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ORGANIC CHEMISTRY

E. F. MacTaggart

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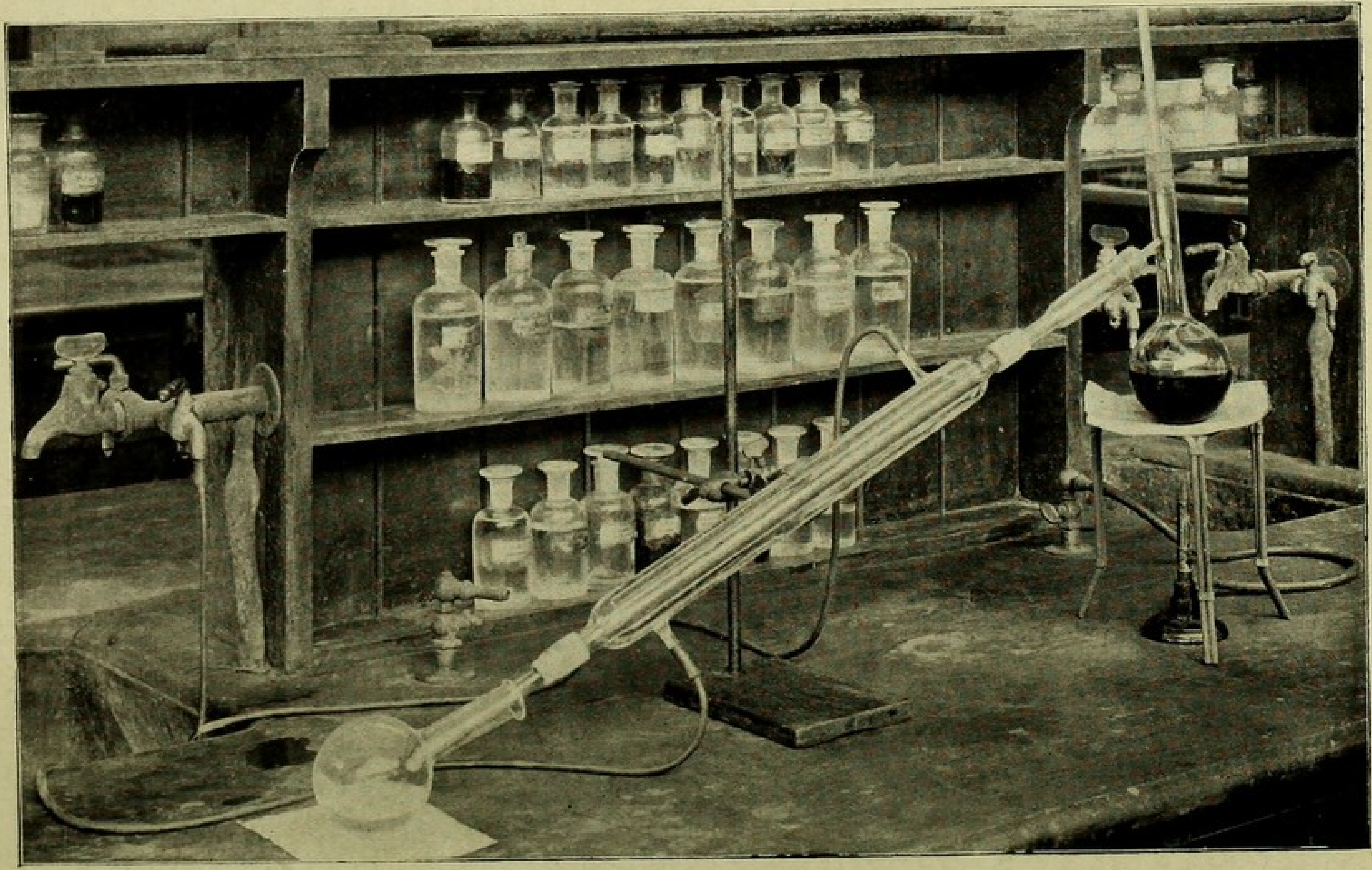
INTRODUCTION TO THE STUDY
OF
ORGANIC CHEMISTRY



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Frontispiece.]

INTRODUCTION TO THE STUDY
OF
ORGANIC CHEMISTRY

A TEXT-BOOK FOR STUDENTS IN THE UNIVERSITIES
AND TECHNICAL SCHOOLS

BY
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PREFACE

This book is intended as a guide to students commencing Organic Chemistry. The subject is treated experimentally from the outset, without preliminaries, the hypotheses and theories which form so essential a scaffolding being introduced as the facts require them. At the same time, every stress is laid on the importance of theory, and every opportunity taken of showing how concrete results have been led up to by theoretical considerations. By this combination, it is believed that it will be more readily understood how the Science has developed, and more readily discerned later how and in what directions the development is likely to continue.

The book proceeds as far as possible from the familiar to the unfamiliar. The first substances to be studied are the typical alcohol and acid akin to the Inorganic bases and acids, and the study of these leads to the theory of radicles. The other simple alcohols and acids are next dealt with, and the ideas of homology and isomerism introduced. The construction of the network of cross-connections typical of Organic Chemistry is now commenced with the aid of the ammonia derivatives and cyanogen compounds, and the necessity of the theory of structure shown. The structural formulæ of the various compounds having been duly established, the simple aldehydes are introduced, and with them the conception of polymerism; then the simple ketones and secondary alcohols, with the theory of position isomerism; and the iso-alcohols and acids, with the theory of branching-chain isomerism. Finally, the simple hydrocarbons are dealt with, and the preceding work codified in the theory of substitution.

The second and third parts of the book, which deal respectively with the more complex aliphatic derivatives, and the benzenoid compounds, are of course more deductive in treatment, but as far as possible the same plan is followed. The theory of stereoisomerism, for example, is considered in connection with the lactic acids, and the constitution of benzene is developed only after a considerable number of benzenoid compounds have been dealt with.

As the book is, to a large extent, parallel in sequence with the historical development of the subject, the names of investigators and dates of their discoveries are introduced wherever practicable. The chapters are short, to facilitate assimilation, and their contents are summarised in charts, which the author has used for many years past, and believes will be found of material assistance both to teachers and students. To ensure accuracy, the proof-sheets have been collated with Beilstein's standard *Handbuch der Organischen Chemie*. The practical details of quantity and manipulation, which will be found in an appendix, have in the majority of cases been tested many times in the classes under the author's charge.

University students will find that their syllabuses have been duly considered, and that the theoretical and practical work demanded by the various examining bodies is dealt with in detail. As a knowledge of qualitative analysis is required at most of the examinations, a second short appendix is devoted to that subject.

GUY'S HOSPITAL, LONDON, S.E.
October, 1897.

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SECTION I

THE ALCOHOLS AND ACIDS: ORGANIC RADICLES

CHAPTER I

PREPARATION OF PURE ALCOHOL

Organic and Inorganic Compounds: Alcohol.—Organic Chemistry deals with the Compounds of Carbon. There is no essential difference between the carbon compounds and those of the other elements, but they are so numerous and intimately related, that it is usual to consider them apart. The name was originally given to compounds such as sugar, which are formed in living organisms, and to their immediate derivatives, such as alcohol, as it was thought that products of this type could not be made in the laboratory, and were radically different from the mineral or Inorganic compounds. It has long been proved that this view was incorrect, and that the Organic compounds can be made from their elements, but the division and name are retained for convenience sake.

One of the longest known and simplest organic compounds is the alcohol to which the properties of fermented liquors are due. Wine and beer have been made from very early times, and it was known to the Arabians, the inventors of the retort, that the properties of such preparations were due to a volatile constituent or "spirit," which can be separated from them by distillation. In the course of time some of the details have been modified, but the substance is still made in practically the same way.

Although much alcohol is prepared by distilling or "burning" wine (brandy=*Branntwein*), the bulk of that used for chemical and industrial purposes is made directly from sugar or starch. When beet or cane molasses for instance is fermented with yeast, a quantity of alcohol is formed, and a similar transformation is brought about in brewing by the action of yeast on wort, the sweet liquid obtained by mashing malt and crushed barley with warm water. Potato spirit is made in the same way from malt and steamed potatoes. As the mechanism of these processes is complex, they will be considered in detail later (p. 176), and this course will commence with the study of the ready formed alcohol, the amount of which varies from 4 or 5 per cent. in beer to 20 per cent. in the heavy wines.

Purification of Alcohol: Distillation.—The first step in a chemical investigation, whether organic or inorganic, is of course to obtain the substance in a pure state, in which its properties are constant and uninfluenced by the presence of foreign matter. Pure water, it will be remembered, is known by the constancy of its boiling and freezing points and density, and by its crystalline form when solidified, the presence of impurities causing departure from this fixity.

The processes used in the purification of organic compounds—washing, crystallisation, sublimation, distillation—are in the main similar to those with which the student is already familiar, but owing to the greater volatility of the carbon derivatives, especially those of comparatively simple nature, distillation is much more frequently used than in dealing with mineral products.

The distilling apparatus in ordinary use is represented in the frontispiece. It is the same in principle as the common retort and receiver, but somewhat more complicated in detail. The liquid is boiled in a flask provided with a side exit for the vapour, so that a thermometer may be placed in the latter, indicating the boiling point of the substance* (Wurtz). The vapour is condensed in a long, wide glass tube, which is cooled by a water-jacket, and slopes downwards towards the receiver (Liebig).

The distillation as thus effected serves a double purpose, for on distilling a complex mixture such as wine or beer, not only do the volatile constituents pass over uncontaminated with solids and colouring matter, but their nature is to some extent indicated by the temperatures at which they distil. Thus water of course is volatile, as well as alcohol, and that the spirit which passes over is accompanied by the inorganic liquid, is evident, not only from the incombustibility of the later portions of the distillate, but also from the steady rise in its boiling point and specific gravity during the whole operation.

Purification of Alcohol: Fractional Distillation.—By simple distillation the alcohol is thus obtained mixed with water, and as will be seen later, with small quantities of other volatile substances. The main problem is to eliminate the water, and is partially solved by utilising the greater volatility of the spirit.

---

* See Appendix I.

As just noted, the first portions of the distillate are much richer in alcohol than those which pass over later; and as the same graduation is repeated in miniature on redistilling the separate portions of the distillate, it is possible by systematic work to effect a fairly complete separation of the two liquids.

This process, which is applicable to all mixtures of unequally volatile liquids having no chemical action on each other, and is consequently much used in organic work, is termed fractional distillation or fractionation. The mixture in the first place is steadily distilled almost to dryness, and the successive fractions collected according to their boiling points in separate receivers.

First fractionation of a mixture of 50 *c.c. of alcohol and* 50 *c.c. of water.*

Fraction. .	x–82° (head)	82–87°	87–92°	92–97°	97–x° (tail)
Volume . .	20 c.c.	16 c.c.	13 c.c.	21 c.c.	29 c.c.

These are then successively redistilled, but owing to their altered composition, no longer pass entirely over at the original temperatures. The alcohol distils the faster from the stronger fractions, and the water from the weaker, so that the result of the second fractionation is to increase the bulk of the end fractions at the expense of the intermediate ones.

Second fractionation.

Fraction. .	x–82° (head)	82–87°	87–92°	92–97°	97–x° (tail)
Volume . .	32 c.c.	5 c.c.	11 c.c.	14 c.c.	36 c.c.

The separation is rapidly increased by each subsequent fractionation. By the end of the third, in fact, the greater part of the alcohol and water have already passed into the head and tail fractions, and the boiling points and specific gravities of these now approximate to those of the pure liquids.

Third fractionation.

Fraction. .	x–82° (head)	82–87°	87–92°	92–97°	97–x° (tail)
Volume . .	44 c.c.	0 c.c.	1 c.c.	11 c.c.	42 c.c.
Sp. gr. . .	0·856	—	—	—	0·991
Sp. gr. of original constituents . .	0·835				1·000

This somewhat tedious process is accelerated by partially condensing the vapours before they enter the condenser, and returning the less volatile portions, and in this manner a fairly complete separation can often be effected in a single distillation. The vapours may be condensed in the upper part of the neck of the flask, made specially long for the purpose, or in a long wide tube or fractionating column, fitted to an ordinary flask (Fig. 1). Various devices have been contrived also to enlarge the condensing surface, and provide for washing the vapour with condensed liquid.

In Hempel's column, for example, the vertical tube is filled with glass beads, and in Glinsky's (Fig. 1), this tube consists of a vertical series of bulbs, separated by blown glass ball valves. The beads and valves retain some of the liquid. In distilleries, similar appliances made of metal are used, the rectifier in Coffey's still, for example, consisting of a copper chamber traversed by perforated plates, which act in the same way as the beads or valves in the laboratory apparatus.

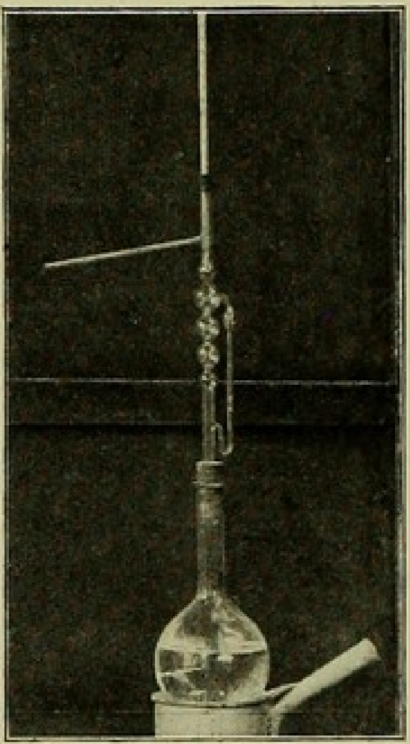
Fig. 1.—Glinsky's Fractionating Column.

Purification of Alcohol: Absolute Alcohol.—The strongest alcohol obtainable by fractional distillation is known as rectified spirit, and has a specific gravity of 0·835 at 15°. Methylated spirit consists of this rectified spirit, mixed with some crude wood spirit and a little paraffin, to render it unfit for drinking, and thus exempt from duty. It can be obtained for chemical purposes without paraffin, and after boiling with a little solid caustic soda to eliminate acetone, etc. (p. 37), and redistilling, may be used instead of the more expensive pure alcohol.

