl ethylsalicylate*, $C_6H_4(OC_2H_5)\cdot COOCH_3$. On hydrolysis with alcoholic potash, only the alkyl of the carboxyl-group is removed from di-alkyl compounds of this kind; methyl ethylsalicylate, for example, yields the potassium salt of *ethylsalicylic acid*,

$$C_6H_4\begin{<}{COOCH_3}{OC_2H_5} + KOH = C_6H_4\begin{<}{COOK}{OC_2H_5} + CH_3\cdot OH.$$

The other alkyl-group is not eliminated even by boiling alkalis, a behaviour which corresponds with that of the alkyl-group in derivatives of phenols, such as *anisole*, $C_6H_5\cdot OCH_3$ (p. 440). Just, however, as anisole is decomposed into phenol and methyl iodide when it is heated with hydriodic acid,

so ethylsalicylic acid under similar conditions yields the phenolic-acid (compare p. 540),

$$C_6H_4<\begin{matrix}COOH\\OC_2H_5\end{matrix} + HI = C_6H_4<\begin{matrix}COOH\\OH\end{matrix} + C_2H_5I.$$

Salicylic acid, $C_6H_4(OH)\cdot COOH$ (o-hydroxybenzoic acid), occurs in the blossom of *Spiræa ulmaria*, and is also found in considerable quantities, as *methyl salicylate*, in oil of wintergreen (*Gaultheria procumbens*). It used to be prepared, especially for pharmaceutical purposes, by hydrolysing this oil with potash.

The methyl alcohol (p. 92) was then distilled, the solution treated with excess of dilute sulphuric acid, and the precipitated salicylic acid purified by recrystallisation from water.

Salicylic acid may be obtained by oxidising *salicylaldehyde* (p. 459), or *salicylic alcohol* (saligenin, p. 452), with chromic acid, by treating o-*aminobenzoic acid* (anthranilic acid, p. 475) with nitrous acid, and also by boiling *phenol* with caustic soda and carbon tetrachloride.

It is now prepared on the large scale by treating sodium phenate with carbon dioxide under pressure, and then heating the *sodium phenylcarbonate*, $C_6H_5\cdot O\cdot COONa$, which is thus formed, at 120–140° under pressure, when it undergoes intramolecular change into sodium salicylate (p. 488).

Salicylic acid is sparingly soluble in cold (1 in 400 parts at 15°), but readily in hot, water, from which it crystallises in needles, melting at 156°; its neutral solutions give with ferric chloride an intense violet colouration. When rapidly heated it sublimes, and only slight decomposition occurs; but when distilled slowly, a large proportion decomposes into phenol and carbon dioxide, this change being complete if the acid is distilled with lime.

When salicylic acid is reduced with sodium and boiling amyl alcohol, it is converted into normal *pimelic acid*, $COOH\cdot[CH_2]_5\cdot COOH$, the next higher homologue of adipic acid (p. 253); in a similar manner, certain other o-phenolic-

acids (but not the m- or p-compounds) may be transformed into homologues of pimelic acid.

Salicylic acid is a powerful antiseptic, and, as it has no smell, it is frequently used as a disinfectant instead of phenol; it is also extensively employed in medicine and as a food preservative.

The mono-metallic salts of salicylic acid, as, for example, *potassium salicylate*, $C_6H_4(OH)\cdot COOK$, and *calcium salicylate*, $\{C_6H_4(OH)\cdot COO\}_2Ca$, are prepared by neutralising a hot aqueous solution of the acid with metallic *carbonates;* they are, as a rule, soluble in water. The di-metallic salts, such as $C_6H_4(OK)\cdot COOK$ and $C_6H_4<\begin{matrix}-O-\\COO\end{matrix}>Ba$, are obtained in a similar manner, employing excess of the metallic *hydroxides*. With the exception of the salts of the alkali metals, these di-metallic compounds are insoluble in water; they are all decomposed by carbonic acid, with formation of the mono-metallic salts,

$$2C_6H_4<\begin{matrix}COOK\\OK\end{matrix} + CO_2 + H_2O = 2C_6H_4<\begin{matrix}COOK\\OH\end{matrix} + K_2CO_3.$$

Methyl salicylate, $C_6H_4(OH)\cdot COOCH_3$, prepared in the manner described (p. 490), or by distilling a mixture of salicylic acid, methyl alcohol, and sulphuric acid (p. 196), is an agreeably smelling oil, boiling at 224°; *ethyl salicylate*, $C_6H_4(OH)\cdot COOC_2H_5$, boils at 231·5°.

Phenyl salicylate, $C_6H_4(OH)\cdot COOC_6H_5$, is prepared by heating a mixture of sodium salicylate and sodium phenate with phosphorus oxychloride,

$$2C_6H_4(OH)\cdot COONa + 2C_6H_5\cdot ONa + POCl_3 = 2C_6H_4(OH)\cdot COOC_6H_5 + 3NaCl + NaPO_3;$$

it melts at 42–43°, is almost odourless, and is much employed in medicine and in surgery, under the name of *salol*, in place of salicylic acid. *Naphthyl salicylate*, $C_6H_4(OH)\cdot COOC_{10}H_7$, *quinine salicylate*, $C_6H_4(OH)\cdot COO\cdot C_{20}H_{23}N_2O$, and many other esters of salicylic acid are similarly employed; also acidyl

derivatives, such as *acetylsalicylic acid*, $C_6H_4(OAc)\cdot COOH$ (*aspirin*, m.p. 135°), which is obtained by heating salicylic acid with acetic anhydride or acetyl chloride.

Methyl methylsalicylate, $C_6H_4(OCH_3)\cdot COOCH_3$, is formed when methyl salicylate is heated with methyl iodide and potash (1 mol.) in alcoholic solution; it is an oil, boiling at 228°.

Methylsalicylic acid, $C_6H_4(OCH_3)\cdot COOH$, is obtained when its methyl ester is hydrolysed with potash; it melts at 98·5°, and when heated with hydriodic acid it is decomposed, giving salicylic acid and methyl iodide; the other halogen acids have a similar action.

m-*Hydroxybenzoic acid* is prepared by fusing **m**-*sulphobenzoic acid* with potash, and also by the action of nitrous acid on **m**-*aminobenzoic acid*. It melts at 200°, does not give a colouration with ferric chloride, and, when distilled with lime, it is decomposed into phenol and carbon dioxide.

p-*Hydroxybenzoic acid* is formed, together with salicylic acid, by the action of carbon tetrachloride and potash on phenol; it may also be obtained from **p**-*sulphobenzoic acid* by fusion with potash, or by the action of nitrous acid on **p**-*aminobenzoic acid*.

It is prepared by heating potassium phenate in a stream of carbon dioxide at 220° so long as phenol distils over; if, however, the temperature be kept below 150°, potassium salicylate is formed. The residue is dissolved in water, and the acid is precipitated from the filtered solution with hydrochloric acid, and purified by recrystallisation from water. **p**-Hydroxybenzoic acid melts at 210°, and is completely decomposed on distillation into phenol and carbon dioxide; its aqueous solution gives no colouration with ferric chloride.

Anisic acid, $C_6H_4(OCH_3)\cdot COOH$ (**p**-methoxybenzoic acid), is obtained by oxidising *anethole*, $C_6H_4(OCH_3)\cdot CH{:}CH\cdot CH_3$ (the principal component of oil of aniseed), with chromic acid; it may also be prepared from **p**-*hydroxybenzoic acid* by means of reactions analogous to those employed in the formation of ethylsalicylic acid from salicylic acid (p. 490).

Anisic acid melts at 185°, and when distilled with lime it is decomposed, with formation of *anisole* (p. 440); when heated with fuming hydriodic acid, it yields **p**-*hydroxybenzoic acid* and methyl iodide.

There are six *dihydroxybenzoic acids*, $C_6H_3(OH)_2\cdot COOH$, two of which are derived from catechol, three from resorcinol, and one

from quinol; the most important of these is **protocatechuic acid** [OH:OH:COOH = 1:2:4], one of the two isomeric *catecholcarboxylic acids*. This compound is formed when many resins, such as catechu and gum benzoïn, and also certain alkaloids, are fused with potash, and it may be prepared synthetically by heating catechol with water and ammonium hydrogen carbonate at 140°.

It crystallises from water, in which it is very soluble, in needles, melts at 199°, and when strongly heated it is decomposed into catechol and carbon dioxide; its aqueous solution gives with ferric chloride a green solution, which becomes violet and then red on the addition of sodium hydrogen carbonate.

Gallic acid, $C_6H_2(OH)_3 \cdot COOH$, [3OH:COOH = 1:2:3:5] (or pyrogallolcarboxylic acid), is a trihydroxybenzoic acid; it occurs in gall-nuts, tea, and many other vegetable products, and is best prepared by boiling *tannin* (see below) with dilute acids. It crystallises in needles, and melts at 220°, being at the same time resolved into pyrogallol (p. 448) and carbon dioxide; it is readily soluble in water, and its aqueous solution gives with ferric chloride a bluish-black precipitate. Gallic acid is a strong reducing agent, and precipitates gold, silver, and platinum from solutions of their salts.

Tannin, $C_{14}H_{10}O_9$ (digallic acid, tannic acid), occurs in large quantities in gall-nuts, sumach, and in many kinds of bark, from which it may be extracted with boiling water. It is an almost colourless, amorphous substance, and is readily soluble in water; its solutions have a very astringent taste, and give with ferric chloride an intense dark-blue solution, for which reason tannin is largely used in the manufacture of inks.

When boiled with dilute sulphuric acid, tannin is completely converted into gallic acid, a fact which seems to show that it is the anhydride of this acid,

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5,$$

but the constitution of tannin is not known. Tannin is used largely in dyeing, as a mordant, owing to its property of forming insoluble coloured compounds with many dyes. It is also extensively employed in tanning. When animal skin or membrane, after suitable preliminary operations, is

placed in a solution of tannin, or in contact with moist bark containing tannin, it absorbs and combines with the tannin, and is converted into a much tougher material; such tanned skins constitute leather.

Mandelic acid, $C_6H_5 \cdot CH(OH) \cdot COOH$ (phenylglycollic acid), is an example of an aromatic hydroxy-acid containing the hydroxyl-group in the *side-chain*. It may be obtained by boiling amygdalin (which contains benzaldehyde cyanohydrin, combined with glucose, p. 453) with hydrochloric acid, but it is usually prepared by treating benzaldehyde with hydrogen cyanide and hydrolysing the resulting hydroxycyanide, a method analogous to that employed in the synthesis of lactic acid from aldehyde (p. 242),

$$C_6H_5 \cdot CHO + HCN = C_6H_5 \cdot CH(OH) \cdot CN,$$
$$C_6H_5 \cdot CH(OH) \cdot CN + 2H_2O = C_6H_5 \cdot CH(OH) \cdot COOH + NH_3.$$

Mandelic acid melts at 133°, is moderately soluble in water, and shows in many respects the greatest resemblance to lactic acid (methylglycollic acid); when heated with hydriodic acid, for example, it is reduced to *phenylacetic acid* (p. 482), just as lactic acid is reduced to propionic acid (p. 241),

$$C_6H_5 \cdot CH(OH) \cdot COOH + 2HI = C_6H_5 \cdot CH_2 \cdot COOH + I_2 + H_2O.$$

The character of the hydroxyl-group in mandelic acid is, in fact, quite similar to that of the hydroxyl-group in the fatty hydroxy-acids and in the alcohols, so that there are many points of difference between mandelic acid and acids such as salicylic acid, which contain the hydroxyl-group united with carbon of the nucleus. When, for example, *ethyl mandelate*, $C_6H_5 \cdot CH(OH) \cdot COOC_2H_5$, is treated with caustic alkalis it does *not* yield an alkali derivative, but the hydrogen of the hydroxyl-group *is* displaced when the ester is treated with sodium or potassium.

Mandelic acid, like lactic acid, exists in optically different forms. The synthetical acid (m.p. 118°) is optically inactive, but the acid (m.p. 133°) prepared from amygdalin is levorotatory.

CHAPTER XXXII.

Naphthalene and its Derivatives.

All the aromatic hydrocarbons hitherto described, with the exception of diphenyl, diphenylmethane, and triphenylmethane (p. 379), contain only *one* closed-chain of six carbon atoms, and are very closely and directly related to benzene; most of them may be prepared from benzene, and reconverted into this hydrocarbon, by comparatively simple reactions, so that they may all be classed as benzene derivatives. The exceptions just mentioned are also related to benzene, but at the same time they might be regarded as hydrocarbons of quite another class, since diphenyl and diphenylmethane contain two, and triphenylmethane contains three, closed-chains of six carbon atoms. There are, in fact, numerous classes or types of aromatic hydrocarbons, and, just as benzene is the parent substance of a vast number of derivatives, so also other hydrocarbons form the starting-points of other homologous series.

The hydrocarbons *naphthalene* and *anthracene*, which are now to be described, are perhaps second only to benzene in importance; each is the parent substance of a great number of compounds, many of which are extensively employed in the manufacture of dyes.

Naphthalene, $C_{10}H_8$, occurs in coal-tar in larger quantities than any other hydrocarbon, and is easily isolated from this source in a pure condition. The crystals of crude naphthalene, which are deposited from the fraction of coal-tar passing over between 170° and 230° (p. 337), are first pressed to get rid of liquid impurities, then washed with caustic soda, and finally warmed with a small quantity of concentrated sulphuric acid, which converts most of the foreign substances into soluble sulphonic acids; the naphthalene is then distilled or sublimed.

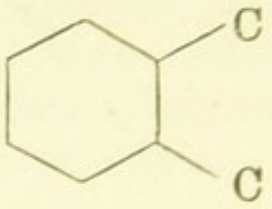
Naphthalene crystallises in large, lustrous plates, melts at 79°, and boils at 218°. It has a highly characteristic smell,

and is extraordinarily volatile, considering its high molecular weight—so much so, in fact, that only part of the naphthalene in crude coal-gas is deposited in the condensers (p. 335); the rest is carried forward into the purifiers, and even into the gas-mains, where in cold weather it is deposited in crystals and frequently causes stoppages at the bends of the pipes. It is insoluble in water, but dissolves freely in hot alcohol and ether, from either of which it may be crystallised. Like many other aromatic hydrocarbons, it combines with picric acid when the two substances are dissolved together in alcohol, forming *naphthalene picrate*, $C_{10}H_8,C_6H_2(NO_2)_3\cdot OH$, a yellow crystalline compound which melts at 149°.

As the vapour of naphthalene burns with a highly luminous flame, the hydrocarbon is used to some extent for carburetting coal-gas—that is to say, for increasing its illuminating power; for this purpose the gas is passed through a vessel which contains coarsely powdered naphthalene, gently heated by the gas-flame, so that the hydrocarbon volatilises and burns with the gas. Naphthalene is also employed as a disinfectant, but its principal use is for the manufacture of a number of derivatives which are employed in the colour industry.

Constitution.—Naphthalene has the characteristic properties of an aromatic compound—that is to say, its behaviour under various conditions is similar to that of benzene and its derivatives, and different from that of fatty compounds; when treated with nitric acid, for example, it yields *nitro*-derivatives, and with sulphuric acid it gives *sulphonic acids*. This similarity between benzene and naphthalene at once suggests a resemblance in constitution, a view which is confirmed by the fact that naphthalene, like benzene, is a very stable compound, and is resolved into simpler substances only with difficulty. When, however, naphthalene is boiled with dilute nitric or chromic acid, or heated with sulphuric acid (p. 478), it is slowly oxidised, yielding carbon dioxide, water, and (*ortho*-)phthalic acid, $C_6H_4(COOH)_2$.

Now the formation of phthalic acid in this way is a fact of very great importance, since it is a proof that the molecule of naphthalene contains the group,

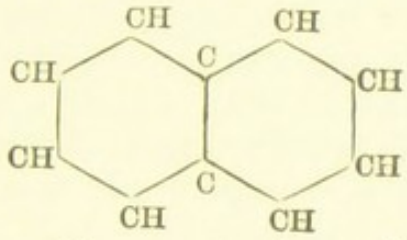
$C_6H_4<\begin{matrix}C\\C\end{matrix}$ or 

—that is to say, that it contains a benzene nucleus to which two carbon atoms are united in the *ortho*-position to one another. This fact alone, however, is insufficient to establish the constitution of the hydrocarbon, since there are still two atoms of carbon and four of hydrogen to be accounted for, and there are many different ways in which these might be united with the $C_6H_4<\begin{matrix}C\\C\end{matrix}$ group.

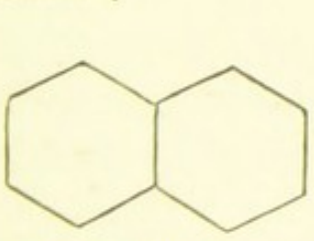
Clearly, therefore, it is important to ascertain the structure of that part of the naphthalene molecule which has been oxidised to carbon dioxide and water—to obtain, if possible, some decomposition product of known constitution, in which these carbon and hydrogen atoms are retained in their original state of combination.

Now this can be done in the following way :—When *nitronaphthalene*, $C_{10}H_7 \cdot NO_2$, a simple mono-substitution product of the hydrocarbon, is boiled with dilute nitric acid, it yields *nitrophthalic acid*, $C_6H_3(NO_2)(COOH)_2$; naphthalene, therefore, contains a benzene nucleus, and the nitro-group in nitronaphthalene is combined with this nucleus. If, however, the *same* nitronaphthalene is reduced to *aminonaphthalene*, $C_{10}H_7 \cdot NH_2$, and the latter is oxidised, *phthalic acid* (and not aminophthalic acid) is obtained. This last fact can only be explained on the assumption either that the benzene nucleus, which is known to be united with the amino-group, has been destroyed, or that the amino-group has been displaced by *hydrogen* during oxidation. Since, however, the latter alternative is contrary to all experience, the former must be

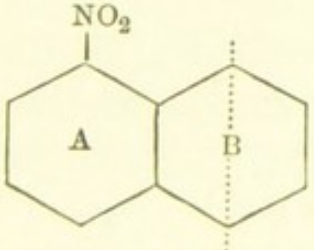
accepted, and it must be concluded that the benzene nucleus which is contained in the oxidation product of aminonaphthalene is *not the same* as that present in the oxidation product of nitronaphthalene; in other words, different parts of the naphthalene molecule have been oxidised to carbon dioxide and water in the two cases, and yet in both these reactions the group, $C_6H_4<\overset{C}{\underset{C}{}}$, remains. The constitution of naphthalene, therefore, must be expressed by the formula,



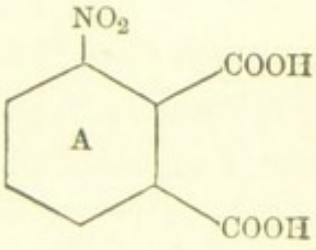
The necessity for this conclusion will be obvious if the above changes are represented with the aid of this formula. When nitronapthalene is oxidised, the nucleus, B (see below), which does not contain the nitro-group, is destroyed (as indicated by the dotted lines), the product being nitrophthalic acid; when, on the other hand, aminonaphthalene is oxidised, the nucleus, A, combined with the amino-group, is attacked, the amino-group is oxidised and eliminated, and phthalic acid is formed,



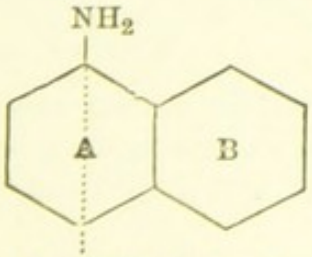
Naphthalene.



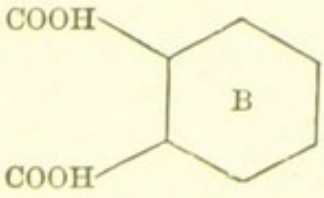
Nitronaphthalene.



Nitrophthalic Acid.



Aminonaphthalene.



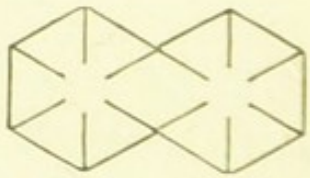
Phthalic Acid.

The constitution of naphthalene was first established in this way by Graebe in 1880, although the above formula

had been suggested by Erlenmeyer as early as 1866; that the hydrocarbon is composed of two closed-chains of six carbon atoms *condensed** together in the o-position, as shown above, has since been confirmed by syntheses of naphthalene and its derivatives, but even more conclusively by the study of the isomerism of its substitution products.

The difficulty of determining and of expressing the actual state or disposition of the fourth unit of valency of each of the carbon atoms in naphthalene is just as great as in the case of benzene. If the carbon atoms are represented as united by alternate double linkings, as in the formula on the left-hand side (see below), there is the objection that the carbon atoms do not show, as indicated, the behaviour of those in fatty unsaturated compounds, as explained more fully in the case of benzene. For this reason the formula on the right-hand side (see below) has been suggested as perhaps preferable, the lines drawn towards the centres of the nuclei having the same significance as in the centric formula for benzene (p. 346). The simple, double-hexagon formula given above is usually employed for the sake of convenience.





Naphthalene may be obtained synthetically by passing the vapour of *phenylbutylene*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$† (or of *phenylbutylene dibromide*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CHBr \cdot CH_2Br$), over red-hot lime; the change involves loss of hydrogen, as in the formation of other aromatic, from fatty, hydrocarbons (p. 340),

$$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2 = C_6H_4 \begin{matrix} CH{:}CH \\ | \\ CH{:}CH \end{matrix} + 2H_2.$$

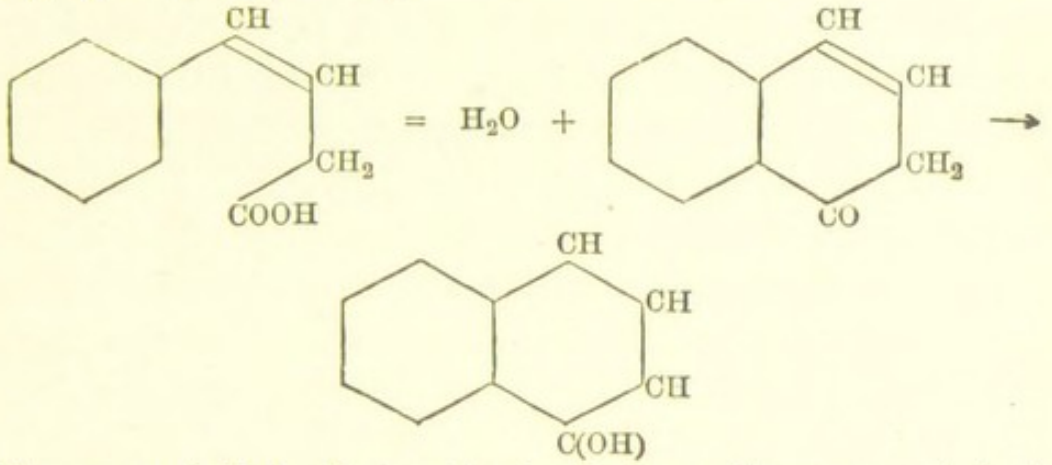
* The term *condensed* used in this and in similar cases signifies that certain carbon atoms are contained in, or are common to, both nuclei.

† *Phenylbutylene* is obtained by treating a mixture of benzyl chloride and allyl iodide with sodium,

$$C_6H_5 \cdot CH_2Cl + CH_2I \cdot CH{:}CH_2 + 2Na = C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2 + NaCl + NaI.$$

It is a liquid, boiling at 178°, and, like butylene, it combines directly with one molecule of bromine, yielding the dibromide.

A most important synthesis of naphthalene was accomplished by Fittig, who showed that *α-naphthol* (α-hydroxynaphthalene) is formed when phenylisocrotonic acid (p. 484) is heated at about 300°. This change probably takes place in two stages, the first product being a keto-derivative of naphthalene, which passes into α-naphthol by intramolecular change (compare p. 205),



The α-naphthol thus obtained may be converted into naphthalene by distillation with zinc-dust, just as phenol may be transformed into benzene (p. 370).

Isomerism of Naphthalene Derivatives.—As in the case of benzene, the study of the isomerism of the substitution products of naphthalene affords the most convincing evidence in favour of the structural formula given above. In the first place, naphthalene differs from benzene in yielding *two* isomeric *mono*-substitution products; there are, for example, two *monochloronaphthalenes*, two *monohydroxynaphthalenes*, two *mononitronaphthalenes*, &c. This fact is readily accounted for with the aid of the above constitutional formula, which may be conveniently written,



(numbered or lettered as shown, the symbols C and H being omitted for the sake of simplicity), and which shows that the eight hydrogen atoms are not all similarly situated

relatively to the rest of the molecule. If, for example, the hydrogen atom (1) were displaced by chlorine, hydroxyl, &c., the substitution product would not be identical with the corresponding compound produced by the displacement of the hydrogen atom (2). In the first case the substituent would be united with a carbon atom, which is itself directly combined with one of the carbon atoms common to both nuclei, whereas in the other case this would not be so. Further, it will be seen that no more than *two* such isomerides could be obtained, because the positions 1.4.1′.4′ (the four α-positions) are identical, and so also are the positions 2.3.2′.3′ (the four β-positions). Clearly, then, the fact that the *mono*-substitution products of naphthalene exist in *two* isomeric forms is in accordance with the above constitutional formula; these isomeric mono-substitution products are usually distinguished with the aid of the letters α and β.

When *two* hydrogen atoms in naphthalene are displaced by two identical groups or atoms, *ten* isomeric di-derivatives may be obtained. The positions of the substituents being indicated by the numerals already used, these isomerides would be,

1:2, 1:3, 1:4, 1:4′, 1:3′, 1:2′, 1:1′, 2:3, 2:3′, 2:2′,

and all other possible positions would be identical with one of these; 2:4′, for example, is the same as 1:3′, 2′:4 and 3:1′, and 1′:4 is identical with 1:4′. The constitution of such a di-derivative is usually expressed with the aid of numerals in this manner, as it is necessary to show whether the substituents are combined with the same or with different nuclei.

When the two atoms or groups are present in one and the same nucleus, their relative position is similar to that of groups in the o-, m-, or p-position in benzene. The positions 1:2, 2:3, and 3:4 correspond with the *ortho*-, 1:3 and 2:4 with the *meta*-, and 1:4 with the *para*-position, and similarly in the case of the other nucleus. The position 1:1′ or 4:4′, however, is different from any of these, and is termed

the *peri*-position; groups thus situated behave in much the same way as those in the o-position in the benzene and naphthalene nuclei.

Derivatives of Naphthalene.

The *homologues of naphthalene*—that is to say, its *alkyl substitution products*—are of comparatively little importance; they may be prepared from the parent hydrocarbon by methods similar to those employed in the case of the corresponding benzene derivatives, as, for example, by treating naphthalene with alkyl halogen compounds in presence of aluminium chloride,

$$C_{10}H_8 + C_2H_5I = C_{10}H_7 \cdot C_2H_5 + HI,$$

and by treating the bromonaphthalenes with an alkyl halogen compound and sodium,

$$C_{10}H_7Br + CH_3Br + 2Na = C_{10}H_7 \cdot CH_3 + 2NaBr.$$

α-Methylnaphthalene, $C_{10}H_7 \cdot CH_3$, is a colourless liquid, boiling at 240–242°, but *β-methylnaphthalene* is a solid, melting at 32°, and boiling at 242°; both these hydrocarbons occur in coal-tar.

The *halogen mono-substitution products* of naphthalene are also of little importance. They may be obtained by treating the hydrocarbon, at its boiling-point, with the halogens (chlorine and bromine), but only the α-derivatives are formed in this way. Both the α- and the β-compounds may be obtained by treating the corresponding naphthols (p. 507), or, better, the naphthalenesulphonic acids (p. 509), with pentachloride or pentabromide of phosphorus,

$$C_{10}H_7 \cdot SO_3H + PCl_5 = C_{10}H_7 \cdot SO_2Cl + POCl_3 + HCl,$$
$$C_{10}H_7 \cdot SO_2Cl + PCl_5 = C_{10}H_7Cl + POCl_3 + SOCl_2;$$

also by converting the naphthylamines (p. 506) into the corresponding diazonium-compounds, and decomposing the latter with a halogen cuprous salt or with copper powder (pp. 414, 416),

$$C_{10}H_7 \cdot NH_2 \rightarrow C_{10}H_7 \cdot N_2Cl \rightarrow C_{10}H_7Cl.$$

All these methods correspond with those described in the case of the halogen derivatives of benzene, and are carried out practically in a similar manner.

α-Chloronaphthalene, $C_{10}H_7Cl$, is a liquid, boiling at about 263°, but the *β-derivative* is a crystalline substance, melting at 56°, and boiling at 265°.

α-Bromonaphthalene, $C_{10}H_7Br$, is also a liquid at ordinary temperatures, and boils at 279°, but the *β-derivative* is crystalline, and melts at 59°.

The chemical properties of these, and of other halogen derivatives of naphthalene, are similar to those of the halogen derivatives of benzene; the halogen atoms are very firmly combined, and cannot be displaced by hydroxyl-groups with the aid of aqueous alkalis, &c.

Naphthalene tetrachloride, $C_{10}H_8Cl_4$, is an important halogen *additive product*, which is produced when chlorine is passed into coarsely powdered naphthalene, at ordinary temperatures. It forms large colourless crystals, melts at 182°, and is converted into *dichloronaphthalene*, $C_{10}H_6Cl_2$ (a substitution product of naphthalene), when it is heated with alcoholic potash; it is readily oxidised by nitric acid, yielding phthalic and oxalic acids, a fact which shows that all the chlorine atoms are present in one and the same nucleus; the constitution of the compound, therefore, is expressed by the formula, $C_6H_4\begin{<}{CHCl\cdot CHCl}{CHCl\cdot CHCl}\begin{>}$.

The formation of this additive product shows that naphthalene, like benzene, is not really a saturated compound, although it usually behaves as such. Many other compounds, formed by the reduction of naphthalene derivatives with sodium and boiling amyl alcohol, are known; when one of the nuclei is thus reduced, the atoms or groups directly united with it acquire the properties which they have in fatty compounds, whereas those united to the unreduced nucleus retain the properties which they have in simple substitution products of benzene. The amino-group in ac.-*tetrahydro-β-naphthylamine* of the constitution, $C_6H_4\begin{<}{CH_2\cdot CH\cdot NH_2}{CH_2\cdot CH_2}$, for example, has the same

character as that in fatty amines, whereas in the case of the isomeric **ar.**-*tetrahydro-β-naphthylamine*, $NH_2 \cdot C_6H_3 \begin{matrix} CH_2 \cdot CH_2 \\ \quad\quad\quad | \\ CH_2 \cdot CH_2 \end{matrix}$, the amino-group has the same properties as that in aniline, because it is combined with the unreduced nucleus. Such tetrahydro-derivatives of naphthalene are distinguished by the prefixes **ar.**- (aromatic) or **ac.**- (alicylic), according as the substituent is contained in the unreduced or in the reduced nucleus. α-Naphthylamine and α-naphthol are reduced to **ar.**-tetrahydro-compounds, but β-naphthylamine and β-naphthol give the **ac.**-tetrahydro-compounds as principal products, and smaller quantities of the **ar.**-tetrahydro-derivatives. **ar.**-Tetrahydronaphthol is phenolic in character, but the **ac.**-isomeride has the properties of an aliphatic alcohol.

Nitro-Derivatives.—Naphthalene, like benzene, is readily acted on by concentrated nitric acid, yielding nitro-derivatives, one, two, or more atoms of hydrogen being displaced according to the concentration of the acid and the temperature at which the reaction is carried out; the presence of sulphuric acid facilitates nitration. The chemical properties of the nitro-naphthalenes are in nearly all respects similar to those of the nitro-benzenes.

α-Nitronaphthalene, $C_{10}H_7 \cdot NO_2$, is best prepared in small quantities by dissolving naphthalene in acetic acid, adding concentrated nitric acid, and then heating the solution on a water-bath during half-an-hour; the product is poured into water, and the nitronaphthalene is purified by recrystallisation from alcohol. On the large scale it is prepared by treating naphthalene with nitric and sulphuric acids, the method being similar to that employed in the case of nitrobenzene (p. 394). It crystallises in yellow prisms, melts at 61°, and boils at 304°; on oxidation with nitric acid, it yields nitrophthalic acid (p. 499).

β-Nitronaphthalene is not formed by nitrating naphthalene, but it may be prepared by dissolving *β-nitro-α-naphthylamine* (a compound obtained by treating α-naphthylamine with *dilute* nitric acid) in an alcoholic solution of hydrogen chloride,

adding finely divided sodium nitrite, and then heating the solution of the diazonium-compound (compare p. 414),

$$C_{10}H_6(NO_2)\cdot N_2Cl + C_2H_5\cdot OH = C_{10}H_7\cdot NO_2 + N_2 + HCl + C_2H_4O.$$

It crystallises in yellow needles, melting at 79°.

The **amino-derivatives** of naphthalene are very similar in properties to the corresponding benzene derivatives, except that even the monamino-compounds are crystalline solids. They have a neutral reaction to litmus, and yet are distinctly basic and form salts with acids; these salts, however, are hydrolysed to some extent by water, and are decomposed by the hydroxides and carbonates of the alkalis. The amino-compounds may be converted into diazonium-compounds, aminoazo-compounds, &c., by reactions similar to those employed in the case of the amino-benzenes, and many of the substances obtained in this way, as well as the amino-compounds themselves, are extensively employed in the manufacture of dyes.

α-**Naphthylamine**, $C_{10}H_7\cdot NH_2$, may be obtained by heating *α-naphthol* with ammonio-zinc chloride or ammonio-calcium chloride * at 250°,

$$C_{10}H_7\cdot OH + NH_3 = C_{10}H_7\cdot NH_2 + H_2O,$$

but it is best prepared by reducing *α-nitronaphthalene* with iron-filings and acetic acid,

$$C_{10}H_7\cdot NO_2 + 6H = C_{10}H_7\cdot NH_2 + 2H_2O.$$

It is a colourless, crystalline substance, melting at 50°, and boiling at 300°; it has a disagreeable smell, turns red on

* Prepared by passing ammonia over anhydrous zinc chloride or calcium chloride. These compounds decompose when they are heated, giving ammonia, and, therefore, are conveniently employed in many reactions requiring the presence of ammonia at high temperatures; the chloride of zinc or calcium resulting from their decomposition also favours the reaction in those cases in which water is formed, as both substances are powerful dehydrating agents. Ammonium acetate may be employed for a similar purpose, as it dissociates at comparatively low temperatures, but its action is less energetic.

exposure to the air, and its salts give a blue precipitate with ferric chloride and other oxidising agents. On oxidation with a boiling solution of chromic acid, it is converted into *α-naphthaquinone* (p. 510).

β-**Naphthylamine** is not prepared from *β*-nitronaphthalene (as this substance is itself only obtained with difficulty), but by heating *β-naphthol* with ammonium chloride and caustic soda at 160° under pressure. It crystallises in colourless plates, melts at 112°, and boils at 294°; it differs markedly from α-naphthylamine in being odourless, and its salts give no colouration with ferric chloride. On oxidation with potassium permanganate, it yields phthalic acid.

The two **naphthols**, or monohydroxy-derivatives of naphthalene, correspond with the monohydric phenols, and are compounds of considerable importance, as they are extensively employed in the colour industry. They both occur in coal-tar, but only in small quantities, and, therefore, are prepared either by diazotising the corresponding naphthylamines,

$$C_{10}H_7\cdot NH_2 \longrightarrow C_{10}H_7\cdot N_2Cl \longrightarrow C_{10}H_7\cdot OH,$$

or by fusing the corresponding sulphonic acids with caustic soda (compare p. 435),

$$C_{10}H_7\cdot SO_3Na + NaOH = C_{10}H_7\cdot OH + Na_2SO_3.$$

Their properties, on the whole, are very similar to those of the phenols, and, like the latter, they dissolve in caustic alkalis, yielding metallic derivatives, which are decomposed by carbonic acid; the hydrogen of the hydroxyl-group in the naphthols may also be displaced by an acetyl- or an alkyl-group, just as in phenols, and on treatment with pentachloride or pentabromide of phosphorus, a halogen atom is substituted for the hydroxyl-group. The naphthols further resemble the phenols in giving colour reactions with ferric chloride.

In some respects, however, the naphthols differ from the phenols, inasmuch as the hydroxyl-groups in the former more readily undergo change; when, for example, a naphthol is heated with ammonio-zinc chloride at 250°, it is converted into the corresponding amino-

compound (see above), whereas the conversion of phenol into aniline requires a temperature of 300–350°, other conditions remaining the same. Again, when a naphthol is heated with an alcohol and hydrogen chloride, it is converted into an alkyl-derivative, whereas alkyl-derivatives of phenols cannot, as a rule, be obtained in this way. In some respects the naphthols form, as it were, a connecting-link between the phenols and the alcohols.

α-Naphthol, $C_{10}H_7 \cdot OH$, is formed, as previously stated (p. 501), when phenylisocrotonic acid is heated at about 300°, an important synthesis, which proves that the hydroxyl-group is in the α-position; it is prepared from *α-naphthylamine* or from *naphthalene-α-sulphonic acid* (p. 509). It is a colourless, crystalline substance, melting at 95°, and boiling at 280°; it has a faint smell, recalling that of phenol, and it dissolves freely in alcohol and ether, but is only sparingly soluble in hot water. Its aqueous solution gives with ferric chloride a violet, flocculent precipitate, consisting probably of an iron compound of *α-di-naphthol*, $HO \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot OH$, an oxidation product of the naphthol.

α-Naphthol, like phenol, is very readily acted on by nitric acid, yielding a *dinitro*-derivative, $C_{10}H_5(NO_2)_2 \cdot OH$, which crystallises in yellow needles, and melts at 138°. This nitro-compound, like picric acid, has a much more strongly marked acid character than the hydroxy-compound from which it is derived, and decomposes carbonates, forming deep-yellow salts which dye silk a beautiful golden yellow; its sodium derivative, $C_{10}H_5(NO_2)_2 \cdot ONa, H_2O$, is known commercially as *Martius' yellow*, or *naphthalene yellow*. Another dye obtained from α-naphthol is *naphthol yellow* (p. 662), the potassium salt of *dinitro-α-naphtholsulphonic acid*, $C_{10}H_4(NO_2)_2(OK) \cdot SO_3K$; the acid itself is manufactured by nitrating *α-naphtholtrisulphonic acid* (prepared by heating α-naphthol with anhydrosulphuric acid), in which process two of the sulphonic groups are displaced by nitro-groups.

β-Naphthol, prepared by fusing *naphthalene-β-sulphonic acid* with potash, melts at 122°, and boils at 286°; it is a

colourless, crystalline compound, readily soluble in hot water, and, like the α-derivative, it has a faint, phenol-like smell. Its aqueous solution gives, with ferric chloride, a green colouration and a flocculent precipitate of *β-di-naphthol*, $HO{\cdot}C_{10}H_6{\cdot}C_{10}H_6{\cdot}OH$.

Sulphonic Acids.—Perhaps the most important derivatives of naphthalene, from a commercial point of view, are the various mono- and di-sulphonic acids, which are obtained from the hydrocarbon itself, from the naphthylamines, and from the naphthols, and used in large quantities in the manufacture of dyes. It would be of little use to describe here the very numerous compounds of this class, but some indication of their properties may be afforded by a brief statement of the more important facts.

Naphthalene is readily sulphonated, yielding two *monosulphonic acids*, $C_{10}H_7{\cdot}SO_3H$—namely, the α- and β-compounds, both of which are formed when the hydrocarbon is heated with anhydrosulphuric acid at 80°; if, however, the operation is carried out at 200°, only the β-acid is obtained, because at this temperature the α-acid is converted into the β-acid by intramolecular change, just as phenol-o-sulphonic acid is transformed into the p-acid at 110° (p. 443). The two naphthalenesulphonic acids are crystalline hygroscopic substances, and show all the characteristic properties of acids of this class.

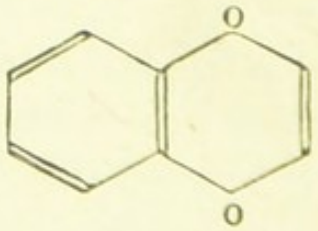
Di-sulphonic acids may be obtained by strongly heating naphthalene with anhydrosulphuric acid.

Fourteen isomeric *naphthylaminemonosulphonic acids*, $C_{10}H_6(NH_2){\cdot}SO_3H$, may theoretically be obtained—namely, seven from α-naphthylamine, and seven from the β-base; as a matter of fact, nearly all these acids are known. The most important, perhaps, is 1:4-*naphthylaminemonosulphonic acid*, or *naphthionic acid*, which is the sole product of the action of sulphuric acid on α-naphthylamine; it is a crystalline compound, very sparingly soluble in cold water, and is used in the manufacture of Congo red and other dyes (p. 661).

The *naphtholmonosulphonic acids* correspond in number with the naphthylaminemonosulphonic acids, and are also extensively used in the colour industry.

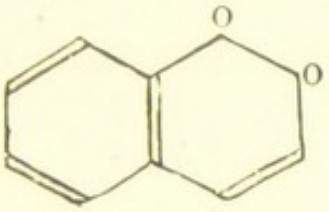
α-Naphthaquinone, $C_{10}H_6O_2$, is a derivative of naphthalene, corresponding with (**p**-benzo)quinone, and, like the latter, it is formed when various mono- and di-substitution products of the hydrocarbon (but only those in which the substituent groups occupy the α-positions) are oxidised with sodium dichromate and sulphuric acid; *α-naphthylamine*, 1:4-*aminonaphthol*, and 1:4-*diaminonaphthalene*, for example, may be employed. As a rule, however, naphthalene itself is oxidised with a boiling solution of chromic acid in acetic acid (a method not applicable for the preparation of quinone from benzene), as the product is then easily obtained in a state of purity.

α-Naphthaquinone crystallises from alcohol in deep-yellow needles, melting at 125°; it resembles quinone in colour, in having a curious pungent smell, and in being very volatile, subliming readily even at 100°, and distilling rapidly in steam. Unlike quinone, it is not reduced by sulphurous acid, but some reducing agents convert it into 1:4-*dihydroxynaphthalene*, $C_{10}H_6(OH)_2$, just as quinone is transformed into quinol (p. 465). This close similarity in properties clearly points to a similarity in constitution, so that α-naphthaquinone may be represented by the formula,



β-Naphthaquinone, $C_{10}H_6O_2$, isomeric with the α-compound, is formed when α-amino-β-naphthol is oxidised with potassium dichromate and dilute sulphuric acid, or with ferric chloride; it crystallises in red needles, decomposes at about 115° without melting, and on reduction with sulphurous acid, is converted into 1:2-*dihydroxynaphthalene*. It differs from

α-naphthaquinone and from quinone in colour, in having no smell, and in being non-volatile, properties which, though apparently insignificant, are of some importance, as they distinguish *ortho*-quinones from *para*-quinones; the latter are generally deep-yellow, volatile compounds, having a pungent odour, whereas the former are red, non-volatile, and odourless. β-Naphthaquinone is an ortho-quinone corresponding with o-benzoquinone (p. 467), and its constitution may be represented by the formula,



Both α- and β-naphthaquinone are oxidised by nitric acid, giving o-phthalic acid, a proof that in both compounds the two oxygen atoms are united with only one nucleus; that the one is a *para*-, the other an *ortho*-quinone is also established by their methods of formation, &c., but the exact disposition of the various carbon valencies is unknown.

The above description of some of the more important naphthalene derivatives will be sufficient to show the close relationship which these compounds bear to the corresponding derivatives of benzene; they are prepared, as a rule, by the same methods as their analogues of the benzene series, and resemble the latter closely in chemical properties; consequently all general reactions and generic properties of benzene derivatives are met with again in the case of naphthalene compounds.

CHAPTER XXXIII.

Anthracene and Phenanthrene.

Anthracene, $C_{14}H_{10}$, is a hydrocarbon of great commercial importance, as it is the starting-point in the manufacture of alizarin, the colouring matter employed in producing Turkey-red dye; it is prepared exclusively from coal-tar. The crude mixture of hydrocarbons and other substances known as '50 per cent. anthracene' (p. 338) is further purified by treatment with various solvents (which extract phenanthrene, &c.), and is then distilled in superheated steam, or recrystallised from pyridine.

Crude anthracene contains, in addition to phenanthrene and other hydrocarbons, considerable quantities of carbazole, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$, a colourless, crystalline substance, melting at 238°, and boiling at 355°.

Anthracene crystallises from benzene in colourless, lustrous plates, which show a beautiful blue fluorescence; it melts at 213°, boils at 351°, and dissolves freely in boiling benzene, but is only sparingly soluble in alcohol and ether. Saturated alcoholic solutions of anthracene and of picric acid, when mixed, give a precipitate of *anthracene picrate*, $C_{14}H_{10},C_6H_2(NO_2)_3\cdot OH$, which crystallises in ruby-red needles, melting at 138°; this compound is resolved into its components when it is treated with a large quantity of alcohol (distinction from phenanthrene picrate, p. 523).

Constitution. — The molecular formula of anthracene ($C_{14}H_{10}$) suggests that this hydrocarbon is related to benzene (C_6H_6), naphthalene ($C_{10}H_8$), and other *closed-chain* compounds, rather than to hydrocarbons of the aliphatic series. The behaviour of anthracene towards chlorine and

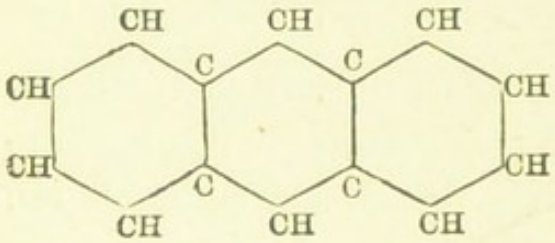
bromine is also, on the whole, similar to that of benzene and naphthalene—that is to say, anthracene yields additive or substitution products according to the conditions; moreover, towards concentrated sulphuric acid it behaves like other aromatic compounds, and is converted into sulphonic acids. When treated with nitric acid, however, instead of yielding a nitro-derivative, as might have been expected, it is oxidised to anthraquinone, $C_{14}H_8O_2$, two atoms of hydrogen being displaced by two atoms of oxygen; this change always takes place, even when dilute nitric acid, or some other oxidising agent, is employed.