By digesting rectified spirit with an appropriate desiccating agent, such as potassium carbonate or quicklime, and redistilling, a spirit is obtained, which has a still lower gravity, and therefore contains less water (Lully, 13th century); but by repeating this treatment, a liquid is ultimately obtained, whose boiling point and specific gravity are constant, and cannot be further reduced. This product is therefore pure, and is termed absolute alcohol.

Small quantities of absolute alcohol can be prepared in the laboratory by digesting rectified or purified methylated spirit in a corked flask with half its weight of quicklime in lumps. The lime gradually slakes and falls to pieces, and after twenty-four hours, the flask containing the alcohol and slaked lime is placed on a water-bath and adjusted to a condenser, and the alcohol completely distilled off into a dry stoppered bottle. The pulverulent lime remains behind chemically combined with the water.

Absolute alcohol (Lowitz, 1796), is a colourless liquid, which has a pleasant odour and burning taste, and burns with a non-luminous flame. It boils at 78° under ordinary pressure, and at -130° freezes to a white crystalline solid. Its specific gravity is 0·794 at 15°. Pure alcohol is very hygroscopic, and this is why it cannot be completely separated from water by fractional distillation alone.

Criteria of Purity.—A substance is pure and a chemical individual, only when its physical properties are constant, and these physical tests are the ultimate criteria of purity. But it is often convenient to prove the absence of specific impurities by direct chemical tests. Thus a fragment of white anhydrous copper sulphate is converted into the blue hydrated salt when added to alcohol containing water. Similarly the yellow solution of barium oxide in pure dry alcohol is rendered milky, owing to the precipitation of the insoluble hydroxide. Paraffin oil also, in which alcohol is soluble, but water insoluble, is rendered turbid by the presence of the latter in the spirit.

Synopsis.—The Organic substance, alcohol, prepared by the fermentation of sugar, is separated from the dissolved solids by distillation, and from most of the water by fractional distillation, but the last portions of the latter are removable only by chemical means. The alcohol thus prepared is known to be pure and a chemical individual by the constancy of its physical properties.

CHAPTER II

ANALYSIS OF ALCOHOL AND DETERMINATION OF ITS FORMULA

General Actions of Alcohol: Necessity of Analysis.—Only when a product has been purified, and its physical properties sufficiently examined to establish its individuality, can its examination from a purely chemical standpoint be commenced. As in all scientific work, the method is that of experiment, guided by analogy. Sometimes the nature of a substance is obvious from the method of its formation, and in such cases only confirmatory evidence is needed, but at other times, when there is no such guide, analogies must be sought for.

Now although alcohol is combustible, and very different physiologically, it is obvious from the outset that it resembles water and the metallic hydroxides in many of its chemical relations. Many salts are dissolved by it, and the crystals which separate from such solutions often contain loosely combined alcohol, analogous to water of crystallisation. Calcium chloride alcoholate, for example, is a definite crystalline compound, which like the hydrate is decomposed by heat. The action of sodium is similar to its action on water, hydrogen being evolved and a sodium derivative formed. The organic liquid partially neutralises acids also, in much the same way as the mineral alkalies.

But although its general character is thus fairly clear, its nature cannot be exactly defined without quantitative examination. The physical differences between organic compounds are much less marked than in parallel inorganic cases, and it is thus necessary to analyse the substances and determine their formulæ before any progress can be made. It is largely for this reason that the systematic study of Organic Chemistry, although the oldest branch of the science, was followed without much success until analytical methods, and the consequent theories, were developed.

Detection and Estimation of Carbon and Hydrogen.—That alcohol contains carbon and hydrogen is proved by burning some, and passing the products of combustion through a cold, empty vessel and a flask of lime water, when water condenses and carbonate of lime is precipitated (Lavoisier, 1794). With the exception of oxygen, the presence of which as a rule can only be established by quantitative analysis, no other element can be detected.

The proportions of carbon and hydrogen are determined by burning the substance in a slow current of air, or oxygen, in presence of copper oxide. The combustion is effected in a hard-glass tube about three feet long, which is heated in a gas furnace of special design (Fig. 2). The granulated oxide having been placed between plugs of asbestos in the middle and further end of the tube, and heated to redness in a current of purified air, to remove all traces of moisture and organic matter, a known weight of the substance, in a small glass bulb, or in the case of solids, in a narrow platinum boat, is introduced into the end next the air inlet, and gradually heated to redness. Most of the substance is burned in the air, whilst the oxidation of any that is volatilised uncombined is completed by the red-hot copper oxide.

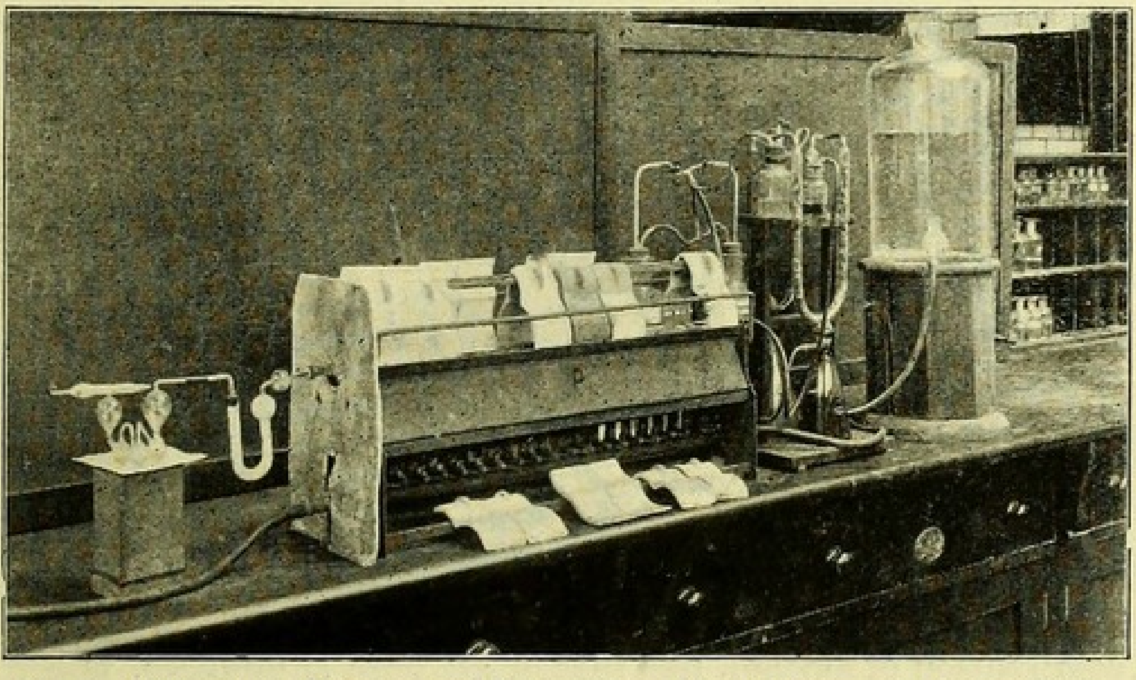

Fig. 2.—Estimation of Carbon and Hydrogen by Combustion with Copper Oxide.

The water from the large jar passes through a T-piece into one or other of the smaller jars behind the furnace, containing respectively air and oxygen. The gases thus expelled pass through a T-piece into the drying apparatus. The large U-tubes are filled with pumice soaked respectively in strong potash solution and concentrated sulphuric acid, which are forced up through T-tubes from the conical reservoir flasks for a few minutes before each combustion. The small bottles at the top contain dilute potash and sulphuric acid, and serve to mark the rate of inflow and outflow of the gas. The purified air passes into the combustion tube, in which the substance and main portion of the copper oxide are situate at the parts from which the clay furnace-tiles have been removed. The burnt gases leaving the tube pass through a U-tube containing sulphuric acid and pumice (most of the water condensing in the small bulb), and then through the three-bulb vessel containing strong potash. The small horizontal tube above the bulbs contains more pumice and sulphuric acid, to retain the moisture given off by the potash solution.

The carbon dioxide and water vapour produced in this manner are carried with the excess of air and nitrogen through a series of two vessels containing calcium chloride and potash, or equivalent absorbent substances, and their amounts are measured by the increase in the weights of the vessels during the combustion (Liebig). The whole operation lasts about two hours.

In careful combustions of alcohol such results as the following are obtained:—

I. 0·2063 gram gives 0·3931 gram CO_2 and 0·2475 gram H_2O.
II. 0·2856 gram „ 0·5427 gram CO_2 and 0·3365 gram H_2O.
III. 0·1989 gram „ 0·3796 gram CO_2 and 0·2351 gram H_2O.

Calculation of Percentage Composition.—Since the percentage compositions of carbon dioxide and water are known, the data for the calculation of that of the alcohol are complete. In the first combustion the weight of the carbon in the portion taken is

$$0{\cdot}3931 \times \frac{3}{11}{}^{*} = 0{\cdot}1072 \text{ gram},$$

and its percentage is therefore

$$51{\cdot}96.^{\dagger}$$

The weight of hydrogen is similarly

$$\frac{0{\cdot}2475}{9} = 0{\cdot}0275 \text{ gram},$$

and its percentage therefore

$$13{\cdot}33.$$

The oxygen is determined by difference, as there is no really satisfactory method for its estimation, and in this case therefore its percentage, since there is no other element present, is

$$100{\cdot}00 - (51{\cdot}96 + 13{\cdot}33) \text{ or } 34{\cdot}71.$$

The duplicate analyses give results which agree with these within the limits of experimental error (p. 9), so that the composition of alcohol, like that of all pure substances, is constant. It was first established by exploding the vapour with oxygen (De Saussure 1808).

Calculation of Empirical Formula.—It will be remembered that all other forms of matter must be thought of from a chemical point of view as composed of atoms of definite weight, and that the relative numbers of the latter are proportional to the quotients of the percentages by the respective atomic weights (Dalton, 1808). Now the ratio in the case of alcohol is

$$N_c:N_h:N_o = \frac{51{\cdot}96}{12}:\frac{13{\cdot}33}{1}:\frac{34{\cdot}71}{16}.$$

and this on simplification becomes

$$N_c:N_h:N_o = 4{\cdot}33 : 13{\cdot}33 : 2{\cdot}17,$$

so that the oxygen atoms are the fewest. But fractions of atoms are inadmissible. Dividing throughout by the smallest number, the numbers become

$$N_c:N_h:N_o = 1{\cdot}99 : 6{\cdot}15 : 1.$$

Here again fractions are obtained, but if it be assumed that

---

[*] $\frac{C}{CO_2} = \frac{12}{44} = \frac{3}{11}$; $\frac{H_2}{H_2O} = \frac{2}{18} = \frac{1}{9}$

[†] $\frac{0{\cdot}1072}{0{\cdot}2063} \times 100.$

the small differences from whole numbers are here due to experimental error the numbers fall into the simple ratio

$$N_c:N_h:N_o=2:6:1,$$

making the formula

$$C_2H_6O.$$

That this assumption is valid is proved by the agreement, within the limits of experimental error, of the percentages calculated from this formula with those worked out from the three analyses, and a formula is always checked in this way, apart from the theoretical considerations.

Analysis of Pure Alcohol.

	Found.			Calculated for C_2H_6O.
	I.	II.	III.	
Carbon .	. 51·96	51·83	52·05	52·17
Hydrogen .	13·33	13·09	13·13	13·04
Oxygen .	. *34·71*	*35·08*	*34·82*	34·79
	100·00	100·00	100·00	100·00

A formula thus showing merely the composition of the substance, and the ratio in which its atoms are combined is termed an empirical formula (Dalton). But it affords no information as to the size of the chemical units or molecules, and until this is determined there is no evidence whether the formula of the reacting unit of the substance is identical with or some multiple of the simple formula. The molecular weight must therefore be next determined.

Determination of Vapour Density and Molecular Weight.—The molecular weight of a volatile liquid, whether organic or inorganic, is deduced from the ratio of the weight of its vapour to that of the same volume of hydrogen at the same temperature and pressure. These volumes, it will be remembered, contain the same number of molecules (Avogadro, 1811), and the weights of the individual molecules are therefore in the same ratio. In practice it is of course inconvenient to compare the vapour directly with hydrogen, and air is used, the density being calculated from the known specific gravity of the lighter gas.

In Victor Meyer's method (1879) the air displaced from an appropriate vessel by the vapour of a known weight of the liquid is collected and measured, and its weight calculated. The displacement vessel (Fig. 3) consists of a long vertical tube having a cylindrical bulb at the lower end, and near the upper end a side tube leading to a small pneumatic trough. The bulb and part of the tube are heated at a constant and sufficiently high temperature by steam or other saturated vapour, which is generated in a cylindrical glass jacket surrounding the displacement tube.

When the air has ceased to expand, a weighed quantity of the liquid in a miniature specimen tube is dropped into the bulb, and the stopper of the displacement vessel quickly replaced. The liquid slowly volatilises, but the vapour being heavier than the air remains at the bottom, and an equal volume of air at the same temperature and pressure is thus expelled into the graduated vessel at the trough. Here it is measured, and its temperature and pressure noted. The air of course contracts on passing into the cold measuring tube; but this is immaterial, as it is the weight which is ultimately required.

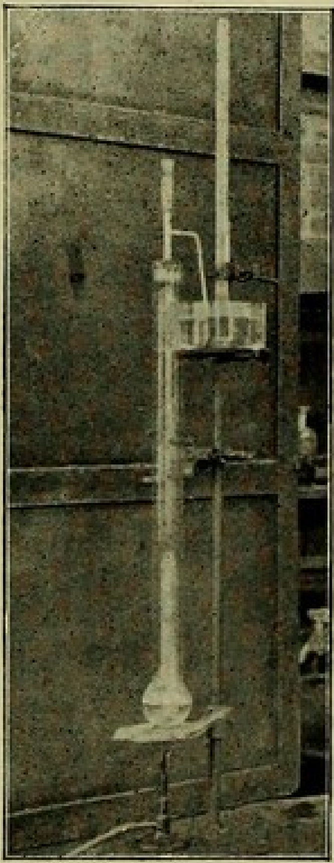
Fig. 3.—Determination of Vapour Density by Air-Displacement method.