Now, the conversion of anthracene into anthraquinone is not only closely analogous to that of naphthalene, $C_{10}H_8$, into α-naphthaquinone, $C_{10}H_6O_2$ (p. 510), but is also an oxidation process of a kind (namely, the substitution of oxygen atoms for an *equal* number of hydrogen atoms) which is unknown in the case of fatty (open-chain) hydrocarbons; anthracene, therefore, is a closed-chain compound. Another highly important fact, bearing on the constitution of anthracene, is that, although the hydrocarbon and most of its derivatives are resolved into simpler substances only with very great difficulty, when this does occur one of the products is always some benzene derivative, usually phthalic acid.

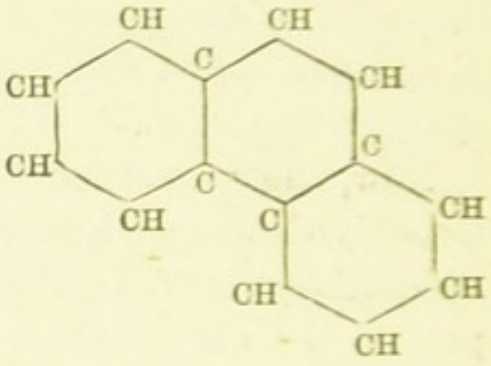
Now, if the molecule of anthracene contained only one benzene nucleus, or even if, like naphthalene, it contained two condensed benzene nuclei, there would still be certain carbon and hydrogen atoms which would have to be regarded as forming *unsaturated* side-chains; but experience has shown that such side-chains in benzene and in naphthalene are oxidised to carboxyl (compare p. 493) with the utmost facility. Consequently, it is impossible to assume their presence in anthracene, a compound which is always oxidised to the neutral substance anthraquinone, without loss of carbon. Arguments of this kind, therefore, lead to the conclusion that the molecule of anthracene is composed *only* of combined or condensed nuclei; as, moreover, the

hydrocarbon may be indirectly converted into phthalic acid, it must be assumed that two of these nuclei are condensed together in the o-position, as in naphthalene.

If, now, an attempt is made to deduce a constitutional formula for anthracene on this basis, and it is further assumed that all the closed-chains are composed of six carbon atoms, as in naphthalene, the following suggest themselves as probable formulæ,



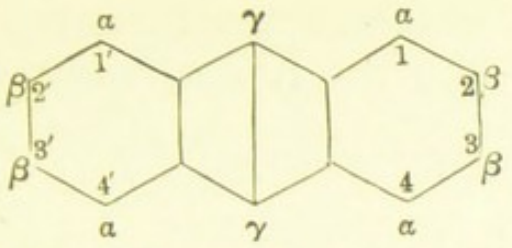
I.



II.

although, of course, neither could be accepted as final without further evidence.

Many facts, however, have led to the conclusion that the constitution of anthracene must be represented by formula I. (formula II. expressing that of phenanthrene, p. 522); this formula accounts satisfactorily for all such facts—amongst others, for a number of important syntheses of the hydrocarbon (see below), for the relation of anthracene to anthraquinone, and for the isomerism of the anthracene derivatives. It is, nevertheless, just as difficult to determine and to express the actual disposition of the fourth valency unit of each carbon atom in anthracene as in the cases of benzene and naphthalene; as, however, there are reasons for supposing that the state of combination of the two central CH groups (that is, those which form part of the central nucleus only) is different from that of all the others (inasmuch as they are generally attacked first), and that the two carbon atoms of these groups are directly united, the above formula (I.) is usually written,



or $C_6H_4\begin{<}{}^{CH}_{CH}{>}C_6H_4$,

the disposition of the carbon valencies in the two $C_6H_4<$ groups being taken to be the same as in the centric formula for benzene.*

Anthracene may be obtained synthetically in various ways. It is produced when benzyl chloride is heated with aluminium chloride,

$$3C_6H_5\cdot CH_2Cl = C_6H_4\begin{<}{}^{CH}_{CH}{>}C_6H_4 + C_6H_5\cdot CH_3 + 3HCl,$$

the *hydranthracene* (p. 516), which is formed as an intermediate product,

$$C_6H_4\begin{<}{}^{H}_{CH_2Cl} + {}^{ClCH_2}_{H}\!>C_6H_4 = C_6H_4\begin{<}{}^{CH_2}_{CH_2}\!>C_6H_4 + 2HCl,$$

being converted into anthracene by loss of hydrogen, which reduces part of the benzyl chloride to toluene (as expressed in the first equation). Anthracene is also formed, together with hydranthracene and phenanthrene (p. 524), when o-*bromobenzyl bromide* (prepared by brominating *boiling* o-*bromotoluene*, $C_6H_4Br\cdot CH_3$) is treated with sodium,

$$2C_6H_4\begin{<}{}^{CH_2Br}_{Br} + 4Na = C_6H_4\begin{<}{}^{CH_2}_{CH_2}\!>C_6H_4 + 4NaBr;$$

here, again, *hydranthracene* is the primary product, and from it anthracene is formed by loss of hydrogen.

Another interesting synthesis may be mentioned—namely, the formation of anthracene when a mixture of *tetrabromethane* and benzene is treated with aluminium chloride,

$$C_6H_4\begin{<}{}^{H}_{H} + {}^{BrCHBr}_{BrCHBr} + {}^{H}_{H}\!>C_6H_4 = C_6H_4\begin{<}{}^{CH}_{CH}\!>C_6H_4 + 4HBr.$$

All these methods of formation are accounted for in a simple

* The letters or numerals serve to denote the constitutions of the anthracene derivatives (p. 516).

manner with the aid of the above constitutional formula, the last one especially indicating that the two central carbon atoms are directly united; the formula, $C_6H_4\langle\begin{matrix}CH\\|\\CH\end{matrix}\rangle C_6H_4$, therefore, will be employed in describing the anthracene derivatives.

Isomerism of Anthracene Derivatives.—Further evidence in support of the above constitutional formula is afforded by the study of the isomerism of the substitution products of anthracene, although, in most cases, all the isomerides theoretically possible have not yet been prepared.

When one atom of hydrogen is displaced, *three* isomerides may be obtained, since there are three hydrogen atoms (α, β, γ), all of which are differently situated relatively to the rest of the molecule; these mono-substitution products are usually distinguished by the letters α, β, γ, according to the position of the substituent (compare formula, p. 515). When two atoms of hydrogen are displaced by similar atoms or groups, *fifteen* isomeric di-substitution products may be obtained.

Hydranthracene, $C_6H_4\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle C_6H_4$, a substance of little importance, is formed when anthracene is reduced with boiling concentrated hydriodic acid, or with sodium amalgam and water. It is a colourless, crystalline compound, melting at 106–108°, and when heated with sulphuric acid it is converted into anthracene, the acid being reduced to sulphur dioxide.

Anthracene dichloride, $C_6H_4\langle\begin{matrix}CHCl\\CHCl\end{matrix}\rangle C_6H_4$, like hydranthracene, is an additive product of the hydrocarbon; it is obtained when chlorine is passed into a *cold* solution of anthracene in carbon disulphide, whereas at 100° substitution takes place, with formation of *monochloranthracene* and *dichloranthracene*,

$$C_6H_4\langle\begin{matrix}CCl\\|\\CH\end{matrix}\rangle C_6H_4 \text{ and } C_6H_4\langle\begin{matrix}CCl\\|\\CCl\end{matrix}\rangle C_6H_4;$$

these substitution products crystallise in yellow needles, melting at 103° and 209° respectively, and they are both converted into

anthraquinone on oxidation, a fact which shows the positions of the chlorine atoms.

Anthraquinone, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, is formed, as already mentioned, when anthracene is oxidised with chromic or nitric acid. It is conveniently prepared by dissolving anthracene (1 part) in boiling glacial acetic acid, and gradually adding a concentrated solution of chromic acid (2 parts) in glacial acetic acid. As soon as oxidation is complete the product is allowed to cool, and the anthraquinone, which separates in long needles, is collected and purified either by sublimation, or by recrystallisation from acetic acid.

Anthraquinone is manufactured by oxidising finely divided '50 per cent. anthracene,' suspended in water, with sodium dichromate and sulphuric acid. The crude anthraquinone is collected on a filter, washed, dried, and heated at 100° with 2–3 parts of concentrated sulphuric acid, by which means the impurities are converted into soluble sulphonic acids, whereas the anthraquinone is not acted on. The almost black product is now allowed to stand in a damp place, when the anthraquinone gradually separates in crystals as the sulphuric acid becomes dilute; water is then added, and the anthraquinone is collected, washed, dried, and sublimed.

Anthraquinone may be produced synthetically by treating a solution of *phthalic anhydride* (p. 479) in benzene with aluminium chloride, the reaction taking place in two stages; *o-benzoylbenzoic acid* is first produced,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + C_6H_6 = C_6H_4<\begin{matrix}CO\cdot C_6H_5\\COOH\end{matrix},$$

o-Benzoylbenzoic Acid.

but by the further action of the aluminium chloride (or of sulphuric acid), this substance is converted into anthraquinone with loss of one molecule of water,

$$\underset{A}{C_6H_4}<\begin{matrix}CO\text{—}\\COOH\end{matrix}\diagdown\underset{B}{C_6H_5} = \underset{A}{C_6H_4}<\begin{matrix}CO\\CO\end{matrix}>\underset{B}{C_6H_4} + H_2O.$$

Anthraquinone, therefore, contains two $C_6H_4<$ groups, united by two $CO<$ groups.

That the two CO< groups occupy the o-position in the one benzene ring (A) is known, because they do so in phthalic acid; that they occupy the o-position in the second benzene ring (B) has been proved, as follows:—When *bromophthalic anhydride* is treated with benzene and aluminium chloride, *bromobenzoylbenzoic acid* is produced, and this, when treated with sulphuric acid, yields *bromanthraquinone*,

$$\underset{\text{A}}{C_6H_3Br\!<\!\begin{matrix}CO\\COOH\end{matrix}}\!\!\diagdown\underset{\text{B}}{C_6H_5}=\underset{\text{A}}{C_6H_3Br\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_4}\underset{\text{B}}{}+H_2O.$$

The formation of this substance from bromophthalic acid proves, as before, that the two CO< groups are united to the ring A in the o-position.

Now, when bromanthraquinone is heated with potash at 160°, it is converted into *hydroxyanthraquinone*, $\underset{\text{A}}{C_6H_3(OH)\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_4}\underset{\text{B}}{}$, which, with nitric acid, yields phthalic acid, $\begin{matrix}COOH\\COOH\end{matrix}\!>\!C_6H_4$, the group A being oxidised; therefore the two CO< groups are attached to B, as well as to A, in the o-position, and anthraquinone has the constitution represented above, a conclusion which affords strong support to the above structural formula of anthracene.

Anthraquinone crystallises from glacial acetic acid in pale-yellow needles, melts at 285°, and sublimes at higher temperatures; it is exceedingly stable, and is only with difficulty attacked by oxidising agents, by sulphuric acid, or by nitric acid. In all those properties which are dependent on the presence of the two carbonyl-groups, anthraquinone resembles the aromatic ketones much more closely than it does the p-quinones. It has no smell, is by no means readily volatile, and is not reduced by sulphurous acid; unlike quinone, therefore, it is not an oxidising agent.

When treated with more powerful reducing agents, however, it is converted into *oxanthranol*, $C_6H_4\!<\!\begin{matrix}—CO—\\CH(OH)\end{matrix}\!>\!C_6H_4$, one of the CO< groups becoming >CH·OH, just as in the reduction of ketones; on further reduction the other CO< group undergoes a similar change, but the product, $C_6H_4\!<\!\begin{matrix}CH(OH)\\CH(OH)\end{matrix}\!>\!C_6H_4$, loses one

molecule of water, yielding *anthranol*, $C_6H_4\langle\begin{matrix}C(OH)\\|\\CH\end{matrix}\rangle C_6H_4$, which is finally reduced to *hydranthracene;* when anthraquinone is distilled with zinc-dust, anthracene is produced.

Anthraquinone is only slowly acted on by ordinary sulphuric acid even at 250°, yielding *anthraquinone-β-monosulphonic acid*, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot SO_3H$; but when heated with a large excess of anhydrosulphuric acid at 160–170°, it yields a mixture of isomeric *disulphonic acids*, $C_{14}H_6O_2(SO_3H)_2$.

Sodium anthraquinone-β-monosulphonate, which is used in such large quantities in the manufacture of alizarin (see below), is prepared by heating anthraquinone with an equal weight of anhydrosulphuric acid (containing 50 per cent. of SO_3) in enamelled iron vessels at 160°. The product is diluted with water, filtered from unchanged anthraquinone, and neutralised with soda; the sparingly soluble sodium anthraquinone-β-monosulphonate separates from the cold solution in glistening plates, and is collected in filter-presses. The more soluble sodium salts of the *anthraquinone-disulphonic acids*, which are always formed at the same time, remain in solution.

Test for Anthraquinone.—When a trace of finely divided anthraquinone is heated with dilute caustic soda and a little zinc-dust, an intense red colouration is produced, but when shaken in contact with air, the solution is decolourised. In this reaction *oxanthranol* (p. 518) is formed, and this substance dissolves in the alkali, forming a deep-red solution; on exposure to the air, however, it is oxidised to anthraquinone, which separates as a flocculent precipitate.

Alizarin, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(OH)_2$, or 1:2-*dihydroxyanthraquinone*, occurs in madder (the root of *Rubia tinctorum*), a substance which has been used from the earliest times for dyeing purposes, and which owes its tinctorial properties to two substances, alizarin and purpurin, both of which are present in the root in the form of glucosides.

Ruberythric acid, the glucoside of alizarin, is decomposed when it is boiled with acids, or when the madder extract is

allowed to undergo fermentation, with formation of alizarin and two molecules of glucose,

$$\underset{\text{Ruberythric Acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + 2C_6H_{12}O_6.$$

A dye of such great importance as alizarin naturally attracted the attention of chemists, and many attempts were made to prepare it synthetically. This was first accomplished in 1868 by Graebe and Liebermann, who found that alizarin could be produced by fusing 1:2-*dibromanthraquinone* * with potash,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2Br_2 + 2KOH = C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(OH)_2 + 2KBr,$$

but the process was not a commercial success.

At the present day, however, madder is no longer used, and the whole of the alizarin of commerce is made from (coal-tar) anthracene in the following manner:—

Anthracene is first oxidised to anthraquinone, and the latter is converted into anthraquinone-β-sulphonic acid by the method already described (p. 519); the sodium salt of this acid is then heated with caustic soda and a little potassium chlorate, and is thus converted into the sodium derivative of alizarin,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3\cdot SO_3Na + 3NaOH + O =$$

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(ONa)_2 + 2H_2O + Na_2SO_3;$$

from this sodium salt, alizarin is liberated with the aid of a mineral acid.

When anthraquinonesulphonic acid is fused with caustic soda, the $-SO_3Na$ group is displaced by $-ONa$ in the usual manner, but the *hydroxyanthraquinone* (sodium derivative) thus produced is further acted on by the alkali, giving alizarin (sodium derivative) and (nascent) hydrogen,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3(ONa) + NaOH = C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(ONa)_2 + 2H.$$

* Obtained by heating anthraquinone with bromine and a trace of iodine in a sealed tube at 160°.

The oxidising agent ($KClO_3$) is added in order to prevent the nascent hydrogen from reducing the still unchanged hydroxy-anthraquinone to anthraquinone.

The operation is conducted as follows :—Sodium anthraquinone-sulphonate (100 parts) is heated in a closed iron cylinder, fitted with a stirrer, with caustic soda (300 parts) and potassium chlorate (14 parts), for two days at 180°. The dark-violet product, which contains the sodium salt of alizarin, is dissolved in water, the solution is filtered, if necessary, and the alizarin is precipitated by the addition of hydrochloric acid. The yellowish crystalline precipitate is collected in filter-presses, washed well with water, and sent on the market in the form of a 10 or 20 per cent. paste. From this product alizarin is obtained in a pure state by recrystallisation from toluene, or by sublimation.

Alizarin crystallises and sublimes in dark-red prisms, which melt at 290°, and are almost insoluble in water, but moderately soluble in alcohol. It is a dihydroxy-derivative of anthraquinone, and, therefore, has the properties of a dihydric phenol ; with aqueous solutions of the alkalis it forms metallic derivatives of the type, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OM)_2$, which are soluble in water, yielding intensely purple solutions. With acetic anhydride it gives a *diacetate*, $C_{14}H_6O_2(OAc)_2$, melting at 180°, and when distilled with zinc-dust it is reduced to anthracene.

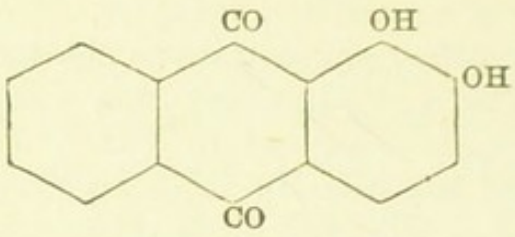
The value of alizarin as a dye lies in the fact that it yields coloured, insoluble compounds ('lakes,' p. 640) with certain metallic oxides ; the ferric compound, for example, is violet-black, the lime compound blue, and the tin and aluminium compounds different shades of red (Turkey-red). A short account of the methods used in dyeing with alizarin is given later (p. 639).

Constitution of Alizarin.—Alizarin may be prepared by heating a mixture of phthalic anhydride and catechol with sulphuric acid at 150°,

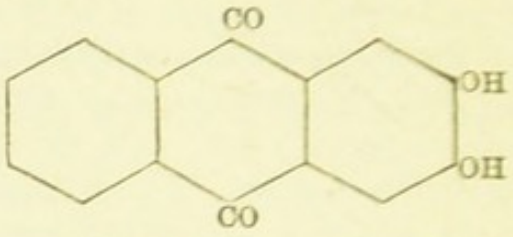
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+C_6H_4<\begin{matrix}OH\\OH\end{matrix}=C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH\\OH\end{matrix}+H_2O.$$

As catechol is o-dihydroxybenzene, it follows that the two

hydroxyl-groups in the product must also be in the o-position to one another; the structure of alizarin, therefore, must be represented by one of the following formulæ :—



I.



II.

Now, alizarin yields two isomeric *mono*-nitro-derivatives, $C_6H_4<^{CO}_{CO}>C_6H(OH)_2\cdot NO_2$, both of which contain the nitro-group in the same nucleus as the two hydroxyl-groups; its constitution, therefore, must be represented by formula I., as a substance having the constitution II. could only yield one such nitro-derivative.

Besides alizarin, several other *dihydroxy-* and also *trihydroxy-anthraquinones* have been obtained, but only those are of value as dyes which contain two hydroxyl-groups in the same positions as in alizarin; two such derivatives, which possess very valuable dyeing properties, may be mentioned.

Purpurin, $C_6H_4<^{CO}_{CO}>C_6H(OH)_3$, or 1:2:4-trihydroxyanthraquinone, is contained in madder, in the form of a glucoside, and may be prepared by oxidising alizarin with manganese dioxide and sulphuric acid. It crystallises in deep-red needles, melts at 253°, and gives, with aluminium mordants, a much yellower shade of red than alizarin; it is used for the production of brilliant reds.

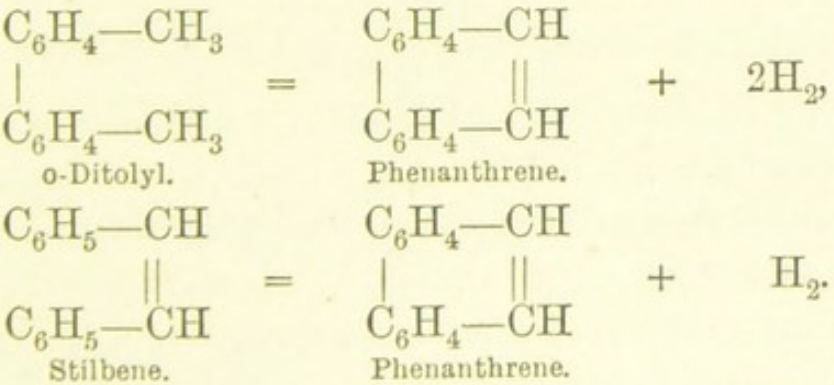
Anthrapurpurin, $C_6H_3(OH)<^{CO}_{CO}>C_6H_2<^{OH_{(1)}}_{OH_{(2)}}$, is isomeric with purpurin, and is manufactured by fusing anthraquinone-disulphonic acid, $C_6H_3(SO_3H)<^{CO}_{CO}>C_6H_3\cdot SO_3H$, with caustic soda and potassium chlorate (p. 521). It crystallises in yellowish-red needles, melts at 330°, and is employed in dyeing yellow shades of Turkey-red.

Phenanthrene, $C_{14}H_{10}$, an isomeride of anthracene, is a hydrocarbon of considerable theoretical interest, although it

has no commercial value. It occurs in large quantities in '50 per cent. anthracene,' from which it may be extracted, as already described (p. 512). The resulting crude phenanthrene is converted into the picrate, which is first recrystallised from alcohol, to free it from anthracene picrate, and then decomposed by ammonia; the hydrocarbon is finally purified by recrystallisation.

Phenanthrene forms lustrous needles, melts at 99°, and distils at about 340°; it is readily soluble in alcohol, ether, and benzene. When oxidised with chromic acid, it is first converted into *phenanthraquinone*, $C_{14}H_8O_2$ (isomeric with anthraquinone), and then into *diphenic acid*, $C_{14}H_{10}O_4$. This acid is decomposed on distillation with lime, yielding carbon dioxide and *diphenyl* (p. 379); it is, therefore, *diphenyldicarboxylic acid*, $COOH \cdot C_6H_4 \cdot C_6H_4 \cdot COOH$, and its formation from phenanthrene shows that the latter contains *two* benzene nuclei.

Further evidence as to the constitution of phenanthrene is obtained by studying its methods of formation. It is formed, for example, when o-*ditolyl* (prepared by treating o-*bromotoluene* with sodium) or *stilbene* * is passed through a red-hot tube; since these two hydrocarbons give the *same* product, the reactions must be expressed as follows :—



* *Stilbene* or *diphenylethylene*, $C_6H_5 \cdot CH{:}CH \cdot C_6H_5$, may be prepared by acting on benzal chloride (p. 390) with sodium,

$$2C_6H_5 \cdot CHCl_2 + 4Na = C_6H_5 \cdot CH{:}CH \cdot C_6H_5 + 4NaCl.$$

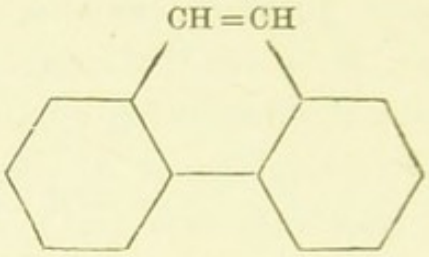
It crystallises in colourless needles, melts at 120°, and, like ethylene, combines with two atoms of bromine, forming *stilbene dibromide*,

$C_6H_5 \cdot CHBr \cdot CHBr \cdot C_6H_5$ (m.p. 237°).

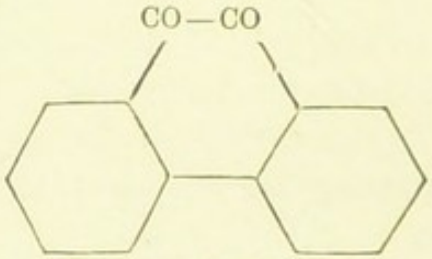
Again, phenanthrene is formed, together with anthracene, by the action of sodium on o-*bromobenzyl bromide* (p. 515),

$$\begin{matrix} Br—C_6H_4—CH_2Br \\ \\ Br—C_6H_4—CH_2Br \end{matrix} + 4Na = \begin{matrix} C_6H_4—CH \\ \vert \quad \Vert \\ C_6H_4—CH \end{matrix} + 4NaBr + H_2.$$

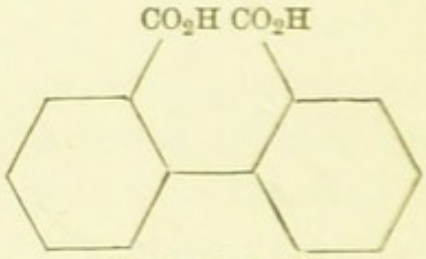
For these and many other reasons, the constitution of phenanthrene is expressed by the formula,



When the hydrocarbon is oxidised to phenanthraquinone, the group, –CH=CH–, becomes –CO—CO–, and on further oxidation to diphenic acid, each carbonyl-group is converted into a carboxyl-group,



Phenanthraquinone.



Diphenic Acid.

Phenanthraquinone, $\begin{matrix} C_6H_4—CO \\ \vert \quad \vert \\ C_6H_4—CO \end{matrix}$, like anthraquinone, is formed by oxidising the hydrocarbon with chromic acid. It crystallises from alcohol in orange needles, and melts at 198°. In chemical properties it shows little resemblance to p-benzoquinone or to α-naphthaquinone, but is more closely related to β-naphthaquinone (p. 510), o-benzoquinone (p. 467), and other ortho-diketones (ortho-quinones); it has no smell, and does not volatilise except when strongly heated, but it is readily reduced by sulphurous acid to *dihydroxyphenanthrene*, $C_{14}H_8(OH)_2$, and it combines with sodium bisulphite, forming a soluble *bisulphite* compound, $C_{14}H_8O_2$, $NaHSO_3$,$2H_2O$; with hydroxylamine it yields a *dioxime*, $C_{12}H_8(C{:}NOH)_2$. The

hydroxy-derivatives of phenanthraquinone, unlike those of anthraquinone, possess no tinctorial properties.

Phenanthraquinone may be readily detected by dissolving a small quantity (0·1 gram) in glacial acetic acid (20 c.c.), adding a few drops of commercial toluene, and then mixing the well-cooled solution with sulphuric acid (1 c.c.). After the lapse of a few minutes, the bluish-green liquid is poured into water and shaken with ether, when the ether acquires an intense reddish-violet colouration. Like the indophenin reaction, this test depends on the formation of a coloured sulphur compound, produced by the condensation of the phenanthraquinone with the *thiotolene*, $C_4H_3S(CH_3)$, which is contained in crude toluene (p. 373).

Diphenic acid, $\begin{matrix} C_6H_4—COOH \\ | \\ C_6H_4—COOH \end{matrix}$, obtained by the oxidation of phenanthrene or of phenanthraquinone with hydrogen peroxide in acetic acid solution, crystallises from water in needles, and melts at 229°. When heated with acetic anhydride it is converted into *diphenic anhydride*, $C_{12}H_8{<}\begin{matrix} CO \\ CO \end{matrix}{>}O$ (m.p. 217°).

This fact is noteworthy, because it shows that anhydride formation may occur even when the two carboxyl-groups are united with *different* benzene nuclei. *Naphthalic acid*, $C_{10}H_6(COOH)_2$, a derivative of naphthalene in which the carboxyl-groups are in the 1:1′- or *peri*-position, also forms an anhydride.

CHAPTER XXXIV.

Pyridine, Quinoline, and Isoquinoline.

Pyridine, *quinoline*, and *isoquinoline* are three very interesting aromatic bases, which, together with their numerous derivatives, form a group of great theoretical interest, and of scarcely less importance than that of the aromatic hydrocarbons; many of these derivatives occur in nature, and

belong to the well-known and important class of compounds termed the 'vegetable alkaloids.'

Coal-tar, though consisting principally of hydrocarbons and phenols, contains also small quantities of *pyridine* and its homologues, *quinoline*, *isoquinoline*, and numerous other basic substances, such as aniline; all these bases are dissolved, in the form of sulphates, in the purification of the hydrocarbons, &c., by treatment with sulphuric acid (compare p. 337), and when the dark acid liquor is afterwards treated with excess of caustic soda, they separate again at the surface of the liquid in the form of a dark-brown oil. By repeated fractional distillation, a partial separation of the various components of this oil may be effected, and crude pyridine, quinoline, &c., may be obtained; on further purification by crystallisation of their salts, or by other methods, some of these bases may be prepared in a state of purity.

Another important source of these compounds is *bone-tar* or *bone-oil*, a dark-brown, unpleasant-smelling liquid formed during the dry distillation of bones in the preparation of bone-black (animal charcoal); this oil contains considerable quantities of *pyridine* and *quinoline*, and their homologues, as well as other bases, and these compounds may be extracted from it with the aid of sulphuric acid, and then separated in the manner mentioned above. Bone-oil, purified by distillation, was formerly used in medicine under the name of *Dippel's oil*.

Pyridine was first obtained from bone-oil. *Quinoline* was first produced by fusing quinine and cinchonine with potash; it is also formed from strychnine under these conditions. *Isoquinoline* was first obtained from coal-tar; derivatives of the base are formed when the alkaloids *papaverine*, *narcotine*, *hydrastine*, &c. are fused with potash.

Pyridine and its Derivatives.

Pyridine, C_5H_5N, is formed during the destructive distillation of various nitrogenous organic substances; hence its presence in coal-tar and in bone-oil.

Pure pyridine is conveniently prepared in small quantities by distilling *nicotinic acid* (p. 533), or other pyridine-carboxylic acid, with soda-lime, just as pure benzene may be prepared from benzoic and phthalic acids in a similar manner,

$$C_5H_4N\cdot COOH = C_5H_5N + CO_2,$$
$$C_5H_3N(COOH)_2 = C_5H_5N + 2CO_2.$$

For commercial purposes it is usually prepared by the repeated fractional distillation of the basic mixture, which is separated from bone-oil or coal-tar as already described; the product consists of pyridine, together with small quantities of its homologues.

Pyridine is a colourless, mobile liquid of sp. gr. 1·003 at 0°; it boils at 115°, is miscible with water in all proportions, and possesses a pungent and very characteristic odour. It is an exceedingly stable substance, as it is not attacked by boiling nitric or chromic acid, and is only slowly acted on by halogens and by sulphuric acid; in the latter case *substitution* products, such as *monobromopyridine*, C_5H_4BrN, and *pyridine sulphonic acid*, $C_5H_4(SO_3H)N$, are formed.

Pyridine is readily reduced by alcohol and sodium, *piperidine* or *hexahydropyridine* (p. 531) being formed,

$$C_5H_5N + 6H = C_5H_{11}N,$$

but when it is heated with hydriodic acid at 300° it gives pentane and ammonia.

Pyridine is a strong base; like the amines, it turns red litmus blue, and forms stable crystalline salts, such as the *hydrochloride*, C_5H_5N,HCl, and the *sulphate*, $(C_5H_5N)_2,H_2SO_4$. The *platinichloride*, $(C_5H_5N)_2,H_2PtCl_6$, crystallises in orange-yellow needles, and is readily soluble in water; when, however, its solution is boiled, a very sparingly soluble yellow salt, $(C_5H_5N)_2PtCl_4$, separates, a fact which may be made use of for the detection of pyridine. Another test for pyridine (and its homologues) consists in heating a few drops

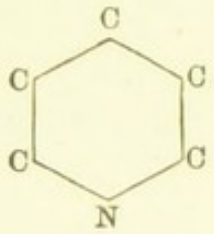
of the base in a test-tube with methyl iodide, when a vigorous reaction takes place, and a yellowish additive product, *pyridine methiodide*, C_5H_5N,CH_3I, is produced; if a piece of solid potash is now added, and the contents of the tube are again heated, the iodine atom is displaced by a hydroxyl-group, and a most pungent and exceedingly disagreeable smell is at once noticed.

When pyridine methiodide is heated alone at 300°, it undergoes isomeric change, and is converted into α- (and γ-) methylpyridine hydriodide; other alkyl halogen additive products (*pyridinium salts*) show a similar behaviour, and the change is analogous to that which occurs in the case of the alkyl anilines (p. 399).

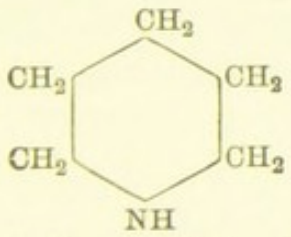
Constitution.—The fact that pyridine is a strong base suggests some relation to the *amines*. It is, however, not a primary amine, because it does not give the carbylamine reaction; nor is it a secondary amine, because it is not acted on by nitrous acid; the necessary conclusion that pyridine is a *tertiary* base is further borne out by its behaviour towards methyl iodide (p. 539). But since pyridine has the molecular formula, C_5H_5N, it is obvious that it cannot be an *open-chain* tertiary amine, because no reasonable constitutional formula founded on this basis could be constructed. The fact that pyridine is extremely stable confirms this conclusion, because if pyridine were a fatty (open-chain) compound it would be highly unsaturated, and should be readily oxidised and resolved into simpler substances. The grounds for doubting its relation to any fatty compound are, in fact, much the same as those which led to the conclusion that the constitution of benzene is totally different from that of dipropargyl (p. 343).

If now the properties of pyridine are compared with those of aromatic compounds, a general analogy is at once apparent; in spite of its great stability, pyridine shows, under certain conditions, the behaviour of an unsaturated compound, and, like benzene, naphthalene, and other closed-chain compounds, yields *additive* products, such as *piperidine*.

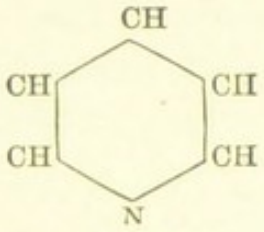
Considerations such as these led Körner, in 1869, to suggest that pyridine, like benzene, contains a closed-chain or nucleus, as represented by the following formula,



and this view has since been confirmed in a great many ways, notably in the following manner:—Piperidine, or hexahydropyridine, the compound which is formed by the reduction of pyridine, and which is reconverted into the latter on oxidation with sulphuric acid (p. 531), has been prepared synthetically by a method (p. 532) which shows it to have the constitution (I.); pyridine, therefore, has the constitution (II.), the relation between the two compounds being the same as that between benzene and hexahydrobenzene,



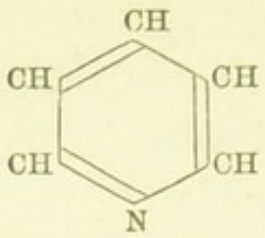
Piperidine (I.).



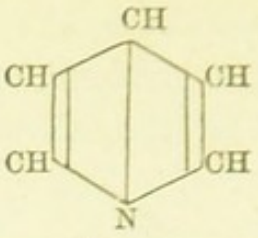
Pyridine (II.).

That the constitution of pyridine is represented by this formula (II.) is also established by a study of the isomerism of pyridine derivatives, and of its relation to quinoline (p. 535); pyridine, therefore, must be regarded as derived from benzene by the substitution of a tervalent nitrogen atom, N≤, for one of the CH≤ groups.

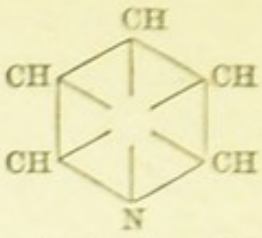
The distribution of the remaining valencies of the nitrogen and carbon atoms is not known, and, as in the case of benzene, several methods of representation (some of which are shown below) have been suggested; of these, the centric formula is perhaps the best, for reasons similar to those already mentioned in discussing the constitution of benzene (pp. 345, 346).



Körner.

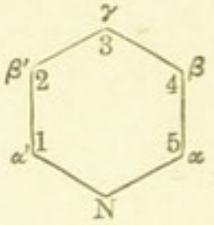


Dewar.

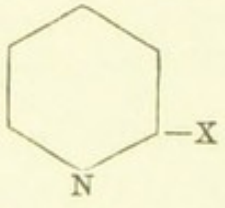


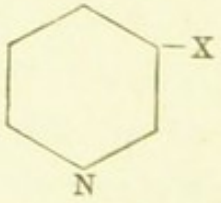
Centric Formula.

Isomerism of Pyridine Derivatives.—The *mono*-substitution products of pyridine, as, for example, the *methylpyridines*, exist in *three* isomeric forms; this fact is clearly accounted for by the accepted constitutional formula for pyridine, in which, for the sake of reference, the carbon atoms may be numbered or lettered * in the following manner, the symbols C and H being omitted as usual :—



Since a *mono*-substitution product may be formed by the displacement of any one of the five hydrogen atoms, it is evident that the following *three*, but not more than three, isomerides may be obtained :—







The positions α and α' are identical, and so also are the positions β and β', but the position γ is different from any of the others.

The *di*-substitution products exist theoretically in *six* isomeric forms, the positions of the substituents in the several isomerides being as follows,

$$\alpha\beta,\ \alpha\gamma,\ \alpha\beta',\ \alpha\alpha',\ \beta\beta',\ \beta\gamma.$$

All other positions are identical with one of these; $\alpha\beta$,

* In the case of pyridine derivatives, letters are generally used instead of numerals.

for example, is the same as $\alpha'\beta'$, and $\beta\gamma$ is identical with $\beta'\gamma$.

As regards the isomerism of its derivatives, pyridine may be conveniently compared with a mono-substitution product of benzene—aniline, for example—the effect of substituting a nitrogen atom for one of the CH< groups in benzene being the same, in this respect, as that of displacing one of the hydrogen atoms by some substituent.

Derivatives of Pyridine.—**Piperidine,** $C_5H_{10}NH$ (hexahydropyridine), is formed, as already stated, when pyridine is reduced with sodium and alcohol; it is usually prepared from pepper, which contains the alkaloid *piperine* (p. 544), a substance which is decomposed by boiling alkalis yielding piperidine and piperic acid.

Powdered pepper is extracted with alcohol, the filtered solution is evaporated, and the residue is distilled with potash; after being neutralised with hydrochloric acid, the distillate is evaporated to dryness, and the residue extracted with hot alcohol, to separate the piperidine hydrochloride from the ammonium chloride which is always present. The filtered alcoholic solution is then evaporated, and the residue is distilled with solid potash; the crude piperidine is purified by fractional distillation over solid potash.

Piperidine is a colourless liquid, boiling at 106°, and is miscible with water; it has a very penetrating odour, recalling that of pepper. Like pyridine, it is a very strong base, turns red litmus blue, and combines with acids forming stable, crystalline salts. When heated with concentrated sulphuric acid at 300°, it loses six atoms of hydrogen, and is converted into pyridine, part of the sulphuric acid being reduced to sulphur dioxide.

Piperidine behaves like a secondary amine towards nitrous acid, and yields *nitroso-piperidine*, $C_5H_{10}N{\cdot}NO$, an oil, boiling at 218°; like secondary amines, moreover, it reacts with methyl iodide, giving N-*methylpiperidine*,* $C_5H_{10}N{\cdot}CH_3$; it is, therefore, a secondary base (compare p. 539).

* The letter N before the name of the substituent signifies that the latter is directly combined with the nitrogen atom.

The important synthesis, already referred to, which establishes the constitution of piperidine, and also that of pyridine, was accomplished by Ladenburg in the following way:—*Trimethylene dibromide** is heated with potassium cyanide in alcoholic solution, and is thus converted into *trimethylene dicyanide*,

$$Br\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br + 2KCN = CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN + 2KBr,$$

a substance which, on reduction with sodium and alcohol, yields *pentamethylene diamine*, just as methyl cyanide under similar conditions yields ethylamine,

$$CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN + 8H = NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2;$$

during this reduction process some of the pentamethylene diamine is decomposed into piperidine and ammonia, and the same change occurs, but much more completely, when the hydrochloride of the diamine is distilled,

$$CH_2\begin{<}{CH_2\cdot CH_2\cdot NH\cdot H \atop CH_2\cdot CH_2\cdot NH_2}\begin{>}{} = CH_2\begin{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}\begin{>}{}NH + NH_3.$$

Piperidine may be reconverted into an open-chain compound in various ways. When, for example, N-benzoylpiperidine is treated with phosphorus pentachloride, it is converted into a dichloro-compound, $CH_2Cl\cdot[CH_2]_4\cdot N{:}CCl\cdot C_6H_5$, which decomposes when it is distilled, and gives 1:5-*dichloropentane*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Cl$, and benzonitrile.

Homologues of Pyridine.—The *alkyl*-derivatives of pyridine occur in coal-tar and bone-oil, and, therefore, are present in the crude pyridine obtained from the mixture of bases in the manner already referred to; they can only be isolated by repeated fractional distillation and subsequent crystallisation of their salts. The three (α, β, γ) isomeric *methylpyridines* or *picolines*, $C_5H_4N\cdot CH_3$, the six isomeric *dimethylpyridines*

* *Trimethylene dibromide*, $C_3H_6Br_2$, is prepared by treating allyl bromide (p. 289) with concentrated hydrobromic acid at 0°,

$$CH_2Br\cdot CH{:}CH_2 + HBr = CH_2Br\cdot CH_2\cdot CH_2Br;$$

it is a heavy, colourless oil, and boils at 164°.

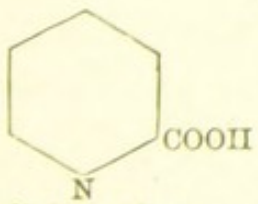
or *lutidines*, $C_5H_3N(CH_3)_2$, and the *trimethylpyridines* or *collidines*, $C_5H_2N(CH_3)_3$, resemble the parent base in most ordinary properties; unlike the latter, however, they undergo oxidation more or less readily on treatment with nitric acid or potassium permanganate, and are converted into *pyridinecarboxylic acids*, just as the homologues of benzene yield benzenecarboxylic acids, the alkyl-groups or side-chains being oxidised to carboxyl-groups,

$$C_5H_4N\cdot CH_3 + 3O = C_5H_4N\cdot COOH + H_2O,$$
$$C_5H_3N(CH_3)_2 + 6O = C_5H_3N(COOH)_2 + 2H_2O.$$

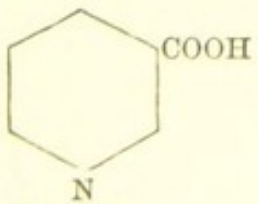
This behaviour has been of great use for the determination of the positions of the alkyl-groups in these homologues of pyridine, because the carboxylic acids into which they are converted are easily isolated, and are readily identified by their melting-points and other properties.

The *pyridinecarboxylic acids*, as a class, are perhaps the most important derivatives of pyridine, chiefly because they are obtained as oxidation products of many of the alkaloids.

The three (α, β, γ) *monocarboxylic* acids may be prepared by oxidising the corresponding *picolines* or *methylpyridines* (see above) with potassium permanganate. The α-carboxylic acid is usually known as **picolinic acid**, because it was first prepared from α-picoline (α-methylpyridine), whereas the β-compound is called **nicotinic acid**, because it was first obtained by the oxidation of nicotine (p. 543); the third isomeride—namely, the γ-carboxylic acid—is called **isonicotinic acid**, and is the oxidation product of γ-picoline.



Picolinic Acid, or Pyridine-α-carboxylic Acid (m.p. 136°).



Nicotinic Acid, or Pyridine-β-carboxylic Acid (m.p. 229°).



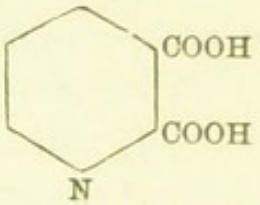
Isonicotinic Acid, or Pyridine-γ-carboxylic Acid (sublimes without melting).

These monocarboxylic acids are all crystalline and soluble in water; they have both basic and acid properties, and form

salts with mineral acids as well as with bases, a behaviour which is similar to that of glycine (p. 329).

The α-carboxylic acid, and all other pyridinecarboxylic acids which contain a carboxyl-group in the α-position (but only such), give a red or yellowish-red colouration with ferrous sulphate. A carboxyl-group in the α-position, moreover, is usually very readily eliminated when the acid is heated; picolinic acid, for example, is much more readily converted into pyridine than is nicotinic or isonicotinic acid.

Quinolinic acid, $C_5H_3N(COOH)_2$ (*pyridine-αβ-dicarboxylic acid*),



a compound produced by the oxidation of quinoline with potassium permanganate, is the most important of the six isomeric dicarboxylic acids. It crystallises in colourless prisms, is only sparingly soluble in water, and gives, with ferrous sulphate, an orange colouration, one of the carboxyl-groups being in the α-position. When heated at 190°, it decomposes into carbon dioxide and nicotinic acid, a fact which shows that the second carboxyl-group is in the β-position. On distillation with lime, quinolinic acid, like all pyridinecarboxylic acids, is converted into pyridine.

In its behaviour when heated alone, quinolinic acid differs in a marked manner from phthalic acid—the corresponding benzenedicarboxylic acid—as the latter is converted into its anhydride (p. 479); nevertheless, when heated with acetic anhydride, quinolinic acid gives an *anhydride*, $C_5H_3N<\begin{matrix}CO\\CO\end{matrix}>O$, a colourless, crystalline substance, melting at 134°. This fact is an indication that the carboxyl-groups are united with carbon atoms, which are themselves directly united (as in the case of phthalic acid), and is further evidence in support of the constitutional formula given above.

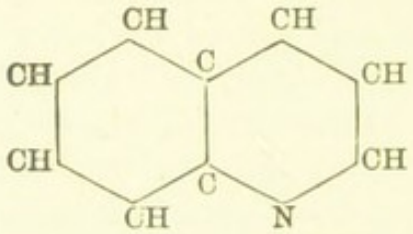
Quinoline and Isoquinoline.

Quinoline, C_9H_7N, occurs, together with *isoquinoline*, in that fraction of coal-tar and bone-oil bases (p. 526) which is collected between 236° and 243°; as, however, it is difficult to obtain the pure substance from this mixture, quinoline is usually prepared synthetically, by *Skraup's reaction*—namely, by heating a mixture of aniline and glycerol with sulphuric acid and nitrobenzene.

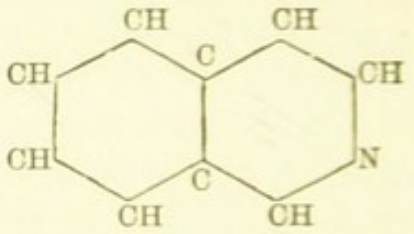
Concentrated sulphuric acid (100 parts) is gradually added to a mixture of aniline (38 parts), nitrobenzene (24 parts), and glycerol (120 parts), and the mixture is then *very cautiously* heated in a large flask (with reflux apparatus) on a sand-bath; when the very violent reaction which first sets in has subsided, the liquid is boiled for about four hours. It is then cooled, diluted with water, and the unchanged nitrobenzene separated by distillation in steam; caustic soda is then added in excess to liberate the quinoline and the unchanged aniline from their sulphates, and the mixture is again steam-distilled. As these two bases cannot well be separated by fractional distillation, the whole of the aqueous distillate is acidified with sulphuric acid, and sodium nitrite is added until nitrous acid is permanently present (p. 415); the solution is then heated in order to convert the diazonium-salt into phenol, rendered alkaline with caustic soda (in order to 'fix' the phenol), and again submitted to distillation in steam. The quinoline is finally separated with the aid of a funnel, dried over solid potash, and purified by fractional distillation.

Quinoline is a colourless, highly refractive oil, of sp. gr. 1·095 at 20°, and boils at 239°. It has a pleasant, characteristic smell, and is sparingly soluble in water. It forms crystalline salts, such as the *hydrochloride*, C_9H_7N,HCl, and the *sulphate*, $(C_9H_7N)_2,H_2SO_4$, which, as a rule, are readily soluble in water. The *dichromate*, $(C_9H_7N)_2,H_2Cr_2O_7$, prepared by adding potassium dichromate to a solution of quinoline hydrochloride, crystallises from water, in which it is only sparingly soluble, in glistening yellow needles, melting at 165°. The *platinichloride*, $(C_9H_7N)_2,H_2PtCl_6,2H_2O$, is only very sparingly soluble in water.

Constitution.—Quinoline is alkaline to litmus, but it does not give the reactions of a primary nor those of a secondary base; on the other hand, it combines with methyl iodide to form the additive product, *quinoline methiodide*, C_9H_7N,CH_3I, and in this and other respects shows the behaviour of a *tertiary* base (p. 539). Now the relation between pyridine, C_5H_5N, and quinoline, C_9H_7N, on the one hand, is much the same as that between benzene, C_6H_6, and naphthalene, $C_{10}H_8$, on the other, both as regards molecular composition (the difference being C_4H_2 in both cases) and chemical behaviour; consequently, quinoline cannot be an *open-chain* compound, but is probably derived from pyridine, just as naphthalene is derived from benzene; if so, its constitution would be expressed by one of the following formulæ :—



I.



II.

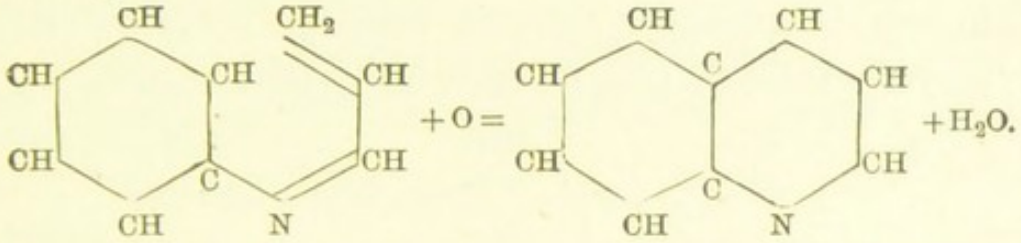
Now, quinoline differs from pyridine, just as naphthalene differs from benzene, in being relatively easily oxidised, and when heated with an alkaline solution of potassium permanganate it yields *quinolinic acid*, $C_5H_3N(COOH)_2$, a derivative of pyridine (p. 534). This fact proves that the molecule of quinoline contains a pyridine nucleus; but it also contains a benzene nucleus, as is shown by its formation from aniline by Skraup's method. Its constitution, therefore, must be expressed by *one* of the above formulæ, as these facts admit of no other interpretation. But formula II. is inadmissible, because it does not account for the formation of quinoline from aniline. For these and other reasons, the constitution of quinoline is represented by formula I. (and that of isoquinoline by formula II. p. 538).

The formation of quinoline from aniline and glycerol may be explained as follows :—The glycerol and sulphuric acid first

interact, yielding acroleïn (p. 290), which then condenses with aniline (as do all aldehydes), forming *acrylaniline*,

$$C_6H_5\cdot NH_2 + CHO\cdot CH{:}CH_2 = C_6H_5\cdot N{:}CH\cdot CH{:}CH_2 + H_2O;$$

this substance, under the oxidising action of the nitrobenzene,* loses two atoms of hydrogen, and is converted into quinoline,



Many derivatives of quinoline may be obtained by Skraup's reaction, using derivatives of aniline instead of aniline itself; when, for example, one of the three toluidines (p. 406) is employed, a *methylquinoline* is formed, the constitution of which depends on that of the toluidine employed.

Derivatives of quinoline are also obtained by the condensation of aniline (or of aniline derivatives) with aldehydes in presence of sulphuric acid (Döbner and Miller); aniline and acetaldehyde, for example, give *α-methylquinoline* (quinaldine),

$$C_6H_5\cdot NH_2 + 2C_2H_4O = C_{10}H_9N + 2H + 2H_2O,$$

a base (b.p. 247°), which on reduction with sodium and alcohol is transformed into dl-*tetrahydroquinaldine*, $C_6H_4\langle{}^{CH_2-CH_2}_{NH\cdot CHMe}\rangle$ (b.p. 247°).

Quinoline itself is formed when the vapour of allylaniline, $C_6H_5\cdot NH\cdot CH_2\cdot CH{:}CH_2$, is passed over strongly heated lead oxide.

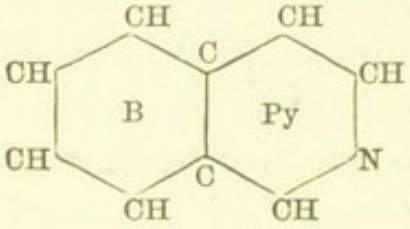
Isoquinoline, C_9H_7N, occurs in coal-tar quinoline, and may be isolated by converting the mixed bases of the fraction boiling at 236–243° into the acid sulphates, C_9H_7N,H_2SO_4, and recrystallising these salts from alcohol (88 per cent.) until the crystals melt at 205°. The sulphate of isoquinoline, thus obtained, is decomposed with potash, and the base purified by distillation. Isoquinoline melts at 23° and boils at

* Nitrobenzene is often employed as a mild oxidising agent, as, in presence of an oxidisable substance, it is reduced to aniline,

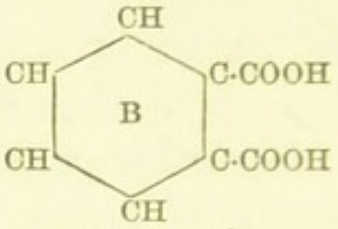
$$C_6H_5\cdot NO_2 + 6H = C_6H_5\cdot NH_2 + 2H_2O.$$

241°; it is very like quinoline in chemical properties, and gives a crystalline *methiodide*, C_9H_7N,MeI (m.p. 159°).

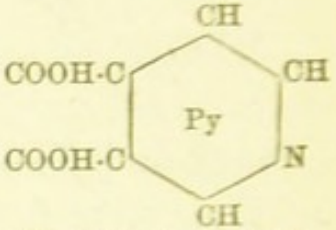
The constitution of isoquinoline is very clearly proved by oxidising the compound with permanganate, when it yields both phthalic acid and *cinchomeronic acid*, $C_5H_3N(COOH)_2$, or pyridine-$\beta\gamma$-dicarboxylic acid; oxidation takes place, therefore, in two directions, in the one case the pyridine (Py), in the other the benzene (B), nucleus being broken up,



Isoquinoline.



Phthalic Acid.



Cinchomeronic Acid.

The constitution of isoquinoline is also established by the following synthesis of the base:—o-Nitrotoluene (p. 396) is converted into o-*cyanotoluene* (o-*tolunitrile*) by methods corresponding with those employed in preparing phenyl cyanide from nitrobenzene (p. 474), and this cyano-derivative is then chlorinated at its boiling-point. The chloro-compound, $CN\cdot C_6H_4\cdot CH_2Cl$, is treated with potassium cyanide, and the product, o-*cyanobenzyl cyanide*, $CN\cdot C_6H_4\cdot CH_2\cdot CN$, is transformed into o-*homophthalic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot COOH$ (a *homo*logue of phthalic acid), by hydrolysis. *Homophthalimide*, $C_6H_4\langle\begin{matrix}CH_2\cdot CO\\CO\cdot NH\end{matrix}\rangle$, prepared by heating the ammonium salt of the acid, may be directly converted into isoquinoline by distillation over strongly heated zinc-dust. This change may also be brought about by treating the homophthalimide with phosphorus oxychloride and then reducing the product (*dichlorisoquinoline*) with hydriodic acid; these reactions may be summarised as follows:—

$$C_6H_4\langle\begin{matrix}CH_2\cdot CO\\CO\cdot NH\end{matrix}\rangle \rightarrow C_6H_4\langle\begin{matrix}CH{:}C(OH)\\C(OH){=}N\end{matrix}\rangle \rightarrow$$

$$C_6H_4\langle\begin{matrix}CH{:}CCl\\CCl{=}N\end{matrix}\rangle \rightarrow C_6H_4\langle\begin{matrix}CH{:}CH\\CH{=}N\end{matrix}\rangle$$

Cyclic Bases.—It will be seen from the above description of piperidine, pyridine, and quinoline that aromatic bases which owe their basic character to the group, $\rangle NH$, or $\rangle\!\!=\!N$, forming *part of a*

closed-chain, show the same chemical behaviour as *open-chain*, secondary or tertiary bases respectively, so far as these particular groups are concerned.

The *secondary* bases, such as piperidine, which contain the >NH-group, yield *nitrosamines*, and, when warmed with an alkyl halogen compound, they are converted into alkyl-derivatives by the *substitution* of an alkyl-group for the hydrogen atom of the >NH-group,

$$>NH + CH_3I = >N\cdot CH_3, HI,$$

just as diethylamine, for example, reacts with ethyl iodide, giving triethylamine,

$$(C_2H_5)_2NH + C_2H_5I = (C_2H_5)_2N\cdot C_2H_5, HI.$$

These alkyl-derivatives of the secondary bases are themselves tertiary bases, and have the property of forming *additive* products with alkyl halogen compounds, giving salts corresponding with the quaternary ammonium salts (p. 215),

$$>N\cdot CH_3 + CH_3I = >N\cdot CH_3, CH_3I, \text{ or } >N(CH_3)_2I.$$

The hydrogen atom of the >NH-group in secondary bases of this kind is also displaceable by the acetyl-group, and by other acid radicles.

The *tertiary* bases, such as pyridine and quinoline, in which the nitrogen atom is not directly united with hydrogen, do not yield nitroso- or acetyl-derivatives, but they unite with *one* molecule of an alkyl halogen compound giving *additive* compounds, corresponding with the quaternary ammonium salts.

CHAPTER XXXV.

Vegetable Alkaloids.

The term *vegetable alkaloid* is generally applied to those *basic nitrogenous substances* which occur in plants, irrespective of any similarity in properties or constitution; as, however, most substances of this kind have some important physiological action, the use of the word may be restricted in this sense.

Most alkaloids are composed of carbon, hydrogen, oxygen, and nitrogen, have a high molecular weight, and are crystalline and non-volatile, but a few, notably *coniine* and *nicotine*, are

composed of carbon, hydrogen, and nitrogen only, and are volatile liquids; with the exception of these liquid compounds, which are readily soluble, the alkaloids are usually sparingly soluble in water, but they dissolve in alcohol, chloroform, ether, and other organic solvents; with acids, they usually form salts, which are soluble in water and crystallise well. Many alkaloids have a very bitter taste, and are excessively poisonous; many, moreover, are extensively used in medicine, and their value in this respect can hardly be overrated.

Generally speaking, the alkaloids are tertiary aromatic bases, but the constitutions of many of them have not yet been fully established, owing partly to their complexity, partly to the difficulty of resolving them into simpler compounds which throw any light on the structure of their molecules. It is known, however, that many alkaloids are derivatives of pyridine, quinoline, or isoquinoline.

It is a remarkable fact that by far the greater number of alkaloids contain one or two, sometimes three or more, methoxy-groups ($-O\cdot CH_3$), united with a benzene nucleus (as in anisole, $C_6H_5\cdot O\cdot CH_3$, p. 440), and the determination of the number of such groups in the molecule is of great importance as a step in establishing the constitution of an alkaloid, because in this way the state of combination of some of the carbon, oxygen, and hydrogen atoms is ascertained. The method employed for this purpose depends on the fact that all substances containing methoxy-groups are decomposed by hydriodic acid, yielding methyl iodide and a hydroxy-compound (compare anisole), in accordance with the general equation,

$$n(-O\cdot CH_3) + nHI = n(-OH) + nCH_3I;$$

by estimating the methyl iodide obtained from a given quantity of a compound of known molecular weight, it is easy, therefore, to determine the number of methoxy-groups in the molecule; ethoxy-groups may also be determined in a similar manner.

This method was first applied by Zeisel, and is of general application; it is conveniently carried out as follows:—

A weighed quantity (0·2–0·4 g.) of the alkaloid is placed in a long-necked distillation flask together with excess (15–25 c.c.) of *distilled* hydriodic acid (b.p. 126°), free from hydrogen sulphide.* The outlet tube of the flask is connected with two small wash-bottles (in series), which contain a concentrated aqueous alcoholic solution of silver nitrate, and a slow stream of carbon dioxide (free from hydrogen chloride) is passed into the hydriodic acid and through the whole apparatus. The distillation flask is heated in an oil- or glycerol-bath, so that the hydriodic acid is just raised to its boiling-point. The methyl iodide which is formed reacts with the silver nitrate, and the precipitated silver iodide is afterwards estimated in the usual way.

Example.—0·3726 gram of substance gave 0·8164 gram of silver iodide, which corresponds with 28·9 per cent. of $-OCH_3$; the substance was $C_8H_4O_3(OCH_3)_2$.

The extraction of alkaloids from plants, and their subsequent purification, are frequently matters of considerable difficulty, partly because in many cases two or more alkaloids occur together, partly because soluble neutral and acid substances, such as the glucosides, sugars, tannic acid, malic acid, &c., are often also present in large quantities. Generally speaking, the alkaloids may be extracted by treating the macerated plant or vegetable product with dilute acids, which convert the alkaloids into soluble salts. The filtered solution may then be treated with soda to liberate the alkaloids, which, being sparingly soluble, are usually precipitated, and may be separated by filtration; if not, the alkaline solution is extracted with ether, chloroform, &c. The products are further purified by recrystallisation, or in some other manner.

Most alkaloids give insoluble precipitates with a solution of tannic, picric, phosphomolybdic, or phosphotungstic acid,

* Hydriodic acid, prepared from iodine with the aid of hydrogen sulphide, often contains the latter; in that case the precipitated silver iodide is contaminated with silver sulphide, and should be boiled with dilute nitric acid before it is collected. Distilled hydriodic acid of constant boiling-point does not lose hydrogen iodide when it is again heated under the same pressure as before.

and with a solution of mercuric iodide in potassium iodide,* &c.; these reagents, therefore, are often used for their detection and isolation.

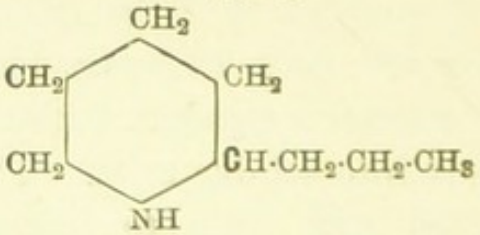
Only the more important alkaloids are described in the following pages.

Alkaloids derived from Pyridine.

Coniine, $C_8H_{17}N$, one of the relatively simple alkaloids, is contained in the seeds of the spotted hemlock (*Conium maculatum*), from which it may be prepared by distillation with caustic soda.

It is a colourless oil, boiling at 167°, and is readily soluble in water; it has a most penetrating odour, and turns brown on exposure to air. Coniine is a strong base; its *hydrochloride*, $C_8H_{17}N,HCl$, and most of its other salts are readily soluble in water. Both the base and its salts are exceedingly poisonous, and cause death in a short time by paralysing the muscles of respiration.

Coniine is dextrorotatory *α-propylpiperidine* (the asymmetric carbon atom is shown in heavy type),



dl-Coniine was first prepared synthetically and resolved into its optically active components by Ladenburg. As this was the first case of an optically active alkaloid having been obtained in the laboratory, its synthesis (described below) is of considerable historical interest.

Piperidine (which can be obtained synthetically, p. 532) is converted into pyridine (p. 531), and from the latter the methiodide is prepared (p. 528). This salt is heated at 300°, whereby it is transformed into α-picoline (α-methylpyridine) hydriodide (p. 528).

* In cases of alkaloid poisoning it is usual, after the stomach-pump has been used, to wash out the stomach with dilute tannic acid, or to administer strong tea (which contains tannin), in order to render the alkaloids insoluble, and therefore harmless.

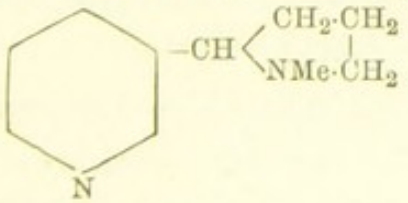
The α-picoline is heated with acetaldehyde (or paracetaldehyde) at 250°, and is thus converted into *α-allylpyridine*, $C_5H_4N(CH{:}CH{\cdot}CH_3)$, which is then reduced to α-propylpiperidine (*dl*-coniine) with sodium and alcohol. The *dl*-coniine is next converted into its *d*-tartrate, and the salt is fractionally crystallised (p. 278); the more sparingly soluble salt of the *d*-base, which crystallises from the solution (leaving the salt of the *l*-base in the mother-liquor), is finally decomposed with potash.

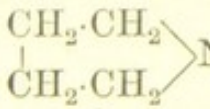
Nicotine, $C_{10}H_{14}N_2$, is present in the leaves of the tobacco-plant (*Nicotiana tabacum*), combined with malic or citric acid.

Tobacco-leaves are extracted with boiling water, and the extract is concentrated, mixed with milk of lime, and distilled; the distillate is acidified with oxalic acid, evaporated to a small bulk, treated with potash, and the liberated nicotine extracted with ether. The crude alkaloid, obtained from the ethereal solution, is purified by distillation in a stream of hydrogen.

It is a colourless oil, which boils at 241°, possesses a very pungent odour, and rapidly turns brown on exposure to air; it is readily soluble in water and alcohol. It is a strong di-acid base, and forms crystalline salts, such as the *hydrochloride*, $C_{10}H_{14}N_2,2HCl$. It combines directly with two molecules of methyl iodide, yielding *nicotine dimethiodide*, $C_{10}H_{14}N_2,2CH_3I$, a fact which shows that it is a di-tertiary base (p. 539). When oxidised with chromic acid it yields nicotinic acid (pyridine-β-carboxylic acid, p. 533); it is, therefore, a pyridine-derivative.

The constitution of nicotine is expressed by the formula,



It is a β-derivative of pyridine, and the substituent is a univalent radicle derived from N-*methyltetrahydropyrrole*,* 

Nicotine contains one asymmetric carbon-group, and is levorotatory. The *dl*-compound has been produced synthetically (Pictet),

* Compare footnote, p. 531. *Pyrrole* is a closed-chain compound (p. 632), and its tetrahydro-derivative is called *pyrrolidine* (p. 634).

and resolved into its optically active components; the synthesis of natural nicotine, like that of coniine, therefore, has been accomplished.

Nicotine is exceedingly poisonous, two or three drops taken into the stomach being sufficient to cause death in a few minutes. It shows no very characteristic reactions, but its presence may be detected by its extremely pungent odour (which recalls that of a foul tobacco-pipe).

Piperine, $C_{17}H_{19}NO_3$, occurs to the extent of about 8–9 per cent. in pepper, especially in black pepper (*Piper nigrum*), from which it is easily extracted.

The pepper is powdered and warmed with milk of lime for fifteen minutes; the mixture is then evaporated to dryness on a water-bath and extracted with ether. The crude piperine, obtained from the ethereal solution, is purified by recrystallisation from alcohol.

It melts at 128°, and is almost insoluble in water; it is only a very weak base, and on hydrolysis it gives piperidine (p. 531) and piperic acid,

$$C_{17}H_{19}NO_3 + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic Acid.}}{C_{12}H_{10}O_4}.$$

Atropine, $C_{17}H_{23}NO_3$ (daturine), is prepared from the deadly nightshade (*Atropa belladonna*).

The plant is pressed, and the juice is mixed with potash and extracted with chloroform (1 litre of juice requires 4 grams of potash and 30 grams of chloroform); the chloroform is then evaporated, the atropine extracted from the residue with dilute sulphuric acid, the solution treated with potassium carbonate, and the precipitated alkaloid recrystallised from alcohol.

This plant, also henbane (*Hyoscyamus niger*), and *Datura Stramonium*, contain various isomeric and closely related alkaloids, of which atropine and *hyoscyamine* are the more important; the latter is optically active and readily undergoes intramolecular change into atropine on treatment with bases. Atropine, in fact, is probably *dl*-hyoscyamine.

Atropine crystallises from aqueous alcohol in prisms, and melts at 115°; it is readily soluble in alcohol, ether, and chloroform, but almost insoluble in water.

It is a strong base, and forms well-characterised salts, of which the *sulphate*, $(C_{17}H_{23}NO_3)_2,H_2SO_4$, is readily soluble, and, therefore, most commonly used in medicine; both the base and its salts are excessively poisonous, 0·05–0·2 gram causing death. Atropine sulphate is largely used in ophthalmic surgery, owing to the remarkable property which it possesses of dilating the pupil when its solution is placed on the eye.

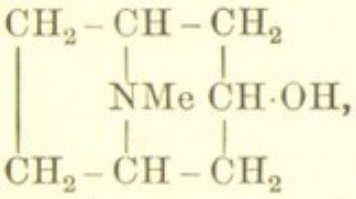
Test for Atropine.—When a trace of atropine is moistened with fuming nitric acid, and evaporated to dryness on a water-bath, it yields a yellow residue, which, on the addition of alcoholic potash, gives an intense violet solution, the colour gradually changing to red.

When atropine is boiled with baryta-water it is readily hydrolysed, yielding *tropic acid* and *tropine*,

$$C_{17}H_{23}NO_3 + H_2O = C_6H_5\cdot CH\begin{matrix}<\text{CH}_2\cdot\text{OH}\\ \text{COOH}\end{matrix} + C_8H_{15}NO.$$

Tropic Acid. Tropine.

Tropine is a hydroxy-base of the constitution,



and atropine is its tropyl-*ester:* in other words, atropine is derived from tropine by the substitution of the *tropyl*-radicle, $HO\cdot CH_2\cdot CHPh\cdot CO$—, for the hydrogen atom of the hydroxyl-group in tropine.

Cocaïne, $C_{17}H_{21}NO_4$, and several other alkaloids of less importance, are contained in coca-leaves (*Erythroxylon coca*).

The coca-leaves are extracted with hot water (80°), the solution is mixed with lead acetate (in order to precipitate tannin, &c.), and the lead in the filtered solution is precipitated with sodium sulphate; the solution is then rendered alkaline with soda, and the cocaïne is extracted with ether and purified by recrystallisation from alcohol.

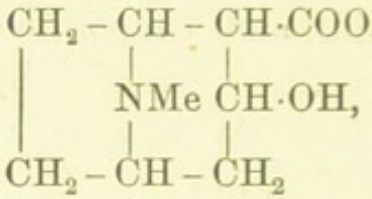
Cocaïne crystallises in colourless prisms, melts at 98°, and is sparingly soluble in water; it forms well-characterised salts, of which the *hydrochloride*, $C_{17}H_{21}NO_4,HCl$, is generally

employed in medicine. Cocaïne is a very valuable local anæsthetic, and is used in minor surgical operations, as its local application takes away all sensation of pain; it is poisonous, however, one grain injected subcutaneously having been attended with fatal results.

When heated with acids or alkalis, cocaïne is readily hydrolysed, with formation of benzoic acid, methyl alcohol, and *ecgonine*,

$$C_{17}H_{21}NO_4 + 2H_2O = C_6H_5 \cdot COOH + CH_3 \cdot OH + C_9H_{15}NO_3.$$

Ecgonine is *tropinecarboxylic acid*,



and cocaïne is the methyl *ester* of *benzoyltropinecarboxylic acid*; cocaïne is formed when the methyl ester of tropinecarboxylic acid is benzoylated—that is to say, when the hydrogen atom of the alcoholic hydroxyl-group is displaced by the benzoyl radicle.

Alkaloids derived from Quinoline.

Quinine, $C_{20}H_{24}N_2O_2$, cinchonine (see below), and several other allied alkaloids, occur in all varieties of cinchona-bark, some of which contain as much as 3 per cent. of quinine. The alkaloids are contained in the bark, combined with tannic and quinic acids.*

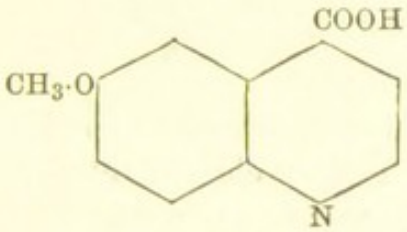
The powdered bark is extracted with dilute sulphuric acid, and the solution of the sulphates is precipitated with caustic soda. The crude mixture of alkaloids, thus obtained, is dissolved in alcohol, the solution is neutralised with sulphuric acid, and the sulphates, which are deposited, are repeatedly recrystallised from water. Quinine sulphate is the least soluble, and separates out first, the sulphates of cinchonine and of the other alkaloids remaining in solution; from the pure sulphate, quinine may be obtained as an amorphous powder by precipitation with ammonium hydroxide.

Quinine crystallises with $3H_2O$, melts at 177° when anhydrous, and is only very sparingly soluble in water; it

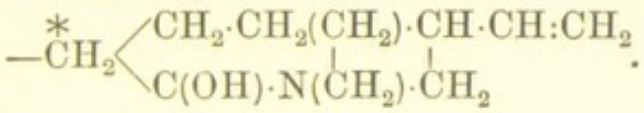
* *Quinic acid*, $C_6H_7(OH)_4 \cdot COOH$, crystallises in prisms, and melts at 162°. It is a tetrahydroxyhexahydrobenzoic acid.

is only a feeble di-acid base, but generally forms well-defined salts, such as the *sulphate*, $(C_{20}H_{24}N_2O_2)_2,H_2SO_4,8H_2O$; many of its salts are soluble in water, and much used in medicine as tonics, and for lowering the body-temperature in cases of fever, &c.

Quinine is a di-tertiary base, because it combines with methyl iodide to form *quinine dimethiodide*, $C_{20}H_{24}N_2O_2,(CH_3I)_2$; it is a derivative of quinoline, because on oxidation with chromic acid it yields *quininic acid* (methoxyquinoline-γ-carboxylic acid),



The carbon atom which remains in the form of the carboxyl-radicle in this acid is probably that marked with an asterisk in a group of the following structure,



Test for Quinine.—When a solution of a salt of quinine is mixed with chlorine- or bromine-water, and ammonium hydroxide is then added, a highly characteristic, emerald-green colouration is produced; quinine is also characterised by the fact that *dilute* solutions of its salts show a beautiful light-blue fluorescence.

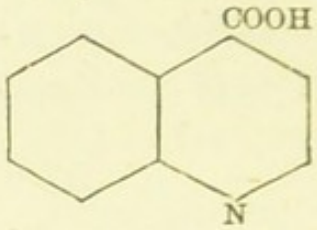
Cinchonine, $C_{19}H_{22}N_2O$, accompanies quinine in almost all the cinchona-barks, and is present in some kinds (in the bark, *Cinchona Huanaco*) to the extent of 2·5 per cent.

In order to prepare cinchonine, the mother-liquors from the crystals of quinine sulphate (see above) are treated with caustic soda, and the precipitate is dissolved in the smallest possible quantity of boiling alcohol; the crude cinchonine, which separates from the cold solution, is then converted into the sulphate, and this salt is crystallised from water.

Cinchonine crystallises in colourless prisms, melts at 255°,

and resembles quinine in ordinary properties; its salts, for example, are antipyretics, but are much less active than those of quinine.

Oxidising agents, such as nitric acid or potassium permanganate, readily attack cinchonine, and convert it into various substances, one of the more important of which is *cinchoninic acid*, or quinoline-γ-carboxylic acid,



The formation of this acid proves that cinchonine is a quinoline-derivative; its structure is very closely related to that of quinine (see above); quinine, in fact, is a *methoxy*cinchonine.

Strychnine, $C_{21}H_{22}N_2O_2$, and brucine, two highly poisonous alkaloids, are contained in the seeds of *Strychnos nux vomica* and of *Strychnos Ignatii* (Ignatius' beans), but they are usually extracted from the former.

Powdered nux vomica is boiled with dilute alcohol, and the filtered solution is evaporated to expel the alcohol, and treated with lead acetate to precipitate tannin, &c. The filtrate is then treated with hydrogen sulphide to precipitate the lead, and the filtered solution is mixed with magnesia and allowed to stand. The precipitated alkaloids are separated, and warmed with a little alcohol, which dissolves out the brucine; the residual *strychnine* is further purified by recrystallisation from alcohol.

The alcoholic solution of the brucine—which still contains strychnine—is evaporated, and the residue dissolved in dilute acetic acid; this solution is now evaporated to dryness on a water-bath, during which process the strychnine acetate decomposes, with loss of acetic acid and separation of the free base. The stable brucine acetate is again dissolved in water, the filtered solution is treated with caustic soda, and the precipitated *brucine* is purified by recrystallisation from dilute alcohol.

Strychnine crystallises in beautiful rhombic prisms, and melts at 284°; although it is very sparingly soluble in water (1 part in 4000 at 15°), its solution has an intensely bitter

taste, and is very poisonous. Strychnine, in fact, is one of the more poisonous alkaloids, half a grain of the sulphate having caused death in twenty minutes.

Although strychnine contains two atoms of nitrogen, it is, like brucine, only a mon-acid base, forming salts, such as the *hydrochloride*, $C_{21}H_{22}N_2O_2,HCl$; many of the salts are soluble in water. It is a tertiary base, because it combines with methyl iodide to form *strychnine methiodide*, $C_{21}H_{22}N_2O_2,CH_3I$.

When distilled with potash, strychnine yields, among other products, *quinoline;* probably, therefore, it is a derivative of this base.

Test for Strychnine.—Strychnine is very readily detected, as it shows many characteristic reactions, of which the following is the most important:—When a small quantity of powdered strychnine is treated with a little concentrated sulphuric acid in a porcelain basin, and a little powdered potassium dichromate is then dusted over the liquid, an intense violet solution, which gradually becomes bright red, and then yellow, is produced.

Brucine, $C_{23}H_{26}N_2O_4$, crystallises in colourless prisms, with $4H_2O$, and melts, when anhydrous, at 178°. It is more readily soluble in water and in alcohol than strychnine, and, although very poisonous, it is not nearly so deadly as the latter (its physiological effect is only about $\frac{1}{24}$th of that of strychnine). Although it contains two atoms of nitrogen, brucine, like strychnine, is a mon-acid base. The *hydrochloride*, for example, has the composition, $C_{23}H_{26}N_2O_4,HCl$; it is also a tertiary base, because it combines with methyl iodide to form *brucine methiodide*, $C_{23}H_{26}N_2O_4,CH_3I$.

Test for Brucine.—When a solution of a brucine salt is treated with nitric acid, a deep brownish-red colouration is obtained, and the solution becomes yellow when it is warmed; if now stannous chloride is added, an intense violet colouration is produced.

This colour reaction serves as a delicate test, both for

brucine and for nitric acid, as it may be carried out with very small quantities.

Alkaloids contained in Opium.

The juice of certain kinds of poppy-heads (*Papaver somniferum*) contains a great variety of alkaloids, of which *morphine* is the most important, but *codeïne*, *narcotine*, *thebaïne*, and *papaverine* may also be mentioned. All these compounds are present in the juice in combination with *meconic acid*,* and partly also with sulphuric acid. When incisions are made in the poppy-heads, and the juice which exudes is left to dry, it assumes a pasty consistency, and is called *opium*. An alcoholic tincture of opium, containing about 1 grain of opium in 15 minims, is know as *laudanum*.

Preparation of Morphine.—Opium is extracted with hot water, and the extract is boiled with milk of lime, and filtered from the precipitate, which contains the meconic acid, and all the alkaloids, except morphine. The filtrate is then concentrated, digested with ammonium chloride until ammonia ceases to be evolved (to convert any lime present into soluble calcium chloride), and kept for some days; the morphine, which separates, is collected and purified by recrystallisation from boiling alcohol.

Morphine, $C_{17}H_{19}NO_3$, crystallises in colourless prisms, with $1H_2O$, and is only sparingly soluble in water and cold alcohol, but dissolves readily in caustic alkalis, from which it is reprecipitated on the addition of acids; it has, in fact, the properties of a phenol. At the same time, it is a mon-acid base, and forms well-characterised salts with acids; the *hydrochloride*, $C_{17}H_{19}NO_3,HCl,3H_2O$, crystallises from water in needles, and is the salt commonly employed in medicine. Morphine is a tertiary base, and gives with methyl iodide *morphine methiodide*, $C_{17}H_{19}NO_3,CH_3I$.

* *Meconic acid*, $C_5HO_2(OH)(COOH)_2$, is a hydroxydicarboxylic acid belonging to the aliphatic series. It gives, with ferric chloride, an intense dark-red colouration. In cases of suspected opium-poisoning this acid is always tested for, owing to the ease with which it can be detected by this colour reaction.

Morphine has a bitter taste, and is so poisonous that one grain of the hydrochloride may be a fatal dose; the system, however, may become so accustomed to the habitual use of opium that, after a time, very large quantities may be taken daily without fatal effects. Morphine is extensively used in medicine as a soporific, especially in cases of intense pain.

Tests for Morphine.—Morphine has the property of liberating iodine from a solution of iodic acid. When a little iodic acid is dissolved in water, and a few drops of a solution of morphine hydrochloride are added, a brownish colouration is at once produced, owing to the liberation of iodine, and the solution then gives, with starch-paste, the well-known deep-blue colouration.

A solution of morphine, or of a morphine salt, gives a deep-blue colouration with ferric chloride, but perhaps the most delicate test for the alkaloid is the following:—A trace of morphine is dissolved in concentrated sulphuric acid, and the solution is kept for fifteen hours; if then treated with nitric acid, it gives a bluish-violet colour, which changes to blood-red. This reaction is very delicate, and is well shown by 0·01 milligramme of morphine.

Morphine contains two hydroxyl-groups, one of which is phenolic, the other alcoholic; it is to the presence of the phenolic hydroxyl-group that morphine owes its property of dissolving in alkalis, and giving a blue colour with ferric chloride.

When heated with potash and methyl iodide, it gives *methyl-morphine*, $C_{17}H_{17}NO(OCH_3)\cdot OH$, a substance which is identical with *codeïne* (p. 550). Codeïne is insoluble in alkalis, and, therefore, is not a phenol; it behaves, however, like an alcohol, and gives, with acetic anhydride, *acetylcodeïne*, $C_{17}H_{17}NO(OCH_3)\cdot OAc$.

It is very remarkable that morphine seems to be a derivative of phenanthrene, as derivatives of this hydrocarbon are very seldom met with in nature. When morphine is distilled with zinc-dust a considerable quantity of this hydrocarbon is obtained, together with pyridine, quinoline, and other substances.

Apomorphine, $C_{17}H_{17}NO_2$, is formed, together with water, when morphine hydrochloride is heated with concentrated hydrochloric acid at 140–150°; its hydrochloride is used in medicine as an emetic.

CHAPTER XXXVI.

Amino-Acids, Uric Acid, and Related Compounds.

* The *amino-acids*, of which glycine (p. 329) is an example, are substances of very great physiological importance. Many of them are obtained by the hydrolysis with acids, alkalis, or digestive enzymes of those highly complex components of animals and plants, which are termed the **proteïns** (p. 575), and for this reason it is believed that the proteïns are produced in organisms from a large number of molecules of relatively simple amino-acids.

The amino-acids, which have hitherto been obtained from natural sources, differ considerably in type, and among them are found representatives of various classes, of which the following are some of the more important :—

Glycine and its homologues (*alanine*, *leucine*, *iso-leucine*).

Alkylamino-acids (*sarcosine*, *betaïne*).

Diamino-fatty acids (*ornithine*, *lysine*).

Monamino-dicarboxylic acids (*aspartic acid*, *glutamic acid*).

Amino-acids which contain closed-chains (*tyrosine*, *tryptophane*).

In some cases a given proteïn may be almost entirely transformed into one amino-acid only ; but as a rule the product of hydrolysis is a complex mixture of (up to ten or more) amino-acids, and the separation of the various components of the mixture is a task of very great difficulty. This difficulty is due partly to the complexity of the mixture, but more particularly to the properties of the amino-acids. These compounds are generally very readily soluble in water, but insoluble in ether and in those other solvents which do not

* The subject-matter of all the following chapters is intended for those who are beyond a *pass* degree standard ; but Chapters XXXVI. and XXXVII. deal more particularly with matters of importance to medical students.

mix with water; consequently they cannot be extracted from their aqueous solutions; further, they cannot be distilled, and, when impure, they do not crystallise readily. During recent years great progress has been made with the chemistry of these compounds, owing mainly to the work of E. Fischer. Improvements have been made in the synthetical methods of preparation of amino-acids, and new processes for their separation and isolation from the products of proteïn hydrolysis have been devised.

The more important synthetical methods of preparation are the following:—

The halogen acids (pp. 170, 171) are treated with alcoholic ammonia,

$$CH_3\cdot CHBr\cdot COOH + 3NH_3 = CH_3\cdot CH(NH_2)\cdot COONH_4 + NH_4Br.$$

The esters of halogen acids are treated with potassium phthalimide, and the products are hydrolysed with hydrochloric acid at about 200° (compare p. 479),

$$CH_2Br\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2 + C_6H_4\begin{<}{}^{CO}_{CO}\end{>}NK = C_6H_4\begin{<}{}^{CO}_{CO}\end{>}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2;$$

$$C_6H_4\begin{<}{}^{CO}_{CO}\end{>}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2 + 4H_2O = C_6H_4(COOH)_2 + NH_2\cdot[CH_2]_4\cdot COOH + 2C_2H_5\cdot OH + CO_2.$$

The cyanohydrin of an aldehyde or ketone is treated with the theoretical quantity of ammonia, and the nitrile of the amino-acid, which is thus formed, is hydrolysed with hydrochloric acid,

$$(CH_3)_2CH\cdot CH_2\cdot CH\begin{<}{}^{OH}_{CN} + NH_3 = (CH_3)_2CH\cdot CH_2\cdot CH\begin{<}{}^{NH_2}_{CN},$$

$$(CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot CN + 2H_2O = (CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot COOH + NH_3.$$

The amino-acids are neutral to indicators, and, in fact, may

be regarded as *salts*, since the –COOH and $-NH_2$ groups in the same or in different molecules neutralise one another, just as do an acid and an amine. When, therefore, an amino-acid is treated with a strong acid, such as hydrochloric acid, it forms a *hydrochloride*, of which glycine hydrochloride (p. 329) is an example; an amino-acid also forms metallic salts, such as *copper glycine* (p. 329). Many amino-acids have a sweet taste.

Esters of the amino-acids may be produced by the usual method of esterification—namely, by passing hydrogen chloride into a solution of the acid in excess of an alcohol. Under these conditions, the *hydrochloride* of the ester is formed; but when this product is treated in the cold with a solution of potassium hydroxide, the hydrochloride is decomposed. The esters themselves, unlike the amino-acids, are soluble in ether; if, therefore, the solution of the liberated ester is immediately extracted with ether, the ester is obtained as an oil, which may be purified by distillation under greatly reduced pressure. The esters of the amino-acids, therefore, are of great use; with their aid the amino-acids may be extracted from the products of hydrolysis of a proteïn, and, to a greater or less extent, separated from one another.

All the amino-acids, with the exception of glycine, which are obtained from natural products, are optically active, whereas the corresponding synthetical compounds, of course, are *dl*-mixtures. Such *dl*-mixtures may be resolved into their enantiomorphously related components by the following method:—The amino-acid is converted into its *benzoyl*-derivative, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}[CH_2]_n{\cdot}COOH$, by the Schotten-Baumann method (p. 473). The amino-group thereby loses its basic character and no longer neutralises the carboxyl-group. Consequently the *benzoylated* acid is a moderately strong acid, and forms salts with bases, such as the alkaloids. The benzoylamino-acid, therefore, may be combined with an optically active base, and the product may then be resolved in the usual way (p. 278). The *d*- and *l*-benzoylamino-acids,

which are regenerated from their salts, are finally reconverted into the *d*- and *l*-amino-acids, respectively, by hydrolysis.

It is thus possible to synthesise many of the *dl*-amino-acids, and then to resolve them into optically active compounds, which are identical with those produced from the proteïns.

It has been stated above that a natural proteïn probably consists of a very large number of molecules of the same or of different amino-acids, which have united together with elimination of water; and the first stage in such a condensation may be represented by the general equation,

$$COOH\cdot[CH_2]_n\cdot NH_2 + COOH\cdot[CH_2]_n\cdot NH_2 = COOH\cdot[CH_2]_n\cdot NH - CO\cdot[CH_2]_n\cdot NH_2 + H_2O.$$

The product so formed from two molecules of an amino-acid is called a *di-peptide;* by condensation with another molecule of the same or of a different acid, a di-peptide may be transformed into a *tri-peptide*, and so on.

In order to throw light on the nature of the proteïns, condensations such as those just indicated were carried out by E. Fischer, and the following methods were used for this purpose:—The ethyl ester of glycine undergoes spontaneous decomposition in presence of water, giving a compound of the constitution, $\begin{matrix} NH\cdot CH_2\cdot CO \\ | \quad\quad | \\ CO\cdot CH_2\cdot NH \end{matrix}$, which is called *glycine anhydride* (or *diketopiperazine*). This product is hydrolysed by hot concentrated hydrochloric acid, giving the hydrochloride of *glycyl-glycine*, $COOH\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NH_2$.

When this *di-peptide*, glycyl-glycine (or its ester), is treated with chloracetyl chloride, it yields a compound of the constitution, $COOH\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, and the latter, with concentrated ammonia, gives a *tri-peptide*,

$$COOH\cdot CH_2\cdot NH\vdots CO\cdot CH_2\cdot NH\vdots CO\cdot CH_2\cdot NH_2.$$

The tri-peptide may now be treated with chloracetyl chloride and ammonia successively, and thus converted into a *tetra-*

peptide; and these processes, by which a $-CO\cdot CH_2\cdot NH_2$ group is substituted for an atom of hydrogen of an amino-group, may be continued.

In another method, the amino-acid is treated with phosphorus pentachloride in acetyl chloride solution, and the acid chloride, which is thus produced, is then caused to react with an ester of an amino-acid,

$$NH_2\cdot[CH_2]_n\cdot COCl + NH_2[CH_2]_n\cdot COOEt = HCl, NH_2\cdot[CH_2]_n\cdot CO\cdot NH[CH_2]_n\cdot COOEt.$$

The product is then made the starting-point of further condensations.

The most complex substance so far produced, by methods such as those just indicated, is an *octadecapeptide*, the molecule of which contains 15 glycyl- or $-NH\cdot CH_2\cdot CO-$ and three *leucyl-* or $-NH\cdot CH(C_4H_9)\cdot CO-$ groups (p. 557); this compound has a molecular weight of 1213, and its constitution is expressed by the formula, $NH_2\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_8\cdot NH\cdot CH_2\cdot COOH$. It is probably the most complex synthetical product ever obtained, and in many respects it resembles the natural proteïns (p. 575).

Glycine and its Homologues.

The simplest amino-acid which is obtained from proteïns—namely, glycine (amino-acetic acid)—has already been described; it is formed in relatively large quantities when glue or gelatine is hydrolysed with dilute sulphuric acid.

dl-**Alanine,** $CH_3\cdot CH(NH_2)\cdot COOH$ (*α-aminopropionic acid*), and its isomeride, *β*-aminopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot COOH$, have been prepared by treating the corresponding bromopropionic acids with ammonia. They resemble glycine in properties.

d-Alanine is one of the principal products of the hydrolysis of fibroïn (the main component of silk); it has been obtained synthetically by the methods already described.

Cystine, $C_6H_{12}N_2O_4S_2$, sometimes separates from urine as a sediment, and is also a component of some gall-stones. It is a derivative of alanine, of the constitution,

$$COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH.$$

The amino-derivatives of butyric and valeric acids may be prepared by the general methods, but they are not of particular physiological interest.

l-**Leucine**, $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$ (*α-aminoisocaproïc acid*), is very widely distributed in the animal kingdom, and is a substance of great physiological importance. It is found in the lymphatic glands, the spleen, and especially in the pancreas; in typhus and some other diseases it is present in considerable quantity in the liver. It is produced during the putrefaction of proteïns; also by the hydrolysis of proteïns, such as hæmoglobin (p. 578), egg-albumin, and caseïn (p. 577), from the last of which it is prepared.

Leucine crystallises in glistening plates, melts at 270°, and when carefully heated sublimes unchanged; when rapidly heated, it decomposes into normal amylamine, $CH_3{\cdot}[CH_2]_4{\cdot}NH_2$, and carbonic anhydride.

It dissolves in 48 parts of water, and is very sparingly soluble in alcohol. Its solution in hydrochloric acid is dextrorotatory, but a solution of the acid itself is levorotatory; when boiled with baryta-water it racemises (pp. 276, 604).

dl-Leucine has been prepared synthetically from isovaleraldehyde (p. 553), and in the form of its benzoyl-derivative, it has been resolved into its components; the *l*-leucine obtained in this way is identical with that prepared from proteïns.