Now the vapour of

0·0623 gram of alcohol

yields approximately

32·5 c.c. of air,

measured over water at 20° and 752 mm. The weight of this volume of air is

0·0396 gram,*

and the specific gravity of the vapour is therefore

$$\frac{0{\cdot}0623}{0{\cdot}0396} \text{ or } 1{\cdot}57.$$

Its vapour density, or specific gravity, referred to hydrogen is thus

$$\frac{1{\cdot}57\dagger}{0{\cdot}0693} \text{ or } 22{\cdot}6,$$

and hence, since the vapour is 22·6 times heavier than hydrogen, the molecular weight of which is 2, the molecular weight of the substance is

$$22{\cdot}6 \times 2 = 45{\cdot}2.$$

The number is more simply obtained by multiplying the specific gravity of the vapour by 28·8 (=2/0·0693).

There are other methods of determining vapour density, of which the chief are Dumas', in which a known volume of the vapour is actually weighed; and Hofmann's, in which the volume of a known weight is directly measured, but they are now little used.

Determination of Molecular Formula from Vapour Density.—Remembering that a molecular formula must either be identical with the empirical formula, or an exact multiple of it, it is

---

* $0{\cdot}0396 = 32{\cdot}5 \times \frac{735}{760} \times \frac{273}{293} \times 0{\cdot}001293$;

0·001293 = weight of 1 c.c. of air at 0° and 760 mm.; pressure of water vapour at 20° = 17 mm.

† 0·0693 = specific gravity of hydrogen referred to air.

now easy to determine the molecular weight. The sum of the atomic weights given by the empirical formula C_2H_6O is 46, and the molecular weight of alcohol is therefore either 46, or some multiple of this, such as 92 or 138, for no other values are consistent with this atomic ratio.

Now the number 45·2 calculated from the vapour density, although not actually coincident with any of these, is so near the first that this must be taken as the actual molecular weight. It must be borne in mind that the determination of vapour density does not give such accurate results as analysis, and the molecular weight calculated from it is used only as an index, and must not be taken as the actual value.

The formula

$$C_2H_6O$$

thus represents the actual number of atoms in the molecule or unit of chemical action as well as the relative numbers in any particular portion (Gerhardt and Laurent, 1845). It here happens to be identical with the empirical formula, but this is not always the case. The molecular formula of acetic acid, for example, is double, and that of benzene six times the empirical formula.

Other Methods of Determining Molecular Weight: the Cryoscopic Method.—There are various other methods of determining molecular weight. When for instance a small quantity of a substance is dissolved in a pure liquid with which it does not interact, the freezing point of the latter is lowered by an amount depending on the molecular weights and relative proportions of the two substances.

The exact relation is given by the equation

$$M = KP/D \text{ (Raoult, 1882),}$$

where M is the molecular weight of the dissolved substance, P the weight dissolved in 100 grams of the solvent, D the depression of the freezing point, and K a constant for each particular solvent. The value of K for water is 19, for acetic acid, 39; and for benzene, 49.

It is usual to measure the depression with specially constructed thermometers graduated in hundredths of a degree, but sufficiently accurate results can be obtained with an ordinary physical thermometer graduated in fifths or tenths of a degree, and reading by estimation to fiftieths or hundredths.

The calculation is simple. Thus

0·492 gram of alcohol

dissolved in

26·8 grams of water,

lowers its freezing point approximately

from 0° to −0·79°,

and from this it follows that the molecular weight is

$$M = \frac{19 \times \frac{0{\cdot}492}{26{\cdot}8} \times 100}{0{\cdot}79} \text{ or } 44.$$

This result, again, is used purely as an index, in the same way as that calculated from the vapour density. The cryoscopic method is of great importance when the substance is not volatile.

An analogous method, based on the fact that the boiling point of a pure liquid is raised by the addition of a soluble substance, is also occasionally used, and there are various chemical methods of determining molecular weight, which will be dealt with as occasion arises.

Synopsis.—Pure alcohol, like pure inorganic substances, is constant in chemical composition, and therefore represented by a definite formula C_2H_6O: and from its vapour density and freezing point of its aqueous solution this formula also represents the number of atoms in its molecule.

CHAPTER III

CHEMICAL NATURE OF ALCOHOL

Action of Sodium on Alcohol: Sodium Ethoxide.—The composition and molecular formula of the substance having been established, its chemical actions can now be studied in detail.

When dry sodium is placed in absolute alcohol, a vigorous action takes place, the metal being dissolved and hydrogen evolved, just as with water. The liquid becomes viscid, and after a time ceases to dissolve the metal, even when heated, and on then cooling, sets to a solid crystalline mass, which is usually brownish from impurity. To purify the product, the mass is filtered, and pressed between filter paper from adherent alcohol, and after picking out undissolved metal is dried in a large test tube at 180°, in a stream of dry hydrogen or coal gas.

The residue consists of a white amorphous powder termed sodium ethoxide. It appears to melt when heated, but is really decomposed, so that here the only criterion of purity is constancy of composition.

Sodium ethoxide obviously cannot contain alcohol as such, but it is an organic compound, for carbon and hydrogen, as well as sodium and oxygen, are present. The presence of the metal is indicated by the flame test, whilst that of the carbon and hydrogen in the difficultly combustible substance, is proved by heating a portion in a test tube with copper oxide, carbon dioxide and steam being evolved. The sodium is estimated by dissolving the ash of the substance in dilute sulphuric acid, and evaporating and weighing the sodium sulphate thus obtained, and the empirical formula found from this and the carbon combustion is

$$C_2H_5NaO.$$

The molecular formula is strictly speaking unknown, for the substance is not volatile, and is decomposed by available solvents, but in the absence of evidence to the contrary, it is assumed to be the same as the empirical formula. The crystalline product first obtained is a molecular compound of the ethoxide with alcohol of crystallisation,

$$C_2H_5NaO, 2C_2H_6O.$$

Rational Formula of Alcohol: Hydrolysis of Sodium Ethoxide.—Sodium ethoxide is thus clearly derived from alcohol in the same way as sodium hydroxide from water, by substitution of sodium for hydrogen; and it follows, therefore, that one of the hydrogen atoms of alcohol is more active than the rest—

$$C_2H_6O+Na=C_2H_5NaO+H;$$
$$H_2O+Na=NaHO+H.$$

Now in Inorganic Chemistry, the reactions of compounds are sufficiently expressed by means of their empirical or molecular formulæ, but the molecular formulæ of organic compounds are so much alike—in some cases, in fact, identical—that a further development is necessary. The above result is accordingly expressed by means of a formula in which the active hydrogen atom is placed apart, and which, as it gives some indication of the chemical relations of the substance, is termed a rational formula (Berzelius)—

$$C_2H_5O.H.$$

But although sodium ethoxide is formed in the same way as the hydroxide, unlike the latter it is decomposed by water, dilute alcohol passing over when its aqueous solution is distilled, and caustic soda remaining in the flask.

In studying such decompositions, the identification of small quantities is often requisite. This is effected in the first instance, when possible, by means of qualitative "test-tube" reactions. Thus the alcohol in the above distillate can be quickly converted without further purification, into iodoform, aldehyde, or ethyl acetate, substances recognisable by their appearance or odour (see Appendix II.). Such tests are of course preliminary. and must be supplemented by the isolation and identification of the suspected substance in the manner previously described.

Small quantities can often be quickly isolated. Thus the alcohol can be roughly separated by dissolving a stick of caustic soda in the head fraction of the distillate. Being insoluble in concentrated soda solution, it slowly rises to the surface, and can thus be separated with a pipette, and dehydrated and distilled for its boiling point. Ammonium sulphate has the same effect, and the organic liquid in such cases is said to be salted out.

The decomposition of sodium ethoxide into alcohol and caustic soda thus established, is termed a hydrolysis—splitting by water—the molecule taking up water, and at the same time being resolved into simpler molecules. In hydration the first stage alone is reached—

$$C_2H_5O.Na+H_2O=C_2H_5O.H+NaHO.$$

Now the hydrogen of caustic soda itself can be displaced by sodium and replaced hydrolytically by the action of water, and in this respect therefore alcohol is chemically analogous to the alkali hydroxide. This relation is represented, however, by the same rational formula as in the first case—

$$NaO.H \longleftrightarrow NaO.Na;\ C_2H_5O.H \longleftrightarrow C_2H_5O.Na.$$

Action of Phosphorus Bromide and Iodide on Alcohol: Ethyl Bromide and Iodide.—The analogy of alcohol to water and caustic soda is amply confirmed by the action of phosphorus bromide and iodide and the mineral acids, the first of which it will be remembered replace the hydroxyl of water by halogen, whilst the last, of course, convert the alkali into salts.

When bromine is slowly added to red phosphorus immersed in absolute alcohol, the phosphorus pentabromide initially formed acts energetically on the latter, and much heat is evolved. The action proceeds with explosive violence if the liquid is not well cooled before each addition. On distilling the red and turbid product from a water-bath, best after the lapse of some hours, a yellowish volatile liquid, termed ethyl bromide, passes over, having a faint odour of garlic. Syrupy phosphoric acid and some unchanged phosphorus remain in the flask.

The liquid is impure, and contains unchanged alcohol and phosphorus bromide, as well as secondary products, but as ethyl bromide is insoluble in dilute alkalies, these may be removed by shaking it with cold dilute caustic soda in a tap-funnel (Fig. 4). The alcohol and phosphorus bromide dissolve in the alkali, whilst the heavy ethyl bromide falls to the bottom and can be drawn off through the tap. If a tap-funnel is not available, a stoppered cylinder or corked test-tube may be used, and the bromide drawn off with a pipette.

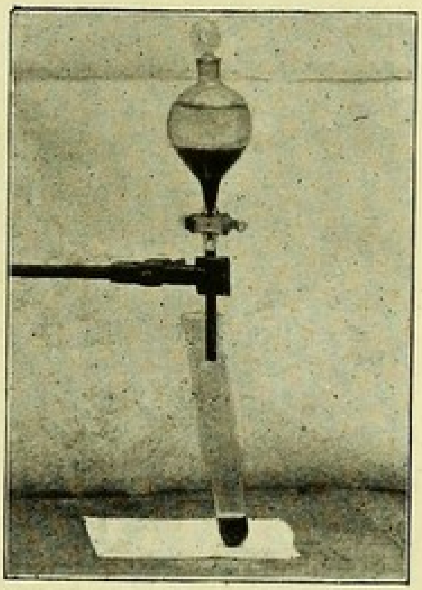

Fig. 4.—Separatory Funnel.

The only impurities now remaining are dissolved water and a small quantity of a secondary product containing phosphorus. The water is removed by placing a few small pieces of recently fused calcium chloride in the liquid for twenty-four hours, and the high-boiling phosphorus compound by fractionating the dry product from a water-bath.

Ethyl bromide, C_2H_5Br (Serullas, 1829), is a liquid of ethereal but garlic odour. It boils at 39°, and its specific gravity is 1·49 at 15°. Like most organic halogen compounds it burns with a green mantled flame, and the presence of halogen is directly demonstrated by bringing a fragment of copper oxide moistened with it into a Bunsen flame. The volatilised copper bromide tinges the flame green.

The bromine is estimated as silver bromide. The liquid, weighed in a small bulb, is heated with the strongest nitric acid and silver nitrate for some hours, at a high temperature. The carbon and hydrogen are completely oxidised, and the bromine unites with the silver, forming silver bromide (Carius). To attain the necessary temperature, 150–250°, the liquid and agents are sealed up in a hard glass tube about twelve inches long, which is enclosed in a strong iron tube to minimise danger from explosion, and heated in an air-bath (Fig. 5). The complete oxidation requires several hours. When the tube has cooled, it is well wrapped up in a cloth, and the drawn out end softened in a flame to allow the confined gases to escape. The end is then cut off, and the silver precipitate washed, dried and weighed in the usual manner, and the percentage of bromine calculated.

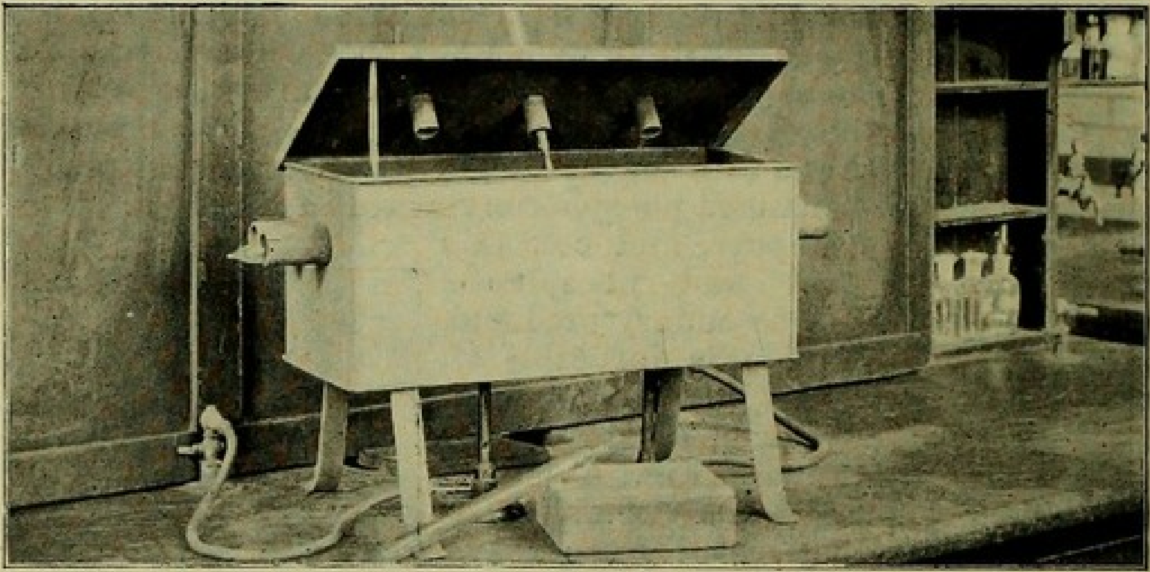

Fig. 5.—Tube-Furnace and Sealed Tubes.

Owing to the presence of the halogen a modification of the carbon combustion is necessary, a long roll of red-hot silver gauze being placed after the copper oxide to decompose the volatile copper bromide, which would otherwise pass into the calcium chloride tube and be weighed as water. The same end is better attained by substituting lead chromate for the oxide.

The empirical formula calculated from the numbers thus obtained, is

$$C_2H_5Br,$$

and as the vapour density is 1·89, this is also the molecular formula of the ethyl bromide.

The action of phosphorus and iodine on alcohol is precisely similar, but not violent, and the product is purified and isolated in the same way.

Ethyl iodide, C_2H_5I (Gay-Lussac, 1815), is a heavy, colourless liquid which boils at 72°, and has a marked garlic odour. It is less stable than the bromide, and when exposed to light becomes brown from liberation of traces of iodine.

Relation of Ethyl Bromide to Alcohol and Sodium Ethoxide: Second Rational Formula of Alcohol.—With phosphorus bromide and iodide, alcohol thus behaves in precisely the same way as water—

$$5C_2H_6O + P + 5Br = 5C_2H_5Br + H_3PO_4 + H_2O;$$
$$5H_2O + P + 5Br = 5HBr + H_3PO_4 + H_2O,$$

and as the organic molecule thus contains hydroxyl, it can be represented by a second rational formula in which this hydroxyl is placed apart from the remaining atoms—

$$C_2H_5.OH.$$

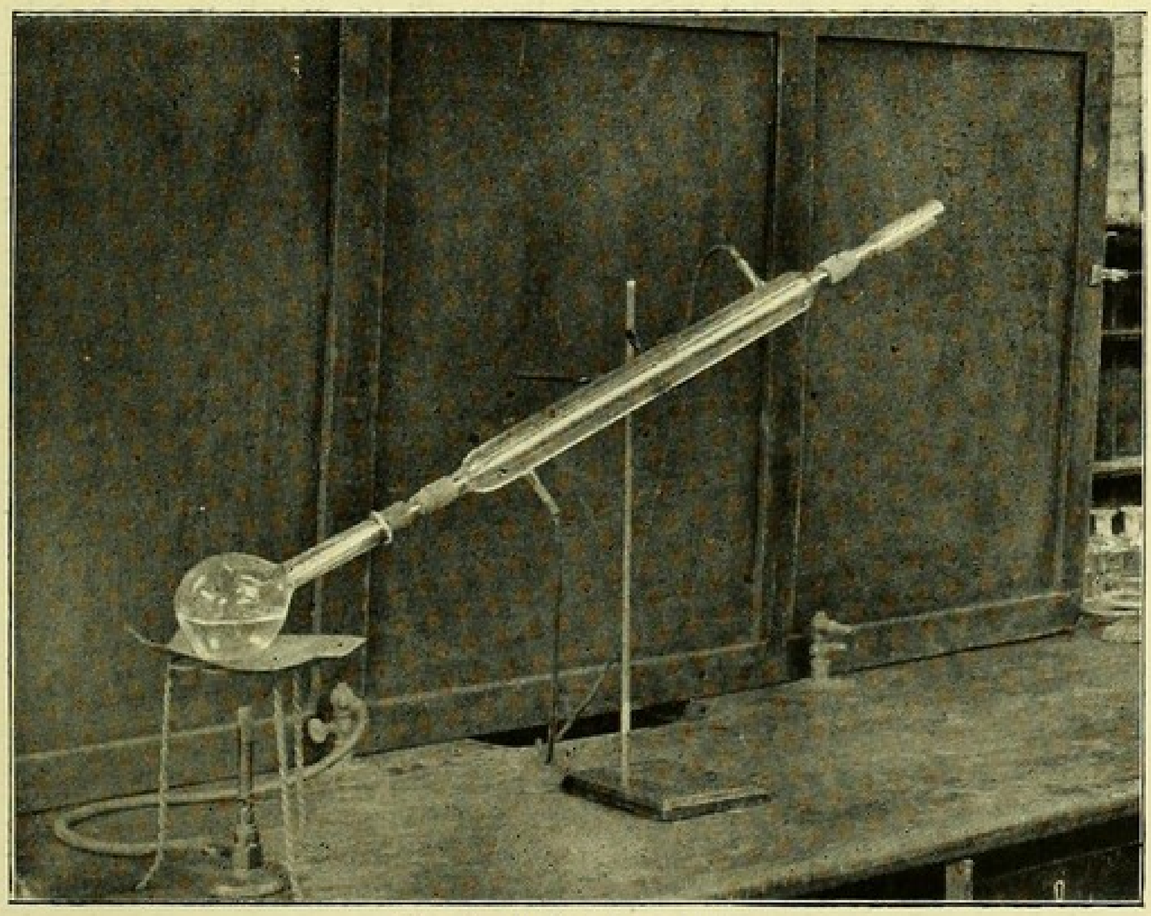

Fig. 6.—Reflux Apparatus.

This result is confirmed, in the first place by the direct conversion of alcohol into ethyl bromide by hydrobromic acid in presence of a dehydrating agent (see Ethyl Chloride below). Here it behaves in the same way as sodium hydroxide—

$$C_2H_5.OH + HBr = C_2H_5.Br + H_2O;$$
$$Na.OH + HBr = Na.Br + H_2O.$$

It is borne out in the second place by the hydrolysis of the bromide to alcohol and hydrobromic acid (sodium bromide), when boiled with caustic soda solution—

$$C_2H_5.Br + NaOH = C_2H_5.OH + NaBr.$$

The conversion is only slowly effected, and to prevent the escape of the volatile liquids the hydrolysis is carried out in a reflux apparatus (Fig. 6), or flask furnished with an inverted condenser, which condenses and returns the vapours (Frankland

and Kolbe, 1848). The boiling is continued until the odour of the bromide is no longer perceptible on disconnecting the flask, and the alcohol is then distilled off, the sodium bromide remaining with the excess of alkali and the water.

The alcohol and its bromide here behave in much the same way as the hydroxide and salt of a heavy metal, lead for example—

$$Pb(OH)_2 + 2HBr = PbBr_2 + 2H_2O:$$
$$PbBr_2 + 2NaOH = Pb(OH)_2 + 2NaBr.$$

The bromine of the organic bromide is much more firmly attached, however, than that of the metallic salt, and is precipitated by silver nitrate only in presence of alcohol and on warming.

Ethyl Chloride.—Alcohol is thus a basic hydroxide intermediate in properties between water and caustic soda. It forms salts, in fact, with most of the acids. Thus ethyl chloride, a volatile liquid resembling the bromide, is made by the direct action of the acid, which in the course of months is partially neutralised. The yield is much increased by the addition of a dehydrating agent (Groves, 1874).

The spirit is boiled with anhydrous zinc chloride in a reflux apparatus in an oil-bath, while dry hydrogen chloride is passed into the mixture. Unattacked alcohol is returned by the condenser, and the ethyl chloride vapour passes from the upper end. After traversing wash-bottles of water and dilute alkali, to remove hydrochloric acid, and of strong sulphuric acid, to remove alcohol and water, it is condensed in a freezing mixture. The zinc chloride retains the liberated water (see also p. 106).

Ethyl chloride, C_2H_5Cl (Basil Valentine, 16th century, "spirit of salt and wine"), is a liquid, which resembles the bromide in odour, but boils at 12°, and has a specific gravity of 0·921 at 0°. As a halogen compound it burns, like the bromide, with a green-mantled flame. On account of its volatility, it is preserved in sealed vessels, or better in alcoholic solution, from which it is set free by gently warming. The vapour is washed with strong sulphuric acid to take up the alcohol. Ethyl chloride is formed in large quantities as a by-product in the manufacture of chloral (p. 118), and is used as a local or refrigerating anæsthetic in dentistry, etc.

The analysis and vapour density of the organic chloride, the chlorine being detected and estimated in precisely the same way as bromine and iodine, lead to the empirical and molecular formula C_2H_5Cl, and the action of hydrochloric acid thus resembles that of hydrobromic acid, the alcohol in both cases behaving as a basic hydroxide—

$$C_2H_5.OH + HCl = C_2H_5.Cl + H_2O.$$

As in the previous case, this is confirmed by the hydrolysis, which on account of the extreme volatility of the chloride must be carried out in a closed vessel—

$$C_2H_5.Cl + NaOH = C_2H_5.OH + NaCl.$$

Synopsis.—In its actions with sodium, the halogen acids, and the phosphorus halogen compounds, alcohol behaves as a basic hydroxide, intermediate to water and caustic soda.

CHAPTER IV

THE ETHYL RADICLE

The Ethyl Sulphates.—That alcohol is a monacid base is confirmed by the existence of two ethyl sulphates, an acid salt and a normal salt. The first is readily formed by the direct action of the acid on alcohol, and is conveniently isolated as the sodium salt.

A mixture of alcohol and strong sulphuric acid is heated in an open flask on a water-bath for an hour, and the ethyl hydrogen sulphate that is formed is cooled, diluted with water, and neutralised in a large basin with a thin cream of calcium carbonate. The resulting solution of ethyl calcium sulphate, for the salt is freely soluble, although a compound of calcium and sulphuric acid is filtered from calcium sulphate and unchanged carbonate, best with the aid of a filter pump, and converted into the sodium salt by cautiously adding sodium carbonate solution as long as a precipitate is formed. The clear solution of ethyl sodium sulphate is boiled down to one-fourth, and then evaporated on a water-bath until it begins to crystallise. After some hours, the crystals are drained and dried between filter paper, and a further quantity obtained by evaporating the mother liquor—

$$C_2H_5.OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O\ ;$$
$$2C_2H_5.HSO_4 + CaCO_3 = Ca(C_2H_5.SO_4)_2 + CO_2 + H_2O\ ;$$
$$Ca(C_2H_5.SO_4)_2 + Na_2CO_3 = 2C_2H_5.NaSO_4 + CaCO_3.$$

Ethyl sodium sulphate, $C_2H_5.NaSO_4$, crystallises in soft, ill-defined cream-coloured masses, having a pleasant odour and somewhat sweet taste. It is deliquescent. Ethyl hydrogen sulphate or sulphovinic acid, $C_2H_5.HSO_4$ (Dabit, 1800), is obtained by exactly precipitating the metal with dilute sulphuric acid from a solution of the calcium, or better, the barium salt. The clear filtered solution is evaporated in a vacuum at the ordinary temperature, over strong sulphuric acid, as the sulphate is decomposed by hot water, and after some days the organic salt remains as a thick, colourless acid syrup, which cannot be made to crystallise—

$$Ba(C_2H_5.SO_4)_2 + H_2SO_4 = 2C_2H_5.HSO_4 + BaSO_4.$$

The second or normal salt, ethyl sulphate, $(C_2H_5)_2SO_4$, is formed in small quantity in the preparation of the acid salt, and can be extracted with ether (p. 71) from the ethyl sodium sulphate mother liquor. It is best prepared, however, by heating ethyl iodide with silver sulphate in a sealed tube, and simply fractionating the liquid product, to separate unchanged iodide—

$$2C_2H_5.OH + H_2SO_4 = (C_2H_5)_2SO_4 + H_2O;$$
$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI.$$

Ethyl sulphate, or "oil of wine" $(C_2H_5)_2SO_4$, is a heavy, colourless liquid, which smells of peppermint, and boils at 208°.

The ethyl sulphates are hydrolysed much more readily than the halogen salts. Thus, on simply boiling ethyl hydrogen sulphate with water, it is resolved into alcohol and sulphuric acid, the alcohol distilling over, and the fixed acid, of course, remaining behind (Hennell, 1821).

Although ethyl sodium sulphate is stable in neutral or alkaline solution, it is converted by acids into ethyl hydrogen sulphate, and when distilled with excess of dilute sulphuric acid is therefore hydrolysed to sodium sulphate and alcohol, which may be detected and isolated in the manner already indicated. Similarly diethyl sulphate is hydrolysed even by warm water to ethyl hydrogen sulphate and alcohol, and by boiling water therefore to alcohol and sulphuric acid—

$$C_2H_5.HSO_4 + H_2O = C_2H_5.OH + H_2SO_4;$$
$$C_2H_5.NaSO_4 + H_2SO_4 = C_2H_5.HSO_4 + NaHSO_4;$$
$$(C_2H_5)_2SO_4 + H_2O = C_2H_5.HSO_4 + C_2H_5.OH.$$

The presence of sulphur in these ethyl sulphates is proved by heating them to redness with sodium, and adding lead acetate to the aqueous extract of the product, when a black precipitate of lead sulphide is thrown down by the sodium sulphide that is formed. The sulphur is estimated as barium sulphate. The substance is completely oxidised by heating it with concentrated nitric acid in a sealed tube, in the same way as in the estimation of halogen, and the sulphuric acid thus formed is precipitated from the diluted product with barium chloride, the sulphate being collected and weighed in the usual manner.

The empirical formulæ calculated from the analyses of the sodium and hydrogen salts are those used above, and the molecular formulæ are assumed to be the same. The molecular formula of the diethyl salt follows from its vapour density.

Ethyl Oxide: Common Ether.—The hydroxide character of alcohol is still further demonstrated by the existence of the corresponding oxide, common ether. Ether is formed by heating ethyl hydrogen sulphate with alcohol instead of with water, and as the action proceeds equally well in presence of excess of sulphuric acid, the sulphate need not be isolated—

$$C_2H_5.HSO_4 + C_2H_5.OH = (C_2H_5)_2O + H_2SO_4.$$

The mixture of alcohol and strong sulphuric acid is heated at 140°, when it boils, and ether and water pass over, and by running in more alcohol at such a rate as to maintain the temperature constant, a continuous stream of the two products is obtained—"continuous process." Theoretically, there should be no end to the action, as the sulphuric acid regenerated acts on a further portion of the alcohol, forming more ethyl hydrogen sulphate, but in practice, owing to secondary actions, the mixture soon becomes charred, and the operation has to be started afresh when about four times the original volume of alcohol has been added.