In contact with *penicillium glaucum*, a solution of *dl*-leucine becomes levorotatory, owing to the destruction of the *d*-modification (p. 279).

d-**Isoleucine**, $CHMeEt{\cdot}CH(NH_2){\cdot}COOH$ (*α-amino-β-methylvaleric acid*), is produced by the hydrolysis of proteïns contained in beetroot sap. It is also formed by the hydrolysis of the proteïns of cereals, potatoes, &c.; and when these

materials are used for the preparation of alcohol, the *d*-isoleucine, which is first produced, is afterwards converted into active amyl alcohol by the action of the enzymes which are present. *l*-Leucine, under similar conditions, gives rise to isobutylcarbinol (p. 111).

Alkylamino-Acids and Related Compounds.

Sarcosine, $CH_3{\cdot}NH{\cdot}CH_2{\cdot}COOH$ (*methylglycine*), was first obtained (Liebig, 1847) by boiling creatine with baryta-water (p. 559); it is also formed when caffeïne is similarly treated. It may be prepared synthetically from chloracetic acid and methylamine,

$$CH_3{\cdot}NH_2 + CH_2Cl{\cdot}COOH = CH_3{\cdot}NH{\cdot}CH_2{\cdot}COOH + HCl.$$

Sarcosine melts and decomposes at 210–220°, giving dimethylamine and carbonic anhydride,

$$CH_3{\cdot}NH{\cdot}CH_2{\cdot}COOH = CH_3{\cdot}NH{\cdot}CH_3 + CO_2.$$

Like glycine, it has both basic and acid properties, and forms well-characterised salts, such as the nitrate, $C_3H_7NO_2,HNO_3$, and the copper salt, $(C_3H_6NO_2)_2Cu,2H_2O$.

Creatine, $NH{:}C(NH_2){\cdot}N(CH_3){\cdot}CH_2{\cdot}COOH$, is a very important substance found in the muscles, nerves, and blood, and also in considerable quantity in meat extract, from which it was isolated by Chevreul in 1834. The muscles contain about 0·3 per cent. of creatine, and it has been calculated that those of a full-grown man contain no less that 90–100 grams of this substance. The name creatine is derived from $\chi\rho\epsilon\alpha s$, meat.

Preparation.—Meat extract (40 grams) is dissolved in water (800 grams), and basic lead acetate is added until no further precipitate is produced; the filtrate is freed from lead with the aid of hydrogen sulphide, and is then concentrated to about 40 c.c. The crystals which separate are washed with dilute alcohol (88 per cent.), and purified by crystallisation from water.

Creatine crystallises from water in hydrated prisms ($1H_2O$); it is moderately soluble in water, very sparingly soluble in alcohol. It has a neutral reaction and a bitter taste, and

forms salts with 1 equivalent of an acid, but it does not appear to possess acid properties. When evaporated with acids it is converted into *creatinine* (see below), and when heated with baryta-water it is decomposed into urea and *sarcosine*,

$$NH{:}C(NH_2)\cdot N(CH_3)\cdot CH_2\cdot COOH + H_2O = NH_2\cdot CO\cdot NH_2 + NH(CH_3)\cdot CH_2\cdot COOH.$$

Creatine has been prepared by heating together cyanamide (p. 324) and sarcosine in alcoholic solution,

$$N{:}C\cdot NH_2 + HN(CH_3)\cdot CH_2\cdot COOH = NH{:}C(NH_2)\cdot N(CH_3)\cdot CH_2\cdot COOH.$$

Creatinine, $NH{:}C\begin{cases}NH - CO\\ N(CH_3)\cdot CH_2\end{cases}$, can be prepared from creatine, into which it is reconverted by alkalis. It is found (about 0·25 per cent.) in urine, and is also present in the muscles, especially after great exertion; in both these cases it is probably produced from creatine.

Creatinine is much more soluble in water than is creatine; it is a strong base, and yields salts, such as the hydrochloride, $C_4H_7N_3O,HCl$. When zinc chloride is added to its aqueous solution, a highly characteristic, sparingly soluble compound, $(C_4H_7N_3O)_2,ZnCl_2$, separates in fine needles, and this compound is used in the estimation of creatinine. Creatinine reduces Fehling's solution, and gives with phosphomolybdic acid a yellow crystalline precipitate.

Betaïne, $COOH\cdot CH_2\cdot N(CH_3)_3\cdot OH$ (*oxyneurine* or *lycine*), may be regarded as a derivative of sarcosine, or of glycine. It occurs in beetroot (Scheibler), and is obtained in large quantities as a by-product in the manufacture of beet-sugar; it is also found in some seeds, especially in those of the cotton-plant.

Preparation.—The mother-liquor, after the extraction of the sugar, is boiled with baryta for twelve hours; the barium is then precipitated with carbon dioxide, and the filtrate is evaporated to dryness. The residue is extracted with alcohol, and the alcoholic

solution precipitated with zinc chloride. The crystalline precipitate, $C_5H_{11}NO_2Cl_2Zn$, is then decomposed with baryta, and the filtrate is freed from barium by means of sulphuric acid, and evaporated to a small bulk, when betaïne chloride separates in crystals.

It is very soluble in water, and gives well-characterised salts, such as the chloride, $COOH{\cdot}CH_2{\cdot}N(CH_3)_3Cl$. When betaïne is heated at 100°, it is converted into a salt of the constitution, $\begin{matrix} CO{\cdot}CH_2 \\ | \quad | \\ O{-}N(CH_3)_3 \end{matrix}$; but at much higher temperatures this compound is decomposed and trimethylamine distils over.

Betaïne chloride has been prepared synthetically by heating together monochloracetic acid and trimethylamine in aqueous solution,

$$COOH{\cdot}CH_2Cl + N(CH_3)_3 = COOH{\cdot}CH_2{\cdot}N(CH_3)_3Cl.$$

Muscarine, $CHO{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH,H_2O$, is an aldehyde closely related to betaïne. It was discovered by Schmiedeberg and Koppe in the poisonous mushroom (*Agaricus muscarius*), and has also been found in putrid fish. It is a strong base, and a powerful poison, acting especially on the heart. Its constitution is proved by the fact that it is formed when choline is oxidised with nitric acid.

Choline, $CH_2(OH){\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$ (*hydroxyethyltrimethylammonium hydroxide*), sometimes called *sinkaline* or *bilineurine*, is an alcohol related to betaïne. It is one of the decomposition products of lecithine (p. 572), and is widely distributed in the animal and vegetable kingdoms. It was discovered by Strecker in bile (χολή), and its constitution was established by Baeyer. Choline is contained in hops, and also in the alkaloid, sinapine, which occurs in mustard-seeds; it is produced in corpses, as the result of putrefactive changes.

Preparation.—Lecithine is boiled during one hour with baryta-water; the barium is then precipitated with carbonic anhydride, the filtrate is evaporated, and the residue extracted with absolute alcohol. The alcoholic extract is mixed with platinic chloride, and the platinichloride of choline, which separates in crystals, is col-

lected, dissolved in water, and decomposed with hydrogen sulphide. The filtrate from the platinum sulphide yields, on evaporation, chloride of choline, $C_5H_{14}NOCl$.

Choline is a strongly alkaline quaternary hydroxide; a characteristic salt is the *platinichloride*, $(C_5H_{14}NO)_2PtCl_6$, which crystallises from water in plates.

When a strong aqueous solution of choline is boiled, glycol and trimethylamine are formed,

$$CH_2(OH)\cdot CH_2\cdot N(CH_3)_3\cdot OH = CH_2(OH)\cdot CH_2\cdot OH + N(CH_3)_3,$$

a decomposition which clearly shows the constitution of the substance. Choline was first synthesised by Würtz, who obtained it by evaporating an aqueous solution of ethylene oxide with trimethylamine,

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O + N(CH_3)_3 + H_2O = CH_2(OH)\cdot CH_2\cdot N(CH_3)_3\cdot OH.$$

Neurine, $CH_2{:}CH\cdot N(CH_3)_3\cdot OH$, is formed when choline is heated with baryta-water, and it is also a decomposition product of lecithine, from which it is doubtless produced by bacterial action after death. It is exceedingly poisonous, and is one of the important ptomaines (p. 563) produced by the action of bacteria on certain proteïns.

Neurine has been prepared synthetically. When choline is heated with hydrobromic acid, the two hydroxyl-groups are displaced by two atoms of bromine, and when the product, $CH_2Br\cdot CH_2\cdot N(CH_3)_3Br$, is treated with silver hydroxide, it yields neurine,

$$CH_2Br\cdot CH_2\cdot N(CH_3)_3Br + 2AgOH = CH_2{:}CH\cdot N(CH_3)_3\cdot OH + 2AgBr + H_2O.$$

d-**Ornithine**, $NH_2\cdot[CH_2]_3\cdot CH(NH_2)\cdot COOH$ (*αδ-diamino-valeric acid*), is produced by the hydrolysis of *arginine*, a substance which occurs among the decomposition products of a great many animal and vegetable proteïns.

Lysine, $NH_2\cdot[CH_2]_4\cdot CH(NH_2)\cdot COOH$ (*αε-diaminocaproïc acid*), occurs among the hydrolytic products of caseïn, egg-albumin, and other proteïns. Both these diamino-acids yield

ptomaines (*tetramethylene diamine* and *pentamethylene diamine* respectively) in presence of putrefactive bacteria.

Aminodicarboxylic Acids.

l-**Asparagine,** $NH_2 \cdot CO \cdot CH_2 \cdot CH(NH_2) \cdot COOH$, a monamide of *aminosuccinic acid* (aspartic acid), is formed in the decomposition of proteïns. It occurs in many plants, particularly in asparagus, and in the young shoots of beans, peas, and lupines, from which it may be obtained by extraction with water. It is readily soluble in water, sparingly soluble in alcohol and ether. When treated with acids or alkalis, it is converted into *l*-aspartic acid.

d-*Asparagine* occurs together with *l*-asparagine in the young shoots of lupines.

It is noteworthy that when an aqueous solution of equal quantities of *d*- and *l*-asparagine is evaporated, crystals of the two active modifications are deposited side by side; a racemic compound (p. 271) is not formed.

d-**Glutamic acid,** $COOH \cdot CH(NH_2) \cdot CH_2 \cdot CH_2 \cdot COOH$ (*aminoglutaric acid*), occurs in the sprouting seeds of various plants, and is an important product of the hydrolysis of caseïn.

Amino-Acids which contain Closed-Chains.

Tyrosine, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$, or **p**-*hydroxyphenyl-α-aminopropionic acid*, is formed in the decomposition of various proteïns. It is found in the liver in some diseases, in the spleen, pancreas, and in cheese (its name is derived from τυρος, cheese). It was first prepared by fusing cheese with potash (Liebig, 1846). Tyrosine is sparingly soluble in water and alcohol, and almost insoluble in ether; it combines with acids and with bases to form salts. With mercuric nitrate in aqueous solution, it gives a yellow precipitate, which, when boiled with dilute nitric acid, acquires an intense red colour; this reaction is used as a delicate test for tyrosine.

Tyrosine decomposes at 270° into carbon dioxide and

p-*hydroxyphenylethylamine*, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, and when fused with potash, it yields **p**-hydroxybenzoic acid (p. 493), acetic acid, and ammonia.

Tyrosine has been synthesised in the following way :—Phenylacetaldehyde (p. 483) yields, with hydrocyanic acid, the nitrile of phenyllactic acid, $C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CN$, which, with alcoholic ammonia, gives the *nitrile* of *phenylaminopropionic acid*, $C_6H_5{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CN$; this nitrile, on hydrolysis, yields *phenylaminopropionic acid* (phenylalanine), $C_6H_5{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$.

Nitric acid converts this amino-acid into **p**-*nitrophenylaminopropionic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$, from which, on reduction, the corresponding *aminophenylaminopropionic acid* is obtained ; the latter, on treatment with nitrous acid, yields tyrosine.

l-**Tryptophane** is an amino-acid derived from indole, C_8H_7N, and its constitution is represented by the formula, $NH\langle\begin{matrix}CH\\C_6H_4\end{matrix}\rangle C{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$. It is a decomposition product of egg- and blood-albumin, and under the influence of putrefactive bacteria, it is converted into *indoleacetic acid*, $NH\langle\begin{matrix}CH\\C_6H_4\end{matrix}\rangle C{\cdot}CH_2{\cdot}COOH$.

Ptomaines or Toxines.—Many of the amino-acids are attacked by various putrefactive organisms, and are converted into highly poisonous basic substances, such as neurine (p. 561), which are classed as ptomaines. These compounds are consequently formed during the putrefaction of fish, meat, and other animal products which contain proteïns, and it is to the presence of ptomaines that the toxic action of such putrid matter is due.

Two other important ptomaines are *putrescine* and *cadaverine*.

Putrescine, $NH_2{\cdot}[CH_2]_4{\cdot}NH_2$ (*tetramethylene diamine*), is crystalline, and melts at 23° ; it has a most unpleasant and penetrating smell. It is miscible with water, and is a strong diacid base.

Putrescine has been obtained synthetically by converting

ethylene dibromide into the dicyanide (p. 249), and then reducing the latter with sodium and alcohol,

$$CN{\cdot}CH_2{\cdot}CH_2{\cdot}CN + 8H = NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2.$$

Cadaverine, or *pentamethylene diamine* (p. 532), is a syrup which boils at 178–179°, and, like putrescine, is a diacid base.

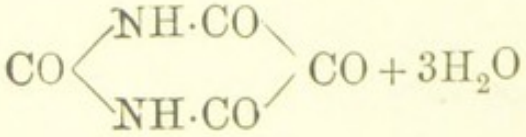
Uric Acid and its Derivatives.

Uric acid (p. 333) is not only itself a compound of great physiological importance, but is also closely related to many other interesting natural products. Discovered long ago (in 1776) by Scheele in urinary calculi, its constitution has been only comparatively recently established, and its synthesis accomplished.

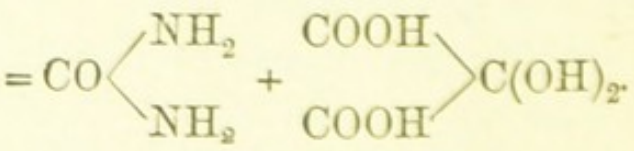
The first important evidence as to the structure of uric acid was obtained by a study of the oxidation products of the compound. When treated with nitric acid, it yields *alloxan*, $C_4H_2N_2O_4$, *parabanic acid*, $C_3H_2N_2O_3$, and *urea* (p. 330).

Alloxan crystallises from water in hydrated prisms, $(4H_2O)$. In contact with the skin its aqueous solution produces, after a time, a purple stain; ferrous salts colour the aqueous solution indigo-blue.

When boiled with alkalis, alloxan is converted into urea and a salt of *mesoxalic acid*;* this and other facts prove that alloxan is **mesoxalylurea**, the constitution and hydrolysis of which are represented below,



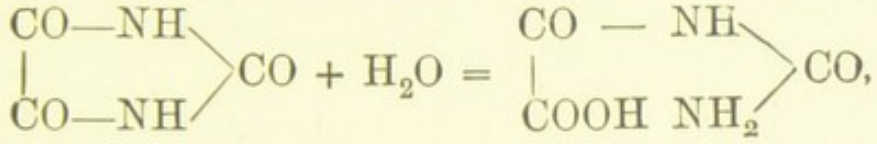
Alloxan
(Mesoxalylurea).



Mesoxalic Acid.

* *Mesoxalic acid*, or *dihydroxymalonic acid*, is formed when dibromomalonic acid, $CBr_2(COOH)_2$, is boiled with baryta-water; it melts at 108°, and is one of the few compounds the molecule of which contains the group, $>C<^{OH}_{OH}$.

Parabanic acid is a crystalline substance, soluble in water and alcohol; it yields a silver derivative, $C_3N_2O_3Ag_2$, and in this respect behaves like a di-basic acid.* When treated with baryta-water, it is hydrolysed in two stages, yielding first *oxaluric acid*, and then oxalic acid and urea; these facts show that parabanic acid is **oxalylurea,** and its structure is expressed by the formula given below,



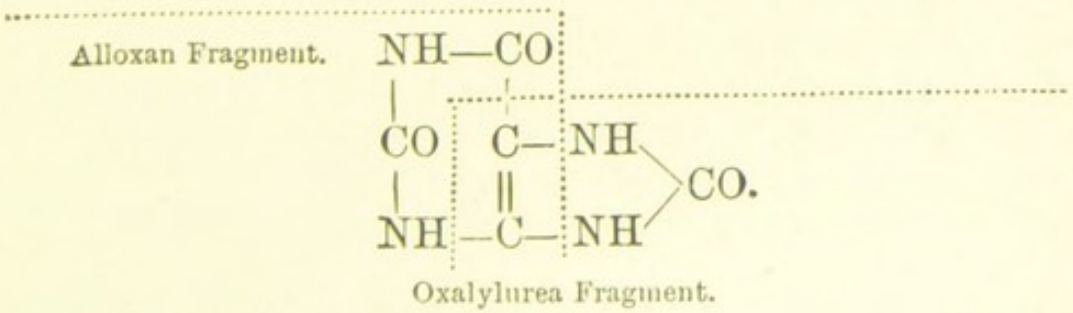
Parabanic Acid. Oxaluric Acid.

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}COOH + H_2O = C_2H_2O_4 + CO(NH_2)_2.$$

The constitution of parabanic acid (*oxalylurea*) is further established by the synthesis of the acid from a mixture of oxalic acid and urea, in presence of phosphorus oxychloride.

Alloxan (mesoxalylurea) and parabanic acid (oxalylurea) are classed as *di-ureïdes*, a term which is applied to di-acidyl (or di-acyl) derivatives of urea; *mono-ureïdes*, such as *acetyl-urea*, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_3$, are also known.

The constitutions and relationships of the above, and of other *degradation* products of uric acid, having been established —in a great measure by the work of Baeyer—it was possible to suggest a probable structural formula for the acid. This was done by Medicus in 1875, and it will be seen that his formula, which is given below, accounts for the formation of the three oxidation products, oxalylurea, alloxan, and urea,



This formula was finally established by the synthesis of

* Parabanic acid is not a carboxylic acid, but its molecule contains two >NH groups, the hydrogen atoms of which are displaceable by metals. (Compare succinimide, p. 252; phthalimide, p. 479; and footnote, p. 567).

uric acid by Behrend and Roosen, and the relationship between uric acid and several other important naturally-occurring compounds was elucidated by the brilliant investigations of E. Fischer, who synthesised not only uric acid, but also caffeïne, theobromine, and many related substances.

Syntheses of Uric Acid.—The first important synthesis of this acid was carried out by Behrend and Roosen in the following manner:—Ethyl acetoacetate * condenses with urea, giving *ethylic β-uramidocrotonate*,

$$\begin{matrix} CH_3\cdot C(OH) \\ \| \\ CH\cdot COOEt \end{matrix} + NH_2\cdot CO\cdot NH_2 = \begin{matrix} CH_3\cdot C\cdot NH\cdot CO\cdot NH_2 \\ \| \\ CH\cdot COOEt \end{matrix} + H_2O;$$

and the corresponding acid, *β-uramidocrotonic acid*, which is obtained by hydrolysis, readily loses water and forms *methyluracil*,

$$\begin{matrix} NH_2 & COOH \\ | & | \\ CO & CH \\ | & \| \\ NH-- & C\cdot CH_3 \end{matrix} = \begin{matrix} NH-- & CO \\ | & | \\ CO & CH \\ | & \| \\ NH-- & C\cdot CH_3 \end{matrix} + H_2O.$$

β-Uramidocrotonic Acid. Methyluracil.

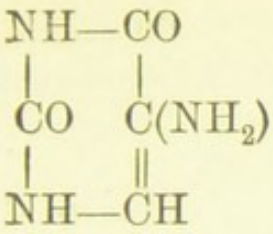
When methyluracil is treated with nitric acid, the methyl- is oxidised to a carboxyl-group, and at the same time a nitro-group is substituted for an atom of hydrogen. The *nitrouracilic acid*, which is thus obtained, is decomposed in boiling alkaline solution, giving *nitrouracil*,

$$\begin{matrix} NH-- & CO \\ | & | \\ CO & C\cdot NO_2 \\ | & \| \\ NH-- & C--COOH \end{matrix} = \begin{matrix} NH-- & CO \\ | & | \\ CO & C\cdot NO_2 \\ | & \| \\ NH-- & CH \end{matrix} + CO_2.$$

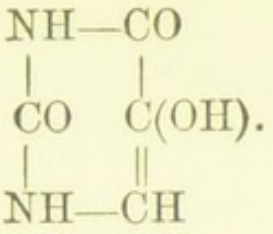
Nitrouracilic Acid. Nitrouracil.

When treated with tin and hydrochloric acid, nitrouracil is converted into a mixture of *aminouracil* and *hydroxyuracil*,

* In this reaction the ethyl acetoacetate, $CH_3\cdot CO\cdot CH_2\cdot COOEt$, is probably first converted into the enolic isomeride, $CH_3\cdot C(OH):CH\cdot COOEt$ (p. 205).

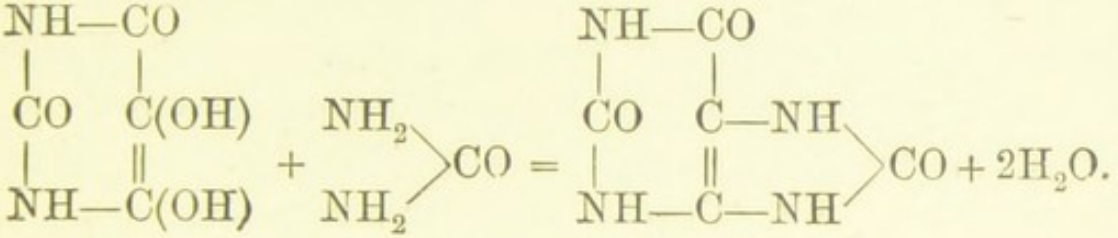


Aminouracil.



Hydroxyuracil.

Bromine-water oxidises hydroxyuracil to *dihydroxyuracil* (*dialuric acid*), which, when heated with urea and sulphuric acid, yields uric acid,

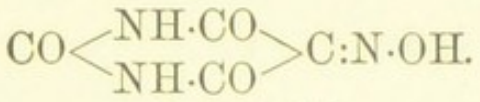


Dialuric Acid. Uric Acid.

Another synthesis of uric acid was accomplished by E. Fischer as follows :—*Malonylurea* (*barbituric acid* *), a diureïde (p. 565), prepared by heating urea with malonic acid, is treated with nitrous acid, by which it is converted into *violuric acid*,*

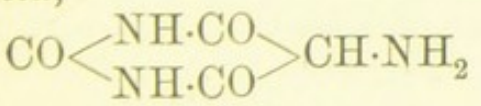


Malonylurea.



Violuric Acid.

On reduction, violuric acid gives *uramil*, which reacts with potassium cyanate in aqueous solution to form *pseudouric acid*,*



Uramil.



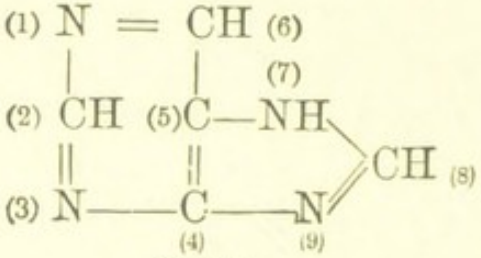
Pseudouric Acid.

* Obviously, barbituric acid, violuric acid, pseudouric acid, and uric acid, like parabanic acid (footnote, p. 565), are not carboxylic acids, and the formation of their metallic derivatives may be preceded by an isomeric change of the *lactam* group –CO·NH– into the *lactim* group –C(OH):N– (compare p. 205). Many other reactions of these compounds may be similarly accounted for; if, for example, pseudouric acid first changes into an enolic form, $CO\langle^{NH\,—\,CO}_{NH\cdot C(OH)}\rangle C\cdot NH\cdot CO\cdot NH_2$, its further conversion into uric acid would seem to be a simple reaction. As a matter of fact, it is not known whether the substances named above are keto- or hydroxy-compounds.

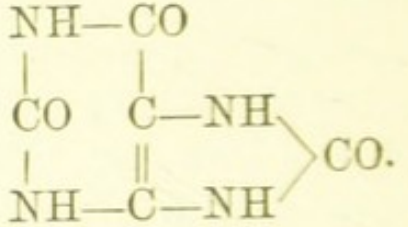
When this acid is heated with hydrochloric acid, or melted with oxalic acid, it loses the elements of water and gives uric acid.

Diethylmalonylurea, $CO\langle{}^{NH\cdot CO}_{NH\cdot CO}\rangle CEt_2$, a crystalline compound melting at 191°, is used as a hypnotic under the name of *veronal*.

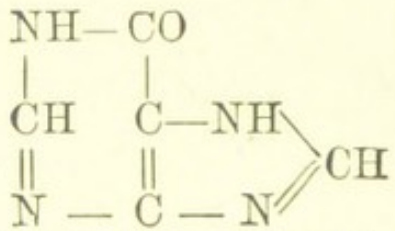
The Purine Derivatives.—Uric acid, and many other important natural products, may be regarded as derived from *purine*, a substance which has been prepared by E. Fischer. The names and formulæ of the more important members of this group are given below, numbers being used to indicate the positions of the substituents in the purine molecule.



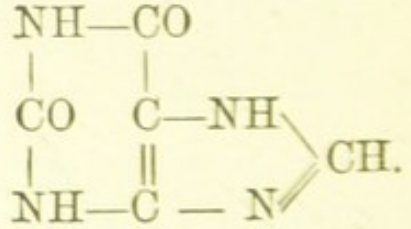
Purine.



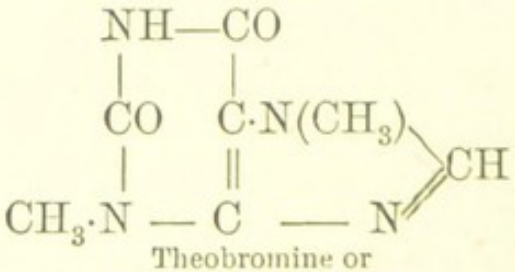
Uric Acid or 2,6,8-Trioxypurine.



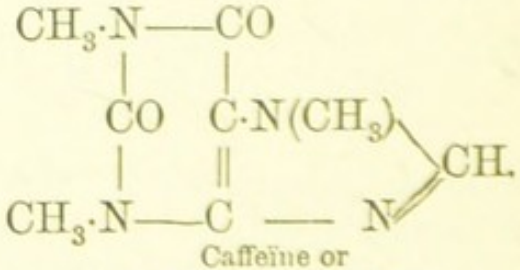
Hypoxanthine or 6-Oxypurine.



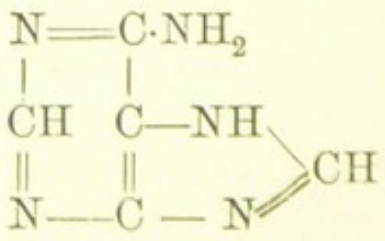
Xanthine or 2,6-Dioxypurine.



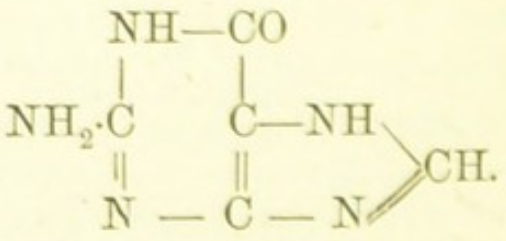
Theobromine or
3,7-Dimethylxanthine.



Caffeïne or
1,3,7-Trimethylxanthine.



Adenine or 6-Aminopurine.



Guanine or 2-Amino-6-oxypurine.

Purine, $C_5H_4N_4$, is obtained by treating *trichloropurine* (see below) with hydriodic acid at 0°, and then reducing the 2,6-*diiodopurine*, which is thus produced,

$$C_5HN_4Cl_3 + 4HI = C_5H_2N_4I_2 + 3HCl + I_2,$$

with zinc-dust in aqueous solution.

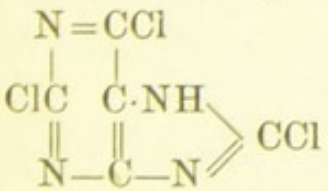
Purine melts at 217°, and is very readily soluble in water; it has both basic and acid properties.

Hypoxanthine, $C_5H_4N_4O$ (*sarkine*, or 6-*oxypurine*), has been found, usually accompanied by xanthine, in blood and urine; also in the muscles, spleen, liver, pancreas, and marrow. It is sparingly soluble in water, but dissolves readily in both acids and alkalis; it may be obtained from adenine, as described below.

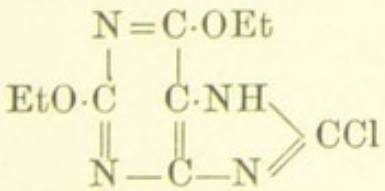
Xanthine, $C_5H_4N_4O_2$ (2,6-*dioxypurine*), occurs in small quantities in the blood, the liver, the urine, and in urinary calculi; it is also present in tea. It may be obtained from guanine (p. 570) by the action of nitrous acid, the amino-group being displaced by hydroxyl in the usual way.*

Xanthine is a white amorphous powder, sparingly soluble in water, but readily soluble in potash; it gives a lead derivative, which, when heated with methyl iodide, yields *theobromine* (p. 570). When oxidised with potassium chlorate and hydrochloric acid, it is resolved into urea and alloxan (p. 564).

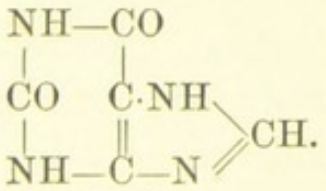
Xanthine has been obtained synthetically by Emil Fischer in the following way:—Uric acid, with phosphorus oxychloride at 160°, yields 2,6,8-trichloropurine,† which, with sodium ethoxide, gives 2,6-*diethoxy*-8-*chloropurine;* this compound is then reduced to xanthine with hydriodic acid,



Trichloropurine.



Diethoxychloropurine.



Xanthine.

* The group –N:C(OH)– in the primary product may then pass into the group –NH–CO–. (Compare footnote, p. 567.)

† Compare footnote, p. 567.

Caffeïne, $C_8H_{10}N_4O_2$ (*theïne*, or *methyltheobromine*), occurs in coffee-beans ($\frac{1}{2}$ per cent.), in tea (2 to 4 per cent.), in kola-nuts (2·5 per cent.), and in other vegetable products.

Tea (1 part) is macerated with hot water (4 parts), milk of lime (1 part) is added, and the mixture is evaporated to dryness on a water-bath; the caffeïne is then extracted by means of chloroform, the extract is evaporated, and the crude base is purified by recrystallisation from water.

Caffeïne forms colourless needles, ($1H_2O$), melts at 225°, and at higher temperatures sublimes unchanged; it has a bitter taste, and is sparingly soluble in cold water and alcohol. Caffeïne is a feeble base, and forms salts with strong acids only; even the *hydrochloride*, $C_8H_{10}N_4O_2$,HCl, is hydrolysed by water.

Tests for Caffeïne.—If a trace of caffeïne is evaporated with concentrated nitric acid, it gives a yellow residue (*amalinic acid*), which on the addition of ammonia becomes intensely violet (murexide reaction); this reaction is also shown by uric acid (p. 333). A solution of caffeïne in chlorine-water yields, on evaporation, a yellowish-brown residue, which dissolves in dilute ammonia, giving a beautiful violet-red solution.

Theobromine, $C_7H_8N_4O_2$ (3,7-*dimethylxanthine*), occurs in cocoa-beans, and resembles caffeïne in properties; when treated with an ammoniacal solution of silver oxide, it yields *silver theobromine*, which reacts readily with methyl iodide, giving caffeïne,

$$C_7H_7N_4O_2Ag + CH_3I = C_7H_7N_4O_2{\cdot}CH_3 + AgI.$$

Adenine, $C_5H_5N_5$ (6-*aminopurine*), may be prepared from the nuclei of cells, and is thus often found in the extracts of animal tissues. It crystallises from water in pearly plates ($3H_2O$). Nitrous acid converts it into *hypoxanthine*, the amino-group being displaced by hydroxyl.* It has been obtained synthetically from trichloropurine (p. 569), which, when treated with ammonia, gives 6-*amino*-2,8-*dichloropurine*; the latter, on reduction with hydriodic acid, gives adenine.

Guanine, $C_5H_5N_5O$ (2-*amino*-6-*oxypurine*), has been found

* Compare footnote, p. 569.

in guano, the liver, the pancreas, and in animal tissues. It is an amorphous powder, which combines with acids to form salts. When treated with nitrous acid, it yields xanthine,* and when oxidised with potassium chlorate and hydrochloric acid, it gives parabanic acid (p. 565) and guanidine.

Guanidine, $NH_2{\cdot}C(NH){\cdot}NH_2$ (*imidourea*), was first prepared by Strecker in 1861 by the oxidation of guanine with potassium chlorate and hydrochloric acid. It may be prepared synthetically by treating cyanogen iodide † with ammonia, cyanamide (p. 324) being formed as an intermediate product,

$$NH_2{\cdot}C{\vdots}N + H{\cdot}NH_2 = NH_2{\cdot}C(NH){\cdot}NH_2.$$

Guanidine is conveniently prepared by heating ammonium thiocyanate at 170–200°, when the thiourea (p. 326), which is first produced, reacts with a further quantity of the ammonium thiocyanate, yielding guanidine thiocyanate,

$$NH_2{\cdot}CS{\cdot}NH_2 + NH_3,HS{\cdot}CN = NH_2{\cdot}C(NH){\cdot}NH_2,HS{\cdot}CN + SH_2.$$

Guanidine forms colourless crystals, and is readily soluble in water; it is a strong monacid base, and of its salts the nitrate, $NH_2{\cdot}C(NH){\cdot}NH_2,HNO_3$, like urea nitrate, is sparingly soluble in water.

When guanidine is treated with a mixture of nitric and sulphuric acids, it yields *nitroguanidine*, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}NO_2$, which, on reduction with zinc-dust and acetic acid, is converted into *aminoguanidine*, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}NH_2$. When the latter is warmed with acids, it yields *semicarbazide*,

$$NH_2{\cdot}C(NH){\cdot}NH{\cdot}NH_2 + H_2O = NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + NH_3,$$

which may be further hydrolysed into ammonia, carbon dioxide, and *hydrazine*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + H_2O = NH_3 + CO_2 + NH_2{\cdot}NH_2.$$

Semicarbazide is an important reagent (p. 141).

* Compare footnote, p. 569.

† Cyanogen iodide sublimes in colourless needles when a mixture of iodine and mercuric cyanide is heated; it is very poisonous.

CHAPTER XXXVII.

Some Complex Components of Animals and Plants.

The substances described in this chapter, with the exception of *lecithine* and *taurine*, are of unknown constitution and cannot be satisfactorily classified. Those which are called the *proteïns* are known to be of very great complexity, and although a few proteïns have been obtained in a crystalline condition, it is not yet certain that they are individual compounds.

Lecithine, $C_{44}H_{90}NPO_9$ (*protagon*), is very widely distributed throughout the animal and vegetable kingdoms. It is found in small quantities in bile and in most organs of the body, and is especially prominent in the brain substance, the blood-corpuscles, and the nerve tissues; it occurs in considerable quantities in yolk of egg (hence its name, from λεχιθος, yolk of egg), and is also found in plants, particularly in the seeds.

Preparation from Yolk of Egg.—The colouring matter of the yolk is first extracted with ether, and the residue is then well washed with water and warmed with absolute alcohol at 40–50°; the filtered solution is evaporated at a low temperature, and the residue again extracted with warm absolute alcohol. The extract is cooled to −10°, and the lecithine which separates is collected and washed with cold alcohol.

Lecithine is a waxy, apparently crystalline, very hygroscopic substance, soluble in alcohol and ether; in contact with water it swells up and forms a kind of emulsion. When treated with acids or baryta-water, it is decomposed into stearic acid,* glycerophosphoric acid,† and choline (p. 560),

$$C_{44}H_{90}NPO_9 + 3H_2O = 2C_{18}H_{36}O_2 + C_3H_9PO_6 + C_5H_{15}NO_2;$$

* Some forms of lecithine yield palmitic or oleïc acid instead of stearic acid.

† *Glycerophosphoric acid*, $C_3H_5(OH)_2{\cdot}O{\cdot}PO(OH)_2$, is a thick syrup, prepared from glycerol and metaphosphoric acid.

it is thus possible that the constitution of lecithine is represented by the following formula :—

$$C_3H_5\begin{cases} O\cdot CO\cdot C_{17}H_{35} \\ O\cdot CO\cdot C_{17}H_{35} \\ O—PO(OH)\cdot O\cdot CH_2\cdot CH_2\cdot N(CH_3)_3\cdot OH. \end{cases}$$

Glycocholic acid, $C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot COOH$, occurs in bile in the form of its sodium salt, $C_{26}H_{42}NO_6Na$.

Preparation.—Fresh bile is mixed with a few drops of hydrochloric acid and rapidly filtered through sand. The filtrate is mixed with concentrated hydrochloric acid and ether, in the proportion of 5 vols. of the former and 30 vols. of the latter to 100 vols. of bile. The crystals of glycocholic acid, which separate, are washed with water containing hydrochloric acid and ether. Taurocholic acid is contained in the mother-liquors.

Glycocholic acid forms colourless needles, melts at 133°, and is soluble in water and alcohol, but very sparingly soluble in ether; its alcoholic solution is dextrorotatory. When boiled with alkalis, it yields *cholalic acid* and glycine,

$$C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot COOH + H_2O = C_{24}H_{40}O_5 + NH_2\cdot CH_2\cdot COOH.$$

Taurocholic acid, $C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H$, occurs in human bile and in the bile of all carnivora. It crystallises in needles, is readily soluble in alcohol, and is dextrorotatory. Like glycocholic acid, it occurs in bile in the form of its sodium salt, $C_{26}H_{44}NO_7SNa$. When boiled with water, it is decomposed into cholalic acid and taurine,

$$C_{24}H_{39}O_4\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H + H_2O = C_{24}H_{40}O_5 + NH_2\cdot CH_2\cdot CH_2\cdot SO_3H.$$

Cholalic acid, $C_{24}H_{40}O_5$, crystallises in plates (m.p. 195°), which are sparingly soluble in water, readily in alcohol and ether; its solutions are dextrorotatory. It is a monobasic acid; but the only known decomposition which throws any light on the constitution of this interesting compound is that in which, when oxidised with permanganate, it yields acetic acid and o-phthalic acid.

Taurine, $NH_2\cdot CH_2\cdot CH_2\cdot SO_3H$ (*aminoisæthionic acid*), was

discovered by Gmelin, in 1824, in ox-gall, in which it occurs in the form of taurocholic acid. It is readily soluble in water, but insoluble in alcohol; it is neutral to indicators, but forms salts, such as the sodium salt, $NH_2 \cdot CH_2 \cdot CH_2 \cdot SO_3Na$, with bases.

Taurine has been prepared by carefully treating alcohol with sulphur trioxide, when *isæthionic acid* is produced,

$$CH_3 \cdot CH_2 \cdot OH + SO_3 = SO_3H \cdot CH_2 \cdot CH_2 \cdot OH.$$

This crystalline and very hygroscopic acid, with phosphorus pentachloride, yields *chlorethylsulphonic acid*, $CH_2Cl \cdot CH_2 \cdot SO_3H$, from which taurine is obtained with the aid of ammonia.

Cholesterol, $C_{27}H_{45} \cdot OH$, is an alcohol which occurs in bile, in the brain, and in considerable quantities in gall-stones and cancerous and tubercular deposits; it is also found in the yolk of egg, in the fat (lanoline) obtained from wool, and in guano.*

It is readily obtained by extracting gall-stones with absolute alcohol and evaporating the extract; the residue is purified by treatment with alcoholic potash, which removes extraneous matter, and is then crystallised from a mixture of ether and alcohol.

Cholesterol separates from water in colourless needles, melts at 145°, and distils at about 360° without decomposing appreciably; it is levorotatory.

Reactions of Cholesterol.—When a few centigrams of cholesterol are dissolved in chloroform (2 c.c.) and the solution is shaken with concentrated sulphuric acid (2 c.c.), the chloroform solution is coloured red and then purple, and the sulphuric acid acquires a green fluorescence. If a few drops of the chloroform solution are poured into a dish, the colour changes to blue, then to green, and lastly to yellow.

Concentrated sulphuric acid containing a little iodine colours cholesterol first violet, then blue, then green, and lastly red. Warmed with dilute (20 per cent.) sulphuric acid, cholesterol crystals are coloured red at the edges.

* A substance very similar to cholesterol, and named paracholesterol or phytosterol, is found in the seeds of certain plants.

The Proteïns.

The 'white of egg,' when separated from the yolk, membrane, and shell, is a thick, colourless, transparent, sticky fluid, miscible with water; on exposure to the air it rapidly loses water, and if dried artificially it quickly shrivels up, giving a translucent amorphous solid (egg-albumin).

When white of egg is put into boiling water it undergoes a remarkable change, and is said to have *coagulated;* it is now insoluble in water and opaque, and forms a solid mass, which, however, still contains a large percentage of water; during coagulation, it is probable that chemical as well as physical changes have occurred.

When white of egg is left exposed to the air under ordinary (non-sterile) conditions it soon begins to putrefy—that is to say, it decomposes under the influence of organisms, yielding a great number of products, among which are hydrogen sulphide, ammonia, ptomaines (p. 563), and various amino-acids (p. 552). Further, when white of egg is heated with dilute mineral acids or with alkalis, it undergoes a profound decomposition, giving in the first place various highly complex products (albumoses, propeptones, peptones), and finally a great number of simpler compounds, of which the amino-acids are the most important. Similar results are obtained with the aid of digestive enzymes, such as pepsin.

This brief account of the behaviour of white of egg will suffice to show that it is an extremely unstable and extraordinarily complex substance, and its physical properties are so indefinite that it is almost impossible to say whether or not it is an individual chemical compound.

Now, white of egg, or egg-albumin, may be taken as the representative of a group of substances, which are classed together as the **proteïns.** These substances form not only the most important part of the contents of the cells of all animals (πρωτεῖον, pre-eminence), but they also occur in considerable quantities in all plants, especially in the seeds or

grain; it is, in fact, from these vegetable proteïns that those contained in animals are formed, since the animal, unlike the plant, is incapable of building up more complex substances from simpler food material, except to a very limited extent. The vegetable proteïns, then, are assimilated by animals, and apparently they are changed very little during this process.

As so little is known of the constitutions of these substances, an attempt to define exactly what is meant by the term proteïn would meet with slight success; the following general statements, however, may be made. The proteïns are insoluble in alcohol and ether, and also, as a rule, in water; but many of them dissolve in salt solutions, and the presence of salts probably accounts for the solubility of the proteïns in the fluids of the animal body. They are all optically active (levorotatory), and they are all colloids. One of the more interesting properties shown by some of the proteïns is that of undergoing *coagulation*, a change which is readily brought about by heat; but different proteïns coagulate at somewhat different temperatures, varying roughly between 55° and 75°, and some are also coagulated by alcohol and by mineral acids.

All proteïns consist of carbon, hydrogen, oxygen, nitrogen, and sulphur; but the determination of the percentage composition of a proteïn is a task of considerable difficulty. As found in nature, all proteïns contain mineral matter, and consequently, on ignition, leave a small percentage of ash; after the removal of these mineral components by repeated precipitation, dialysis, &c., or when their presence is allowed for, the percentage composition of the various proteïns is found to vary within fairly wide limits, as shown by the following numbers:—

Carbon	50·0–55·0 per cent.
Hydrogen	6·9– 7·3 "
Nitrogen	15·0–19·0 "
Oxygen	19·0–24·0 "
Sulphur	0·3– 2·4 "

Egg-albumin has been obtained free from mineral matter and in a crystalline condition; its composition is C = 51·48, H = 6·76, N = 18·14, O = 22·66, S = 0·96 per cent.

The *empirical* formula, calculated from the percentage composition of egg-albumin, or from that of some other proteïn, comes out to something like $C_{146}H_{226}N_{44}SO_{50}$, which requires C = 51·2, H = 6·6, N = 18·0, and S = 0·9 per cent.; as, however, a very slight error in the analytical results would make a very great difference in the empirical formula, that just given is only a rough approximation.

The molecular weights of the proteïns are unknown; attempts have been made to determine them by various methods, but the results are very uncertain, and all that can be said is that the minimum value is probably 15,000, which is about twelve times as great as that of the octadecapeptide synthesised by E. Fischer (p. 556).

The proteïns are classed into various groups, principally according to their physical properties. Those which are coagulated by heat, for example, may be classed as albumins or globulins. The *albumins* (egg-albumin, blood-albumin) are soluble in water, and are not precipitated when their solutions are saturated with sodium chloride or magnesium sulphate. The *globulins* (serum-globulin) are insoluble in water, but dissolve in dilute salt solutions, from which they are precipitated when the solutions are saturated with magnesium sulphate.

The *phospho-proteïns* (caseïn) contain phosphorus and have an acidic character, in consequence of which they dissolve in alkalis, giving solutions which do not coagulate when they are heated.

Many other classes of proteïns are distinguished.

Closely related to the proteïns are the complex degradation products (*albumoses*, *propeptones*, *peptones*, and *polypeptides*) which are successively formed when proteïns are hydrolysed with the aid of digestive enzymes or chemical reagents.

Tests for Proteïns.—All proteïns are coloured violet-red by a solution of mercuric nitrate containing traces of nitrous acid.

This reagent (called *Millon's reagent*) is prepared by dissolving one part by weight of mercury in two parts of strong nitric acid and diluting the solution with twice its bulk of water; after some time the supernatant liquid is decanted from the precipitate.

When a proteïn is warmed with nitric acid it gives a yellow colour, which becomes bright orange on the addition of ammonia. This reaction, called the *xanthoproteïc reaction*, is stated to be the most delicate test for proteïns. If a few drops of copper sulphate solution are added to a proteïn, and then excess of potash, a red to violet colouration is produced; this reaction is called the *biuret reaction*, because it resembles the colour-reaction obtained in a similar manner with biuret (p. 332).

Hæmoglobins.—**Hæmoglobin** is the name given to the proteïn which constitutes the pigment of the red blood-corpuscles. 'It exists in the blood in two conditions; in arterial blood, it is loosely combined with oxygen, and is called *oxyhæmoglobin;* the other condition is the deoxygenated or reduced hæmoglobin (often simply called *hæmoglobin*), which occurs in venous blood—that is, the blood which is returning to the heart, after it has supplied the tissues with oxygen. Hæmoglobin is thus the oxygen-carrier of the body, and it may be called a respiratory pigment.'*

Oxyhæmoglobin can be obtained by mixing defibrinated blood with salt solution (1 vol. of saturated salt solution to 9 vols. of water), which precipitates the blood-corpuscles. These are washed with salt water of the same strength, mixed with a little water, and extracted with ether, which removes cholesterol, &c., all these operations being conducted as nearly as possible at 0°. The aqueous solution is then filtered, and the filtrate is mixed with one-fourth of its vol. of alcohol, and cooled to −10°, when crystals of oxyhæmoglobin separate. These may be purified by recrystallisation from ice-cold aqueous alcohol.

Oxyhæmoglobin forms light-red rhombic crystals, which dissolve readily in water and are reprecipitated by alcohol. Its percentage composition is nearly the same as that of egg-albumin (p. 576), except that oxyhæmoglobin always contains 0·4 per cent. of iron. When oxyhæmoglobin, in

* Halliburton, *Chemical Physiology.*

aqueous solution, is placed under greatly reduced pressure, or treated with weak reducing agents, it loses oxygen and is converted into *hæmoglobin*, a substance which has also been obtained in a crystalline form; and, *vice versâ*, hæmoglobin, in aqueous solution, is rapidly converted into oxyhæmoglobin in contact with air. If carbon monoxide is led into a solution of oxyhæmoglobin, the last-named substance loses its oxygen and combines with the carbon monoxide to form *carbonic oxide hæmoglobin*, a compound which crystallises in large, bluish crystals. This compound is not capable of absorbing and giving up oxygen like hæmoglobin—a fact which explains the poisonous action of carbon monoxide. Oxyhæmoglobin, hæmoglobin, and carbonic oxide hæmoglobin all show characteristic absorption spectra, which allow of their being easily identified and distinguished from one another.

Hæmin and Hæmateïn.—When oxyhæmoglobin or dried blood is warmed with a drop of acetic acid and a small crystal of common salt on a microscopic slide, and the mixture is then cooled, reddish-brown crystals separate. These consist of *hæmin*, the chloride of hæmateïn, and have the composition, $C_{32}H_{31}N_4O_3FeCl$. If these crystals are treated with alkali, brownish-red flocks of *hæmateïn*, $C_{32}H_{31}N_4O_3Fe{\cdot}OH$, separate; and this formation of hæmin and hæmateïn serves as a very delicate test for blood.

Chlorophyll is the green colouring matter of plants; it may be extracted from leaves with the aid of alcohol, and thus obtained as a green, amorphous mass. Its composition is unknown, but it is noteworthy that magnesium seems to be an essential constituent.

Chlorophyll, like hæmoglobin, shows a characteristic absorption spectrum, and the absorption spectrum and other properties of certain chlorophyll derivatives are almost identical with those of certain derivatives of hæmoglobin. As the function of hæmoglobin is to absorb oxygen, that of chlorophyll to set free oxygen from carbonic acid, this close relationship between the two compounds is of great physiological interest, and it

is remarkable that the two substances responsible for such different vital functions should appear to be similar in chemical composition.

Gelatin is a substance closely related to the proteïns; it may be obtained by the action of dilute acids on the white fibres of connective tissue.

It is best prepared by digesting bones, first with dilute acids to remove inorganic matter, and then with water under pressure at 110–120°; when the filtered solution is evaporated, commercial gelatin is obtained.

Gelatin is a hard, almost transparent, horn-like substance which is insoluble in alcohol, ether, and in cold water, but dissolves readily in hot water, yielding a solution which sets to a jelly (*gelatinises*) as it cools. If, however, the aqueous solution is boiled for some hours, the power of gelatinising is entirely lost. Gelatin forms an insoluble compound with tannic acid, and the process of tanning consists partly in converting the gelatin in the hides into this hard, insoluble compound by steeping them in tannic acid solution. Gelatin is also rendered insoluble in water when it is treated with formaldehyde. When heated with dilute sulphuric acid, gelatin breaks down, much in the same way as do the proteïns, yielding *glycine*, *leucine*, and other amino-acids.

CHAPTER XXXVIII.

The Terpenes and Related Compounds.

Although the carbohydrates (p. 293), the proteïns (p. 575), and the non-volatile fatty glycerides (olive-, linseed-, palm-oil, &c.) form by far the greater part of the dry matter of plants, there are many other important and interesting compounds obtained from the vegetable kingdom. Nearly all plants contain certain volatile, odoriferous liquids called *essential oils*,

many of which possess a pleasant odour or taste, and are used in the manufacture of essences and perfumes; many of them are also used in medicine.

Most essential oils are complex mixtures; and, although the characteristic properties of any one such oil are usually due to the presence of some particular compound, this compound may be accompanied by many others. It often happens, therefore, that two or more essential oils may have one or more components in common, and yet differ entirely in smell, because each contains, in addition, some highly odoriferous compound which does not occur in the others.

A few essential oils have already been mentioned—as, for example, oil of wintergreen (p. 491), oil of mustard (p. 327), oil of bitter almonds (p. 453), and oil of aniseed (p. 460)—and their main components have been described. The following three compounds are also obtained from essential oils, and are extensively used in perfumery :—

Citral. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CHO.$

Geraniol. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CH_2\cdot OH.$

Linalool. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH\cdot CH_2\cdot CH_2\cdot C(OH)(CH_3)\cdot CH:CH_2.$

Citral, $C_{10}H_{16}O$, occurs in the oils of lemon, orange, and verbena, and may be obtained by oxidising geraniol; it boils at 224–228°.

Geraniol, $C_{10}H_{18}O$, constitutes about 90 per cent. of Indian geranium-oil, and is principally used for the adulteration of oil of roses; it boils at 120–122° (17 mm. pressure).

Linalool, $C_{10}H_{18}O$, occurs in the oils of lavender and bergamot; it boils at 197–199°. Linalool and geraniol are both transformed into terpin (p. 592) when they are shaken with a 5 per cent. aqueous solution of sulphuric acid, and it is possible that the formation of terpenes in plants is the result of reactions of this kind.

The most abundant and perhaps the most generally known

of all the essential oils is the liquid called '*turpentine*,' which is obtained by making shallow cuts in the stems of the pine-trees or coniferæ, and collecting the sap or juice which flows out.

Turpentine consists of a solution of various solids—called *resins*—in a liquid called *oil of turpentine;* when crude turpentine is distilled in steam, the essential oil passes over, leaving a residue of resin or *colophony* (violin rosin).

Oil of turpentine is a colourless, mobile liquid of sp. gr. about 0·86, boiling at about 158–160°; it is, however, a mixture, and shows considerable variations in properties according to the species of pine from which it has been obtained. The oil has a well-known, not unpleasant odour, which is probably not due to its principal component, but to small quantities of substances formed from it by oxidation. On exposure to moist air, oil of turpentine gradually changes; it darkens in colour, becomes more viscous, and is converted into resin and a variety of oxidation products, hydrogen peroxide being also produced during these changes.

Oil of turpentine is practically insoluble in water, but is miscible with most organic liquids; it is an excellent solvent for many substances which are insoluble in water, such as phosphorus, sulphur, and iodine, and it also dissolves resins and caoutchouc; it is used on the large scale in the preparation of varnishes and oil-paints.

The Terpenes.

The principal component of oil of turpentine is a hydrocarbon called *pinene*, a substance which occurs not only in all pine-trees, but also in a great many other plants—as, for example, in the essential oils of eucalyptus, laurel, lemon, parsley, sage, juniper, and thyme.

Pinene, $C_{10}H_{16}$, is a colourless, mobile liquid (sp. gr. 0·858 at 20°), having an odour of 'turpentine.' It boils at 155°, and is readily volatile in steam.

Pinene combines directly with two atoms of bromine, yielding a crystalline *dibromide*, $C_{10}H_{16}Br_2$, and with one molecule of hydrogen chloride, giving *pinene hydrochloride*, $C_{10}H_{17}Cl$, a compound (m.p. 131°) which has the odour and appearance of camphor (p. 594), and is often called 'artificial camphor.'

Pinene also combines directly with nitrosyl chloride (NOCl), giving a crystalline *pinene nitrosochloride*, $C_{10}H_{16}NOCl$, which melts at 103°.

The formation of these additive products seems to show that the molecule of pinene contains one ethylenic linking; the products themselves are of great use for the identification of pinene.

When pinene dibromide is heated alone, at a moderately high temperature, it is converted into *cymene* (p. 378) and hydrogen bromide,

$$C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr;$$

cymene is also produced, together with various other hydrocarbons, when pinene is heated with iodine.

The pinene obtained from American turpentine is *dextro*rotatory (*d*-pinene), whereas that isolated from French turpentine is *levo*-rotatory (*l*-pinene); but it is very difficult to obtain either compound in a state of purity. *dl*-Pinene can easily be obtained by decomposing the nitrosochloride of either of the optically active modifications with aniline.

Camphene, $C_{10}H_{16}$, is a solid hydrocarbon, which occurs in a number of essential oils (ginger-, citronella-, spike-, valerian-oil), and which can also be obtained artificially from various naturally-occurring compounds; it melts at 48°, boils at 160°, and is practically insoluble in water.

Camphene is formed when pinene hydrochloride, $C_{10}H_{17}Cl$ (*isobornyl chloride*), is heated at 200° with sodium acetate and glacial acetic acid, or distilled with lime (compare p. 597); it may also be obtained from camphor by the method described later (p. 598).

Camphene resembles pinene, inasmuch as it unites directly

with one molecule of hydrogen chloride, forming *camphene hydrochloride*, $C_{10}H_{17}Cl$, which melts at 149–151°; it also combines directly with two atoms of bromine, giving *camphene dibromide*, $C_{10}H_{16}Br_2$. It is, however, much more stable than pinene, and is only oxidised with difficulty; on treatment with chromic acid, it gives camphor (p. 594).

Camphene, like pinene, is optically active; the *d*-, *l*-, and *dl*-forms are all known.

Limonene, $C_{10}H_{16}$, like pinene, is an important component of essential oils, and occurs in those of lemon, lime, lavender, caraway, bergamot, celery, turpentine, and many others; it is a colourless, pleasant-smelling, mobile liquid, boiling at 175°. It combines directly with *four* atoms of bromine to form a crystalline *limonene tetrabromide*, $C_{10}H_{16}Br_4$, which melts at 104°; it also unites with two molecules of hydrogen chloride or hydrogen bromide, yielding the crystalline compounds, $C_{10}H_{18}Cl_2$ and $C_{10}H_{18}Br_2$, respectively. On oxidation with concentrated sulphuric acid, it yields *cymene*.

Limonene is optically active. *d*-Limonene is found in lemon-oil, whereas *l*-limonene occurs in pine-needle-oil and in Russian oil of peppermint. *dl*-Limonene was named *di-pentene* before its relation to the active forms was known.

Dipentene is formed (as the result of racemisation: p. 604) when either of the optically active modifications is heated at 250–300°; it is also produced when pinene or camphene is treated in a similar manner—a fact which seems to show that there is a close relationship between these three hydrocarbons. Further, when either of the active limonenes is combined with *two* molecules of hydrogen chloride or bromide, the product, $C_{10}H_{18}Cl_2$ or $C_{10}H_{18}Br_2$, is optically *inactive*, and is named *dipentene dihydrochloride* or *dihydrobromide* as the case may be.

Dipentene occurs naturally in *Oleum cinæ;* it is best prepared by heating terpineol (p. 590) with potassium hydrogen sulphate. *Dipentene tetrabromide*, $C_{10}H_{16}Br_4$, melts at 124°, and the *nitrosochloride*, $C_{10}H_{16}NOCl$, at 102°.

Pinene, camphene, and limonene are three important

members of a group of substances of vegetable origin which are classed together as the **terpenes** (from the word 'turpentine').

The term terpene, however, cannot be accurately defined; although it is more particularly employed to denote certain unsaturated *hydrocarbons* of the molecular formula, $C_{10}H_{16}$, even these compounds differ considerably in constitution, and consequently, also, in properties.

The Constitutions of the Terpenes.

The first fact of general importance which bears on the question of their structures is, that the terpenes combine directly with bromine, hydrogen chloride, hydrogen bromide, and nitrosyl chloride, or at least with one or other of these reagents, forming crystalline additive products. But whereas some of the terpenes combine directly with *four* atoms of bromine or *two* molecules of hydrogen bromide, others unite with only *two* atoms of bromine or *one* molecule of hydrogen bromide. This difference in behaviour admits of a classification of the terpenes into two groups, as follows:—

TYPE I.—Terpenes which combine with $2Br_2$ or with 2HBr.
Limonene.*

TYPE II.—Terpenes which combine with Br_2 or with HBr.
Pinene. Camphene.

Now, their behaviour towards bromine, halogen acids, &c., affords evidence that the terpenes are not *open-chain* hydrocarbons of the molecular formula, $C_{10}H_{16}$. If they were compounds of this type they should unite directly with *six* atoms of bromine or with *three* molecules of a halogen acid, because their molecules would contain either three olefinic bindings or one olefinic and one acetylenic binding, as do those of the

* Several other members of each of these types are known, but as they cannot be described here their names are not given.

two (unknown) open-chain hydrocarbons of the molecular formula, $C_{10}H_{16}$, shown below,

$$CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$
$$CH{:}C{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

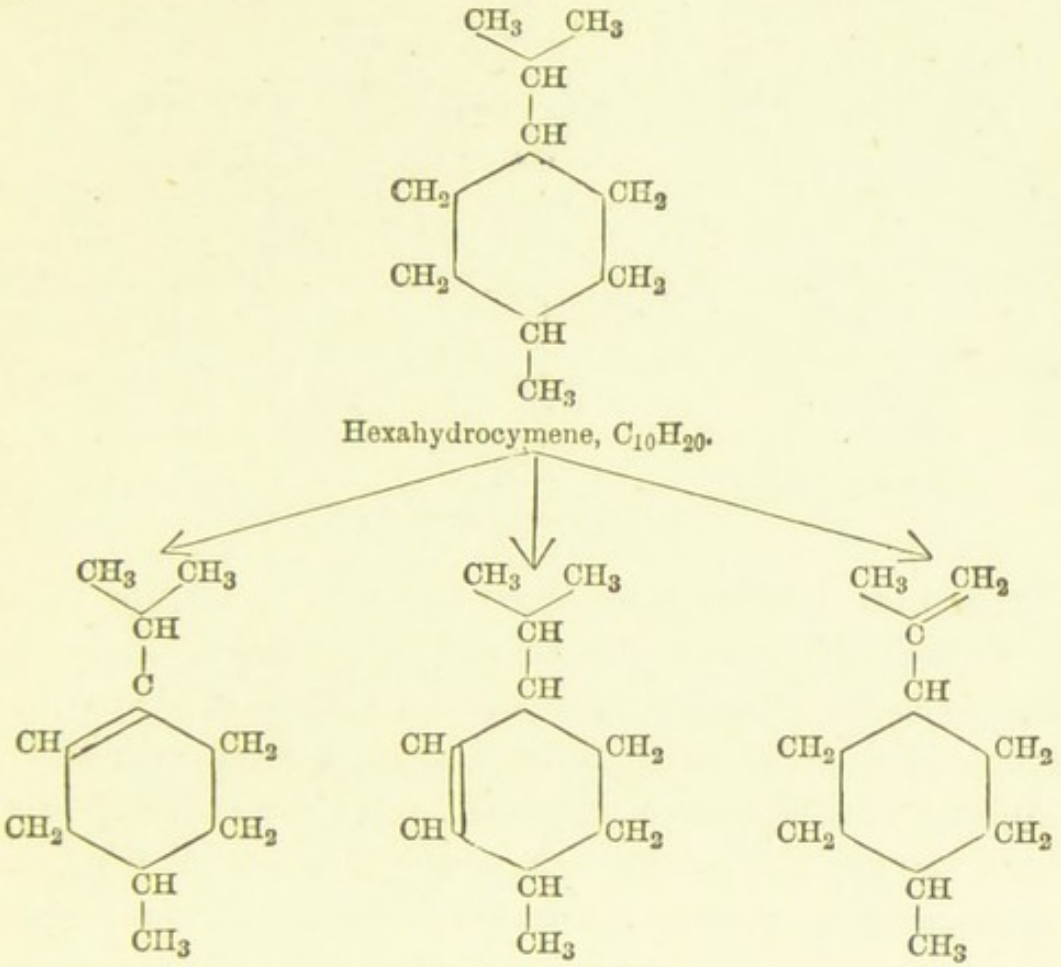
Another fact of general importance is that many of the terpenes are easily transformed into comparatively simple derivatives of benzene, among which is frequently found the well-known hydrocarbon, *cymene* or **p**-*isopropylmethylbenzene*, $C_{10}H_{14}$ (p. 378).

This conversion of terpenes and their derivatives into cymene, and also the fact that cymene often occurs together with the terpenes in essential oils, led to the conclusion that the terpenes were probably derivatives of, or closely related to, cymene—that is to say, that they probably contained the same 'skeleton' of carbon atoms as that which occurs in cymene. Further investigation, more especially the study of their oxidation products (compare p. 589), only served to confirm this view, and in the course of time the constitutions of some of the terpenes were definitely established.

Before the structural formulæ of any of the terpenes are given, the manner in which unsaturated (olefinic) *closed-chain* hydrocarbons might be derived from the aromatic hydrocarbon cymene may be considered. For this purpose a reference may first be made to the description of the reduction products of benzene (pp. 365, 366).

Now, just as benzene is related to the saturated hydrocarbon, cyclohexane, from which unsaturated hydrocarbons (cyclo-olefines) may be prepared, so also cymene is related to the saturated compound, *hexahydrocymene*, from which corresponding cyclo-olefines may be derived. From hexahydrocymene, however, not two but a number of isomeric cyclo-olefines could theoretically be formed by the loss of hydrogen; if, for example, *two neighbouring* atoms of hydrogen were removed, various isomeric hydrocarbons of the molecular formula, $C_{10}H_{18}$, might be obtained. The formulæ of three

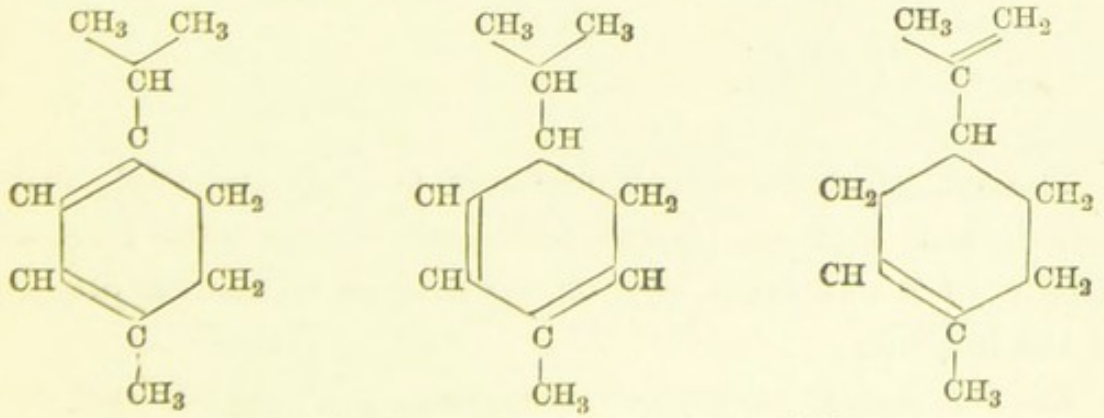
of the numerous isomerides, which are theoretically possible, are given below.



Hexahydrocymene, $C_{10}H_{20}$.

Cyclo-olefines, $C_{10}H_{18}$.

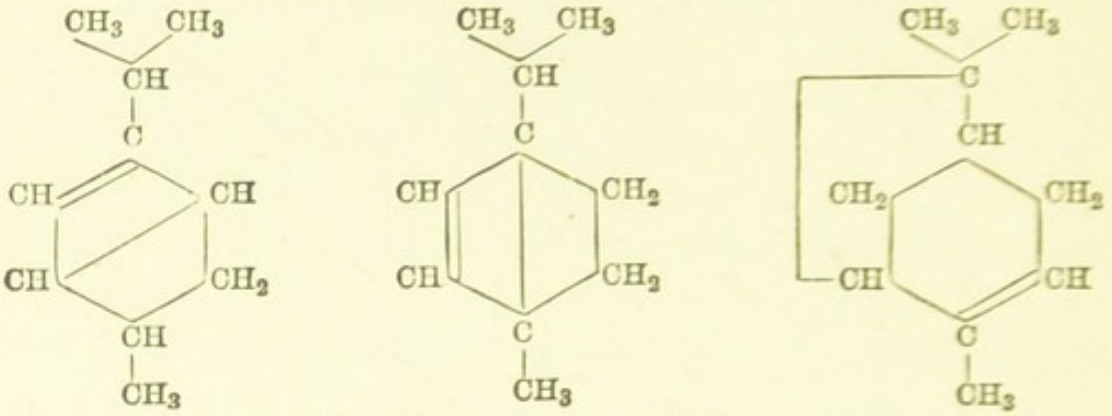
If two more *neighbouring* atoms of hydrogen were removed, hydrocarbons of the molecular formula, $C_{10}H_{16}$, would be obtained—as, for example, the following:—



Type I. Cyclo-diolefines or Cyclo-dienes, $C_{10}H_{16}$.

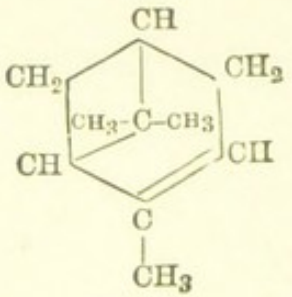
If, on the other hand, the two hydrogen atoms were removed from $-CH_2-$ or $>CH-$ groups, which are not directly

united with one another, each hydrocarbon, $C_{10}H_{18}$, might give various isomeric hydrocarbons, $C_{10}H_{16}$, such as the following:—

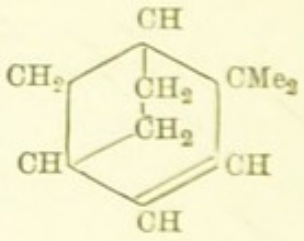


Type II. Cyclo-olefines, $C_{10}H_{16}$.

It is now known that the constitutions of the terpenes are expressed by formulæ of one or other of these types. Limonene, for example, is a cyclo-diolefine of Type I., and its constitution is more fully discussed later. Pinene and camphene are terpenes of Type II., and their constitutions are shown below; their molecules, or the formulæ by which their molecules are represented, are said to contain *bridged rings*.



*Pinene.**



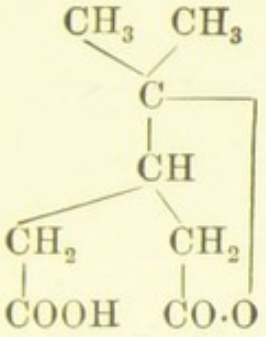
Camphene.

The constitution of camphene is not yet definitely established, but that of pinene has been determined from the results of a careful study of a series of oxidation products of the terpene.

Pinene readily undergoes oxidation, yielding various compounds; among these may be mentioned terephthalic acid

* This formula is identical with the third of the three expressions immediately above.

(p. 480) and two other important oxidation products—namely, terpenylic and terebic acids, the constitutional formulæ of which are given below.



Terpenylic Acid.



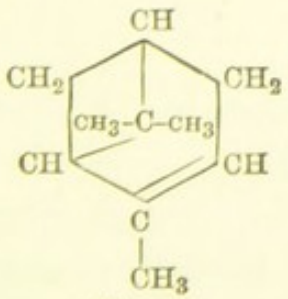
Terebic Acid.

Terpenylic acid, $C_8H_{12}O_4$, is a *lactone* (p. 243) and at the same time a monocarboxylic acid; it is crystalline, and melts at 90°.

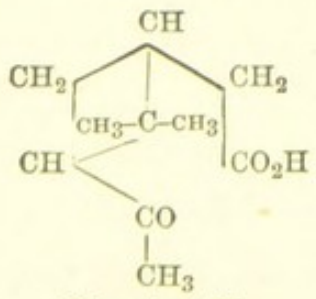
Terebic acid, $C_7H_{10}O_4$, is also a crystalline lactonic monocarboxylic acid (m.p. 175°), and is closely related to terpenylic acid, from which it can be obtained by oxidation with potassium permanganate.

As the constitutions of these two acids have been established, the formation of these oxidation products threw a good deal of light on the constitution of pinene.

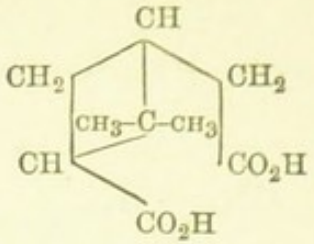
Further, and more conclusive, evidence was obtained by Baeyer, who showed that, on careful oxidation with potassium permanganate, pinene was converted into *pinonic acid.* The constitution of this acid was proved by the fact that, on treatment with an alkali hypobromite, it gave *pinic acid,* which, on further oxidation with chromic acid, was converted into *norpinic acid* (*dimethylcyclobutanedicarboxylic acid*).



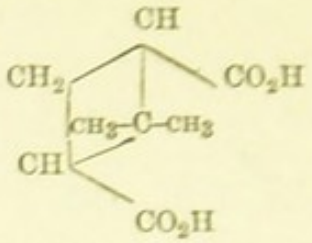
Pinene.



Pinonic Acid.



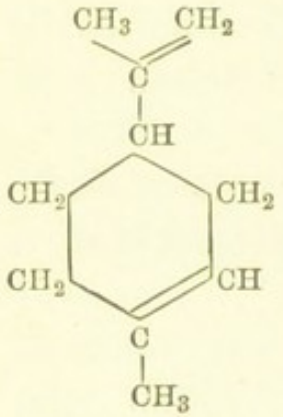
Pinic Acid.



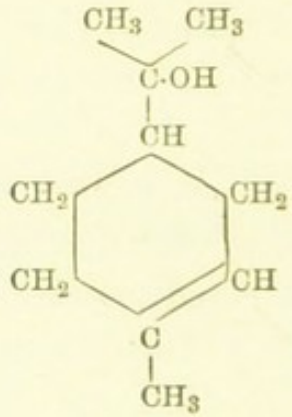
Norpinic Acid.

The Synthesis of dl-*Limonene and of Related Compounds.*

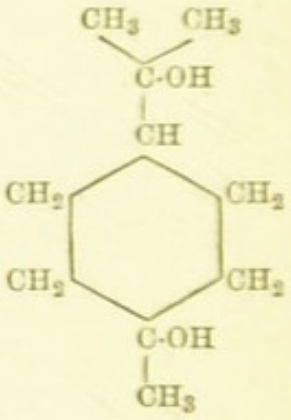
dl-*Limonene* (dipentene, p. 584) and the two compounds *terpineol* and *terpin*, which are closely related to limonene, have been prepared synthetically, and their constitutions are respectively represented by the following formulæ :—



dl-Limonene
(Dipentene).



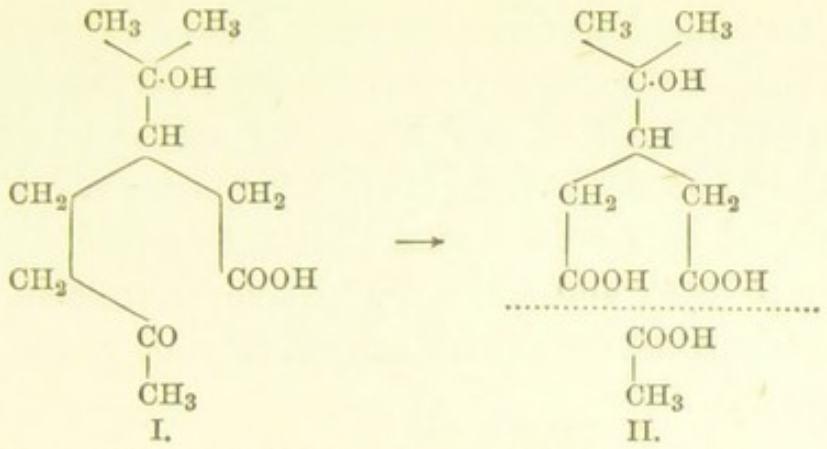
dl-Terpineol.



Terpin.

dl-*Terpineol*, $C_{10}H_{18}O$, is formed when dipentene or limonene is shaken with a 5 per cent. aqueous solution of sulphuric acid, and is manufactured (for use in perfumery) by boiling *terpin hydrate* (p. 593) with dilute sulphuric acid. It melts at 36°, boils at 219°, and has a very strong odour of hyacinths.

On oxidation, terpineol yields a ketonic acid of the constitution given below (formula I.); this product is further oxidised to acetic acid and a dicarboxylic acid (formula II.), the latter of which passes into its lactone, *terpenylic acid* (p. 589),



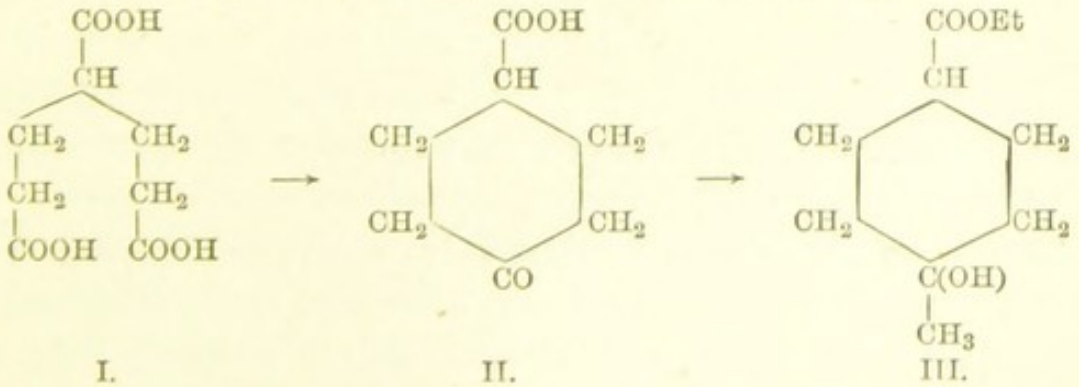
I. II.

A clear indication of the structure of terpineol having been obtained from the study of this series of oxidation products, and in other ways, it was possible to attempt the synthesis of this alcohol; this attempt was successfully made (Perkin) in the following manner:—

The sodium derivative of ethyl cyanoacetate (p. 209) reacts with two molecules of *ethyl β-iodopropionate*, giving *ethyl γ-cyanopentane-αγε-tricarboxylate* (compare footnote, p. 662),

$$CN\cdot CNa_2\cdot COOEt + CH_2I\cdot CH_2\cdot COOEt =$$
$$CN\cdot C(COOEt)\begin{matrix}CH_2\cdot CH_2\cdot COOEt\\CH_2\cdot CH_2\cdot COOEt\end{matrix} + 2NaI.$$

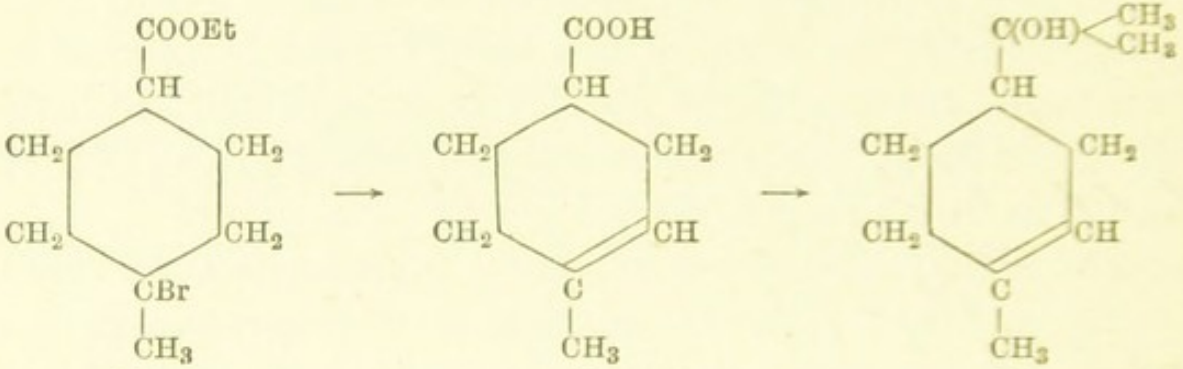
This ester, on hydrolysis with hydrochloric acid, yields *pentane-αγε-tricarboxylic acid* (I.),* which is converted into *δ-ketohexahydrobenzoic acid* (II.) when it is boiled with acetic anhydride and subsequently distilled. Ethyl δ-ketohexahydrobenzoate, treated with magnesium methyl iodide, yields the ester of *δ-hydroxyhexahydro*-p-*toluic acid* (III.),



I. II. III.

* The tetracarboxylic acid, which is first produced by the hydrolysis of the -CN group, decomposes with loss of carbon dioxide.

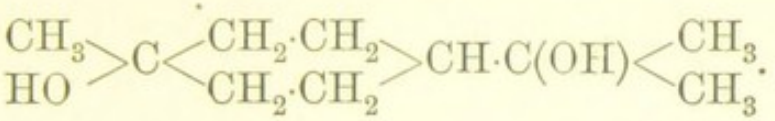
The last-named hydroxy-compound (III.) gives, with hydrobromic acid, the corresponding bromo-derivative (IV.), which on treatment with alkalis loses one molecule of hydrogen bromide and is converted into *tetrahydro*-**p**-*toluic acid* (V.). The ester of this acid reacts with magnesium methyl iodide (compare p. 228), and when the product is treated with water it gives **terpineol** (VI.); the constitution of terpineol is thus established.



Terpineol is converted into **dipentene** (*dl*-limonene) when it is heated with potassium hydrogen sulphate, and, theoretically, this loss of the elements of water might occur in one of two different ways, giving the complex, $>C=C<^{CH_3}_{CH_3}$, or $>CH-C<^{CH_3}_{CH_2}$. But dipentene, being a *dl*-mixture, must contain in its molecule at least one asymmetric carbon group. Consequently, of the above two, the latter complex must be formed, otherwise the molecule of dipentene would not contain an asymmetric group. The constitution of dipentene (and of limonene), therefore, is expressed by the formula already given (p. 590).

Terpin, $C_{10}H_{20}O_2$, is produced by shaking terpineol with dilute sulphuric acid, and is manufactured by treating oil of turpentine with nitric acid and alcohol at ordinary temperatures. It has been synthesised by treating ethyl δ-ketohexahydrobenzoate (p. 591) with excess of magnesium methyl

iodide and decomposing the product with water; its constitution, therefore, is expressed by the formula,



Terpin melts at 104°, and boils at 258°. It combines readily with water, giving **terpin hydrate**, $C_{10}H_{20}O_2,H_2O$, a crystalline compound, which melts at 117°.

Sesquiterpenes and Polyterpenes.

The terpenes of the molecular formula, $C_{10}H_{16}$, are often accompanied in nature by other unsaturated hydrocarbons of higher molecular weight, which are no doubt related to the terpenes more or less closely. Some of these more complex hydrocarbons have the same empirical formula, (C_5H_8), as the terpenes, and their molecular formula, therefore, is $(C_5H_8)_n$, generally $C_{15}H_{24}$ or $C_{20}H_{32}$. It has been suggested, therefore, that all these compounds, including the terpenes, are polymeric modifications of some simple hydrocarbon (C_5H_8); this view finds some support in the fact that the hydrocarbon *isoprene*, C_5H_8 (p. 90), which is formed in the destructive distillation of india-rubber and of some of the terpenes, readily undergoes polymerisation, forming not only terpenes, but also more complex hydrocarbons which are very similar to india-rubber in properties.

In consequence of this relationship in composition, the naturally-occurring hydrocarbons of the molecular formula, $C_{15}H_{24}$, have been named the *sesquiterpenes*, whilst the still more complex ones have been named the *polyterpenes*.

The two best-known sesquiterpenes are *cadinene* and *caryophyllene*, both of which are viscous liquids, boiling at about 274° and 255° respectively.

Cadinene occurs in the essential oils of cubeb, juniper, camphor, &c., and caryophyllene in oil of cloves.

Compounds closely related to the Terpenes.

Although the terpenes are such constant and important components of most essential oils, the specific odour or taste of the latter is usually due to the presence of one or more compounds, which contain *oxygen* as well as carbon and hydrogen; the compounds in question are usually *ketones* (such as camphor and menthone), *phenols* (such as thymol and carvacrol: p. 445), *alcohols* (such as borneol and menthol), or *esters*, and most of them are closely related to the terpenes in constitution. A few of the more important of these naturally-occurring terpene derivatives are described in the following pages; like the terpenes, they are *optically active*.

d-**Camphor**, $C_{10}H_{16}O$, is a component of essential oil of camphor, and is obtained from the camphor-tree (*Laurus camphora*), which grows in Japan, by distilling the leaves in steam. It is a soft, crystalline solid, melting at 175°, and boiling at 204°; it is very volatile, sublimes readily even at ordinary temperatures, and has a highly characteristic smell. It is only sparingly soluble in water, but sufficiently so to impart to the solution a distinct taste and smell (*Aqua camphoræ*), and it dissolves readily in alcohol and most ordinary organic solvents; it is used in medicine, in the manufacture of xylonite, and also in the preparation of a few explosives.

Camphor can be obtained by oxidising camphene (p. 583) with potassium dichromate and sulphuric acid,

$$C_{10}H_{16} + O = C_{10}H_{16}O,$$

a fact which seems to show that it is related to this terpene; it is also produced when the secondary alcohol, borneol (p. 598), is oxidised with nitric acid,

$$C_{10}H_{18}O + O = C_{10}H_{16}O + H_2O.$$

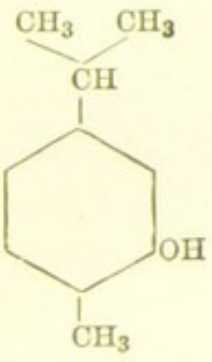
The latter method of formation and its whole chemical behaviour prove that camphor is a *ketone*; with hydroxylamine, for instance, camphor reacts readily, giving a crystalline oxime, *camphoroxime* (m.p. 118°),

$$C_{10}H_{16}O + NH_2{\cdot}OH = C_{10}H_{16}{:}N{\cdot}OH + H_2O;$$

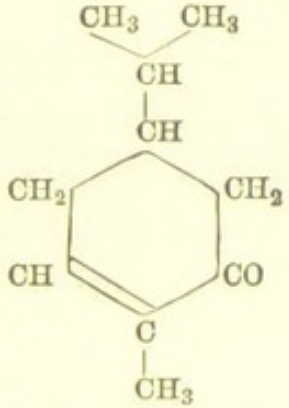
and, on reduction, it is converted into borneol, just as acetone is transformed into the secondary alcohol, isopropyl alcohol,

$$C_{10}H_{16}O + H_2 = C_{10}H_{17}\cdot OH.$$

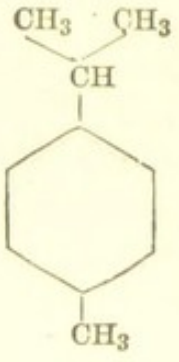
When camphor is heated with iodine, it is converted into *carvacrol* (hydroxycymene, p. 445), and when distilled with phosphorus pentoxide, it is transformed into *cymene* (p. 378). These last two facts seem to show that camphor is very closely related to cymene and carvacrol, and when written in the form of equations, the two reactions appear to be extremely simple; at one time the following constitutional formula was assigned to camphor on account of its supposed relation to these two benzene derivatives :—



Carvacrol.



Kekulé's Formula for Camphor.



Cymene.

There are, however, many other important facts which show clearly that camphor is not directly related to cymene or carvacrol, as represented above, and that its conversion into a benzene derivative is not nearly so simple a change as it appears to be.

In the first place, camphor behaves like a *saturated* ketone, and forms substitution, not additive, products when treated with bromine, chlorine, &c., whereas in accordance with Kekulé's formula it would be an unsaturated compound; in the second place, camphor gives rise to a number of oxidation products of known constitution, and the formation of these substances cannot be accounted for on the basis of the constitutional formula given above.

The first product of the oxidation of camphor with boiling

nitric acid is a dicarboxylic acid of the composition, $C_{10}H_{16}O_4$, called *camphoric acid*,

$$C_8H_{14}\begin{cases}CH_2\\ |\\ CO\end{cases} + 3O = C_8H_{14}\begin{cases}COOH\\ COOH\end{cases};$$

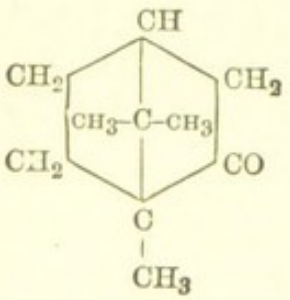
and this compound on further oxidation yields a tricarboxylic acid, $C_9H_{14}O_6$, called *camphoronic acid*,

$$C_{10}H_{16}O_4 + 5O = C_9H_{14}O_6 + CO_2 + H_2O.$$

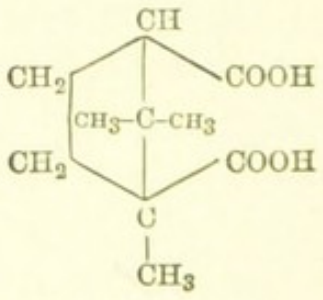
Now, it has been proved that camphoronic acid has the following constitution,

$$\begin{array}{llll} CH_2 & -C(CH_3) & -C(CH_3)_2 \\ | & | & | \\ COOH & COOH & COOH; \end{array}$$

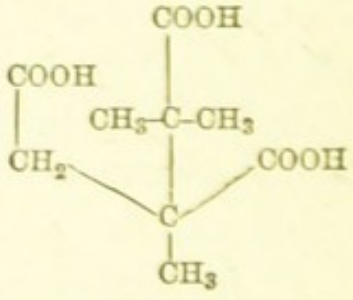
and, as an acid of this constitution could not possibly be obtained by the oxidation of a true cymene or carvacrol derivative, it follows that camphor has not the constitution assigned to it by Kekulé. For these and other reasons the structure of camphor is represented by the following formula (proposed by Bredt), which summarises satisfactorily the behaviour of camphor and its relation to camphoric and camphoronic acids :—



Camphor.



Camphoric Acid.

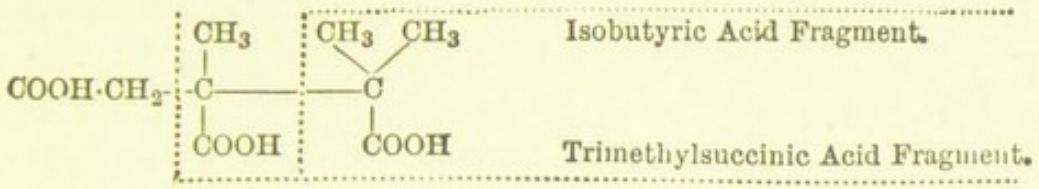


Camphoronic Acid.

d-**Camphoric acid**, $C_8H_{14}(COOH)_2$, the first oxidation product of camphor, is a crystalline substance melting at 187°; it is readily converted into its anhydride, $C_8H_{14}\begin{cases}CO\\ CO\end{cases}O$ (m.p. 221°).

d-**Camphoronic acid**, $C_6H_{11}(COOH)_3$, melts at 137°, and is readily soluble in water; when heated strongly, it is decom-

posed into trimethylsuccinic acid, isobutyric acid, carbon dioxide, water, and carbon,



Camphoronic acid has been prepared synthetically in the following manner:—Ethyl acetoacetate condenses with *ethyl bromisobutyrate*, $(CH_3)_2CBr\cdot COOEt$, in presence of zinc (p. 229) to form a compound,

$$COOEt\cdot CH_2\cdot C(OZnBr)—C(CH_3)_2\cdot COOEt,$$
$$\quad\quad\quad

d-**Borneol,** $C_{10}H_{17}\cdot OH$, occurs in combination with acetic acid as *bornyl acetate*, $C_{10}H_{17}\cdot O\cdot CO\cdot CH_3$, in many essential oils—as, for example, in those of thyme, valerian, and pine-needles; it also occurs in a free condition in the oils of spike and rosemary; its principal source, however, is the *Dryobalanops camphora*, a tree growing in Borneo and Sumatra.

Borneol can be obtained by reducing camphor with sodium and alcohol. It is rather like camphor in physical properties, but is more distinctly crystalline, and, although it has an odour recalling that of camphor, it also smells faintly of peppermint. It melts at 203°, boils at 212°, and is readily volatile in steam.

Borneol is a secondary alcohol; when treated with phosphorus pentachloride, it is converted into bornyl chloride,

$$C_{10}H_{17}\cdot OH + PCl_5 = C_{10}H_{17}Cl + POCl_3 + HCl;$$

and when this product is heated with aniline, it gives camphene, with elimination of the elements of hydrogen chloride,

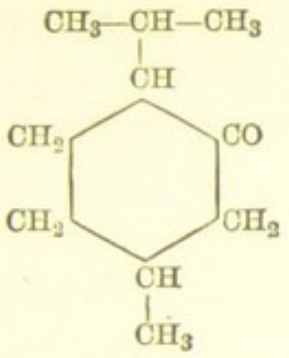
$$C_{10}H_{17}Cl = C_{10}H_{16} + HCl.$$

From these, and many other reactions which cannot be described here, it has been concluded that camphor, borneol, and camphene are related to one another, as shown by the formulæ which have already been given.