The distillate contains sulphurous acid and alcohol in addition to ether and water, and these impurities are withdrawn by shaking it with dilute caustic soda, and then with strong calcium chloride solution, until the washings cease to give the iodoform reaction for alcohol. The light insoluble ether rises to the surface each time, and finally, after separating from the aqueous layer, is dried with fused calcium chloride, and redistilled from a water-bath, in contact with a little sodium.

Ethyl oxide or ether*, $(C_2H_5)_2O$, (Valerius Cordus, 1542), is a mobile and extremely volatile liquid, having a very characteristic odour resembling that of peppermint, but sweeter. It boils at 35°, and the frozen solid melts at $-117°$. The specific gravity is 0·736 at 0°. Ether is a valuable solvent for fats, resins, and other substances insoluble in water, and is therefore much used in the laboratory. It is also used as an anæsthetic, both internally, the vapour producing insensibility when inhaled, and locally as a refrigerant, in the form of spray. The vapour is dangerously inflammable, and the liquid must never be brought near a naked flame.

The percentage composition and vapour density of the substance lead to the molecular formula $C_4H_{10}O$. Its rational formula as ethyl oxide, $(C_2H_5)_2O$, is proved by its formation when ethyl bromide is boiled with excess of sodium ethoxide in a reflux apparatus. The odour of the bromide is soon replaced by that of the ether, and after an hour the conversion is fairly complete (Williamson, 1851; see also p. 42)—

$$C_2H_5Br + C_2H_5.ONa = (C_2H_5)_2O + NaBr.$$

The formula is confirmed by the hydrolysis of ether to alcohol when heated with dilute sulphuric acid in a sealed tube at 150°, and by its conversion into ethyl hydrogen sulphate by concentrated sulphuric acid at a somewhat higher temperature—

$$(C_2H_5)_2O + H.OH = 2C_2H_5.OH;$$
$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5.HSO_4 + H_2O.$$

The Ethyl Radicle: Alkylic Hydroxyl.—From these various actions it follows that the derivatives of alcohol are, on the one hand, parallel to those of water, and, on the other hand, to those of sodium hydroxide, and that the sodium and hydrogen atoms and the atomic group,

$$C_2H_5,$$

are combined with and interchange the same groups or atoms,

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* αἰθήρ = the attenuated upper air; hence "attenuated" spirit.

and pass unchanged through the various transformations. The organic group behaves, in fact, throughout as a weak basic radicle, analogous to the metallic elements, potassium and sodium (Liebig, 1834). Were it not that it can be oxidised to carbon dioxide and water, it might be regarded as an organic element.

SODIUM, ETHYL, AND HYDROGEN COMPOUNDS.

$Na.OH$	$C_2H_5.OH$	$H.OH$
$Na.ONa$	$C_2H_5.ONa$	$H.ONa$
$Na.Br$	$C_2H_5.Br$	$H.Br$
$Na.Cl$	$C_2H_5.Cl$	$H.Cl$
$Na.HSO_4$	$C_2H_5.HSO_4$	$H.HSO_4$
Na_2SO_4	$(C_2H_5)_2SO_4$	H_2SO_4.
Na_2O	$(C_2H_5)_2O$	H_2O

On account of its persistence and stability, this group is assigned a special name, ethyl * (Liebig, ether and ὕλη=stuff, matter), and a special symbol, Et, so that the formula of alcohol as ethyl hydroxide becomes

$$Et.OH,$$

and those of its derivatives, $Et.ONa$, $Et.Br$, Et_2O, etc. Further, on account of the analogy in function of the ethyl radicle to the alkali metals, it is termed an alkyl radicle, and the hydroxyl with which it is associated, alkylic hydroxyl. Radicles play so important a part in Organic Chemistry that it was termed at one time the Chemistry of Compound Radicles (Berzelius).

Synopsis.—Alcohol is the hydroxide of a basic or alkylic radicle, ethyl, C_2H_5 or Et, analogous to the alkali metals in function. To indicate this its formula is written as $C_2H_5.OH$ or $Et.OH$. The corresponding oxide is common ether.

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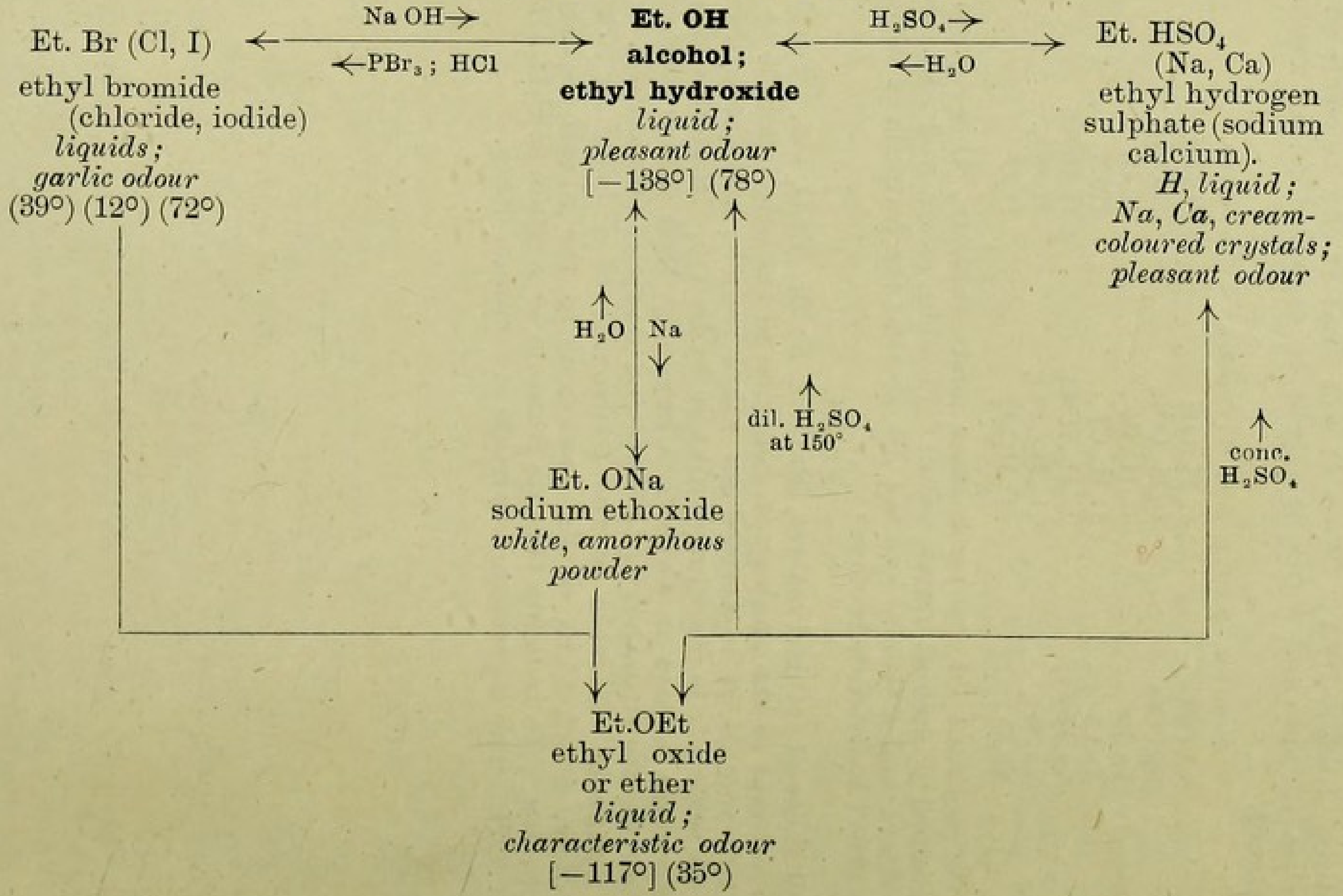
* Ēthȳl.

ALCOHOL AND THE ETHYL RADICLE.



CHAPTER V

PREPARATION AND COMPOSITION OF ACETIC ACID

Oxidation of Alcohol to Acetic Acid: Vinegar and Wood Vinegar.—Although alcohol resembles water and sodium hydroxide in so many respects, it differs from them radically in that it is convertible into a substance having marked acid properties. It has long been known that wine and beer become sour on exposure to air and warmth, and the vinegar thus generated was in fact the only acid with which the ancients were acquainted (ὄξος, *acetum* = vinegar; ὀξύς, *acidum* = sharp). The mechanism of the change thus brought about was not of course understood in those times, but the process is now known to be one of oxidation, for the oxygen gradually disappears from the adjacent air, and the change is equally well brought about by the ordinary oxidising agents (Lavoisier, 1794).

When, for instance, alcohol is boiled in a reflux apparatus with potassium permanganate and dilute sulphuric acid, the permanganate is decolourised, and on distilling the product after action has ceased, a liquid passes over, which has the sharp, characteristic odour of vinegar, and an acid reaction and taste. It is in fact identical with distilled vinegar.

Vinegar is always made by the natural oxidation of alcohol. In warm climates, the wine is simply added to hot strong vinegar placed in casks provided with air holes. Under the influence of the ferment (p. 177), the wine is gradually oxidised by the air, and is drawn off and replenished from time to time. Malt vinegar is made from fermented wort in much the same way. "White vinegar" is manufactured by oxidising dilute spirit by the quick vinegar process. The spirit is caused to trickle through perforated casks, which are filled with shavings impregnated with the ferment, a convection current of air being kept moving through the apparatus by the heat generated in the action (Schützenberger, 1823).

The acetic acid used for chemical and industrial purposes, however, is usually made by distillation of wood. When a hard wood such as beech or box is heated to redness in a retort, gases are first evolved, and then a liquid passes over which separates into two layers, a light aqueous layer of wood vinegar or pyroligneous acid, and a heavy insoluble layer of wood tar (16th century). Charcoal remains in the retort. This pyroligneous acid is simply impure acetic acid (Fourcroy and Vauquelin, 1800).

Purification of Acetic Acid: Crystallisation: Glacial Acetic Acid.—On distilling the dilute acid obtained by any of these methods the water passes over the more quickly, and by careful fractionation a fairly strong product can be obtained (Basil Valentine, 16th century). In a somewhat analogous manner, on freezing the dilute acid, the solvent water separates as ice, whilst the dissolved acetic acid remains in solution (Stahl, 1697). In this case also the process has its limits, for at a certain concentration the dissolved substance and solvent freeze together. Conversely, the strong acid obtained by fractional distillation may itself be concentrated by freezing, the acid now being the solvent and the water remaining in solution as the dissolved substance.

But these methods are tedious, and in practice a chemical process is used. The dilute acid is exactly neutralised with sodium carbonate and boiled to dryness, and the residue fused and poured on a cold slab. The anhydrous crystalline mass of sodium acetate is then broken up and distilled with concentrated sulphuric acid, and the distillate redistilled with a few fragments of the salt to eliminate mechanically carried sulphuric acid (Stahl, 1692).

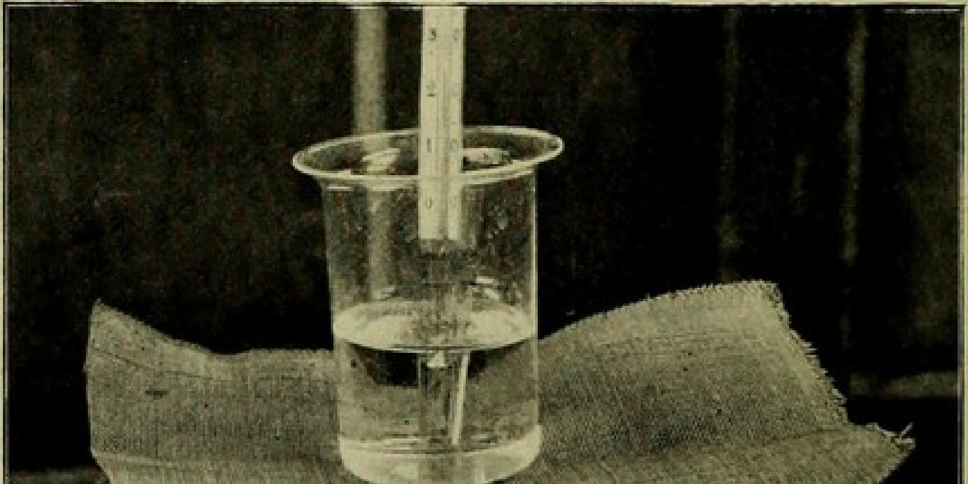


Fig. 7.—Determination of Melting-Point by Capillary Tube method.

On a large scale, pyroligneous acid is roughly distilled to separate the accompanying wood spirit (p. 37), and then neutralised with milk of lime. The calcium acetate is evaporated to dryness and heated at 200° to carbonise tarry impurities, and finally distilled with hydrochloric acid.

The acid prepared by any of these methods is termed glacial acetic acid, as it freezes at ordinary winter temperatures, but it still contains a little water, and this is eliminated by the process of fractional crystallisation mentioned above. A quantity of the concentrated acid is partially frozen, and the unfrozen portion having been drained off, the crystals are melted and the operation repeated until the melting point is constant (Fig. 7).* The boiling point and specific gravity are now also constant, and the product is pure.

Composition and Formula of Acetic Acid: Determination of Molecular Weight by Silver Method.—Pure acetic acid, $C_2H_4O_2$, (De Lauraguais, 1759) is a pungent, inflammable, hygroscopic liquid, or colourless crystalline solid. It melts at 16·7°, and boils at 118°, and has a specific gravity of 1·051 at 20°. The acid is much more stable than alcohol, and resists the action of even chromic trioxide, so that it is used as a solvent in oxidising organic substances with this agent. By prolonged boiling with acid permanganate, however, it is oxidised to carbon dioxide and water, whilst with alkaline permanganate it yields oxalic acid (p. 124).