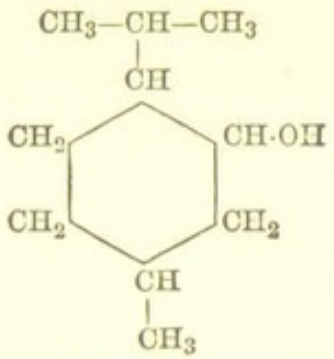
l-**Menthone,** $C_{10}H_{18}O$, is one of the numerous components of oil of peppermint, the essential oil of *Mentha piperita*, which also contains menthol (see below), pinene, cadinene (p. 593), and many other compounds.

Menthone is a colourless liquid, boiling at 206°, and its chemical behaviour stamps it as a ketone; on reduction with sodium and alcohol, it is converted into the secondary alcohol, menthol.

Menthone is a *ketohexahydrocymene;* its constitution and that of menthol are respectively expressed by the following formulæ:—



Menthone.



Menthol.

l-**Menthol,** $C_{10}H_{19}\cdot OH$, is related to menthone in the same way as borneol is related to camphor; it occurs in oil of peppermint both in the free state and as *menthyl acetate*, $C_{10}H_{19}\cdot O\cdot CO\cdot CH_3$, and it is principally to the presence of this alcohol that oil of peppermint owes its very powerful odour.

Menthol is crystalline, and melts at 142°; on reduction with hydriodic acid, it is converted into hexahydrocymene.

CHAPTER XXXIX.

Carbohydrates.

Aldoses.—The three monosaccharoses, glucose (p. 294), mannose (p. 297), and galactose (p. 297), are identical in structure, and are optically isomeric; they are all *aldehydes*, and at the same time *pentahydric alcohols*, derived from normal hexane.

Compounds of corresponding structures may be derived from the lower, and also from the higher, paraffins. The simplest of these hydroxyaldehydes is glycollic aldehyde, $CH_2(OH)\cdot CHO$ (p. 237), and next in order of molecular weight comes glyceraldehyde, $CH_2(OH)\cdot CH(OH)\cdot CHO$; the compounds, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$ and $CH_2(OH)\cdot$

$CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$, form links between glyceraldehyde and the monosaccharoses.

All such hydroxyaldehydes are termed **aldoses**, and are classed as *di-*, *tri-*, *tetr-*, *pent*-aldoses, &c., according to the number of carbon atoms in their molecules.

Aldoses may be prepared by cautiously oxidising the corresponding alcohols; just as glycol gives glycollic aldehyde and glycerol gives glyceraldehyde, so also the higher polyhydric alcohols, such as erythritol, arabitol, mannitol, &c. (p. 292), give the corresponding tetroses, pentoses, hexoses, &c.

The oxidation of a polyhydric alcohol may generally be accomplished with the aid of nitric acid, or of bromine and water, but hydrogen peroxide in presence of a trace of a ferrous salt is often the most suitable reagent (p. 237).

Aldoses may also be prepared from the corresponding acids in the manner described later (p. 603).

Erythrose, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$, is an example of an *aldotetrose;* it is obtained, mixed probably with the isomeric *ketotetrose*, $CH_2(OH)\cdot CH(OH)\cdot CO\cdot CH_2\cdot OH$, by the oxidation of erythritol.

l-**Arabinose** and *l*-**xylose** are optically isomeric *aldopentoses* of the constitution, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$. l-*Arabinose* is obtained by boiling cherry-gum, or gum-arabic, with dilute sulphuric acid; it melts at 160°, and is dextrorotatory.* l-*Xylose* is obtained by boiling wood-gum (xylan) with dilute sulphuric acid; it melts at 143°, and is dextrorotatory.*

Both these aldopentoses are formed when bran, straw, and various other vegetable products are boiled with dilute sulphuric acid. Like the aldohexoses, they have a sweet taste, and reduce Fehling's solution, but they do not ferment

* Although these aldopentoses are both dextrorotatory, they are both distinguished from their enantiomorphously related isomerides (d-*arabinose* and d-*xylose*) by the letter *l*, which generally denotes a levorotatory compound; the reason of this is explained later (p. 614).

with yeast; when warmed with hydrochloric acid and a little phloroglucinol (p. 449), they give a cherry-red solution. They both yield furfuraldehyde (p. 632) when they are distilled with hydrochloric or dilute sulphuric acid; this reaction may be used for their detection and also for their estimation, since the furfuraldehyde which is present in the distillate may be isolated and weighed in the form of its very sparingly soluble hydrazone.

The aldoses are closely related in chemical properties, and show the following very important reactions:—

They are reduced by sodium amalgam and water to the corresponding polyhydric alcohols; an aldohexose, for example, gives a hexahydric alcohol or *hexitol* (p. 292), an aldopentose, a pentahydric alcohol or *pentitol*, and so on.

They are oxidised by nitric acid, by bromine and water, and by other reagents. The first product is a *mono*-carboxylic acid, produced by the oxidation of the aldehyde-group; glucose, for example, gives *gluconic acid*, mannose gives the optically isomeric *mannonic acid*, xylose gives *xylonic acid*, and so on. These mono-carboxylic acids, on further oxidation, are transformed into *di*-carboxylic acids by the conversion of the $-CH_2\cdot OH$ into the carboxyl-group; thus gluconic acid gives *saccharic acid*, $COOH\cdot[CH(OH)]_4\cdot COOH$, mannonic acid gives the optically isomeric *mannosaccharic acid*, and xylonic acid gives *trihydroxyglutaric acid*, $COOH\cdot[CH(OH)]_3\cdot COOH$.

These changes may be summarised as follows:—

$$CH_2(OH)\cdot[CH(OH)]_n\cdot CHO \rightarrow CH_2(OH)\cdot[CH(OH)]_n\cdot COOH \rightarrow COOH\cdot[CH(OH)]_n\cdot COOH.$$

The aldoses combine directly with hydrogen cyanide, forming *hydroxy-cyanides*, which may be hydrolysed to mono-carboxylic acids. An aldo*hexose* is thus converted into an acid which is structurally identical with the oxidation product of an aldo*heptose* (compare p. 302), and similarly in other cases the final result is the transformation of the $-CHO$ group into $-CH(OH)\cdot COOH$. The aldoses react with hydroxylamine,

giving oximes, and with phenylhydrazine, giving either a hydrazone or an osazone, according to the conditions of the experiment (p. 300).

They react with alcohols in presence of hydrogen chloride, forming ether-like compounds, which are called *alkyl-glucosides.**

When *d*-glucose, for example, is dissolved in methyl alcohol, and hydrogen chloride is passed into the solution, two stereoisomeric (α- and β-) *methylglucosides* of the composition, $C_6H_{11}O_6 \cdot CH_3$, are formed. These compounds do not reduce Fehling's solution, and do not react with phenylhydrazine, so that probably their molecules do not contain an aldehyde-group. It seems, therefore, that in the formation of these derivatives, a change has occurred not unlike that by which an acetal is produced from an aldehyde and an alcohol (p. 148),

$$R \cdot CHO + 2HO \cdot R = R \cdot CH(OR)_2 + H_2O,$$

and that the aldehyde-group of glucose has reacted with *one* hydroxyl-group of methyl alcohol and *one* hydroxyl-group (probably that in the γ- position) belonging to the glucose molecule. According to this view, the constitution of the optically isomeric methyl glucosides is expressed by the formula,

$$CH_2(OH) \cdot CH(OH) \cdot CH(O) \cdot CH(OH) \cdot CH(OH) \cdot CH < \overset{\frown}{} OCH_3.$$

Polyhydric Monocarboxylic Acids.—The monocarboxylic acids, produced by the oxidation of the aldoses, are readily soluble in water, and most of those derived from the aldopentoses and the higher aldoses pass spontaneously into their *lactones* (p. 243), with loss of one molecule of water; gluconic acid, $C_6H_{12}O_7$, for example, gives *glucolactone*, $C_6H_{10}O_6$, mannonic acid gives the optically isomeric *mannolactone*, and so on. These lactones are crystalline compounds, which, in aqueous solution, pass into the corresponding acids, until a condition of equilibrium is attained [$C_6H_{10}O_6 + H_2O \longleftrightarrow C_6H_{12}O_7$]; they are completely hydrolysed in presence of excess of alkali.

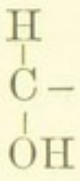
Many of these lactones may be reduced with sodium

* Compare p. 619.

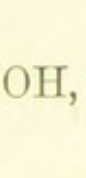
amalgam and water, in presence of carbonic acid,* and thus converted into the corresponding *aldoses* (E. Fischer). This is a reaction of great importance, as it serves as a means of passing from the acid to the corresponding aldose, which may then be reduced to the alcohol. The following changes, for example, are thus rendered possible :—

$$CH_2(OH)\cdot[CH(OH)]_n\cdot COOH \rightarrow CH_2(OH)\cdot[CH(OH)]_n\cdot CHO \rightarrow CH_2(OH)\cdot[CH(OH)]_n\cdot CH_2\cdot OH.$$

The polyhydric monocarboxylic acids undergo a very interesting change when they are heated with pyridine or quinoline at moderately high temperatures (about 150°) ; thus *d*-gluconic acid, treated in this way, is partly transformed into its optical isomeride, *d*-mannonic acid, whereas *d*-mannonic acid, under the same conditions, is partly converted into *d*-gluconic acid. The reason of this is, that the asymmetric carbon group, to which the carboxyl-radicle is directly united, undergoes *optical inversion.* An *l*- or – group, the configuration of



which may be represented by $R-\overset{H}{\underset{OH}{C}}-COOH$, is transformed



into a *d*- or + group, $R-\overset{OH}{\underset{H}{C}}-COOH$, and *vice versâ.* The optical inversion, however, is restricted to this particular asymmetric group, so that the configuration of the rest of the molecule is unchanged. Since, moreover, optical inversion is a reversible process, the change, *d*-gluconic acid ⟷ *d*-mannonic acid, may proceed in either direction until a condition of equilibrium is reached.†

* Unless carbon dioxide is continuously passed into the solution, the sodium hydroxide, produced from the sodium amalgam and water, hydrolyses the lactone ; the acids themselves, or their salts, are *not* reduced.

† In the case of substances containing *one* asymmetric group, the optical inversion continues until equal quantities of the *d*- and *l*-isomerides are present; similarly, if the molecule contains *two* asymmetric carbon-

Polyhydric Dicarboxylic Acids.—The more important acids of this class—namely, *d*-saccharic acid (p. 297), *d*-mannonic acid (p. 601), and mucic acid (p. 298)—have been already referred to. The first two compounds are optically active, but mucic acid is optically inactive (internally compensated).

When *d*-saccharic acid, in the form of its *lactone*, $C_6H_8O_7$, is reduced with sodium amalgam and water, it is converted first into *glucuronic acid*, $CHO\cdot[CH(OH)]_4\cdot COOH$, and then into d-*gulonic acid*, $CH_2(OH)\cdot[CH(OH)]_4\cdot COOH$. *d*-Gulonic acid is optically isomeric with *d*-gluconic acid; on reduction, in the form of its lactone, it gives d-*gulose*, an aldohexose, which is an optical isomeride of glucose, mannose, and galactose.

The Ascent and Descent of the Aldose Series.—An aldose containing n carbon atoms may be transformed into an aldose containing $n+1$ carbon atoms by the following series of reactions:—The aldose is combined with hydrogen cyanide, and the cyanohydrin is hydrolysed to the carboxylic acid; the lactone of this acid is then reduced in the usual manner,

$$CH_2(OH)\cdot[CH(OH)]_n\cdot CHO \rightarrow CH_2(OH)\cdot[CH(OH)]_n\cdot CH(OH)\cdot CN \rightarrow CH_2(OH)\cdot[CH(OH)]_n\cdot CH(OH)\cdot COOH \rightarrow CH_2(OH)\cdot[CH(OH)]_n\cdot CH(OH)\cdot CHO.$$

The conversion of *d*-mannose, $C_6H_{12}O_6$, into the aldoheptose, d-*mannoheptose*, $C_7H_{14}O_7$, was thus accomplished by E. Fischer, who, in a similar manner, transformed *d*-mannoheptose into d-*mannooctose*, $C_8H_{16}O_8$, and the latter into d-*mannononose*, $C_9H_{18}O_9$; these aldoses, like many of the aldohexoses synthesised by E. Fischer, do not, so far as is known, occur in nature, but they are very similar to the natural monosaccharoses in many of their properties.

groups, the optical inversion *may* involve them both, and continue until an optically inactive product, consisting of the *dl*- mixture and the internally compensated form (or of two *dl*- mixtures), is produced. The optically active substance is then said to be completely *racemised* (compare p. 276).

An aldose containing n carbon atoms may be transformed into an aldose containing $n-1$ carbon atoms in the following manner:—The oxime of the aldose is heated with acetic anhydride and sodium acetate, whereby the hydrogen atoms of the hydroxyl-groups are displaced by acetyl-radicles and the group $-CH{:}N{\cdot}OH$ is transformed into $-CN + H_2O$. The product is a polyacetyl derivative of a polyhydric nitrile; it gives, with an ammoniacal solution of silver hydroxide, a precipitate of silver cyanide, and is subsequently hydrolysed, with formation of an aldose. These changes are indicated below,

$$CH_2(OH){\cdot}[CH(OH)]_n{\cdot}CH(OH){\cdot}CHO \longrightarrow CH_2(OH){\cdot}[CH(OH)]_n{\cdot}CH(OH){\cdot}CH{:}N{\cdot}OH \longrightarrow CH_2(OAc){\cdot}[CH(OAc)]_n{\cdot}CH(OAc){\cdot}CN \longrightarrow CH_2(OAc){\cdot}[CH(OAc)]_n{\cdot}CH(OAc){\cdot}OH^* \longrightarrow CH_2(OH){\cdot}[CH(OH)]_n{\cdot}CHO.$$

A similar transformation may sometimes be accomplished in a simpler manner by oxidising the aldose to the corresponding mono-carboxylic acid, and then treating the latter with hydrogen peroxide in presence of ferric acetate,

$$CH_2(OH){\cdot}[CH(OH)]_n{\cdot}CH(OH){\cdot}CHO \longrightarrow CH_2(OH){\cdot}[CH(OH)]_n{\cdot}CH(OH){\cdot}COOH \longrightarrow CH_2(OH){\cdot}[CH(OH)]_n{\cdot}CHO.^\dagger$$

Ketoses.—The polyhydric ketones, the *ketoses*, corresponding with fructose in structure, are not so well known as the aldoses; the simplest ketose is dihydroxyacetone (p. 300); but various compounds of this type, such as *erythrulose*, $CH_2(OH){\cdot}CH(OH){\cdot}CO{\cdot}CH_2{\cdot}OH$, *arabinulose*, $CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CO{\cdot}CH_2{\cdot}OH$, and *sorbose* (an optical isomeride of fructose), are known. The three compounds just named, and also fructose, have been obtained with the aid of the sorbose bacterium, which has the property of bringing about the oxidation of the corresponding polyhydric alcohols (erythritol, arabitol, and sorbitol) to ketoses, and

* $R-CH(OAc){\cdot}CN + AgOH = R{\cdot}CH(OAc){\cdot}OH + AgCN$
$R{\cdot}CH(OAc){\cdot}OH + H_2O = R{\cdot}CH(OH)_2 + C_2H_4O_2$
$R{\cdot}CH(OH)_2 = R{\cdot}CHO + H_2O.$

† $R{\cdot}CH(OH){\cdot}COOH + H_2O_2 = R{\cdot}CHO + CO_2 + 2H_2O.$

also that of the aldoses to the corresponding monocarboxylic acids.

The ketoses reduce Fehling's solution, and when treated with sodium amalgam and water they are transformed into the corresponding polyhydric alcohols; on oxidation they are converted into two (or more) relatively simple acids, as explained in the case of fructose (p. 299).

The Configurations of some of the Carbohydrates.

The molecules of an aldohexose, and those of the *mono*carboxylic acids derived from them, contain four asymmetric carbon-groups, and it can be shown that, theoretically, there are sixteen optically isomeric aldohexoses of the constitution $CH_2(OH)\cdot[CH(OH)]_4\cdot CHO$, and sixteen optically active monocarboxylic acids corresponding with them. These sixteen optically isomeric forms may be classed in eight pairs, the compounds forming any pair being enantiomorphously related (p. 270). Thus, corresponding with *d*-glucose (ordinary glucose), there is an aldohexose (*l*-glucose) which is identical with *d*-glucose in all respects, except that it is levorotatory and its crystals are enantiomorphously related to those of the *d*-isomeride. The relationship between *d*- and *l*-glucose, in fact, is the same as that between *d*- and *l*-lactic acids or *d*- and *l*-tartaric acids. Similarly, *l*-mannose and *d*-mannose (ordinary mannose), *l*-gulose and *d*-gulose (p. 604), are enantiomorphously related.

The molecules of a hexahydric alcohol of the constitution, $CH_2(OH)\cdot[CH(OH)]_4\cdot CH_2\cdot OH$, and those of the corresponding *di*carboxylic acids also contain four asymmetric groups, but in the case of these compounds only ten optical isomerides are theoretically possible. The reason of this is, that whereas all the four asymmetric carbon-groups in the molecule of an aldohexose or monocarboxylic acid are *structurally* different, the molecule of a hexitol or of a dicarboxylic acid contains only two structurally different asymmetric groups, and *two* optically isomeric aldohexoses may correspond with,

and be converted into, *one* hexitol or *one* dicarboxylic acid only.

This point may be illustrated by a simple case. A compound such as tartaric acid, the molecule of which contains two structurally identical asymmetric carbon-groups, exists in three optically isomeric forms, which may be represented by + +, − −, and + − respectively (p. 274). If, however, *one* of the −COOH groups in this acid were to be converted into $-CH_2{\cdot}OH$, four optical isomerides, namely, + +, − −, + −, and − +, would be possible; the two asymmetric groups having different structures, the configurations + − and − + are no longer identical. Of these four optical isomerides, the first two are enantiomorphously related, optically active forms. The second two are also enantiomorphously related, and both are optically *active;* neither would correspond with + − or mesotartaric acid, because in the molecule of the latter the + and − groups are structurally identical and enantiomorphously related, in consequence of which the acid is an internally compensated (optically inactive) compound. In other words, whereas a compound of the constitution, $CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH$, would exist in four optically active forms, two of these (the + − and the − +) would give one and the same inactive dicarboxylic acid; in an analogous manner sixteen optically active aldohexoses give only ten optically isomeric hexitols, or ten dicarboxylic acids.

The molecules of an aldopentose, such as *l*-arabinose, and those of the corresponding monocarboxylic acids, contain *three* asymmetric carbon-groups, and eight optical isomerides of each of these types are possible; in each case these eight isomerides constitute four pairs of enantiomorphously related compounds. The molecules of a pentitol, $CH_2(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, and those of a normal $\alpha\beta\gamma$-trihydroxy-

$$\overset{\alpha}{}\qquad\overset{\beta}{}\qquad\overset{\gamma}{}$$

glutaric acid, $COOH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH$, derived from an aldopentose, contain two asymmetric carbon-

groups only, because in these compounds the β-carbon atom is combined with two structurally *identical* groups—namely, either [$-CH(OH)\cdot CH_2\cdot OH$] or [$-CH(OH)\cdot COOH$], and has lost its asymmetry. When the α- and γ-groups have the same configurations, + and +, or − and −, the compound is optically active, just as in the case of the tartaric acids (p. 274); when, however, these two asymmetric groups have different configurations (one being + and the other −), thus causing internal compensation, the presence of the $\beta >CH(OH)$ group renders possible the existence of *two* such internally compensated (inactive) forms.* There are, therefore, *four* optically isomeric pentitols, of which two are enantiomorphously related and optically active, and two are inactive by internal compensation. The optically isomeric trihydroxyglutaric acids correspond in number with the pentitols.

Now it has been found possible to establish not only the structural relationships of the various aldoses and of their immediate derivatives, but also to determine the manner in which they are related in *configuration*, and to assign to each compound a particular *stereochemical* formula.

In order to represent these configurations, the signs + and − may be used, as in the case of the tartaric acids (p. 274), to distinguish any two enantiomorphously related groups; the configurations of two enantiomorphously related aldopentoses, for example, may be expressed by

$$CH_2(OH)\cdot\overset{+}{C}H(OH)\cdot\overset{-}{C}H(OH)\cdot\overset{+}{C}H(OH)\cdot CHO \text{ and}$$

$$CH_2(OH)\cdot\overset{-}{C}H(OH)\cdot\overset{+}{C}H(OH)\cdot\overset{-}{C}H(OH)\cdot CHO,$$

every asymmetric group in the one molecule having a *different* sign from that of the corresponding group in the other molecule.

* This point can only be made clear with the aid of the usual models (footnote, p. 269).

Before this question of configurational relationship is considered further, the following facts bearing on this matter must be stated :—

d-Glucose and *d*-mannose give one and the same osazone.

This fact proves that the molecules of these two aldohexoses differ in configuration only as regards that particular asymmetric group which is directly united to the aldehyde-group. In the formation of the osazone from either molecule, this asymmetric group, $\begin{matrix}\text{CH·OH}\\ \text{CHO}\end{matrix}$, is converted into $\begin{matrix}\text{C:N}_2\text{HPh}\\ \text{CH:N}_2\text{HPh}\end{matrix}$, and loses its asymmetry; as the other three asymmetric groups in the molecules remain unchanged (compare the case of glucose and fructose, p. 301), and yet both compounds give the same product, the difference between them must be that stated above.

l-Xylose, on reduction with sodium amalgam and water, is converted into an *optically inactive* pentitol, whereas *l*-arabinose gives an *optically active* pentitol.

Since the *two* asymmetric groups in the molecule of an optically *inactive* pentitol must be enantiomorphously related (otherwise they could not condition internal compensation), these groups must be represented by different signs. Consequently, the corresponding groups in *l*-xylose must also be represented by different signs, while those in *l*-arabinose must be represented by identical signs, otherwise an inactive configuration would be assigned to the optically active reduction product of this aldopentose (compare p. 608).

l-Arabinose combines with hydrogen cyanide, and the cyanohydrin thus obtained is converted on hydrolysis into two structurally identical, but optically isomeric, acids.

These two acids are *l*-gluconic acid and *l*-mannonic acid, and the formation of two optically isomeric acids in this way is explained as follows :—By the combination of the aldehyde-group with hydrogen cyanide, a new asymmetric group is synthesised, and consequently *both* the theoretically possible forms of this new group may be produced, just as in the synthesis of lactic acid from acetaldehyde (p. 242). There are, therefore, two optically isomeric products, both of which contain the three asymmetric groups of the original aldopentose, but which differ in configuration as regards the new asymmetric group. If, for example, the original aldopentose had the configuration, + + −, the products would be the + + − ⊕, and the + + − ⊖ isomerides, the new asymmetric groups being indicated by the circles.

l-Gluconic acid is enantiomorphously related to *d*-gluconic acid, and is derived from *l*-glucose, which is enantiomorphously related to *d*-glucose.

l-Mannonic acid is enantiomorphously related to *d*-mannonic acid, and *l*-mannose is similarly related to *d*-mannose.

d-Glucose and *d*-gulose (p. 604) give on oxidation one and the same optically active dicarboxylic acid (*d*-saccharic acid), and on reduction one and the same optically active hexitol (*d*-sorbitol).

This fact proves that certain configurations cannot be assigned to either of these aldohexoses ; thus neither of these compounds could have the configuration + + + +, because a dicarboxylic acid or a hexitol having the corresponding configuration could not be produced from two different aldohexoses. Similarly, neither *d*-glucose nor *d*-gulose could have the configuration, + − − +. In other words, if *d*-saccharic acid or *d*-sorbitol had either of these configurations, neither compound could correspond with, or be obtained from, two different aldohexoses.

The stereochemical relationships of some of the more

important members of the carbohydrate group may now be considered in the light of these facts and with the help of the following table, in which the configurations of all the theoretically possible (normal) aldopentoses and aldohexoses are shown :—

Aldopentoses.	1	2	3	4	5	6	7	8
$CH_2 \cdot OH$								
(*a*) CH·OH.....	+	+	−	−	+	+	−	−
* CH·OH.....	+	−	+	−	+	−	+	−
(*b*) CH·OH.....	−	−	+	+	+	+	−	−
CHO								

Aldohexoses.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.
$CH_2 \cdot OH$																
CH·OH.....	+	+	+	+	−	−	−	−	+	+	+	+	−	−	−	−
CH·OH.....	+	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−
CH·OH.....	−	−	−	−	+	+	+	+	+	+	+	+	−	−	−	−
** CH·OH.....	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−
CHO																

The eight optically isomeric aldopentoses are represented by the configurations 1 to 8. The first question to decide is, what conclusions can be drawn from the behaviour of *l*-xylose and of *l*-arabinose?

l-Xylose gives one of the optically inactive pentitols and one of the optically inactive trihydroxyglutaric acids; its configuration, therefore, must be represented by 1, 2, 3, or 4, because these are the only configurations from which it would be possible to derive an internally compensated pentitol or dicarboxylic acid—that is to say, a pentitol in which the

two asymmetric carbon-groups (*a*) and (*b*) are of *different* signs.

l-Arabinose, on the other hand, gives one of the optically active pentitols, and consequently its configuration is represented by 5, 6, 7, or 8, because only from one of these aldopentoses could there be derived a pentitol in which the two asymmetric groups (*a*) and (*b*) are of the *same* sign.

l-Arabinose can be converted into a mixture of *l*-gluconic and *l*-mannonic acids (p. 610); and these acids on reduction, in the form of their lactones, give *l*-glucose and *l*-mannose respectively. In these changes the asymmetric group, distinguished by two asterisks in the structural formula of the aldohexoses, is synthesised. The configurations of all the aldohexoses which could thus be obtained from *l*-arabinose (5, 6, 7, or 8) are represented above the numerals IX. to XVI. Hence one of these eight configurations must represent *l*-glucose and another *l*-mannose.

Now, *l*-glucose and *l*-mannose, on oxidation, give optically active *di*carboxylic acids, and on reduction optically active hexitols. Neither of these aldohexoses, therefore, can have the configuration XII. or XIII., because the *di*carboxylic acids and hexitols derived from these would be optically inactive by internal compensation—that is to say, in compounds represented by [COOH + − + − COOH] or [CH_2(OH) + − + − CH_2(OH)], the asymmetric groups in corresponding positions in the structural formula are enantiomorphously related and cause internal compensation.

These facts and arguments prove that the configurations of *l*-glucose and of *l*-mannose must be two of the following:—

+	+	+	−	−	−
+	+	−	+	−	−
+	+	+	−	−	−
+	−	+	−	+	−
IX.	X.	XI.	XIV.	XV.	XVI.

But it is known that *d*-glucose and *d*-mannose differ in configuration only as regards one of their four asymmetric groups—namely, that distinguished by two asterisks in the structural formula (see table); the relation between *l*-glucose and *l*-mannose, therefore, must be of the same kind, since *d*-glucose and *l*-glucose, likewise *d*-mannose and *l*-mannose, are enantiomorphously related.

An examination of the six configurations just given shows that XI. and XIV. cannot represent either *l*-glucose or *l*-mannose, because these configurations would still be different even if the lowermost asymmetric groups were identical; in other words, the other three asymmetric groups in these configurations (XI. and XIV.) are not identical, as they are known to be in the case of *l*-glucose and *l*-mannose. Consequently, the configurations of these two aldohexoses must be represented by two chosen from IX., X., XV., and XVI.

Now, these four configurations represent two pairs of enantiomorphously related compounds; the forms IX. and XVI. (+ + + +) and (− − − −) are so related, likewise the forms X. and XV. (+ + + −) and (− − − +). But from the relationship between *d*-glucose and *d*-gulose it is known that *d*-glucose cannot have the configuration IX. or XVI. (p. 610); it follows, therefore, that *l*-glucose cannot have either of these configurations, and in consequence must be represented by X. or XV.

Since, in these configurational formulæ, the signs + and − were originally chosen quite arbitrarily, and the same relations would hold if every sign had been reversed, *one* of these configurations may now be arbitrarily assigned to *d*-glucose, the other to *l*-glucose. When, however, this choice has been made, the configurations of all the other substances considered above are also fixed in relationship to those of *d*- and *l*-glucose.

If, then, the configuration XV. be assigned to *l*-glucose, *d*-glucose must be represented by X., *d*-mannose by IX.,

l-mannose by XVI., *d*-gulose by V. (see table, p. 611), and *l*-gulose by IV. The configurations of the corresponding hexitols and of the mono- and di-carboxylic acids are also determined.

l-Arabinose, from which *l*-glucose and *l*-mannose are obtained, must be represented by (8); *d*-arabinose by (5). *l*-Xylose (from which *l*-gulose is derived) must have the configuration (2). Similarly, the configurations of the pentitols and of the mono- and di-carboxylic acids derived from the aldopentoses are settled.

The configuration of *d*-fructose (ordinary fructose) is also proved to be [$CH_2(OH)$ + + + $CO{\cdot}CH_2{\cdot}OH$], because it is known that the three asymmetric groups in *d*-fructose are stereochemically identical with the corresponding three groups in *d*-glucose and *d*-mannose; this is proved by the fact that all three compounds give the same osazone (pp. 301, 609). Further, when fructose is reduced to a hexitol it gives both *d*-sorbitol and *d*-mannitol. In the conversion of the $>CO$ group into $>CH{\cdot}OH$, a new asymmetric group is synthesised, and both the + and the − configurations of this group are formed, just as in the synthesis of *l*-gluconic acid and *l*-mannonic acid from *l*-arabinose. As the two reduction products are *d*-sorbitol (+ + + −) and *d*-mannitol (+ + + +), *d*-fructose must have the above configuration.

The optical relationships of various other members of the carbohydrate group have been established by methods analogous to those illustrated above.

In some examples already given, as in that of ordinary fructose, and in those of arabinose and xylose (p. 600), the levorotatory form is distinguished by *d*, and the dextrorotatory by *l*. This is because ordinary (levorotatory) fructose is directly related to *d*-glucose in configuration, whereas the dextrorotatory forms of arabinose and xylose are directly related to *l*-glucose and *l*-gulose respectively. As suggested by E. Fischer, the choice between the letters, *d* and *l*, is made

to depend on the relationships of the compound rather than on the direction in which the substance rotates the plane of polarised light; in the above cases, the important sugar, *d*-glucose, serves as a standard.

The Synthesis of Sugars and their Derivatives.

The synthesis of the naturally-occurring 'sugars,' glucose and fructose, is one of the brilliant triumphs of organic chemistry, and was accomplished by E. Fischer, who also succeeded in preparing many new optically isomeric aldohexoses, in addition to heptoses, octoses, nonoses (p. 604), and a great number of related compounds.

Although it is impossible to give here an adequate description of these researches, or to convey any idea of the great difficulties which had to be overcome, the more important results of this work may be very briefly summarised.

The product obtained by treating glycerose with a solution of sodium hydroxide (p. 300) gave, with phenylhydrazine, a mixture of osazones. One of the osazones isolated from this mixture was named *α-acrosazone*. This compound was converted into the corresponding *osone* (*α-acrosone*) by the method described in the case of glucosazone (p. 301), and the osone was then reduced to a compound of the composition, $C_6H_{12}O_6$, which was named *α-acrose*, and which was found to ferment with yeast. On further reduction, α-acrose was converted into a hexahydric alcohol, $C_6H_{14}O_6$, which was found to be very similar in properties to naturally occurring *d*-mannitol (p. 292); but, whereas *d*-mannitol was optically active, α-acritol was optically inactive.

The possibility suggested itself that α-acritol might be *dl*-mannitol—that is to say, a mixture of the enantiomorphously related *d*- and *l*-mannitols; but as *dl*-mannitol was then unknown, and as only about 0·2 gram of α-acritol was obtained from 1 kilo of glycerol, even if the identity of α-acritol

and *dl*-mannitol were established, the preparation of this synthetical product would remain an extremely difficult matter.

Now, *d*-mannitol, on oxidation, gave first the corresponding aldohexose, *d*-mannose (which was afterwards obtained from vegetable-ivory nuts, &c.), and then the corresponding monocarboxylic acid, *d*-mannonic acid. The enantiomorphously related *l*-mannonic acid was obtained from *l*-arabinose, with the aid of hydrogen cyanide (p. 610).

A mixture of equal quantities of *d*- and *l*-mannonic acids when reduced (in the form of their lactones) gave first an aldohexose, *dl*-mannose, and on further reduction a hexitol, *dl*-mannitol; the *dl*-mannitol thus prepared was proved to be identical with α-acritol. It was thus possible to obtain α-acritol by *comparatively* easy methods, and to investigate it further.

dl-Mannonic acid, which *could* be prepared from α-acritol, just as *d*-mannonic acid is prepared from *d*-mannitol (but which was actually obtained by mixing the *d*- and *l*-acids), was resolved into its enantiomorphously related components with the aid of its strychnine or morphine salt (p. 278), and the *d*-mannonic acid was then reduced, first to *d*-**mannose**, and then to *d*-**mannitol**.

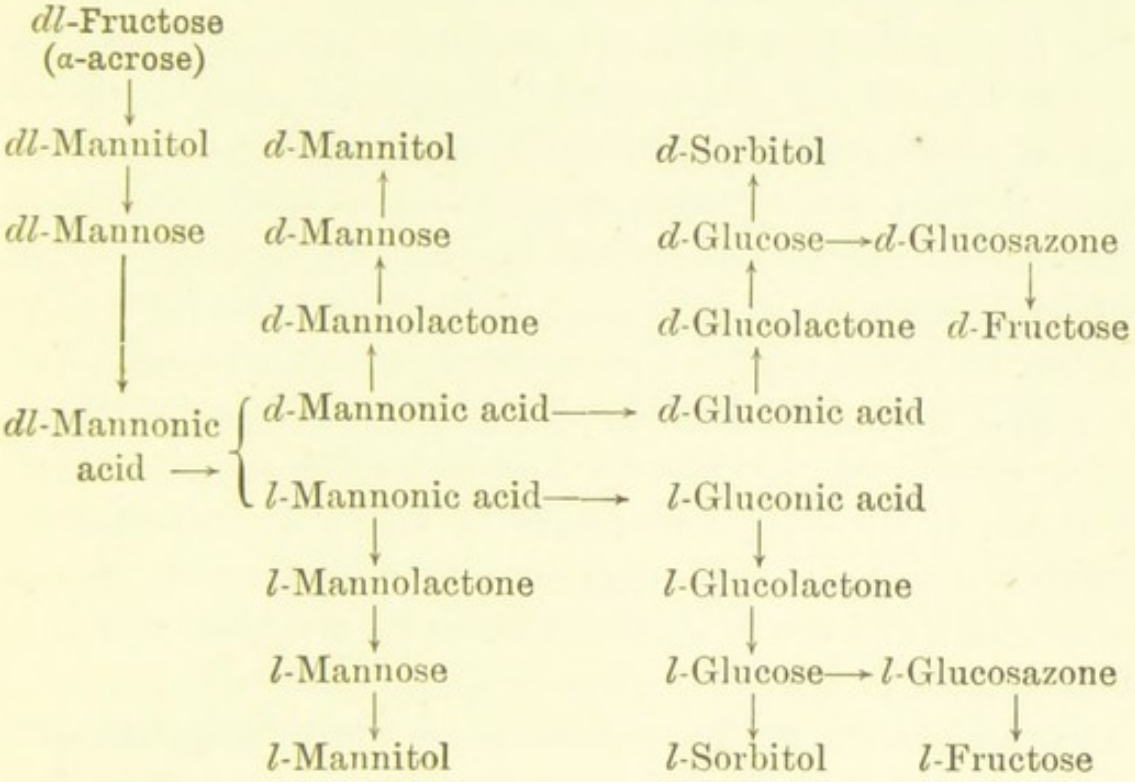
In a similar manner *l*-**mannose** and *l*-**mannitol** were obtained from *l*-mannonic acid.

d-Mannonic acid was heated with quinoline, and was partly transformed into *d*-gluconic acid (p. 603); the latter was then reduced to *d*-**glucose** and *d*-**sorbitol**. In a similar manner *l*-gluconic acid was obtained from *l*-mannonic acid, and reduced to *l*-**glucose** and *l*-**sorbitol**.

d-**Fructose** was obtained from *d*-glucose with the aid of the osazone in the manner already described (p. 302), and *l*-**fructose** was prepared in the same way from *l*-glucose. It was also proved that α-acrose, the first synthetical product, was *dl*-fructose.

These results are summarised in the following table; the

starting-point is α-acrose, and the arrows indicate the directions in which the transformations occur :—



Di-saccharoses.—Although it is known that the di-saccharoses (p. 303) are condensation products formed from two molecules of the same or of different hexoses, the manner in which this condensation occurs is still uncertain. Some of the di-saccharoses, such as lactose and maltose, may be oxidised with bromine and water, and thus converted into monocarboxylic acids of the molecular formula, $C_{12}H_{22}O_{12}$. Lactose, for example, gives *lactobionic acid*, and maltose, *maltobionic acid*.

Now, the formation of an acid by the direct combination of a molecule with one atom of oxygen proves that that molecule contains an aldehyde-group ; hence, when lactose and maltose are produced by the condensation of two aldohexose molecules, the aldehyde-group of *one* of the aldohexoses is not directly concerned in the process. Sucrose, unlike lactose and maltose, cannot be oxidised to an acid of the molecular formula, $C_{12}H_{22}O_{11}$, and consequently its molecule does not contain an aldehyde-group.

Lactobionic acid and maltobionic acid, like the di-saccharoses from which they are derived, are readily hydrolysed ; lactobionic acid is thus transformed into *d*-galactose and *d*-gluconic acid, whereas maltobionic acid is converted into *d*-glucose and *d*-gluconic acid.

The Fermentation of Aldoses and Ketoses.—The action of the enzymes of yeast (invertase and zymase) on some of the aldoses and ketoses has already been stated (p. 102), and it has been pointed out that zymase brings about the alcoholic fermentation of *d*-glucose and of *d*-fructose. Of the other hexoses, *d*-mannose ferments quickly, and *d*-galactose ferments slowly; but *l*-glucose, *l*-mannose, and all the optically isomeric aldohexoses not mentioned immediately above, seem to be incapable of undergoing alcoholic fermentation. The tetroses, pentoses, heptoses, and octoses, also, are not attacked by yeast, but mannononose (p. 604) undergoes alcoholic fermentation, and glycerose (p. 300) undergoes changes which result in the formation of propionic acid. It would seem, therefore, that the only molecules which are attacked by zymase are those which contain three, or a multiple of three, carbon atoms.

It is obvious from the behaviour of the aldohexoses that the action of the enzyme depends not only on the structure, but also on the configuration of the molecule, and it is a noteworthy fact that of two structurally identical, enantiomorphously related compounds, such as *d*- and *l*-glucose, the enzyme attacks the one and leaves the other unchanged.

A similar instance of the selective action of an enzyme is observed in the case of the methylglucosides (p. 602); one of them, the α-compound, is readily hydrolysed by invertase, and converted into glucose and methyl alcohol, whereas the optical isomeride is not attacked. Another example is met with in the case of the enzyme, maltase, which hydrolyses maltose but has no action on sucrose.

It is, in fact, a general rule that the specific action of an enzyme is restricted to one or to a few substances, and in cases such as those considered above, the selective action may possibly be conditioned by the asymmetry of the enzyme itself.

Muta-rotation.—The specific rotation of *d*-glucose in a freshly prepared aqueous solution is about $[\alpha]_D + 110°$; but

this value rapidly decreases, and in the course of about twenty-four hours it becomes constant at $[\alpha]_D + 52{\cdot}6°$; when the solution is boiled, or treated with small quantities of alkali hydroxides, it attains this minimum value in the course of a few minutes.

Many other members of the carbohydrate group, and also many optically active compounds of widely different types, show an analogous behaviour; in freshly prepared solutions they have a different (greater or smaller) specific rotation from that which is ultimately attained.

This phenomenon, originally called bi-rotation, now termed *muta-rotation*, is due to the occurrence of some change in the dissolved molecules. In many cases it is known to be the result of keto-enolic transformation or other types of tautomeric change, or to the combination of the dissolved substance with the water or other solvent. In the case of *d*-glucose, the muta-rotation is due to the partial conversion of the ordinary form of the sugar (α-glucose, $[\alpha]_D + 110°$) into β-glucose ($[\alpha]_D + 19°$), until a condition of equilibrium is attained, but the nature of the relationship between the α- and β-forms has not been determined.

The Glucosides.—The glucosides (footnote, p. 316), of which various examples have been given (pp. 327, 447, 452), are believed to be analogous to the methylglucosides (p. 602) in structure—that is to say, their molecules probably contain some univalent group, which may be of a highly complex nature, in place of the methyl-group in a compound of the character of the methylglucosides. They are all levorotatory and are all hydrolysed by mineral acids, giving a sugar (usually *d*-glucose) and one or more other products, which may belong to widely different types of compounds. Most glucosides are also hydrolysed by particular enzymes, such as emulsin and myrosin.

Among the interesting glucosides not yet mentioned, those which occur in the leaves of the foxglove (*Digitalis purpurea* and *lutea*) are of physiological importance, and pass under the

name of *digitalin;* this preparation stimulates the action of the heart, and at the same time diminishes the frequency of the pulse.

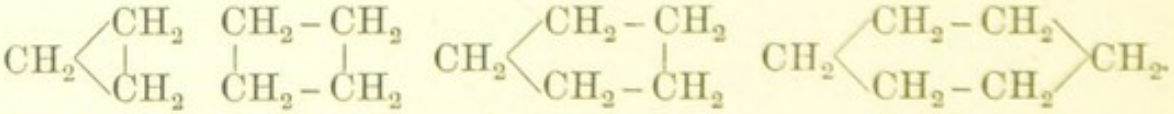
CHAPTER XL.

Cycloparaffins, Cyclo-olefines, and other Types of Closed-Chain Compounds.

It has been pointed out that benzene, cymene, and other aromatic compounds may combine directly with hydrogen under suitable conditions. The closed-chain compounds which are formed in this and in many other ways are classed as *cycloparaffins* when they are fully saturated, and as *cyclo-olefines* when they are unsaturated (compare p. 365). Hexahydrobenzene, for example, is called cyclohex*ane*, whereas tetrahydrobenzene is called cyclohex*ene*, and dihydrobenzene, cyclohexa*diene*.

The terms cycloparaffin and cyclo-olefine, however, are not restricted to those compounds the molecules of which contain closed-chains of six carbon atoms; they are also applied to corresponding compounds, the molecules of which contain closed-chains of 3, 4, 5, 7, &c. carbon atoms.

Cycloparaffins and their Derivatives.—The cycloparaffins are also frequently referred to as the polymethylenes (footnote, p. 364); the nomenclature of such compounds may be illustrated by the following examples:—



Cyclopropane (Trimethylene). Cyclobutane (Tetramethylene). Cyclopentane (Pentamethylene). Cyclohexane (Hexamethylene).

The names of the alcohols derived from the cycloparaffins end in **ol**, those of the aldehydes in **al**, and those of the ketones in **one**, as will be seen from examples given below. The positions of the substituents in the closed-

chain are shown by numbering the carbon atoms *in order*, and using these numbers in the name of the compound; it is immaterial, of course, from which carbon atom the numbering starts.

The *cycloparaffins* may be prepared directly by treating certain dihalogen derivatives of the paraffins with zinc or with sodium,

$$CH_2\begin{cases}CH_2Br\\CH_2Br\end{cases} + Zn \text{ (or } 2Na) = CH_2\begin{cases}CH_2\\|\\CH_2\end{cases} + ZnBr_2 \text{ (or } 2NaBr);$$

such reactions may be summarised by the general equation,

$$[CH_2]_n\begin{cases}CH_2X\\CH_2X\end{cases} + Zn \text{ (or } 2Na) = [CH_2]_n\begin{cases}CH_2\\|\\CH_2\end{cases} + ZnX_2 \text{ (or } 2NaX),$$

but dibromides, such as $CH_3{\cdot}CHBr{\cdot}[CH_2]_n{\cdot}CH_2Br$, and other dihalogen derivatives, may also be employed.

The *hydroxy*-derivatives of the cycloparaffins may be obtained by treating certain halogen derivatives of open-chain ketones with magnesium, in presence of ether—an application of the Grignard reaction which corresponds with the preparation of a tertiary alcohol from a ketone (p. 228). Acetobutyl bromide, for example, yields 1-*methylcyclopentan*-1-*ol*, when the product of the reaction,

$$\begin{matrix}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3\\|\\CH_2{\cdot}CH_2Br\end{matrix} + Mg = \begin{matrix}CH_2{\cdot}CH_2\\|\\CH_2{\cdot}CH_2\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_3\\O{\cdot}MgBr'\end{matrix}$$

is decomposed with a dilute acid.

The *dihydroxy*-derivatives may be prepared by reducing certain open-chain di-ketones; this reaction is analogous to that which occurs in the formation of pinacone from acetone (p. 145),

$$CH_2\begin{cases}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3\\CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3\end{cases} + 2H = CH_2\begin{cases}CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3\\CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3\end{cases}.$$

2,8-Nonadione. 1,2-Dimethylcycloheptan-1,2-diol.