The empirical formula of acetic acid (Berzelius, 1814) is

$$CH_2O,$$

and as its vapour density is about 30°, its molecular weight is 60°, and its molecular formula,

$$C_2H_4O_2.$$

The molecular weight indicated by the cryoscopic method varies with the concentration of the solution, owing to the dissociation of the dissolved acid, but the value calculated from the vapour density is confirmed by analysis of the silver salt.

The silver salts of organic acids are easily prepared and readily purified and analysed, and they are almost invariably anhydrous. Silver acetate for example is a white crystalline substance, which is made by dissolving the freshly precipitated oxide or carbonate in the dilute acid, and evaporating the filtered solution to dryness. When it is heated to redness in a porcelain crucible it is reduced to the metal,

0·5276 gram

yielding approximately

0·3412 gram of silver,

and so on in like proportion. Now acetic acid forms only one silver salt, whatever the proportion in which it is heated with the oxide. It is therefore monobasic, and the molecular weight of the salt may thus be represented by the expression

$$M - 1 + 108,$$

where M is the molecular weight of the acid. An atom of silver replaces one of hydrogen. But as the molecule contains one atom of silver, the relative weight of the metal is as

$$108 : (M - 1 + 108),$$

---

* See Appendix I.

and hence, since

$$108:(M-1+108)=0{\cdot}3412:0{\cdot}5276,$$
$$M=60{\cdot}02,$$

agreeing with the formula

$$C_2H_4O_2.$$

Acetic acid is thus derived from alcohol by the substitution of an atom of oxygen for two atoms of hydrogen—

$$C_2H_6O+2O=C_2H_4O_2+H_2O.$$

Synopsis.—The acetic acid obtained by distillation of vinegar, and by the destructive distillation of wood, is also formed by the direct oxidation of alcohol.

CHAPTER VI

CHEMICAL NATURE OF ACETIC ACID: THE ACETYL RADICLE

The Metallic Acetates: Rational Formula of Acetic Acid.—As already noted, acetic acid readily decomposes the alkali carbonates, and potassium acetate, $C_2H_3KO_2$, prepared in this way from vinegar and wood ashes, was used as a medicine by the Romans. The same salts are formed by the action of the alkali hydroxides, or in some cases of the metals themselves on the acid.

The acetates are the oldest artificial salts known, the gray-green basic copper acetate or verdigris having been made by the Greeks by allowing grape skins to remain in contact with copper plates. The acetic acid, formed by successive fermentation of the sugar, attacks the copper in presence of the air, and the salt is still made in essentially the same way by exposing sheet copper to the vapour of crude pyroligneous acid.

Ordinary copper acetate, $Cu(C_2H_3O_2)_2+H_2O$, made by dissolving copper oxide or carbonate in the warm dilute acid and evaporating to crystallisation, is a well defined, dark green crystalline salt. Lead acetate (Basil Valentine, 16th century) is prepared in a similar manner by dissolving litharge in the acid, and is known as sugar of lead, from its resemblance to cane sugar in appearance and taste. The taste, however, is metallic and astringent as well as sweet, and the salt is of course poisonous.

The ferric acetates are used in dyeing, and are also useful in detecting small quantities of the acid. When ferric chloride is added to a neutral acetate, the solution assumes a deep red colour, owing to the formation of the normal acetate, $Fe(C_2H_3O_2)_3$. This is decomposed and decolourised by dilute hydrochloric acid, and by simply boiling with water, is partially hydrolysed to an insoluble, brown, basic salt, part of the acid being set free—

$$Fe(C_2H_3O_2)_3+H_2O=Fe(OH)(C_2H_3O_2)_2+C_2H_4O_2.$$

From the existence of these various salts it is evident that, as in alcohol, one of the hydrogen atoms of the acetic acid molecule is more active than the rest, and that the substance may be represented by a rational formula,

$$C_2H_3O_2.H.$$

analogous to that of the basic hydroxide. But it is noteworthy that the unique hydrogen atom is much more active than in alcohol. The sodium derivative, for example, is much more easily formed, and conversely much more stable. It may be heated with water at any temperature without being decomposed.

Action of Phosphorus Chlorides on the Acetates: Acetyl Chloride: Second Rational Formula of Acetic Acid.—The resemblance of the acid to alcohol extends to its action with the phosphorus halogen compounds, although, as has been seen, there is no action with acids.

When glacial acetic acid is mixed with half its volume of phosphorus trichloride, heat is evolved, and after a time the mixture separates into two layers, the upper consisting of the chloro-derivative mixed with some unchanged trichloride, and the lower of a solution of phosphorous acid in acetic acid.

On fractionating the upper layer, the main fraction boils at 50–58°, the more volatile portions consisting chiefly of unchanged trichloride. After purification by repeated redistillation over small quantities of fused sodium acetate, the product boils at a constant temperature—

$$3C_2H_4O_2+PCl_3=3C_2H_3OCl+H_3PO_3.$$

Acetic or acetyl chloride, $C_2H_3O.Cl$ (Gerhardt, 1851), is a colourless, mobile liquid, which fumes strongly in the air, and corrodes animal and vegetable tissues. It boils at 51°, and has a specific gravity of 1·130 at 0°. The analysis and vapour density lead to the molecular formula C_2H_3OCl, and the action of phosphorus trichloride on acetic acid is thus similar to that of the pentabromide on alcohol, hydroxyl again being replaced by halogen. Phosphorus pentachloride and oxychloride have the same effect, and sodium acetate, for example, may in this way be directly converted into the acid chloride. The action, however, here proceeds farther, acetic oxide being also formed.

Not only is acetyl chloride formed in the same way as ethyl bromide, but it is decomposed in the same manner by hydrolytic agents. But the action is much more readily effected. When acetyl chloride is poured into cold water it at first sinks to the bottom. It soon dissolves, however, with evolution of heat, and the solution now contains only acetic and hydrochloric acids. The vapour of the chloride is hydrolysed in the same way by the moisture of the air, whence the fuming—

$$C_2H_3O.Cl+H.OH=C_2H_3O.OH+HCl.$$

The phosphorus haloids thus serve to show the presence of hydroxyl both in the alcohol and the acid, and as will be seen later, all forms of hydroxyl are detected by means of these agents. They have virtually the same action as hydrochloric acid, but one much wider in its scope, and act as a stronger acid of this class might be expected to act.

Acetyl Oxide.—It has been seen that ethyl bromide and sodium ethoxide interact to form ethyl oxide, and an analogous acetyl oxide may therefore be expected from the acetyl derivatives (Williamson, 1851). This is actually the case, but as might be anticipated, acetyl oxide, although analogous in composition and manner of formation to ethyl oxide, has very different properties.

To make the oxide, acetyl chloride is simply boiled with excess of recently fused and powdered sodium acetate, in a reflux apparatus in an oil bath, until the clear liquid is free from chlorine. The product is then distilled off, and after redistillation is pure. A more economical method consists in boiling the acetate with phosphorus oxychloride, the acetyl chloride initially formed acting at once further with excess of the salt. The purification is effected as in the first method—

$$C_2H_3O.Cl + C_2H_3O.ONa = (C_2H_3O_2)_2O + NaCl.$$

Acetyl or acetic oxide $(C_2H_3O_2)_2O$, (Gerhardt, 1853), or acetic anhydride, as it is also termed from its relation to the acid, is a colourless liquid of unbearably pungent odour. It boils at 138°, and its specific gravity is 1·073 at 20°. The empirical and molecular formula anticipated by theory is confirmed by the analysis and vapour density, and the rational formula is proved by the manner of formation and decomposition.

Like the chloride, it is hydrolysed much more easily than the corresponding ethyl compound, the decomposition again being effected by simply pouring the liquid into water. If the quantity of the latter is limited, the excess of the oxide falls to the bottom, as it is not affected by the acid, but otherwise it slowly dissolves. The hydrolysis is much hastened by warming the mixture, or by adding caustic soda solution—

$$(C_2H_3O_2)_2O + H_2O = 2C_2H_3O.OH.$$

Reduction of Acetic Acid to Alcohol.—By means of acetic chloride or oxide the acid can be reconverted into alcohol, for when either of these liquids is kept for some days in a loosely stoppered vessel in contact with sodium amalgam, it is slowly reduced by the moisture that enters. The alcohol may be separated by distilling the diluted product after boiling it with alkali to destroy impurities. As both the chloride and the oxide are so readily made from the acid, the action is practically the reverse of the oxidation of alcohol (Linneman, 1868)—

$$C_2H_3O.Cl + 4H = C_2H_5.OH + HCl.$$

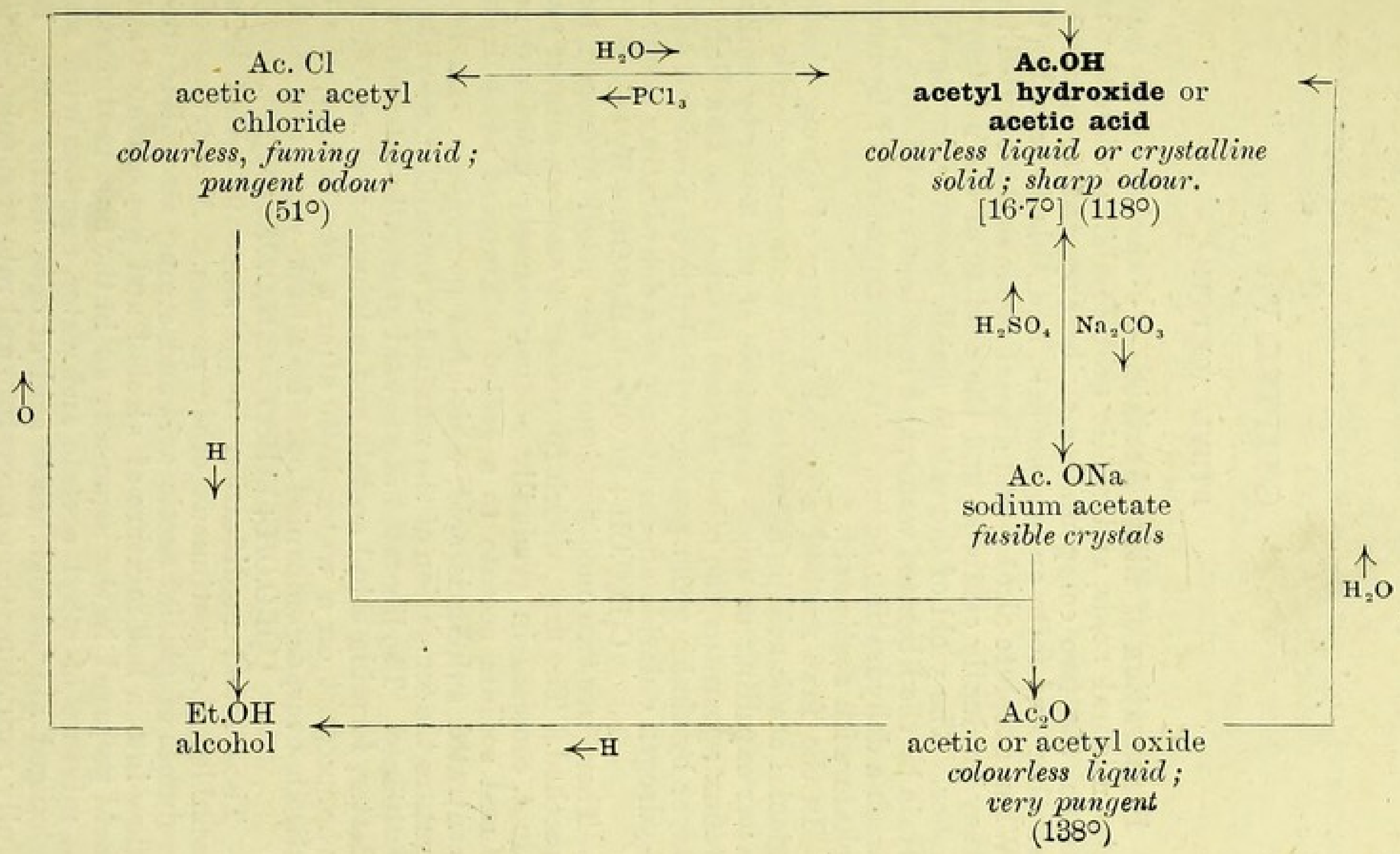
The Acetyl Radicle: Oxylic Hydroxyl.—From these actions it is evident that in the oxidation of alcohol it is the ethyl radicle which is affected, and that it is transformed into an oxidised radicle of the formula

$$C_2H_3O.$$

This is termed acetyl, and assigned the symbol Ac, so that acetic acid is acetyl hydroxide. This negative radicle, thus formed by the substitution of oxygen in the positive ethyl group, is analogous to the radicles of the inorganic acids. It is termed an oxylic or acidic radicle, and the hydroxyl with which it is associated, oxylic hydroxyl. The hydrogen of oxylic hydroxyl is thus more active than that of alkylic hydroxyl.

Synopsis.—From the action of acetic acid with phosphorus chloride and the mineral bases, it is the hydroxide of an acid or oxylic radicle, acetyl, C_2H_3O or Ac, analogous to the inorganic hydroxyacids, and its formula may be written as $C_2H_3O.OH$ or Ac.OH. The phosphorus haloids serve to detect both alkylic and oxylic hydroxyl.

ACETIC ACID AND THE ACETYL RADICLE.



CHAPTER VII

ETHYL ACETATE

Preparation of Ethyl Acetate.—As alcohol forms salts with the mineral acids, and acetic acid combines with the mineral bases, the two compounds may be expected to neutralise one another and form an organic salt, and this is actually the case. When absolute alcohol and glacial acetic acid are boiled together, they gradually combine, and the acidity of the mixture diminishes. The yield of the salt is small, however, owing to hydrolysis by the liberated water, and it is best to withdraw the latter with a dehydrating agent, or to decompose ethyl hydrogen sulphate with acetic acid.