The *keto*-derivatives may be prepared by heating the calcium salts of certain dicarboxylic acids, a reaction which corresponds with that employed in the preparation of ketones from mono-

carboxylic acids; the calcium salt of adipic acid (p. 244), for example, gives *cyclopentanone*,

$$\begin{matrix}CH_2\cdot CH_2\cdot COO\\ |\\ CH_2\cdot CH_2\cdot COO\end{matrix}\!\!>\!Ca = \begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>\!CO + CaCO_3.$$

The *carboxy*-derivatives may be prepared by treating certain dihalogen derivatives of the paraffins with the sodium compound of ethyl malonate, ethyl acetoacetate, or ethyl cyanoacetate (p. 209),*

$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + CNa_2(COOEt)_2 = \begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!C(COOEt)_2;$$

Ethyl Cyclopropane-1,1-dicarboxylate.

also by treating certain dihalogen derivatives of the paraffins (1 mol.) with two molecular proportions of ethyl sodiomalonate, then forming the sodium derivatives of the products, and submitting the latter to the action of bromine or iodine,

$$CH_2\!<\!\begin{matrix}CH_2Br\\ CH_2Br\end{matrix} + 2CHNa(COOEt)_2 = CH_2\!<\!\begin{matrix}CH_2\cdot CH(COOEt)_2\\ CH_2\cdot CH(COOEt)_2\end{matrix} + 2NaBr,$$

$$CH_2\!<\!\begin{matrix}CH_2\cdot CNa(COOEt)_2\\ CH_2\cdot CNa(COOEt)_2\end{matrix} + Br_2 = CH_2\!<\!\begin{matrix}CH_2\cdot C(COOEt)_2\\ |\\ CH_2\cdot C(COOEt)_2\end{matrix} + 2NaBr.$$

Ethyl Cyclopentane-1,1,2,2-tetracarboxylate.

Carboxy-derivatives of cyclo-ketones may be prepared by treating the esters of certain dicarboxylic acids with sodium,

$$CH_2\!<\!\begin{matrix}CH_2\cdot COOEt\\ CH_2\cdot CH_2\cdot COOEt\end{matrix} + Na = CH_2\!<\!\begin{matrix}CH_2\cdot C(ONa)\\ \|\\ CH_2\cdot C\text{–}COOEt\end{matrix} + C_2H_5\cdot OH.$$

In this reaction the sodium derivative of the *enol* (p. 205) is formed, as in the case of the preparation of ethyl acetoacetate; but when the product is treated with a dilute acid, the keto-isomeride (*ethyl cyclopentan*-1-*one*-2-*carboxylate*) is obtained.

Carboxy-derivatives of cyclo-diketones (cyclo-di*ones*) may

* Such reactions really occur in two stages, but for the sake of brevity the two changes are summarised in the one equation; the operations are carried out in much the same way as described in the synthesis of derivatives of ethyl acetoacetate (p. 201) and ethyl malonate (p. 207).

be prepared in a somewhat analogous manner, by condensing the esters of certain dicarboxylic acids with ethyl oxalate, with the aid of sodium or of sodium ethoxide,

$$CH_2\begin{<}CH_2\cdot COOEt \\ CH_2\cdot COOEt\end{>} + \begin{matrix}COOEt \\ |\\ COOEt\end{matrix} = CH_2\begin{<}CH(COOEt)\cdot CO \\ CH(COOEt)\cdot CO\end{>} + 2C_2H_5\cdot OH.$$

Ethyl Cyclopentan-1,2-one-3,5-dicarboxylate.

This reaction corresponds with the preceding one, and also with that which occurs in the preparation of ethyl oxalacetate (p. 209).

The above examples show that any reaction which brings about the union of carbon atoms, and results in the formation of an open-chain compound, may be applied to the preparation of a closed-chain compound, provided always that the latter is stable under the conditions of the experiment.

A method of great general importance for the preparation of cyclo-paraffins and their derivatives is that of Sabatier and Senderens, which consists in passing the vapour of aromatic or of cyclo-olefine derivatives (p. 365), together with hydrogen, over finely divided nickel* heated at about 200°. Under these conditions benzene, for example, yields cyclohexane, and phenol, cyclohexanal.

Another method, particularly useful in connection with the terpenes and their derivatives, consists in treating the unsaturated compound with hydrogen in the presence of colloidal palladium.† Under these conditions many unsaturated compounds absorb hydrogen rapidly at the ordinary temperature, and are transformed into cycloparaffin derivatives.

Properties of the Cycloparaffins.—Except that the cycloparaffins and their derivatives usually boil at higher temperatures than the corresponding saturated open-chain compounds, the two types of compounds resemble one another in physical properties. The boiling-points of some typical substances are compared in the following table :—

* Prepared by reducing the oxide in a stream of hydrogen.

† Prepared by treating a solution of palladium chloride with hydrogen in the presence of gum-arabic.

Cyclopentane, C_5H_{10}.....	50°	Pentane, C_5H_{12}.....	38°
Cyclohexane, C_6H_{12}.....	81°	Hexane, C_6H_{14}.....	71°
Cyclobutanol, $C_4H_7{\cdot}OH$	123°	Normal butyl alcohol, $C_4H_9{\cdot}OH$.....	117°
Cyclopropanecarboxylic acid, $C_3H_5{\cdot}COOH$....	183°	Normal butyric acid, $C_3H_7{\cdot}COOH$.....	163°

In chemical properties also there is a close resemblance between the two types of compounds. Thus, the esters obtained by any of the above methods may be hydrolysed to the corresponding *acids*, and when the latter contain the group, $>C(COOH)_2$, they may be transformed into the corresponding monocarboxylic acids in the ordinary way (p. 208). The ketones may be reduced to secondary alcohols, or caused to undergo most of the other usual reactions of open-chain ketones; but when they are oxidised the ring is 'broken' and a dicarboxylic acid is formed,

$$[CH_2]_n\begin{<}{CH_2}{CH_2}\end{>}CO + 3O = [CH_2]_n\begin{<}{CH_2{\cdot}COOH}{COOH}.$$

The secondary alcohols may be transformed into the corresponding halogen compounds, or changed in other ways, just as may the open-chain secondary alcohols.

The cycloparaffins, as a rule, are not acted on by reducing agents, and towards oxidising agents—such as an alkaline solution of potassium permanganate—and towards the halogens and halogen acids, they and their derivatives usually behave like the corresponding compounds of the paraffin series.

In certain respects, nevertheless, some of the cycloparaffins resemble the olefines (with which they are isomeric). Whereas propane, for example, is not acted on by hydrogen bromide or by bromine, cyclopropane is immediately attacked by hydrogen bromide even in the cold, with formation of propyl bromide; and, although it is not readily attacked by bromine, it slowly combines with this halogen and gives trimethylene dibromide, $CH_2Br{\cdot}CH_2{\cdot}CH_2Br$ (p. 532). Derivatives of cyclopropane behave in a similar manner. Cyclopropane-1,1-dicarboxylic acid, for example, although only very slowly

attacked by bromine at ordinary temperatures, is transformed into *bromethylmalonic acid*, $CH_2Br{\cdot}CH_2{\cdot}CH(COOH)_2$, by cold hydrobromic acid. It is also noteworthy that the stability of a cyclopropane derivative depends not only on the nature of the compound, but also on the positions of the substituents in the closed-chain. Thus, whereas cyclopropane-1,1-dicarboxylic acid is readily attacked by hydrobromic acid, as just stated, the isomeric 1,2-dicarboxylic acid is not changed, even when it is heated with the halogen acid.

Cyclobutane and its derivatives, on the whole, are more readily formed, and are much more stable, than the corresponding cyclopropane compounds; they are not acted on by bromine or by hydrogen bromide at ordinary temperatures, but a few of them are attacked at higher temperatures.

Cyclopentane and its derivatives are produced with far greater ease than the corresponding cyclobutane compounds, and do not combine either with bromine or with hydrogen bromide.

Cyclohexane and its derivatives, although stable towards the two reagents just mentioned, are not formed so easily as the corresponding cyclopentane compounds, and, in fact, are sometimes transformed into the latter in the course of reactions which occur at high temperatures; thus, when benzene is reduced with hydriodic acid at 250°, it yields *methylcyclopentane*, probably because the cyclohexane which is first produced undergoes an isomeric change.

The Spannungtheorie.—In order to account for this graded stability of the cycloparaffins, Baeyer proposed the so-called *Spannungtheorie* or *strain theory*, which may be explained as follows:—When a carbon atom is represented by a small ball, and its four units of valency by flexible rods, which are directed from the centre of the ball towards the angles of a regular tetrahedron (compare p. 267), then any two of these rods enclose an angle of 109·28°. When now the union of two or more carbon atoms is represented by linking the balls together with the aid of these rods, and

various models of *closed-chains* of carbon atoms are thus constructed, it will be found that strains are set up in the models owing to the necessary angular deflections of the rods. In the model, which consists of two balls (*cycloethane*), the closed-chain is produced by joining the balls together by *two* rods; the strain which is thereby produced may be supposed to be due to a deflection of each of the rods through an angle of $\frac{109{\cdot}28^\circ}{2}$, because this is the deflection which each would undergo if it were brought parallel with the other. In the model composed of three balls (*cyclopropane*), the rods would form an equilateral triangle, and the deflection of each would be $\frac{109{\cdot}28^\circ - 60^\circ}{2}$. Similarly, in the cases of the models composed of 4, 5, 6, &c. balls, the deflections may be calculated. These deflections, which may be regarded as measures of the strains set up in the molecules, are tabulated below :—

Cycloethane (ethylene).....	54·44°	$\frac{(109{\cdot}28^\circ)}{2}$
Cyclopropane	24·44°	$\frac{(109{\cdot}28^\circ - 60^\circ)}{2}$
Cyclobutane.....	9·44°	$\frac{(109{\cdot}28^\circ - 90^\circ)}{2}$
Cyclopentane	0·44°	$\frac{(109{\cdot}28^\circ - 108^\circ)}{2}$
Cyclohexane.....	−5·16°	$\frac{(109{\cdot}28^\circ - 120^\circ)}{2}$
Cycloheptane	−9·33°	$\frac{(109{\cdot}28^\circ - 128{\cdot}34^\circ)}{2}$
Cyclooctane.....	−12·51°	$\frac{(109{\cdot}28^\circ - 135^\circ)}{2}$.

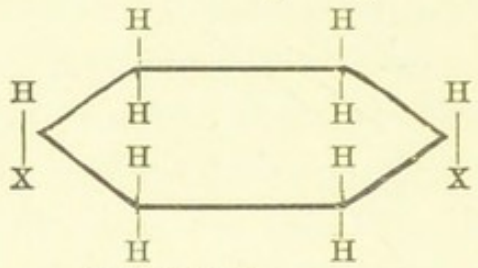
It is thus evident that the deflection is greatest in the case of the model composed of two balls, which represents the molecule of ethylene; if, therefore, ethylene is regarded as the simplest cycloparaffin, its molecule should be the least stable, since ring-formation is accompanied by the greatest

strain. In accordance with this view, the cycloethane ring is readily 'broken'—as, for example, when ethylene combines with bromine or with hydrogen bromide. From this hypothesis it would also be inferred that the relative stabilities of the other cycloparaffins gradually increase up to cyclopentane, and then decrease again; and, judging from facts such as those recorded above, this is the case. It has also been found from the heats of combustion of the cycloparaffins, that the heat developed by the combustion of one $-CH_2-$ group decreases from ethylene to cyclopentane, and then increases again; as the heat of combustion includes the heat generated during the disintegration of the molecule, these measurements also support Baeyer's views.

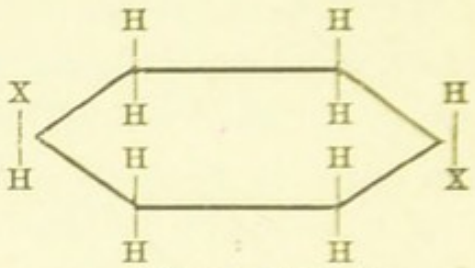
The great difference in behaviour between α-, β-, γ-, δ-, &c. hydroxy-acids as regards the readiness with which they form *lactones* (p. 243), and of dicarboxylic acids as regards the readiness with which they form *inner anhydrides*, is also accounted for by the strain theory; in molecules, such as those of valerolactone (p. 243) and succinic anhydride (p. 250), which are very readily formed, there is presumably a smaller strain than in those which are composed of closed-chains containing a greater or smaller number of atoms. The facility with which closed-chains are generally produced from certain **o**-derivatives of benzene, and not from **m**- or **p**-compounds, is also accounted for in a similar manner.

Cis- and Trans-isomerism of Closed-Chain Compounds.—In the models referred to above, which represent the molecules of the cycloparaffins, the balls (carbon atoms) are all in one plane, from either side of which project in a symmetrical manner the two remaining rods of each of the balls. When, therefore, two hydrogen atoms of two different $-CH_2-$ groups in a cycloparaffin are displaced by two identical or dissimilar substituents, if the models of such molecules are constructed, it will be seen that two different arrangements are possible. As a matter of fact, compounds of the type here considered are found to exist in *stereo-*

isomeric forms; there are, for example, two stereoisomeric *cyclohexane*-1,4-*dicarboxylic acids*, which may be respectively represented by the following projections (where X is the –COOH group):—



Cis-modification.



Trans-modification.

As this type of stereoisomerism is analogous to that which occurs in the case of unsaturated open-chain compounds (p. 279), such isomerides are distinguished by the prefixes *cis-* and *trans-*, which are chosen in the manner previously indicated.

Cyclo-olefines.

The cyclo-olefines are related to the cycloparaffins just as the olefines are related to the paraffins, and some examples of this class of compound have already been described (compare pp. 365, 587). They may be prepared from ketones and alcohols of the cycloparaffin series by reactions corresponding with those used in the formation of olefines from open-chain compounds; the following changes,

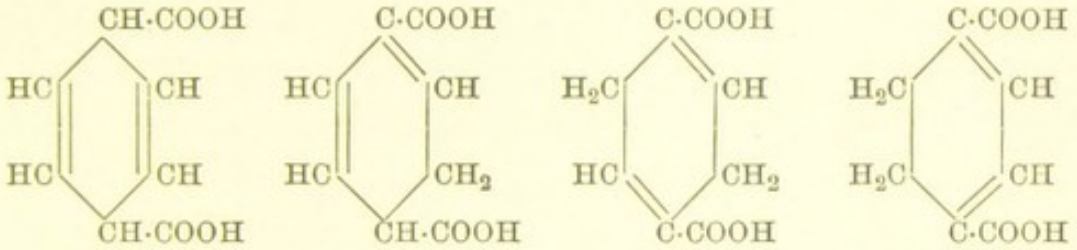
$$-CH_2{\cdot}CO- \longrightarrow -CH_2{\cdot}CH(OH)- \longrightarrow -CH_2{\cdot}CH_2Br- \longrightarrow -CH{:}CH-,$$

for example, may be brought about by the usual methods.

The cyclo-olefines and their derivatives may also be prepared by the reduction of aromatic compounds. When aromatic acids are treated with vigorous reducing agents, such as sodium amalgam and water, or sodium and an alcohol, the benzene nucleus in many, but not in all, cases is reduced. Benzoic acid, for example, with sodium and alcohol, gives *cyclohexanecarboxylic acid*; the toluic acids may also be reduced in a similar manner; but apparently reduction occurs only in the case of those acids in which the carboxyl-group is directly united to the nucleus.

The reduction products of phthalic, isophthalic, and terephthalic acids formed the subject of a long series of investigations by Baeyer, who obtained the di-, tetra-, and hexa-hydro-derivatives of all the three isomerides; his results may be illustrated by a short summary of his work in the case of terephthalic acid.

The *dihydroterephthalic acids* (*cyclohexadienedicarboxylic acids*) exist in the following four structurally isomeric forms :—



Δ-2:5-acid. Δ-1:5-acid. Δ-1:4-acid. Δ-1:3-acid.

In naming such isomerides, the symbol Δ is used to denote the double binding (or bindings), and the positions of the double bindings are shown by numbers; the numbering starts from one of the carboxyl-groups.

Of the above four structural isomerides, the Δ-2:5-acid exists in *cis*- and *trans*-forms, corresponding with the two stereoisomeric cyclohexanedicarboxylic acids (p. 628).

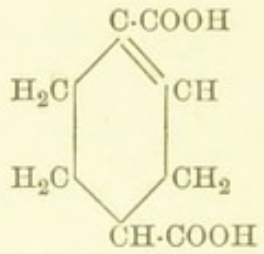
When terephthalic acid is reduced with sodium amalgam and water, it yields in the first place a mixture of the *cis*- and *trans*-forms of the Δ-2:5-acid. In the molecules of these compounds the double bindings are in a *labile* (or unstable) position—namely, in the $\beta\gamma$-position, $-CH{:}CH{\cdot}CH_2{\cdot}COOH$; and such compounds, whether of the open- or of the closed-chain series, show a great tendency, especially when heated with alkalis, to pass into $\alpha\beta$-unsaturated carboxylic acids, $-CH_2{\cdot}CH{:}CH{\cdot}COOH$ (p. 486). This change takes place even when the Δ-2:5-acid is boiled with water.

The Δ-1:5-acid, which is thus produced, also undergoes an isomeric change when its alkaline solution is boiled, the $\beta\gamma$-double binding passing to the $\alpha\beta$-position, with formation of the Δ-1:4-acid. The Δ-1:4-acid, therefore, is always the main product when terephthalic acid is reduced with sodium

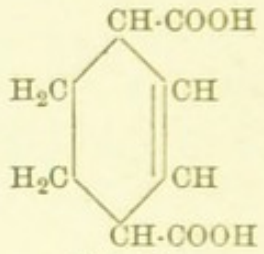
amalgam and water, unless the sodium hydroxide in the solution is neutralised as fast as it is formed.

The Δ-1:3-acid is prepared from hexahydroterephthalic acid; for this purpose the latter is converted into 1,4-*dibromocyclohexane*-1,4-*dicarboxylic acid* (*αα-dibromohexahydroterephthalic acid*), which, when treated with boiling alcoholic potash, loses two molecules of hydrogen bromide, giving Δ-1:3-dihydroterephthalic acid.

The *tetrahydroterephthalic acids* (*cyclohexenedicarboxylic acids*) exist in the following two structurally isomeric forms :—



Δ-1-acid.



Δ-2-acid.

The Δ-2-compound shows *cis*- and *trans*-isomerism.

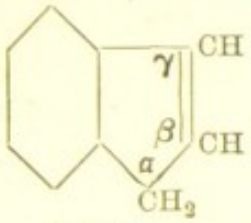
Both the stereoisomeric Δ-2-acids are produced by the reduction of Δ-1:3- or Δ-1:5-dihydroterephthalic acid with sodium amalgam; they both undergo isomeric change when they are boiled with a solution of sodium hydroxide, the double binding 'wandering' from the $\beta\gamma$- to the $\alpha\beta$-position in the usual manner, with formation of the Δ-1-acid.

The *hexahydroterephthalic acids* (*cyclohexane*-1,4-*dicarboxylic acids*) exist only in the two stereoisomeric forms mentioned above, and a mixture of these compounds is produced when the tetrahydro-acids are combined with bromine and the dibromo-additive products are reduced with zinc-dust and acetic acid.

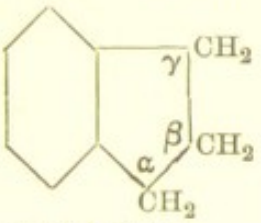
Indene, Hydrindene, and Hydrindone.

Many closed-chain compounds of a mixed type are known—as, for example, substances which combine the properties of benzene with those of a cycloparaffin or cyclo-olefine. *Indene*, *hydrindene*, and *hydrindone* are compounds of this kind, and

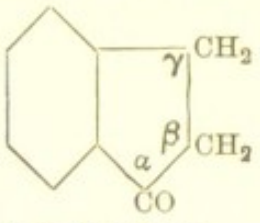
are respectively represented by the following formulæ; the letters serve to distinguish their isomeric derivatives :—



Indene.



Hydrindene.



α-Hydrindone.

Indene is contained in that fraction of coal-tar which is collected from 176° to 182°, and is isolated from this product by precipitation with picric acid (p. 443); the *picrate* is purified by recrystallisation and then distilled in steam, whereby it is hydrolysed and indene passes over. Indene boils at 178°, and readily undergoes polymerisation; when reduced with sodium and alcohol, it is converted into **hydrindene** (b.p. 177°), a much more stable compound.

Indene has been synthesised by a method analogous to one of those employed in the synthesis of the cycloparaffins (p. 622). o-Xylene (1 mol.) is treated with bromine (4 mols.) at 150°, and the o-*xylylene dibromide*, which is thus produced, is warmed with ethyl sodiomalonate (compare footnote, p. 622),

$$C_6H_4\begin{<}{CH_2Br}{CH_2Br}+CNa_2(COOEt)_2=C_6H_4\begin{<}{CH_2}{CH_2}\end{>}C(COOEt)_2+2NaBr.$$

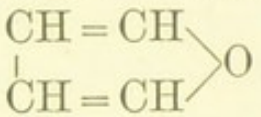
The *ethyl hydrindenedicarboxylate*, so formed, is hydrolysed, the dicarboxylic acid is converted into the monocarboxylic acid in the usual manner, and the barium salt of the *hydrindene-β-carboxylic acid* is distilled, whereby it is converted into indene, barium carbonate, and hydrogen.

α-**Hydrindone** is obtained, together with hydrogen chloride, by warming *phenylpropionyl chloride*, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$, with aluminium chloride. It melts at 41°, boils at 244°, and forms an *oxime* (m.p. 146°); when this oxime is reduced with sodium amalgam and water, it is converted into α-**hydrindamine**, an externally compensated base (b.p. 220°), which may be resolved into its optically active components. When hydrindamine hydrochloride is heated alone, it decomposes into indene and ammonium chloride.

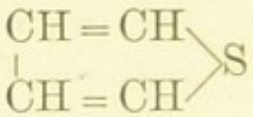
β-Hydrindone, $C_6H_4\begin{<}{l}CH_2\\CH_2\end{>}CO$, is produced when the calcium salt of *phenylene-o-diacetic acid* * is heated, a reaction similar to that which occurs in the formation of cyclopentanone from calcium adipate (p. 622); it melts at 61°, boils at 220–225°, and shows the ordinary reactions of a ketone.

Furan, Thiophene, and Pyrrole.

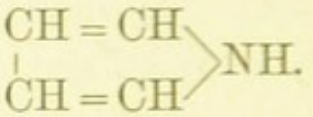
The molecules of these three substances contain closed-chains of five atoms, and are respectively represented by the following formulæ :—



Furan.



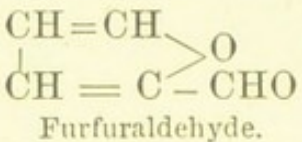
Thiophene.



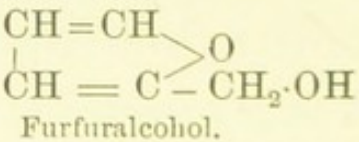
Pyrrole.

Each of these compounds is the parent substance of a great many derivatives.

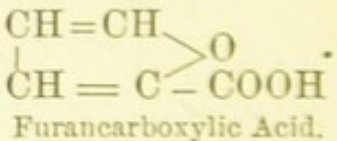
Furan, C_4H_4O, is obtained by heating the barium salt of *furancarboxylic acid* (*pyromucic acid*) with soda-lime; it is a colourless liquid, boiling at 32°. Its more important derivatives are :—



Furfuraldehyde.



Furfuralcohol.



Furancarboxylic Acid.

Furfuraldehyde, $C_4H_3O{\cdot}CHO$ (*furfural*), is obtained in theoretical quantities when pentoses are distilled with hydrochloric acid (p. 601), and is usually prepared by distilling bran with dilute sulphuric acid. It boils at 162°, and yields a hydrazone (m.p. 96°). Owing to the fact that the molecule of furfuraldehyde contains an unsaturated closed-chain directly united to the aldehyde-group, it shows most of the properties of benzaldehyde. Thus, when shaken with caustic potash, it yields a mixture of furfuralcohol and furancarboxylic acid, just as benzaldehyde gives benzyl alcohol and benzoic acid

* This acid is obtained by treating o-xylylene dibromide (p. 631) with potassium cyanide, and hydrolysing the *o-xylylene dicyanide* which is thus formed.

(p. 456). It may also be successively transformed into *furoïn*, $C_4H_3O{\cdot}CO{\cdot}CH(OH){\cdot}C_4H_3O$, and *furil*, $C_4H_3O{\cdot}CO{\cdot}CO{\cdot}C_4H_3O$, by reactions exactly analogous to those by which benzaldehyde is converted into benzoïn and benzil (p. 457).

Furfuraldehyde may be very readily detected by the deep-red colour which it gives when aniline is added to its alcoholic solution.

Furancarboxylic acid, $C_4H_3O{\cdot}COOH$ (*pyromucic acid*), is obtained when mucic acid (p. 298) is distilled under reduced pressure; it melts at 134°, and closely resembles benzoic acid in physical and in chemical properties.

Thiophene, C_4H_4S, was discovered by V. Meyer as a result of the observation that whereas coal-tar benzene shows the indophenine reaction (p. 340), pure benzene (from benzoic acid) does not.*

Thiophene is extracted from coal-tar benzene (which contains about 0·6 per cent. of this sulphur compound) by shaking the crude hydrocarbon with concentrated sulphuric acid; the thiophene dissolves in the form of *thiophenesulphonic acid*, $C_4H_3S{\cdot}SO_3H$, which may be isolated by one of the usual methods (p. 429), and converted into its lead salt; when the latter is heated with ammonium chloride, thiophene passes over.

Thiophene is most conveniently prepared by heating sodium succinate with phosphorus trisulphide; it may be assumed that in this reaction the succinic acid is first converted into the enolic isomeride, and that the *dihydroxythiophene*, which is first produced,

$$\begin{matrix} CH_2{\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{matrix} \longrightarrow \begin{matrix} CH{:}C(OH)_2 \\ | \\ CH{:}C(OH)_2 \end{matrix} \longrightarrow \begin{matrix} CH{:}C(OH) \\ | \\ CH{:}C(OH) \end{matrix} \!\!>\!\! S,$$

is then reduced by the hydrogen sulphide, which is formed

* It was at first thought that the blue colouring matter, called indophenine (p. 340), was a compound of the composition, $C_{14}H_9NO_4$, produced by the condensation of one molecule of isatin with one molecule of benzene. V. Meyer showed that indophenine has the composition, $C_{12}H_7ONS$, and that it is produced from isatin and thiophene.

during the reaction. Under similar conditions, levulic acid (p. 205) is converted into *methylthiophene*, C_4H_3MeS (*thiotolene*), a compound which occurs in crude coal-tar toluene (p. 373).

Thiophene and its derivatives show an extraordinarily close resemblance to benzene and its derivatives; corresponding compounds have almost the same boiling-points, and are very similar in chemical properties.

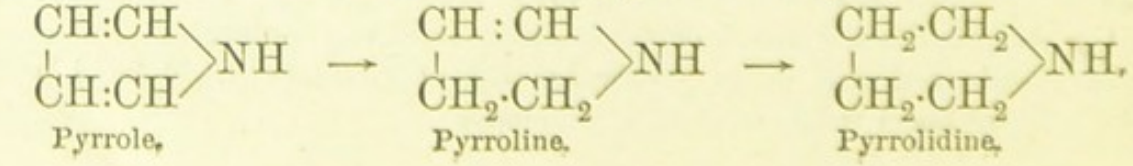
Pyrrole, C_4H_5N, was discovered in bone-oil by Runge, and was more fully investigated by Anderson.

The fraction of bone-oil, collected from 100° to 150°, is washed with dilute sulphuric acid to free it from pyridine bases, and is then warmed with caustic potash in order to hydrolyse the nitriles which are present. The oil is again distilled, and the portion collected from 120° to 140° is heated with excess of solid caustic potash; the solid *potassium pyrrole* is then separated from the oil, which consists of benzene derivatives, and decomposed with water. The liberated pyrrole is afterwards distilled in steam and further purified by fractional distillation; it boils at 131°.

Pyrrole and its derivatives impart a crimson colouration to a pine-chip moistened with hydrochloric acid and held in the vapour of the substance; in contact with strong acids, pyrrole is rapidly converted into an orange-red substance (pyrrole red), hence the name, pyrrole, from πυρρός, red.

Pyrrole is a very feeble base, because the >NH-group is combined with the two strongly negative –CH:CH– groups; these groups, in fact, like the >CO groups in succinimide (p. 252), confer acid properties on the >NH-group, in consequence of which pyrrole forms a *potassium* derivative, C_4H_4NK, when it is warmed with potassium, but the compound is hydrolysed by water.

When pyrrole is reduced with zinc and acetic acid, it yields *pyrroline* (b.p. 91°), which on further reduction with sodium and alcohol is transformed into *pyrrolidine* (b.p. 87°).



Pyrrole. Pyrroline. Pyrrolidine.

The reduction of the negative group, $-CH{:}CH-$, to the positive group, $-CH_2{\cdot}CH_2-$, is accompanied by a great increase in the basic nature of the substance; pyrroline gives stable salts with acids, and pyrrolidine is as strongly basic as diethylamine, or piperidine.

Pyrrolidine has been synthesised by reactions exactly similar to those employed in the synthesis of piperidine (p. 532), which may be summarised as follows:—

$$CH_2Br{\cdot}CH_2Br \longrightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}CN \longrightarrow NH_2{\cdot}[CH_2]_4{\cdot}NH_2 \longrightarrow \begin{matrix} CH_2{\cdot}CH_2 \\ | \quad\quad \rangle NH. \\ CH_2{\cdot}CH_2 \end{matrix}$$

Synthesis of Furan, Thiophene, and Pyrrole Derivatives.—Derivatives of these three closed-chain compounds may be prepared from 1,4- or γ-diketones such as *acetonylacetone*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$,* which contain the grouping, $-CO{\cdot}CHR{\cdot}CHR{\cdot}CO-$. When such diketo-compounds are treated with (*a*) sulphuric or hydrochloric acid, (*b*) hydrogen sulphide (in the form of phosphorus trisulphide), or (*c*) ammonia, they are transformed into derivatives of (*a*) furan, (*b*) thiophene, and (*c*) pyrrole respectively. In these changes the diketo-compound probably reacts in the enolic form, $-C(OH){:}CR{\cdot}CR{:}C(OH)-$, which then loses the elements of water, giving a furan derivative, or reacts with the hydrogen sulphide or ammonia, giving a thiophene or pyrrole derivative as the case may be.

Acetonylacetone, for example, yields the following compounds:—

$$\begin{matrix} CH_3{\cdot}C=CH \\ | \quad\quad \rangle O \\ CH_3{\cdot}C=CH \end{matrix}$$

$\beta\beta_1$-Dimethylfuran.

$$\begin{matrix} CH_3{\cdot}C=CH \\ | \quad\quad \rangle S \\ CH_3{\cdot}C=CH \end{matrix}$$

$\beta\beta_1$-Dimethylthiophene.

$$\begin{matrix} CH_3{\cdot}C=CH \\ | \quad\quad \rangle NH. \\ CH_3{\cdot}C=CH \end{matrix}$$

$\beta\beta_1$-Dimethylpyrrole.

Many other derivatives of these types have been prepared by similar methods.

Antipyrine, $C_{11}H_{12}N_2O$, is a 1,2,3-phenyldimethyl-derivative

* Acetonylacetone is obtained when the sodium derivative of ethyl acetoacetate is treated with chloracetone, $CH_2Cl{\cdot}CO{\cdot}CH_3$, and the product is then submitted to ketonic hydrolysis.

of a closed-chain compound, which is called *pyrazolone*, and which has the structure, $CH\langle^{NH\cdot NH}_{CH\cdot CO}\rangle$. It was first obtained by Knorr as follows :—

Ethyl acetoacetate is heated with phenylhydrazine,

$$CH_3\cdot C(OH){:}CH\cdot COOEt + NH_2\cdot NH\cdot C_6H_5 =$$
$$CH_3\cdot C(OH){:}CH\cdot CO\cdot NH\cdot NH\cdot C_6H_5 + H_2O,$$

$$CH_3\cdot C(OH){:}CH\cdot CO\cdot NH\cdot NH\cdot C_6H_5 =$$
$$CH_3\cdot C\langle^{NH\cdot NC_6H_5}_{CH\cdot CO}\rangle + H_2O,$$

and the product (1-*phenyl*-3-*methylpyrazolone*) is then treated with methyl iodide,

$$CH_3\cdot C\langle^{NH\cdot NC_6H_5}_{CH\cdot CO}\rangle + CH_3I = CH_3\cdot C\langle^{NMe\cdot NC_6H_5}_{CH{-}CO}\rangle, HI.$$

Antipyrine is a crystalline compound (m.p. 113°), and is readily soluble in water; it is a strong mon-acid base, and is a powerful antipyretic. Its *salicylate* is also used as an antipyretic, under the name of *salipyrine*.

CHAPTER XLI.

Dyes and their Application.

Although most organic compounds are colourless, some, especially certain classes of the aromatic series, are intensely coloured substances, amongst which representatives of almost every shade occur; most of the principal dyes used at the present day, in fact, are aromatic compounds, the primary source of which is coal-tar—hence the well-known expression 'coal-tar colours.'

That a dye must be a coloured substance is, of course, obvious, but a coloured substance is not necessarily a dye, in the ordinary sense of the word, unless it is also capable of fixing itself, or of being fixed, in the fabric to be dyed, in

such a way that the colour is not removed when the fabric is rubbed, or washed with water; azobenzene, for example, is intensely coloured, but it would not be spoken of as a dye, because it does not fulfil the second condition.

Again, when a piece of *silk* or *wool* is dipped into a solution of picric acid, it is dyed yellow, and the colour is fixed in such a way that it is not removed when the material is washed with water. When, however, a piece of *calico* or other *cotton* material is treated in the same way, the picric acid does not fix itself, and is dissolved out again by water. A given substance, therefore, may be a dye for certain materials, but not for others; silk and wool fix picric acid, and are dyed by it, but cotton does not—a behaviour which is repeatedly met with in the case of other colouring matters.

Now, materials such as wool, cotton, silk, &c., consist of minute fibres, which may be very roughly described as long, cylindrical, or flattened tubes (except in the case of silk, the fibres of which are solid), the walls of which, like parchment paper and certain membranes, allow of the passage of water and of dissolved crystalloids by diffusion, but not that of colloid substances, or, of course, of matter in suspension. If, therefore, picric acid were present in a fibre, *as* picric acid, it would be extracted from this fibre by water; as, in the case of silk and wool, this does not occur, it must be assumed that the picric acid has actually combined with some substance in the fibre, and has been converted into a yellow compound, which is either insoluble or a colloid.

The nature of the insoluble compound which is formed when a material is dyed is not known, but there are reasons for supposing that certain components of the fibre unite with the dye to form an insoluble salt. This seems probable from the fact that nearly all dyes which thus fix themselves directly on the fabric are either basic or acid in character. Azobenzene, as already mentioned, is not a dye, probably because it is a neutral substance; if, however, some group, such as an amino-, hydroxyl-, or sulphonic-group, which confers basic or acid properties, is introduced into the

molecule of azobenzene, then the resulting derivative is a dye, because it has the property of combining directly with the fibres of certain materials.

Another fact which leads to the same conclusion may be quoted. Certain dyes—as, for example, rosaniline—are salts of bases which are themselves colourless, and yet some materials may be dyed simply by immersion in *colourless* solutions of these bases, the same colour being obtained as with the coloured salt (that is, the dye itself); this can only be explained on the assumption that some component of the fibre combines with the colourless base, forming with it a salt of the same colour as the dye.

Some fibres, especially silk and wool, seem to contain both acid and basic components, as they are often dyed directly both by basic and by acid dyes; cotton, on the other hand, seems to be almost free from salt-forming components, as, except in rare cases, it does not combine with colouring matters.

Since the fixing of a dye within the fibre is probably the result of the conversion of the dye into some insoluble compound, it seems reasonable to suppose that, even if a colouring matter is incapable of combining with any component of the fibre, it might still be employed as a dye, provided that, after it had once passed through the walls of the fibre, it could be there converted into some insoluble compound; this principle is applied in the case of many dyes, and the substances used to fix them in the fibre are termed *mordants*.

Dyes, therefore, may be roughly divided into two classes with respect to their behaviour towards a *given* fabric: (*a*) those which fix themselves on the fabric, and (*b*) those which do so only with the aid of a mordant.

Mordants are substances which (usually after having undergone some preliminary change) combine with dyes, forming insoluble coloured compounds; the colour of the dyed fabric in such cases depends, of course, on that of the compound thus produced, and not on that of the dye itself, so that by using different mordants different shades or colours are often obtained.

As an example of dyes of the second class, alizarin may

be taken, as its applications illustrate very clearly the use of mordants.

If a piece of calico is dipped into an aqueous solution of alizarin, it is coloured *yellow*, but the colour is not fixed, and is easily removed with the aid of soap and water. If, however, a piece of calico which has been previously mordanted with a suitable aluminium salt (in the manner described below) is treated in the same way, it is dyed a fast *red*, the alizarin having combined with the aluminium compound in the fibre to form a red insoluble substance; if, again, the calico has been mordanted with a ferric salt, it is dyed a fast *dark purple*.*

Substances very frequently employed as mordants are certain salts of iron, aluminium, chromium, and tin, more especially those, such as the acetates, thiocyanates, and alums, which are readily hydrolysed by water, yielding either an insoluble metallic hydroxide or an insoluble basic salt.

The process of mordanting usually involves two operations: firstly, the fabric is passed through, or soaked in, a solution of the mordant, in order that its fibres may become impregnated with the metallic salt; secondly, the fabric is treated in such a way that the salt is decomposed within the fibres, and there converted into some insoluble compound.

The second operation, the fixing of the mordant, so that it will not be washed out when the fabric is brought into the dye-bath, is accomplished in many ways. One method is to pass the mordanted material through a solution of some weak alkali (ammonia, sodium carbonate, lime), or of some salt, such as sodium phosphate or arsenate, which reacts with the metallic salt in the fibre, forming an insoluble metallic hydroxide, or a phosphate, arsenate, &c. Another method, applicable more especially in the case of mordants which are salts of *volatile acids*, consists in exposing the fabric to the

* A colouring matter, such as alizarin, which can thus be used for the production of different colours is sometimes termed 'polygenetic;' a dye which gives only one colour is then called 'monogenetic.'

action of steam, at a suitable temperature; under these conditions the metallic salt is hydrolysed, the acid volatilises with the steam, and an insoluble hydroxide or basic salt remains in the fibre.

In the case of silk and woollen fabrics, the operations of mordanting and fixing the mordant may often be carried out simultaneously, by merely soaking the materials in a boiling dilute solution of the mordant; under these conditions the metallic salt is partially hydrolysed in the fibre, and is there deposited in an insoluble form; silk is sometimes simply soaked in a cold, concentrated solution of the mordant, and then washed with water to cause the hydrolysis of the metallic salt.

In cases where only parts of the fabric are to be dyed, as, for example, in *calico-printing*, a solution of a suitable mordant may be mixed with the dye, and with some thickening substance, such as starch, dextrin, gum, &c., and printed on the fabric in the required manner, the thickening being used to prevent the mordant from spreading to other parts; the material is then submitted to a steaming process, when the metallic hydroxide which is produced within the fibre combines with and fixes the dye.

All these processes are identical in principle, the object being to deposit some insoluble metallic compound within the fibre; when the mordanted material is afterwards treated with a solution of a suitable dye, the latter unites with the metallic hydroxide, forming a coloured compound, which is fixed in the fibre. The coloured substances produced by the combination of a dye with a metallic hydroxide are termed *lakes*, and those dyes which form lakes belong to the class of *acid* dyes.

Tannin (p. 494) is an example of a different class of mordants—namely, of those which are employed with *basic dyes*, such as malachite green (p. 644) and rosaniline (p. 648); its use depends on the fact that, being an acid, it combines with dyes of a basic character, forming with them insoluble

coloured salts (tannates), which are thus fixed in the fibre. The fabric is mordanted by being passed first through a solution of tannin, and then through a weak solution of tartar emetic, or stannic chloride, which converts the tannin into an insoluble antimony or tin tannate, and thus fixes it in the fibre.

All colouring matters are converted into colourless compounds on reduction; in the case of some dyes, the reduction product cannot be directly reconverted into the dye by oxidation, as, for example, in that of aminoazobenzene, which, when treated with *powerful* reducing agents, yields aniline and p-phenylenediamine,

$$C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH_2 + 4H = C_6H_5\cdot NH_2 + NH_2\cdot C_6H_4\cdot NH_2.$$

When, however, the colourless reduction product differs from the dye in such a way that it may be readily reconverted into the dye by oxidising agents, the reduction product is called a *leuco-compound*.

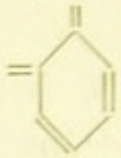
Aminoazobenzene, for example, the hydrochloride or oxalate of which is known as *aniline yellow*, on treatment with *mild* reducing agents, such as zinc-dust and acetic acid, yields aminohydrazobenzene, which is only slightly coloured,

$$C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH_2 + 2H = C_6H_5\cdot NH\cdot NH\cdot C_6H_4\cdot NH_2.$$

The last-named substance is readily oxidised to aminoazobenzene when its alcoholic solution is shaken with precipitated mercuric oxide, and is, therefore, *leuco*-aminoazobenzene.

When an insoluble dye yields a soluble leuco-compound, which is very readily reconverted into the dye on oxidation, it may be applied to fabrics in a special manner, as, for example, in the case of indigo-blue. Indigo-blue, $C_{16}H_{10}N_2O_2$ (p. 663), is insoluble in water, but on reduction it is converted into a readily soluble leuco-compound, $C_{16}H_{12}N_2O_2$, known as *indigo-white*. In dyeing with indigo, a solution of indigo-white is prepared by reducing indigo, suspended in water, with grape-sugar and sodium hydroxide, or with ferrous sulphate

and sodium hydroxide, and the fabric is then passed through this solution, whereupon the indigo-white diffuses into the fibres through their walls; on subsequent exposure to the air the indigo-white is reconverted into indigo-blue by oxidation, and the insoluble dye is thus fixed in the fabric.

The molecules of nearly all intensely coloured substances contain at least one group of atoms, called a *chromophore*, to the presence of which the colour may be attributed. Among these chromophores, the nitro- and the azo-groups, and the p- and o-quinone rings,  and  , are the more important. Thus, in the case of azobenzene the chromophore is the group, $-N{:}N-$; a change in this part of the molecule, such as that which occurs when azobenzene is converted into hydrazobenzene, destroys the colour, whereas a change in other parts of the molecule, such as the substitution of various groups for hydrogen atoms of the nucleus, merely modifies the colour.

The substance which contains the chromophore is called the *chromogen*, and the salt-forming group which converts the inert chromogen into a dye is called the *auxochrome*. The amino-, hydroxyl-, and sulphonic-groups are the more important auxochromes.

Some of the more important dyes may now be described. As, however, it is impossible to discuss the constitutions of all these compounds, it must be understood that the formulæ employed in the following pages are those commonly accepted, and that most of them have been satisfactorily established.

Derivatives of Triphenylmethane.

Triphenylmethane, $C_6H_5{\cdot}CH(C_6H_5)_2$ (p. 380), or, more strictly speaking, triphenyl carbinol, $C_6H_5{\cdot}C(C_6H_5)_2{\cdot}OH$, is the parent substance of a number of dyes, which are of very

great technical importance on account of their brilliancy; as examples, *malachite green*, *pararosaniline*, and *rosaniline* may be mentioned, and in the case of each of these compounds the **leuco-base**, the **colour-base**, and the **dye** itself may be described.

The *leuco-base* (p. 644) is an amino-derivative of triphenylmethane; in the case of malachite green, for example, the leuco-base is tetramethyldiaminotriphenylmethane,

$$C_6H_5\cdot CH\begin{<}C_6H_4\cdot NMe_2\\C_6H_4\cdot NMe_2\end{.}$$

The *colour-base* is an amino-derivative of triphenyl carbinol, and is produced from the leuco-base by oxidation, just as triphenyl carbinol results from the oxidation of triphenylmethane (p. 380); the colour-base of malachite green, for example, is tetramethyldiaminotriphenyl carbinol,

$$C_6H_5\cdot C(OH)\begin{<}C_6H_4\cdot NMe_2\\C_6H_4\cdot NMe_2\end{.}$$

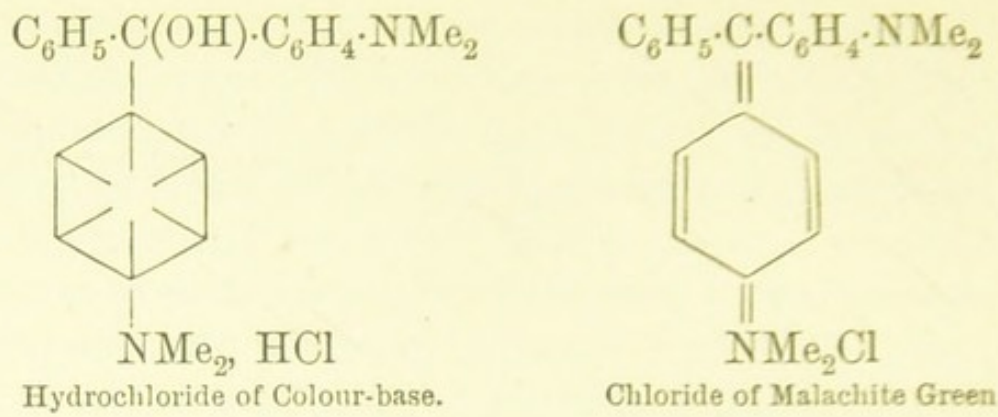
Both the leuco-base and the colour-base are usually colourless, and the latter also yields colourless, or only slightly coloured, salts, on treatment with *cold* acids; when *warmed* with acids, however, the colour-base gives highly coloured salts, which constitute the dye, water being eliminated,

$$\underset{\text{Malachite Green Base.}}{C_{23}H_{26}N_2O} + HCl = \underset{\text{Chloride of Malachite Green.}}{C_{23}H_{25}N_2Cl} + H_2O.$$

This loss of water is probably due to combination taking place between the hydroxyl-group and the hydrogen atom of the acid employed, and the conversion of the colourless into the coloured salt may be expressed as follows:—

$$C_6H_5\cdot C(OH)\begin{<}C_6H_4\cdot NMe_2\\C_6H_4\cdot NMe_2,HCl\end{.} = C_6H_5\cdot C\begin{<}C_6H_4\cdot NMe_2\\C_6H_4{=}NMe_2Cl\end{.} + H_2O.$$

This change—namely, the elimination of two univalent atoms or groups—resembles the conversion of colourless quinol into highly coloured quinone (p. 464), and also that of **p**-aminophenol into quinonechlorimide (p. 467), and may be represented in a similar manner,



Exactly similar changes may be assumed to take place in the formation of the pararosaniline and rosaniline dyes, and, in fact, a great many colouring matters may be regarded as derivatives of quinones.

Malachite green (of commerce) is a double salt, formed by the combination of the chloride of tetramethyldiaminotriphenyl carbinol with zinc chloride, and the first step in its manufacture is the preparation of *leuco-malachite green* or *tetramethyl*-**p**-*diaminotriphenylmethane*, $C_6H_5 \cdot CH(C_6H_4 \cdot NMe_2)_2$.

Leuco-malachite green is manufactured by heating a mixture of benzaldehyde (1 mol.) and dimethylaniline (2 mols.) with zinc chloride,

$$C_6H_5 \cdot CHO + \begin{matrix} C_6H_5 \cdot NMe_2 \\ C_6H_5 \cdot NMe_2 \end{matrix} = C_6H_5 \cdot CH \begin{matrix} C_6H_4 \cdot NMe_2 \\ C_6H_4 \cdot NMe_2 \end{matrix} + H_2O.$$

It is a colourless, crystalline substance, which, when treated with oxidising agents, such as manganese dioxide and sulphuric acid, or lead dioxide and hydrochloric acid, yields *tetramethyldiaminotriphenyl carbinol*,

$$C_6H_5 \cdot CH(C_6H_4 \cdot NMe_2)_2 + O = C_6H_5 \cdot C(OH)(C_6H_4 \cdot NMe_2)_2.$$

This oxidation product is a colourless base, which with *cold* acids yields colourless solutions of its salts; when, however, such solutions are warmed, the colourless salts lose one molecule of water, intensely green solutions being obtained. The formation of the chloride, for example, is expressed by the equation just given (p. 643); and the double salt which the chloride forms with zinc chloride (or the oxalate of the base), constitutes the malachite green (Victoria green, benzaldehyde green) of commerce.

Preparation of Malachite Green.—Dimethylaniline (10 parts) and benzaldehyde (4 parts) are heated with zinc chloride (4 parts) in a porcelain basin or enamelled iron vessel during two days at 100°, the mixture being constantly stirred. The product is submitted to distillation in steam, to get rid of the unchanged dimethylaniline, and the insoluble leuco-compound is then separated. This product is washed with water, dissolved in as little hydrochloric acid as possible, and the calculated quantity of freshly precipitated lead dioxide is added to the diluted solution. The filtered dark-green solution is then mixed with sodium sulphate to precipitate any lead, again filtered, and the colouring matter precipitated in the form of its zinc double salt, $3C_{23}H_{25}N_2Cl,2ZnCl_2,2H_2O$, by the addition of zinc chloride and common salt; this salt is finally purified by recrystallisation.

Malachite green, and other salts of the base, such as the oxalate, $2C_{23}H_{24}N_2,3C_2H_2O_4$, form deep-green crystals, and are readily soluble in water; they are decomposed by alkalis, with separation of the *colour-base*, tetramethyldiaminotriphenyl carbinol.

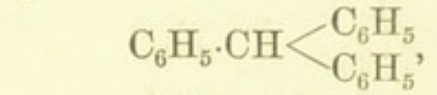
Malachite green dyes silk and wool directly an intense dark-bluish green, but cotton must first be mordanted with tannin and tartar emetic (p. 641), and then dyed in a bath gradually raised to 60°.

Many other dyes, closely allied to malachite green, are prepared by condensing benzaldehyde with tertiary alkylanilines (p. 407). *Brilliant green*, for example, is finally obtained when diethylaniline is employed, instead of dimethylaniline, in the above-described process, whereas *acid green* is obtained from benzaldehyde and ethylbenzylaniline,* $C_6H_5{\cdot}N(C_2H_5){\cdot}C_7H_7$, in a similar manner. The salts of these two colouring matters are very sparingly soluble in water, and, therefore, are of little use as dyes; for this reason the bases are treated with anhydrosulphuric acid, and thus converted into mixtures of readily soluble sulphonic acids, the sodium salts of which constitute the commercial dyes. Silk and wool are dyed in a bath acidified with sulphuric acid (hence the name acid green), and very bright greens are obtained, but these dyes are not suitable for cotton.

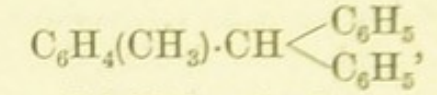
Pararosaniline and *rosaniline* are exceedingly important

* Produced by treating aniline with benzylchloride and ethyl bromide successively.

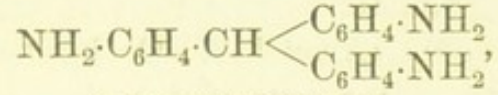
dyes, which, like malachite green, are derived from triphenylmethane. Whereas, however, malachite green is a derivative of *diamino*-triphenylmethane, the rosanilines are all *triamino*-triphenylmethane derivatives, as will be seen from the following formulæ :—



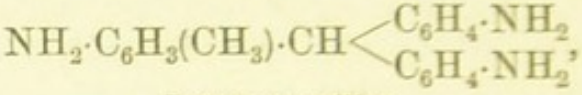
Triphenylmethane.



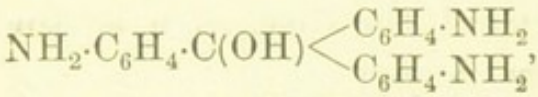
Tolyldiphenylmethane (Methyltriphenylmethane).



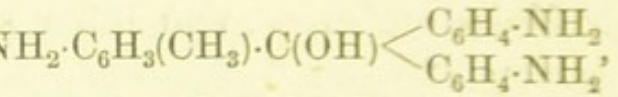
Leuco-pararosaniline. Triaminotriphenylmethane.



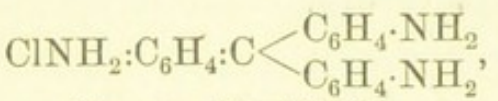
Leuco-rosaniline. Triaminotolyldiphenylmethane.



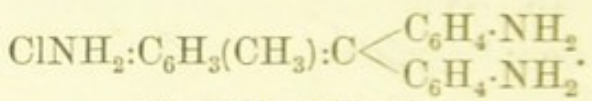
Pararosaniline Base. Triaminotriphenyl Carbinol.



Rosaniline Base. Triaminotolyldiphenyl Carbinol.



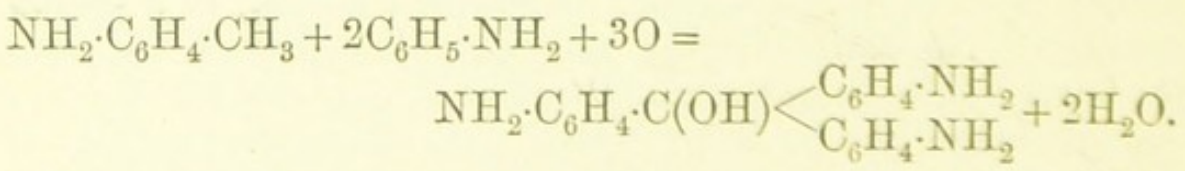
Pararosaniline Chloride.



Rosaniline Chloride.

In all these compounds the amino-groups are in the *para*-position to the methane carbon atom.

Pararosaniline (of commerce) is the chloride of triaminotriphenyl carbinol, a base which is most conveniently prepared by oxidising a mixture of **p**-toluidine (1 mol.) and aniline (2 mols.) with arsenic acid, or nitrobenzene (compare rosaniline, p. 648),



Probably the **p**-toluidine is first oxidised to **p**-aminobenzaldehyde, $NH_2 \cdot C_6H_4 \cdot CHO$, which then condenses with the aniline (as in the case of the formation of leuco-malachite green) to form leuco-pararosaniline; this compound is then converted into the pararosaniline base on further oxidation.

The salts of pararosaniline have a deep-magenta colour, and are soluble in warm water; they dye silk, wool, and cotton

under the same conditions as described in the case of malachite green; pararosaniline, however, is not so largely used as rosaniline.

Triaminotriphenyl carbinol, the pararosaniline colour-base, is obtained, as a colourless precipitate, when alkalis are added to a solution of the chloride, or of some other salt; it crystallises from alcohol in colourless needles, and when treated with acids, gives the intensely coloured pararosaniline salts.

Leuco-pararosaniline or triaminotriphenylmethane, $NH_2 \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NH_2)_2$, is prepared by reducing triaminotriphenyl carbinol with zinc-dust and hydrochloric acid,

$$NH_2 \cdot C_6H_4 \cdot C(OH)(C_6H_4 \cdot NH_2)_2 + 2H = NH_2 \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NH_2)_2 + H_2O.$$

It crystallises in colourless plates, melts at 148°, and forms salts, such as the hydrochloride, $C_{19}H_{19}N_3,3HCl$, with three equivalents of an acid. When the hydrochloride is treated with nitrous acid it is converted into a tri-diazonium compound, $CH(C_6H_4 \cdot N_2Cl)_3$, which, when boiled with water, yields *aurin*, $C_{19}H_{14}O_3$ (p. 653), and when heated with alcohol, is converted into triphenylmethane, just as phenyldiazonium chloride, under similar conditions, yields phenol or benzene.

Constitution of Pararosaniline.—Since triphenylmethane can be obtained from pararosaniline in this way, the latter is a derivative of this hydrocarbon (an important fact, first established by E. and O. Fischer in 1878). Moreover, pararosaniline may be prepared from triphenylmethane, as follows:—Triphenylmethane, with the aid of fuming nitric acid, is converted into trinitrotriphenylmethane, $NO_2 \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NO_2)_2$, a compound in which all the nitro-groups are in the **p**-position to the methane carbon atom; this nitro-compound, on reduction, yields leuco-pararosaniline, which, on oxidation, is readily converted into the colour-base, triaminotriphenyl carbinol. When this base is treated with acids it yields salts of pararosaniline, with elimination of water,

$$HCl,\overset{(4)}{N}H_2\cdot C_6H_4\cdot\overset{(1)}{C}(OH)\begin{matrix}<\\ \end{matrix}\begin{matrix}C_6H_4\cdot NH_2^{(4)}\\ C_6H_4\cdot NH_2^{(4)}\end{matrix}=$$

Hydrochloride of Pararosaniline Base.

$$ClNH_2{:}C_6H_4{:}C\begin{matrix}<\\ \end{matrix}\begin{matrix}C_6H_4\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix}+H_2O.$$

Chloride of Pararosaniline.

Rosaniline (of commerce), fuchsine, or magenta, is the chloride (or acetate) of triaminotolyldiphenyl carbinol, a base which is produced by the oxidation of equal molecular proportions of aniline, o-toluidine, and p-toluidine (with nitrobenzene, arsenic acid, mercuric nitrate, &c.), the reaction being similar in all respects to the formation of the pararosaniline base from aniline (2 mols.) and p-toluidine (1 mol.),

o-Toluidine.

$$NH_2\cdot C_6H_4\cdot CH_3+\begin{matrix}C_6H_4Me\cdot NH_2\\ C_6H_5\cdot NH_2\end{matrix}+3O=$$

p-Toluidine. Aniline.

$$NH_2\cdot C_6H_4\cdot C(OH)\begin{matrix}<\\ \end{matrix}\begin{matrix}C_6H_3Me\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix}+2H_2O.$$

Rosaniline Base.

Rosaniline is usually manufactured at the present time by what is termed the '*nitrobenzene process*,' or the '*arsenic acid process*.'

To the requisite mixture of aniline, o-toluidine, and p-toluidine* (38 parts), hydrochloric acid (20 parts) and nitrobenzene (20 parts) are added, and the whole is gradually heated to 190°, small quantities of iron-filings (3–5 parts) being added from time to time (see below). At the end of five hours the reaction is complete, and steam is then led through the mass to drive off any unchanged aniline, toluidine, or nitrobenzene, after which the residue is powdered and extracted with boiling water, under pressure; lastly, the extract is mixed with salt, and the crude rosaniline chloride, which separates, is purified by recrystallisation.

In this reaction the nitrobenzene acts only indirectly as the oxidising agent; the ferrous chloride, produced by the action of the hydrochloric acid on the iron, is oxidised by the nitrobenzene to ferric chloride, which in its turn oxidises the mixture of aniline

* Crude 'aniline-oil,' a mixture of these three bases, has sometimes been used instead of the pure compounds.

and toluidines to rosaniline, and is itself again reduced to ferrous chloride; the action, therefore, is continuous, and only a small quantity of iron is necessary.

The salts of the rosaniline base with one equivalent of an acid, as, for example, the chloride, $C_{20}H_{20}N_3Cl$, form magnificent crystals, which show an intense green metallic lustre; they dissolve in warm water, forming deep-red solutions, and dye silk, wool, and cotton a brilliant magenta colour, the conditions of dyeing being the same as in the case of malachite green.

The addition of alkalis to a saturated solution of the chloride of rosaniline destroys the colour, and causes the precipitation of the colour-base, *triaminotolyldiphenyl carbinol*, $C_{20}H_{20}N_3 \cdot OH$ (p. 646), which crystallises in colourless needles, and is at once reconverted into the intensely coloured salts when it is warmed with acids. When reduced with tin and hydrochloric acid, the rosaniline salts yield *leuco-rosaniline*, $C_{20}H_{21}N_3$ (p. 646), a colourless, crystalline substance, which, when treated with oxidising agents, is again converted into rosaniline.

Leuco-rosaniline has been converted into diphenyl-m-tolylmethane, $CH_3 \cdot C_6H_4 \cdot CH(C_6H_5)_2$, by methods similar to those used in the transformation of pararosaniline into triphenylmethane (p. 647); leuco-rosaniline, therefore, has the constitution,

$$\begin{matrix} {}^{(3)}CH_3 \\ {}^{(4)}NH_2 \end{matrix} > C_6H_3 \cdot {}^{(1)}CH < \begin{matrix} C_6H_4 \cdot NH_{2\,(4)} \\ C_6H_4 \cdot NH_{2\,(4)} \end{matrix},$$

and the rosaniline salts are derived from this base, just as those of pararosaniline and of malachite green are derived from leuco-pararosaniline and leuco-malachite green respectively.

Derivatives of Pararosaniline and Rosaniline.

The hydrogen atoms of the three amino-groups in pararosaniline and rosaniline may be displaced by alkyl-groups, by heating the dye with alkyl halogen compounds; under these

conditions tri-alkyl substitution products are obtained as primary products, one of the hydrogen atoms of each of the amino-groups being displaced. When, for example, rosaniline is heated with methyl chloride, it yields, in the first place, the chloride of *trimethyl*-rosaniline,

$$NHMe\cdot C_6H_4\cdot C\begin{cases} C_6H_4\cdot NHMe \\ C_6H_3(CH_3):NHMeCl \end{cases}$$

This compound is a reddish-violet dye; the corresponding *triethyl*-rosaniline chloride is the principal component of *Hofmann's violet*, *dahlia*, *primula*, &c., dyes, which have now been superseded by more brilliant violets.

By the continued action of methyl iodide on rosaniline, the iodide of *tetramethyl*-rosaniline is obtained. This substance is a magnificent bluish-violet dye, but is now little used; it is a tertiary base, and forms an additive compound of the composition, $C_{20}H_{16}N_3Me_4I,MeI,H_2O$, which, curiously enough, is green, and was formerly used under the name, '*iodine green*.'

The substitution of methyl-groups for hydrogen in the molecule of rosaniline, which is a brilliant red dye, brings about a change in colour—first to reddish-violet, and then to bluish-violet, as the number of alkyl-groups increases. This change is more marked when ethyl-groups are introduced, and still more so when phenyl- or benzyl-groups are substituted for hydrogen; in the latter case, pure blue dyes are produced (see below). In fact, by varying the number and character of the substituents, almost any shade from red to blue can be obtained.

Lastly, it is interesting to note that when a violet dye, like tetramethylrosaniline, combines with an alkyl halogen compound, it is converted into a bright-green dye, which, however, is somewhat unstable, and on being warmed readily decomposes into the alkyl halogen compound and the original violet dye. A piece of paper, for example, which has been dyed with 'iodine green' becomes violet

when warmed (over a Bunsen burner), and methyl iodide is evolved.

The alkyl-derivatives of pararosaniline and of rosaniline are no longer prepared by heating the dyes with alkyl halogen compounds, but are obtained by more economical methods. The dyes of this class now actually manufactured, examples of which are described below, are, with few exceptions, derivatives of pararosaniline.

Methyl violet appears to consist principally of the chloride of *pentamethyl*-pararosaniline; it is usually manufactured by heating a mixture of dimethylaniline, potassium chlorate, cupric chloride (or sulphate), and sodium chloride, at 50–60°, during about eight hours;* the product is heated with hot water, the copper is removed with hydrogen sulphide, and the dye is precipitated from the concentrated solution by the addition of salt.

Methyl violet comes into the market in the form of hard lumps, which have a green, metallic lustre; it is readily soluble in alcohol and hot water, forming beautiful violet solutions, which dye silk, wool, and cotton under the same conditions as are employed in the case of malachite green (p. 645).

Crystal violet is the chloride of *hexamethylpararosaniline*, and is manufactured by what is called the 'phosgene process': —Carbonyl chloride (phosgene) reacts readily with dimethylaniline to form tetramethyldiaminobenzophenone (Michler's ketone), and the hydrochloric acid, which is simultaneously produced, combines with the excess of dimethylaniline. Tetramethyldiaminobenzophenone condenses with dimethylaniline, in the presence of phosphorus oxychloride, giving the colour-base of crystal violet,

$$\overset{(4)}{N}Me_2\cdot C_6H_4\cdot \overset{(1)}{C}O\cdot C_6H_4\cdot \overset{(4)}{N}Me_2 + C_6H_5\cdot NMe_2 = HO\cdot C(C_6H_4\cdot NMe_2)_3,$$

Tetramethyldiaminobenzophenone. Colour-base of Crystal Violet.

* The changes which take place during this remarkable process are doubtless very complex, and cannot be discussed here.

which is then transformed into hexamethylpararosaniline chloride.

This dye is manufactured in large quantities; its applications and properties are similar to those of methyl violet.

When rosaniline is treated with aniline at 100°, in the presence of some weak acid, such as acetic, benzoic, or stearic acid, phenyl-groups displace the hydrogen atoms of the amino-groups just as in the formation of diphenylamine from aniline and aniline hydrochloride (p. 410). Here, as in the case of the alkyl-derivatives of rosaniline, the colour of the product depends on how many phenyl-groups have been introduced into the molecule; the mono- and di-phenyl-derivatives are reddish-violet and bluish-violet respectively, whereas triphenylrosaniline is a pure blue dye, known as *aniline blue*.

Aniline blue, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}C\begin{matrix}C_6H_4{\cdot}NH{\cdot}C_6H_5\\ C_6H_3(CH_3){:}NH(C_6H_5)Cl\end{matrix}$ (triphenylrosaniline chloride), is prepared by heating rosaniline with benzoic acid and an excess of aniline at 180° during about four hours, and until the mass dissolves in dilute acids, forming a pure blue solution. The product, which contains the aniline blue in the form of the colour-base, is then treated with hydrochloric acid, whereupon the chloride crystallises out in a slightly impure condition.

Aniline blue is very sparingly soluble in water, and in dyeing with it, the operation has to be conducted in alcoholic solution. In order to get over this difficulty, the insoluble dye is treated with anhydrosulphuric acid, and thus converted into a mixture of sulphonic acids, the sodium salts of which are readily soluble, and come on the market under the names, '*alkali blue*,' '*water blue*,' &c.

In dyeing silk and wool with these colouring matters, the material is first dipped into alkaline solutions of the salts, when a light-blue tint is obtained, and it is not until it has been immersed in dilute acid (to liberate the sulphonic acid) that the true blue colour is developed. Cotton is

dyed in the same way, but must first be mordanted with tannin.

The tri-hydroxy-derivatives of triphenyl carbinol and of tolyl-diphenyl carbinol, which correspond with the tri-amino-compounds described above, are respectively represented by the following formulæ :—

$HO\cdot C_6H_4\cdot C(OH)<^{C_6H_4\cdot OH}_{C_6H_4\cdot OH}$, $HO\cdot C_6H_3(CH_3)\cdot C(OH)<^{C_6H_4\cdot OH}_{C_6H_4\cdot OH}$.

Trihydroxytriphenyl Carbinol. Trihydroxytolyldiphenyl Carbinol.

These compounds may be obtained from the corresponding tri-amino-derivatives (the colour-bases of pararosaniline and of rosaniline) with the aid of the diazo-reaction ; in other words, the amino-compounds are treated with nitrous acid, and the solutions of the diazonium-salts are then heated. The hydroxy-compounds thus produced, however, are unstable, and readily lose one molecule of water, yielding coloured compounds—*aurin* and *rosolic acid*—which correspond with the pararosaniline and rosaniline dyes in constitution,

$HO\cdot C_6H_4\cdot C<^{C_6H_4\cdot OH}_{C_6H_4=O}$, $HO\cdot C_6H_3(CH_3)\cdot C<^{C_6H_4\cdot OH}_{C_6H_4=O}$.

Aurin. Rosolic Acid.

These substances are of little use as dyes, owing to the difficulty of fixing them.

The Phthaleïns.

The phthaleïns, like malachite green and the rosanilines, are derivatives of triphenylmethane, inasmuch as they are substitution products of *phthalophenone*, a lactone (p. 243) formed from *triphenylcarbinol*-o-*carboxylic acid*, by loss of one molecule of water,

$$CO<^{-C_6H_4-}_{OH\ HO}>C(C_6H_5)_2 = CO<^{C_6H_4}_{-O-}>C(C_6H_5)_2 + H_2O.$$

Phthalophenone is prepared by treating a mixture of phthalyl chloride (p. 478) and benzene with aluminium chloride,

$$CO<^{C_6H_4}_{-O-}>CCl_2 + 2C_6H_6 = CO<^{C_6H_4}_{-O-}>C(C_6H_5)_2 + 2HCl.$$

It crystallises in colourless needles, melts at 115°, and

dissolves in alkalis, yielding salts of triphenylcarbinol-o-carboxylic acid. This acid, on reduction with zinc-dust in alkaline solution, is converted into *triphenylmethane-o-carboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}CH(C_6H_5)_2$, from which, by distillation with lime, *triphenylmethane* is obtained—a proof that the phthaleïns are derivatives of this compound.

Phenolphthaleïn, $C_{20}H_{14}O_4$ (dihydroxyphthalophenone), is prepared by heating phthalic anhydride (3 parts) with phenol (4 parts) and zinc chloride (5 parts), at 115–120°, during eight hours,

$$CO\langle{}^{C_6H_4}_{\ \ O\ \ }\rangle CO + 2C_6H_5{\cdot}OH = CO\langle{}^{C_6H_4}_{\ \ O\ \ }\rangle C(C_6H_4{\cdot}OH)_2 + H_2O;$$

the product is washed with water, dissolved in a solution of sodium hydroxide, and the phenolphthaleïn precipitated from the filtered solution with acetic acid.

Phenolphthaleïn separates from alcohol in pale-yellow crystals, and melts at 250°; it dissolves in alkalis, giving solutions which have a deep-pink colour, owing to the formation of coloured salts, but on the addition of acids the colour vanishes, hence the use of phenolphthaleïn as an indicator in alkalimetry. It is, however, of no value as a dye.

The conversion of feebly coloured phenolphthaleïn into an intensely coloured salt is probably due to its transformation into a derivative of quinone, just as in the case of the conversion of the colourless salt of tetramethyldiaminotriphenyl carbinol into the green dye (p. 644), and may be expressed as follows :—

$$\underbrace{CO\langle{}^{C_6H_4}_{\ \ O\ \ }\rangle C\langle{}^{C_6H_4{\cdot}OH}_{C_6H_4{\cdot}OH}}_{\text{Phenolphthaleïn.}} \longrightarrow \underbrace{COONa{\cdot}C_6H_4{\cdot}C(OH)\langle{}^{C_6H_4{\cdot}OH}_{C_6H_4{\cdot}OH}}_{\text{Intermediate Product.}} \longrightarrow$$

$$\underbrace{COONa{\cdot}C_6H_4{\cdot}C\langle{}^{C_6H_4{\cdot}OH}_{C_6H_4{=}O}}_{\text{Coloured Salt.}} + H_2O.$$

Fluoresceïn, $C_{20}H_{12}O_5$, is a very important dye-stuff, produced by heating phthalic anhydride with resorcinol,

$$CO\langle{}^{C_6H_4}_{\ \ O\ \ }\rangle CO + 2C_6H_4\langle{}^{OH}_{OH} = \underbrace{CO\langle{}^{C_6H_4}_{\ \ O\ \ }\rangle C\langle{}^{C_6H_3(OH)}_{C_6H_3(OH)}\rangle O}_{\text{Fluoresceïn.}} + 2H_2O.$$

In this change, two hydrogen atoms of the two benzene

nuclei unite with the oxygen atom of one of the >CO groups of the phthalic anhydride (as in the formation of phenolphthaleïn), and a molecule of water is also eliminated from the hydroxyl-groups of the two resorcinol molecules.

Phthalic anhydride (1 mol.) and resorcinol (2 mols.) are heated together at 200° until the mass becomes quite solid; the dark product is then washed with hot water, dissolved in alkali, the filtered alkaline solution acidified with sulphuric acid, and the fluoresceïn extracted with ether.

Fluoresceïn separates from alcohol in dark-red crystals; it is almost insoluble in water, but dissolves readily in alkalis, forming dark, reddish-brown solutions, which, when diluted, show a most magnificent yellowish-green fluorescence (hence the name, fluoresceïn). In the form of its sodium salt, $C_{20}H_{10}O_5Na_2$, fluoresceïn comes into the market as the dye, '*uranin*.' Wool and silk are dyed yellow, and at the same time show a beautiful fluorescence, but the colours are faint, and soon fade; hence fluoresceïn has a very limited application alone, and is generally mixed with other dyes in order to impart fluorescence. Some of the derivatives of fluoresceïn are very important dyes.

Eosin, $CO\begin{<}{C_6H_4}{-O-}\end{>}C\begin{<}{C_6HBr_2(OH)}{C_6HBr_2(OH)}\end{>}O$ (tetrabromofluoresceïn), is formed when fluoresceïn is treated with bromine, four atoms of hydrogen in the resorcinol nuclei being displaced.

Fluoresceïn is treated with the theoretical quantity of bromine in acetic acid solution, and the eosin which separates is collected, washed with a little acetic acid, and dissolved in dilute potash. The filtered solution is then acidified, and the eosin extracted with ether.

Eosin separates from alcohol in red crystals, and is almost insoluble in water, but dissolves readily in alkalis, forming deep-red solutions, which, on dilution, exhibit a beautiful green fluorescence, but not nearly to the same extent as solutions of fluoresceïn.

Eosin comes into the market in the form of its potassium salt, $C_{20}H_6Br_4O_5K_2$ (a brownish powder), and is much used for dyeing silk, wool, cotton, and especially paper, which fixes the dye without the aid of a mordant. Silk and wool are dyed with eosin directly, in a bath acidified with a little acetic acid; but cotton must first be mordanted with tin, lead, or aluminium salts. The shades produced are a beautiful pink, and the materials also show a very beautiful fluorescence.

Tetriodofluoresceïn, $C_{20}H_8I_4O_5$, is also a valuable dye. Its sodium salt, $C_{20}H_6I_4O_5Na_2$, comes into the market under the name, '*erythrosin*.'

Many other phthaleïns have been prepared by condensing phthalic acid and its derivatives with other phenols, and then treating the products with bromine or iodine.

Azo-Dyes.

The azo-dyes contain the chromophore, –N:N–, to each of the nitrogen atoms of which a benzene or naphthalene nucleus is directly united. Azobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_5$, the simplest of all azo-compounds, is not a dye, although it is intensely coloured (compare p. 637), and this is true also of other *neutral* azo-compounds; if, however, one or more hydrogen atoms in such compounds are displaced by amino-, hydroxyl-, or sulphonic-groups, the products, as, for example, aminoazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$, hydroxyazobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$, azobenzenesulphonic acid, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H$, are yellow or brown dyes.

Azo-dyes are usually prepared by one of two general methods—namely, by treating a *diazonium*-salt with an *amino-compound*,*

* In cases where a diazoamino-compound is first produced (p. 420), an excess of the amino-compound is employed, and the mixture is warmed until the intramolecular change into the aminoazo-compound is complete (p. 420).

$$C_6H_5\cdot N_2Cl + C_6H_5\cdot NMe_2 = C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NMe_2,HCl,$$

Dimethylaminoazobenzene Hydrochloride.

$$CH_3\cdot C_6H_4\cdot N_2Cl + CH_3\cdot C_6H_4\cdot NH_2 = CH_3\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(CH_3)\cdot NH_2,HCl,$$

Aminoazotoluene Hydrochloride.

or by treating a *diazonium*-salt with a *phenol*,

$$C_6H_5\cdot N_2Cl + C_6H_5\cdot OH = C_6H_5\cdot N{:}N\cdot C_6H_4\cdot OH + HCl,$$

Hydroxyazobenzene.

$$C_6H_5\cdot N_2Cl + C_6H_4(OH)_2 = C_6H_5\cdot N{:}N\cdot C_6H_3(OH)_2 + HCl.$$

Dihydroxyazobenzene.

In the first case the products—aminoazo-compounds—are *basic* dyes, whereas in the second case they are *acid* dyes.

Another method of some general application for the direct preparation of azo-dyes containing a sulphonic-group, consists in treating the diazonium-derivative of sulphanilic acid (p. 431) with an amino-compound or with a phenol,

$$SO_3H\cdot C_6H_4\cdot N_2\cdot OH + C_6H_5\cdot NH_2 = SO_3H\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NH_2 + H_2O,$$

Aminoazobenzenesulphonic Acid.

$$SO_3H\cdot C_6H_4\cdot N_2\cdot OH + C_6H_5\cdot OH = SO_3H\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH + H_2O.$$

Hydroxyazobenzenesulphonic Acid.

As, however, the yield is generally a poor one, such dyes are usually prepared by sulphonating the aminoazo- or hydroxyazo-compounds.

In all these reactions the group, $-N_2-$, displaces hydrogen of the benzene nucleus from the **p**-position to one of the amino- or hydroxyl-groups; substances such as **p**-toluidine, in which the **p**-position is occupied, either do not react with diazonium-salts, or do so only with great difficulty.

The technical operations involved in the production of azo-colours, as a rule, are very simple. In 'coupling' diazonium-compounds with phenols, for example, the amino-compound (1 mol.) is diazotised (p. 415), and the solution of the diazonium-salt is then slowly run into the *alkaline* solution of the phenol, or its sulphonic acid, care being taken to keep the solution slightly alkaline, other-

wise interaction ceases, owing to the liberated hydrochloric acid. After a short time the solution is mixed with salt, which causes the colouring matter to separate in flocculent masses; the product is then collected in filter-presses and dried, or sent on the market in the form of a paste.

The 'coupling' of diazonium-compounds with amino-compounds is generally brought about by simply mixing the aqueous solution of the diazonium-salt with that of the salt of the amino-compound (compare footnote, p. 656), and then precipitating the colouring matter by the addition of common salt; in some cases, however, the reaction takes place in alcoholic solution only.

Acid azo-colours (that is, hydroxy- and sulphonic-derivatives) are taken up by animal fibres directly from an acid bath, and are principally employed in dyeing wool; they can be fixed on cotton with the aid of mordants (tin and aluminium salts being generally employed), but, as a rule, only with difficulty; nevertheless some acid dyes, notably those of the *congo-group* (p. 661), dye cotton directly without a mordant.

Basic azo-dyes are readily fixed on cotton which has been mordanted with tannin, and are very largely used in dyeing calico and other cotton goods.

At the present time a great many azo-colours are manufactured, but only a few of the more typical are mentioned here.

Chrysoïdine, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2$ (diaminoazobenzene), is produced by mixing molecular proportions of phenyldiazonium chloride and **m**-phenylenediamine (p. 407) in aqueous solution. The hydrochloride crystallises in reddish needles, is moderately soluble in water, and dyes silk and wool directly, and cotton mordanted with tannin, an orange-yellow colour.

Bismarck brown, $NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2$ (triaminoazobenzene), is prepared by treating **m**-phenylenediamine hydrochloride with nitrous acid; one half of the base is converted into the diazonium-compound, which then interacts with the other half, producing the dye,

$$NH_2{\cdot}C_6H_4{\cdot}N_2Cl + C_6H_4(NH_2)_2 = NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NH_2)_2,HCl.$$

The hydrochloride is a dark-brown powder, and is largely used in dyeing cotton (mordanted) and leather a dark brown.

Helianthin (dimethylaminoazobenzenesulphonic acid) is very easily prepared by mixing aqueous solutions of diazotised sulphanilic acid and dimethylaniline hydrochloride,

$$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}OH + C_6H_5{\cdot}NMe_2 = SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NMe_2 + H_2O.$$

The sodium salt (*methylorange*) is a brilliant orange-yellow powder, and dissolves freely in hot water, forming a yellow solution, which is coloured red on the addition of acids; hence its use as an indicator. It is seldom employed as a dye, on account of its sensibility to traces of acid.

Resorcin yellow (tropæölin O) is prepared by 'coupling' diazotised sulphanilic acid and resorcinol, and has the constitution, $SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(OH)_2$. Its sodium salt is a moderately brilliant orange-yellow dye, and is not readily acted on by acids; it is chiefly employed, mixed with other dyes of similar constitution, in the production of olive-greens, maroons, &c.

By using various benzene derivatives, and 'coupling' them, as in the above examples, *yellow* and *brown* dyes of almost any desired shade can be obtained; in order, however, to produce a *red* azo-dye, a compound containing at least one naphthalene nucleus must be prepared. This can be readily done by 'coupling' a phenyldiazonium-compound with a naphthylamine, naphthol, naphthalenesulphonic acid, &c., just as described above. The dyes thus obtained give various shades of reddish-brown or scarlet, and are known collectively as 'Ponceaux' or 'Bordeaux.'

When, for example, xylyldiazonium chloride is combined with β-naphtholdisulphonic acid, a scarlet dye (scarlet R) of

the composition, $C_6H_3Me_2{\cdot}N{:}N{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$, is formed; another scarlet dye (Ponceau 3R) is produced by the interaction of pseudocumyldiazonium chloride and β-naphtholdisulphonic acid, and has the composition, $C_6H_2Me_3{\cdot}N{:}N{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$.

Paranitraniline red, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$, is an important azo-dye, which is applied to cotton fabrics in the following manner:—The fabric is steeped in an alkaline solution of β-naphthol, and, when it has been dried, it is treated with a solution of diazotised **p**-nitraniline. A brilliant red dye-stuff is thus produced within the fibres,

$$NO_2{\cdot}C_6H_4{\cdot}N_2Cl + C_{10}H_7{\cdot}OK = \overset{(4)}{N}O_2{\cdot}C_6H_4{\cdot}\overset{(1)}{N}_2{\cdot}C_{10}H_6{\cdot}\overset{(2)}{O}H + KCl.$$

This is an example of the development process, which is often applied in the production of blues and blacks on cotton. The material is impregnated with an aminoazo-compound, which is then diazotised and coupled with an amino-compound, or with a phenol, whereby the dye is produced within the fibres. Obviously, such dye-stuffs contain more than one azo-group; and, in fact, dyes containing as many as four azo-groups find general application.

Rocellin, $SO_3H{\cdot}C_{10}H_6{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH$, a compound produced by coupling β-naphthol with the diazonium-compound of naphthionic acid (p. 509), may be mentioned as an example of an azo-dye containing two naphthalene nuclei. It gives beautiful red shades, very similar to those obtained with the natural dye, cochineal, which rocellin and other allied azo-colours have, in fact, almost superseded.

Within recent years many very valuable colouring matters have been prepared from benzidine, $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$ (p. 425), and its derivatives.

Benzidine may be compared with two molecules of aniline, and when diazotised it yields the salt of a *diphenyltetrazonium hydroxide*, $ClN_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2Cl$. This substance reacts with amino-compounds, phenols, and their sulphonic acids, just as does phenyldiazonium chloride (but with 2 mols.),

producing a variety of most important colouring matters, known as the dyes of the *congo-group*.

Congo red, a dye produced by the combination of diphenyltetrazonium chloride with naphthionic acid, is one of the very valuable compounds of this class. Its sodium salt,

$$SO_3Na\cdot(NH_2)C_{10}H_5\vdots N{:}N\cdot C_6H_4\cdot C_6H_4\cdot N{:}N\vdots C_{10}H_5(NH_2)\cdot SO_3Na,$$

is a scarlet powder, which on the addition of acids turns blue, owing to the liberation of the free sulphonic acid.

The congo-dyes possess the unusual property of giving, with unmordanted cotton, brownish-red shades which are fast to soap. They are much used for dyeing cotton; but they become dull in time, in any atmosphere which contains traces of acid fumes—as, for example, in the air of manufacturing towns—owing to the liberation of the blue sulphonic acids.

The tetrazonium derivatives of tolidine* and of dianisidine,† as well as that of benzidine, may be coupled with numerous amino- and phenolic compounds of the benzene or of the naphthalene series, and several hundreds of such compounds have been placed on the market. The great majority of them are quite stable towards acid fumes, and they form one of the very important groups of dye-stuffs, chiefly on account of their brilliancy of shade and their property of dyeing unmordanted cotton direct from a soap-bath.

Tolidine, and to a greater extent dianisidine, give rise to bluer shades than does benzidine; whilst, as regards the second component, the naphthylamines yield red, and the naphthols yield blue, dye-stuffs. These points are brought out in the following series of dye-stuffs, each of which is of a bluer shade than the preceding one:—

* *Tolidine*, $NH_2\cdot MeC_6H_3\cdot C_6H_3Me\cdot NH_2$, is produced from nitrotoluene by reactions similar to those by which benzidine is produced from nitrobenzene; when its salts are treated with nitrous acid, they yield salts of ditolyltetrazonium hydroxide, just as benzidine gives salts of diphenyltetrazonium hydroxide.

† *Dianisidine*, $NH_2(OMe)\cdot C_6H_3\cdot C_6H_3(OMe)\cdot NH_2$, is prepared from nitroanisole, $NO_2\cdot C_6H_4\cdot OMe$, by a corresponding series of reactions (p. 425).

Name of Dye.	Tetrazotised Base.	Compound, or Compounds, coupled with the Tetrazotised Base.
Congo red (scarlet)	Benzidine	Naphthionic acid. + Naphthionic acid.
Benzopurpurin 4B (blue red)	Tolidine	Naphthionic acid. + Naphthionic acid.
Benzopurpurin 10B (blue red)	Dianisidine	Naphthionic acid. + Naphthionic acid.
Congo corinth B (violet)	Tolidine	Naphthionic acid. + α-Naphtholsulphonic acid.
Azo blue (blue violet)	Tolidine	α-Naphtholsulphonic acid. + α-Naphtholsulphonic acid.
Benzoazurine G (pure blue)	Dianisidine	α-Naphtholsulphonic acid. + α-Naphtholsulphonic acid.

Various Colouring Matters.

Martius' yellow, $C_{10}H_5(NO_2)_2 \cdot OH$ (dinitro-α-naphthol), is obtained by the action of nitric acid on α-naphtholmono- or di-sulphonic acid, the sulphonic group or groups being eliminated during nitration. The commercial dye is the sodium salt, $C_{10}H_5(NO_2)_2 \cdot ONa$; it is readily soluble in water, and dyes silk and wool directly an intense golden yellow.

When α-naphtholtrisulphonic acid is nitrated, two of the sulphonic groups are eliminated, and the resulting substance has the formula, $C_{10}H_4(NO_2)_2(OH) \cdot SO_3H$; it is, in fact, the sulphonic acid of Martius' yellow. This valuable dye-stuff is called **naphthol yellow**, and comes on the market in the form of its potassium salt, $C_{10}H_4(NO_2)_2(OK) \cdot SO_3K$; it is very largely used, as the yellow shades which it gives are faster to light than those of Martius' yellow.

Methylene blue, $C_{16}H_{18}N_3ClS$, was first prepared by Caro, in 1876, by the oxidation of dimethyl-**p**-phenylenediamine (p. 409) with ferric chloride in presence of hydrogen sulphide.

Nitrosodimethylaniline (p. 409) is reduced in strongly acid solution with zinc-dust, or with hydrogen sulphide, and the solution of dimethyl-**p**-phenylenediamine, thus obtained, is treated with ferric chloride in presence of excess of hydrogen sulphide. The

intensely blue solution, thus produced, is mixed with salt and zinc chloride, which precipitate the colouring matter as a zinc double salt, and in this form it comes on the market.

Methylene blue is readily soluble in water, and is a valuable cotton-blue, as it dyes cotton, mordanted with tannin, a beautiful blue, which is very fast to light and soap; it is not much used in dyeing silk or wool.

Indigo, $C_{16}H_{10}N_2O_2$, is a natural dye which has been used from the earliest times. It is contained in the leaves of the indigo-plant (*Indigofera tinctoria*) and in woad (*Isatis tinctoria*) in the form of 'indican,' $C_8H_6ON(C_6H_{11}O_5)$, a colourless, crystalline glucoside of indoxyl (p. 664); when the leaves are macerated with water, this glucoside is hydrolysed into glucose and indoxyl, the latter undergoes atmospheric oxidation, and indigo separates as a blue scum.

Indigo comes on the market in an impure condition in the form of dark-blue lumps, which, especially when rubbed, show a remarkable copper-like lustre. It is insoluble in water and most other solvents, but dissolves readily in hot aniline, from which it crystallises as the solution cools; it sublimes in the form of a purple vapour, and condenses as a dark-blue crystalline powder, which consists of pure 'indigotin' or indigo-blue, the principal and most valuable component of commercial indigo.

Reducing agents convert indigotin into its leuco-compound, *indigo-white*, which, in contact with air, is rapidly reconverted into indigo-blue, a property made use of in dyeing with this substance (p. 641); concentrated sulphuric acid dissolves indigotin, with formation of *indigodisulphonic acid*, $C_{16}H_8N_2O_2(SO_3H)_2$, the sodium salt of which is used in dyeing under the name 'indigo carmine.'

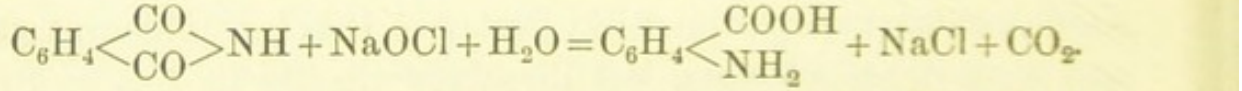
The great value of indigotin (indigo-blue) as a dye naturally made it an attractive subject for investigation, and as the result of laborious research on the part of many chemists, the constitution of indigo-blue was established about 1880, chiefly by the work of Baeyer and his pupils. During his investigations, Baeyer succeeded in preparing indigo-blue artificially by various methods, two of

which have already been described (pp. 457 and 487), but these and several other methods subsequently discovered were found to be unsuitable for the manufacture of the dye at a price which would enable it to compete with the natural product.

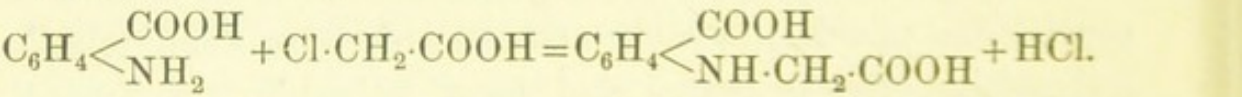
Recently, however, by the application of scientific knowledge and of untiring energy, processes have been worked out in Germany by which it is possible to produce indigo-blue synthetically on the large scale and at a profit.

The most important of these methods is based on a discovery of Heumann, who found that indigo-blue could be obtained by heating phenylglycine (phenylaminoacetic acid) with alkalis in presence of air. The whole process may be summarised as follows:—Naphthalene is oxidised to phthalic anhydride by heating it with sulphuric acid in presence of mercuric sulphate (p. 478). Phthalic anhydride is converted into phthalimide (p. 479) by heating it with ammonia under pressure.

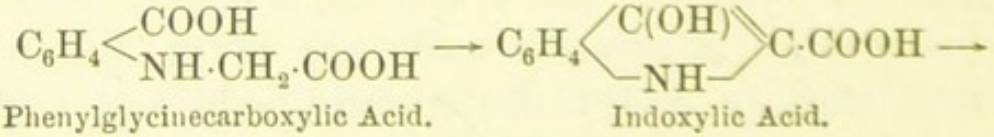
Phthalimide is converted into anthranilic acid (o-aminobenzoic acid, p. 475) by treating it with an alkali hypochlorite, a method discovered by Hoogewerf, which is analogous to that used by Hofmann in converting amides into amines (p. 211),



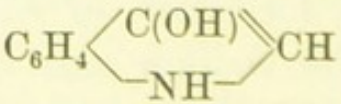
Anthranilic acid is then treated with chloracetic acid to obtain phenylglycinecarboxylic acid,



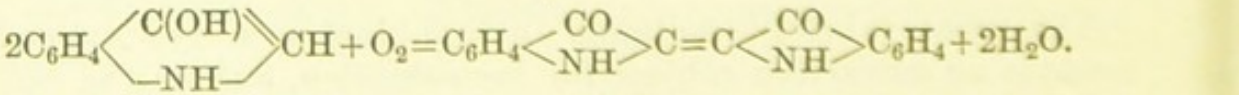
This compound, like phenylglycine itself, is converted into indigo-blue when it is fused with alkalis, the change taking place in several stages which may be indicated as follows:—



Phenylglycinecarboxylic Acid. Indoxylic Acid.



Indoxyl.



Indoxyl. Indigo-blue.

The last reaction—namely, the conversion of indoxyl into indigo-blue—is carried out by dissolving the fused mass in water and passing a stream of air through the alkaline solution.

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[Where more than one reference is given, one being in heavy type, that reference is usually to the systematic description of the substance.]

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