In the first method a cooled mixture of strong alcohol and glacial acetic acid is saturated with hydrogen chloride gas, and after expelling as much as possible of the latter by boiling in a reflux apparatus, the ethyl acetate is salted out as a light mobile layer by shaking the product with brine or powdered salt. The hydrogen chloride appears to act as a dehydrating agent—

$$C_2H_3O.OH + Et.OH = C_2H_3O.OEt + H_2O$$

There are two modifications of the ethyl hydrogen sulphate method. The first, which furnishes at once an almost pure product, consists in gradually adding coarsely powdered, recently fused sodium acetate to a cooled mixture of alcohol and concentrated sulphuric acid, which has previously been heated to ensure the formation of the maximum amount of ethyl hydrogen sulphate. The liberated acetic acid gradually interacts with the latter, forming ethyl acetate and sulphuric acid, and on heating the product on a water bath after a day or two, the acetate distils over, accompanied only by a little water and alcohol—

$$C_2H_3O.OH + EtHSO_4 = C_2H_3O.OEt + H_2SO_4.$$

The second modification is the same in principle, and resembles the continuous ether process. A mixture of equal volumes of glacial acetic acid and strong alcohol is allowed to flow into a hot mixture of alcohol and concentrated sulphuric acid prepared in the same way as in the first modification, and a mixture of ethyl acetate and water, together with some unchanged alcohol and acetic acid at once distils over. By carefully regulating the temperature and rate of supply, eight or ten times the original volume of alcohol can thus be converted.

The product obtained by the second process merely requires drying with calcium chloride, and redistilling, but the others must first be washed with sodium carbonate solution until neutral, and then shaken with brine or concentrated calcium chloride solution to remove alcohol. In both operations the light ethyl acetate floats on the wash liquid.

Composition and Formula of Ethyl Acetate: its Hydrolysis or Saponification.—Ethyl acetate, $C_2H_3O.OEt$ (De Lauraguais, 1759), or as it is sometimes termed, acetic ether or ester, is a colourless, mobile, neutral liquid, having a fragrant vinous odour. It boils at 77°, and its specific gravity is 0·924 at 0°. The empirical formula is C_2H_4O, and as the vapour density is about 44, the molecular formula is $C_4H_8O_2$, which agrees with the anticipated rational formula.

The latter is also confirmed by the hydrolysis, which is readily effected by boiling the liquid with caustic soda solution in a reflux apparatus until its odour is no longer perceptible. Alcohol can be distilled at once from the product, and acetic acid, after strongly acidifying the residue with dilute sulphuric acid—

$$C_2H_3O.OEt + NaOH = C_2H_3O.ONa + Et.OH.$$

The ethereal salt is thus resolved into acid and alcohol, just as a metallic salt is decomposed into acid and base. The process is sometimes termed saponification, from the analogy of the action to that involved in soap making (p. 44).

Further confirmation of the rational formula is afforded by other methods of preparation. Thus when ethyl bromide is heated in a sealed tube with dry silver acetate, the white acetate is converted into the yellowish silver bromide, and on opening the tube the odour of the bromide is replaced by that of ethyl acetate, which is also distinguished by its higher boiling point. The action is analogous to the formation of ether from ethyl bromide and sodium ethoxide, and to that of acetic oxide from acetic chloride and sodium acetate—

$$Et.Br + Ac.OAg = Ac.OEt + Ag.Br.$$

On this account ethyl acetate may be regarded as a compound ether or oxide of the ethyl and acetyl radicles, and as a matter of fact it is intermediate to the ethyl and acetyl oxides in the degree of ease with which it is hydrolysed.

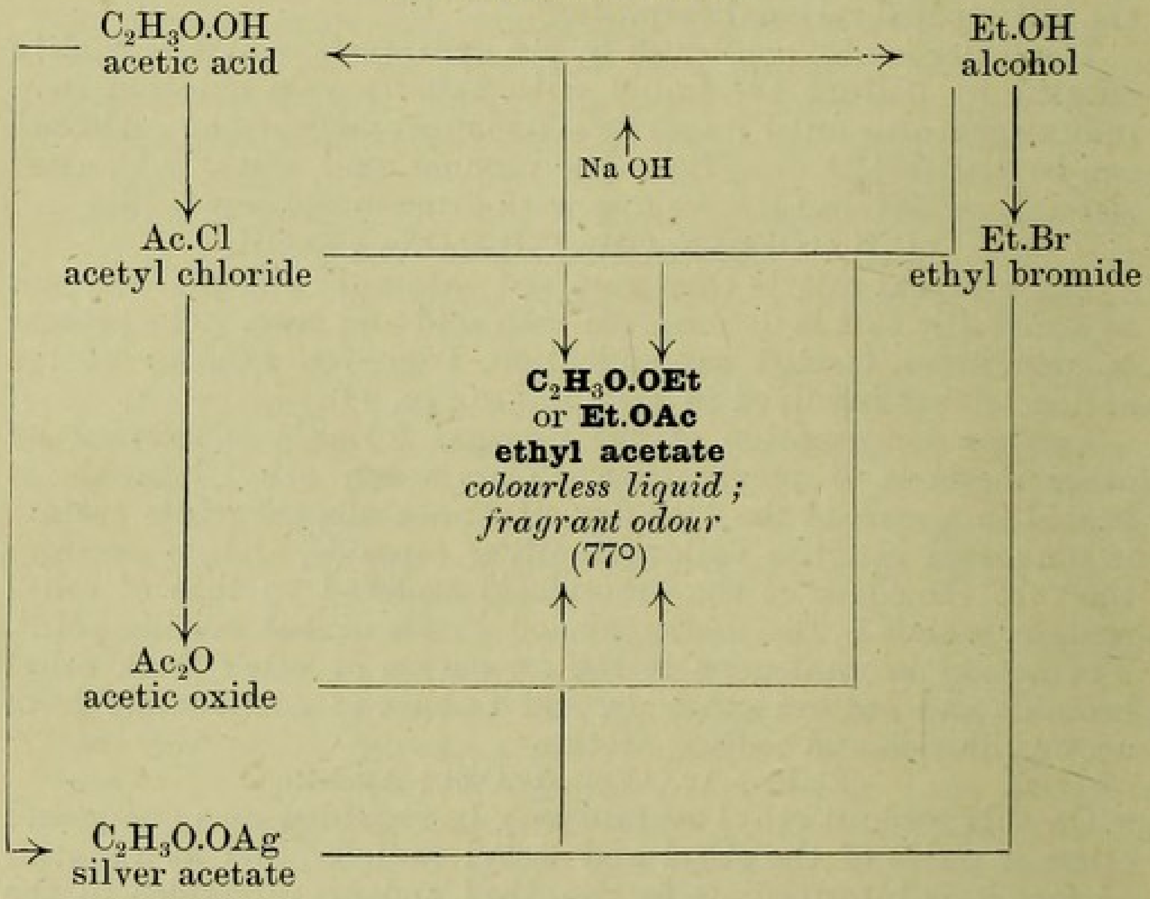
Action of Acetyl Chloride and Oxide on Alcohol: Differentiation of Alkylic from Oxylic Hydroxyl.—Again, when acetic chloride is mixed with absolute alcohol, there is a brisk action, and hydrogen chloride is evolved, and on diluting the product with water, and neutralising it with caustic soda solution, the odour of ethyl acetate is noticeable. The acetate can be isolated by shaking the product with salt, and identified in the manner described above. The action of acetic oxide is similar, except that water is eliminated instead of hydrogen chloride, and that the mixture must be warmed—

$$C_2H_5.OH + AcCl = C_2H_5.OAc + HCl.$$

Now as the acetyl radicle thus takes the place of the hydrogen of the alkylic hydroxyl, and as it is evident from the mode of preparation of the chloride and oxide that they do not affect acids, these substances serve as reagents to differentiate alkylic from oxylic hydroxyl (Schützenberger, 1865). As will be seen later, this is very important.

Synopsis.—Alcohol and acetic acid form a compound, ethyl acetate, which is analogous on the one hand to the metallic salts, and is hence termed an ethereal salt, and on the other hand to ethyl and acetyl oxides. Acetyl chloride and oxide serve to differentiate alkylic from oxylic hydroxyl.

ETHYL ACETATE.



CHAPTER VIII

THE ALCOHOLS AND ACIDS OF THE ACETIC SERIES

Methyl Alcohol and the Methyl Radicle.—Alcohol, acetic acid, and ethyl acetate are types of three large classes of organic compounds: the alcohols, the acids, and the ethereal salts.

The simplest of all the alcohols is methyl alcohol, which is formed in the dry distillation of wood, and thus accompanies acetic acid in crude pyroligneous acid. The head fraction obtained in the purification of this acid is a volatile inflammable liquid termed wood spirit (Boyle, 1661), and consists chiefly of acetone and the new alcohol. To isolate the latter, the crude spirit is repeatedly boiled with quicklime, to eliminate acetic acid and water, and hydrolyse methyl acetate, and is then fractionated to separate the acetone.

The alcohol is also prepared on a large scale, together with several other products, by the dry distillation of "vinasses," the residual liquor from the alcoholic fermentation of beet molasses (p. 172), and it occurs naturally in the oil of the winter-green, a shrub indigenous to New Jersey. The chief constituent of this oil is methyl salicylate (p. 304), an ethereal salt from which the methyl alcohol is set free by hydrolytic agents.

Commercial methyl alcohol still contains some acetone, which is best eliminated by boiling with anhydrous oxalic acid, with which the alcohol forms a crystalline ethereal salt. The methyl oxalate, which separates on cooling the solution, is washed with cold water until the washings cease to give the iodoform reaction, and is then hydrolysed in precisely the same way as ethyl acetate. Finally, the alcohol is distilled off and fractionated, and dehydrated over quicklime (Wöhler).

Pure methyl alcohol, CH_4O (Taylor, 1812), is a colourless liquid, which closely resembles ordinary or ethyl alcohol, but boils at 66°, and has a specific gravity of 0·798 at 15°. Its chemical behaviour is similar to that of the more complex compound in practically every respect. Sodium dissolves in it, forming a crystalline compound, which when heated yields sodium methoxide, $CH_3.ONa$, a white amorphous powder resembling sodium ethoxide, and this is reconverted by water into caustic soda and the alcohol.

The actions of phosphorus bromide and hydrochloric acid are also similar. Methyl bromide, CH_3Br (Bunsen, 1844), formed in the same way as ethyl bromide, is a similar colourless liquid, boiling at 4°, and is hydrolysed by caustic soda to methyl alcohol and sodium bromide. Similarly, the methyl chloride, CH_3Cl (Dumas, 1831), formed by the action of hydrochloric acid differs from ethyl chloride only in that it boils at $-23°$, and is therefore gaseous at ordinary temperatures.

Methyl hydrogen sulphate, $CH_3.HSO_4$, is a syrupy liquid, and methyl sodium sulphate, $CH_3.NaSO_4$, a soft crystalline solid. Both resemble the corresponding methyl compounds, and are hydrolysed in precisely the same way. Methyl oxide or ether, $(CH_3)_2O$ (Dumas), boils at $-23°$, but has the odour of ordinary ether. It is prepared in the same way, and is therefore present in ether made from methylated spirit. Methyl acetate, $C_2H_3O.OCH_3$, made by the action of acetic acid on methyl hydrogen sulphate, is a fragrant liquid which boils at 57°, but is otherwise similar to ethyl acetate, and is hydrolysed by caustic soda in precisely the same manner.

In fact, setting aside physical differences and differences of composition, everything that has been said of ethyl alcohol and its derivatives may be said of methyl alcohol and its derivatives. The simpler alcohol is therefore the hydroxide of an alkylic radicle methyl,

$$CH_3 \text{ or } Me,$$

(Dumas and Péligot, 1834; μέθυ=wine: ὕλη=wood), its rational formula being

$$CH_3.OH \text{ or } Me.OH.$$

Formic Acid and the Formates.—When methyl alcohol is boiled with acid permanganate, it is completely oxidised to carbon dioxide and water, but by exposing it to the mild oxidising action of air in presence of platinum black, an acid oxidation product is obtained (Dumas, 1831). This is identical with the formic acid prepared by macerating and distilling red ants (*formicæ*) or stinging nettles. Formic acid can also be made by distilling starch with manganese dioxide and dilute sulphuric acid (Scheele, 1770), but it is best prepared by the interaction of oxalic acid and glycerol (Berthelot, 1856),

The two substances are simply heated at 120–130° in a distilling flask. Dilute formic acid passes over if crystallised oxalic acid is used, but 90 per cent. acid if the oxalic acid is previously dehydrated. Carbon dioxide is evolved in either case—

$$C_2H_2O_4 = CH_2O_2 + CO_2 \text{ (see p. 125).}$$

The concentrated formic acid is conveniently dehydrated by boiling it in a reflux apparatus with boric anhydride or anhydrous oxalic acid. On distilling the product from an oil bath a glacial acid is obtained, from which the last traces of water can be eliminated by fractional crystallisation as in the case of acetic acid. An older but less convenient method of preparing the anhydrous acid consists in decomposing the lead salt with dry sulphuretted hydrogen at 100°.

Potassium formate is formed quantitatively when a moist stick of potash is exposed to an atmosphere of carbon monoxide at 100°, the absorption being complete in about three days (Berthelot, 1855)—

$$CO + KOH = CHO.OK,$$

and sodium formate is produced by the slow reduction of ammonium carbonate with sodium amalgam.

Formic acid, CHO.OH (Ray, 1670), is a colourless, corrosive liquid, or crystalline solid, which resembles acetic acid, but is more powerful. It fumes slightly in the air, and its odour is much more pungent, recalling that of sulphurous acid. It melts at 8°, and boils at 101°, and its specific gravity is 1·243 at 0°.

The empirical formula is CH_2O_2, and this is the molecular formula calculated from the vapour density, and by the silver method, so that the formation from methyl alcohol is precisely analogous to that of acetic acid from ethyl alcohol—

$$CH_4O + 2O = CH_2O_2 + H_2O.$$

Formic acid resembles acetic acid almost as closely as methyl resembles ethyl alcohol, and its salts are indistinguishable from the acetates except in composition. Thus sodium formate is a crystalline substance, resembling sodium acetate. The soluble red ferric formate, $Fe(CHO_2)_3$, made in the same way as ferric acetate, is hydrolysed by boiling water in a similar manner, to formic acid, and an insoluble, brown, basic salt.

Copper formate, $Cu(CHO_2)_2 + H_2O$, prepared from copper oxide, forms well-defined blue crystals, and lead formate also crystallises well, and is sweet and astringent like lead acetate (Ray).

Methyl formate, CHO.OMe, also, made by the interaction of calcium formate with methyl alcohol saturated with hydrogen chloride gas, or by dry-distilling sodium formate with methyl sodium sulphate—

$$CHO.ONa + MeNaSO_4 = CHO.OMe + Na_2SO_4,$$

is a fragrant liquid boiling at 32°, and like the acetate is hydrolysed to its proximate constituents by alkalies. Ethyl formate is similar, but boils at 54°.

The chloride and anhydride of the formyl radicle, CHO, of which formic acid is the hydroxide, and which might be expected from the analogy to acetic acid, have never been prepared, the product of the action of phosphorus trichloride on the acid at once decomposing into carbon monoxide and hydrogen chloride—

$$3CHO.OH + PCl_3 = 3CO + 3HCl + H_3PO_3.$$

For a similar reason the anhydrous acid cannot be made by the action of sulphuric acid on the sodium salt, formic acid being decomposed into pure carbon monoxide and water by dehydrating agents—

$$CHO.OH = CO + H_2O.$$

As the acid also is so readily oxidised, it has marked reducing powers. When for instance a solution of silver nitrate, to which enough ammonia has been added to exactly redissolve the oxide at first precipitated, is warmed with a neutral solution of a formate, metallic silver is precipitated, usually as a mirror—

$$2AgNO_3 + CH_2O_2 + 4NH_3 + H_2O = 2Ag + 2NH_4NO_3 + (NH_4)_2CO_3,$$

and similarly mercuric chloride is reduced to calomel when its solution is heated with a formate.

Apart from its instability towards oxidising and dehydrating agents, however, formic acid is a true analogue of acetic acid.

Propyl Alcohol, Propionic Acid, and the Higher Alcohols and Acids.—As stated above, there are many alcohols and acids. Several such alcohols of high boiling point are formed in small amount in the alcoholic fermentation of sugar, and as they are sparingly soluble in water, form with the latter a milky tail fraction in the rectification of spirit.

The mixture of alcohols, separated from the accompanying water, is termed fusel oil (Scheele, 1785). Although their boiling points differ considerably, they cannot be completely separated by fractional distillation, probably for the same reason as in the case of alcohol and water. The mixed iodides, however, formed by the action of iodine and red phosphorus on the dry fusel oil, are readily separable in this way, and the separate alcohols obtained by hydrolysing the pure iodides can then be purified and dehydrated much in the same way as ordinary alcohol.

Propyl alcohol, $C_3H_7.OH$ (Chancel, 1853), which constitutes about 3 per cent. of potato fusel oil, is a liquid boiling at 97°, and having a specific gravity of 0·807 at 15°. It resembles ethyl alcohol, but is less pleasant in odour, and burns with a luminous flame, owing to the higher percentage of carbon. Its various derivatives are similar to those of ethyl and methyl alcohols, and there is no need to describe them, the only differences being that the liquid products boil at higher temperatures, and, as a rule, are denser. By the same reasoning as before, therefore, they are the compounds of a propyl radicle, C_3H_7 or Pr.

Propyl alcohol, again, is readily oxidised by acid permanganate, and the acid thus formed is distinguished from acetic acid only by its insolubility in calcium chloride solution. It is salted out as an oily layer (*προτος πιον*=first oil) when this salt is added to its solution.

Propionic acid, $C_3H_5O.OH$ (Gottlieb, 1844), is a colourless liquid, of acid but somewhat rancid odour. It boils at 141°, and freezes at −37°, and its specific gravity is 1·017 at 0°. Its derivatives are precisely similar to those of acetic acid in the manner of their formation and decomposition, and they are therefore compounds of a propionyl radicle, C_3H_5O.

The compounds next in order are butyl alcohol and butyric acid. Butyric acid is found as an ethereal salt in fresh butter (*butyrum*), and can be prepared from butter fat. The clarified fat is heated on a water bath with alcoholic potash until it is entirely dissolved, and the heating is then continued, water being added from time to time until the alcohol is expelled. The product is acidified with dilute sulphuric acid and allowed to cool, and on distilling the clear acid solution, after removing the cake of solid fat acids (p. 45), an aqueous solution of butyric and allied volatile acids passes over. The acids are then salted out with calcium chloride, and separated by fractional neutralisation (p. 96), or by boiling the solution of the calcium salts. Calcium butyrate is much less soluble in hot than in cold water, and separates as a scum. Butyric acid, however, is most easily made by fermentation of lactic acid (p. 141).

Butyric acid, $C_4H_7O.OH$ (Chevreul, 1823), is a somewhat oily liquid, having a sharp and very rancid odour. It melts at $-2°$, and boils at 162°. Its derivatives are precisely similar to those of propionic and acetic acids. Butyl alcohol, $C_4H_9.OH$ (Lieben and Rossi, 1869), a liquid boiling at 117°, and having a distinctly unpleasant odour, occurs to the extent of 6 per cent. in potato fusel oil, but was originally obtained by the reduction of butyric aldehyde (p. 73). It may also be prepared from butyric chloride.

It is unnecessary to mention more than the principal of the remaining analogues of alcohol and acetic acid, although acids and alcohols are known containing all numbers of carbon atoms up to eighteen, and many beyond. Amyl alcohol, $C_5H_{11}.OH$, a liquid boiling at 138° (see also p. 85), is related to valeric acid, $C_5H_9O.OH$, in the same way as butyl alcohol to butyric acid, and both are characterised by their rank, unpleasant odours. Caproïc acid, $C_6H_{11}O.OH$, and capric acid, $C_8H_{15}O.OH$, are oily liquids which occur in combination in goats' butter, and, together with butyric acid, in cows' butter. Octyl alcohol, $C_8H_{17}.OH$, is found in heracleum; pelargonic acid, $C_9H_{17}O.OH$, in the leaves of the geranium.

The Ethereal Salts and Mixed Ethers.—The ethereal salts of many of these alcohols and acids are liquids of very fragrant odour and flavour, and in dilute alcoholic solution are used as fruit essences. The odours and flavours of many of the fruits are, in fact, due to small quantities of these substances. Propyl acetate, for example, has the odour and flavour of pears, and the amyl acetate from fusel oil that of Jargonelle pears. Similarly, ethyl butyrate is used as pineapple flavouring.

Not only, however, are the alkyl radicles variously combined with the acids in these ethereal salts, but they are united with one another in a series of compounds, termed the mixed ethers, the existence of which confirms the view that ordinary ether is ethyl oxide.

Thus methyl ethyl ether, $CH_3.O.C_2H_5$, a liquid boiling at 11°, and resembling ordinary ether, is formed by the interaction both of methyl iodide with sodium ethoxide, and of ethyl iodide with sodium methoxide—

$$CH_3I + NaOC_2H_5 \rightarrow CH_3.O.C_2H_5 \leftarrow CH_3ONa + C_2H_5I,$$

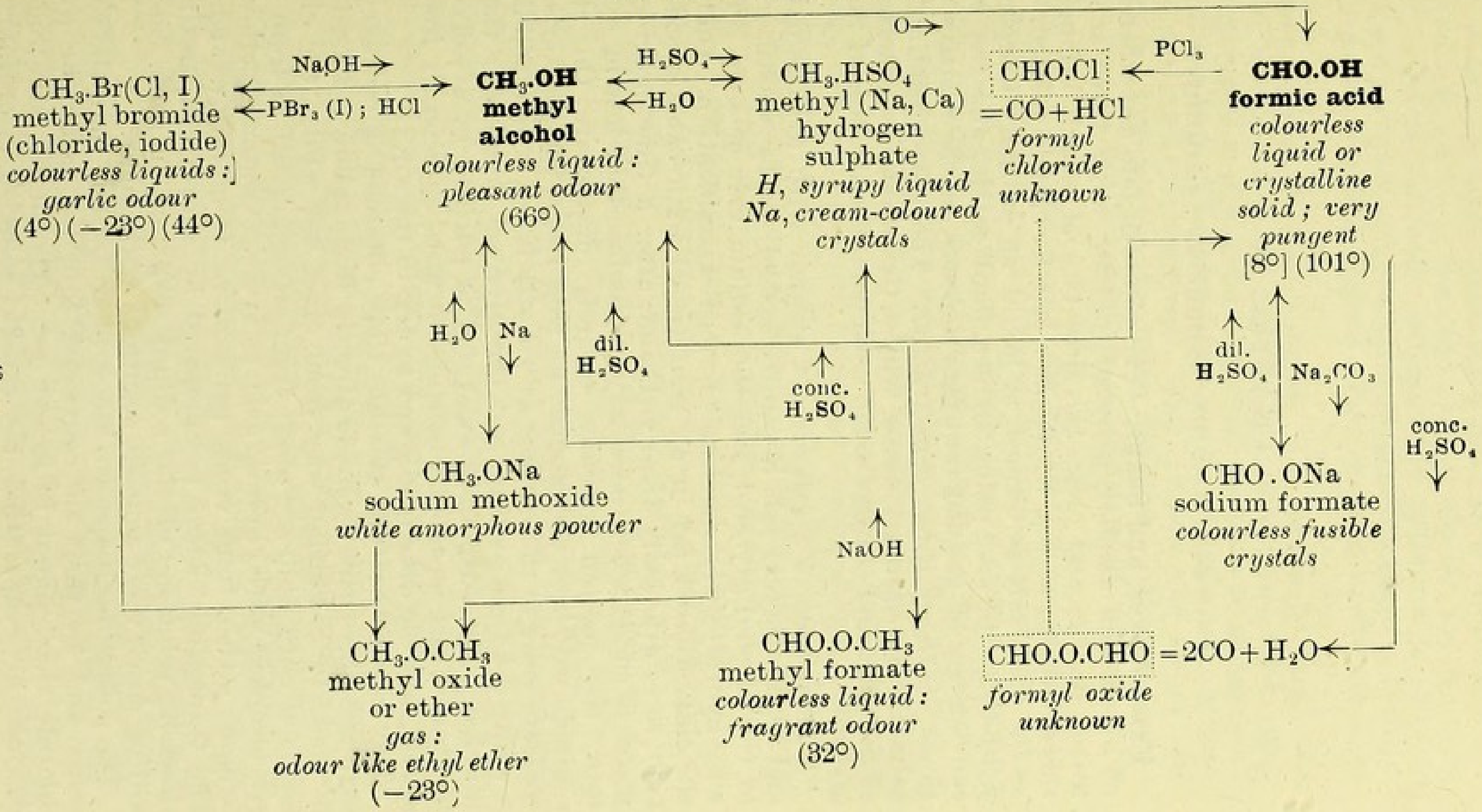
so that the presence of both alkyl radicles cannot be doubted. Similarly, it is formed both by the action of methyl alcohol on ethyl hydrogen sulphate, and by that of ethyl alcohol on methyl hydrogen sulphate, and is therefore present in the ether made from methylated spirit.

A still more striking proof that the conversion of alcohol into ether is due to its interaction with ethyl hydrogen sulphate, and is not a mere process of dehydration, is afforded by the action of ordinary alcohol on a hot mixture of sulphuric acid and amyl alcohol. The mixture initially contains amyl hydrogen sulphate, and the first product is ethyl amyl ether, $C_2H_5.O.C_5H_{11}$, a liquid boiling at 112°. But as the action proceeds, and ethyl hydrogen sulphate is formed, the mixed ether is accompanied by a steadily increasing amount of ordinary ether, until finally the latter alone passes over. The residue in the distilling flask now contains only ethyl hydrogen sulphate, which can be isolated in the manner already described. Before these mixed ethers were made (Williamson, 1851), the mechanism of the formation of ether from alcohol was not clearly understood.

Synopsis.—Alcohol, acetic acid, and ethyl acetate, are types of the three classes of alcohols, acids, and ethereal salts, the members of which form series showing well-marked and analogous gradations in properties.

METHYL ALCOHOL AND FORMIC ACID.

(The Propyl-propionyl and higher charts are similar, with the addition that the acid chlorides and oxides are known.)



CHAPTER IX

THE FATTY ACIDS: HOMOLOGY: ISOMERISM

Fats, Waxes, and Soaps.—The common fats are ethereal salts of a complex alcohol, glycerol (p. 129), with three acids, palmitic, stearic, and oleïc, the first two of which belong to the acetic-butyric series, whilst the last is closely related. Oleïn, as the olëic salt is termed, is liquid at ordinary temperatures, whilst stearin and palmitin are hard solids, and the varying consistency of the different fats depends on the relative proportions of these three constituents. The corresponding alkali salts are the ordinary soaps, whilst the waxes are ethereal salts of the fatty and similar acids with complex alcohols of the ethyl series.

Mutton suet is a mixture of stearin with a little palmitin, and as an ethereal salt is readily hydrolysed by caustic alkalies to the alcohol glycerol, and the sodium salt or soap. This is why hydrolysis is sometimes termed saponification. On boiling the clear filtered fat in an iron vessel with caustic soda solution, it is gradually dissolved, and, after a time, provided that water is added when necessary, to replace that lost by evaporation, the molten globules entirely disappear. On stirring common salt into the product at this stage, the soap or sodium stearate rises to the surface as an oily layer, which solidifies to a white cake on cooling, and the glycerol remains in the alkaline lye. The soap thus separated is purified by dissolving in hot water, and repeatedly salting out until sufficiently free from alkali, and the cake is allowed to dry in the air.

The impure sodium stearate thus obtained is ordinary curd soap, which is usually made directly from tallow. Castile soap is made in a similar way from olive oil, whilst the cheaper forms of curd soap are made from cocoa-nut oil, or from palm-oil, bleached with chromic acid mixture. Common yellow soap is made either from crude palm-oil, or from tallow and resin. The transparent soaps are prepared by simply evaporating the alcoholic solutions of the sodium soaps, or, in some cases, by boiling down their aqueous solutions with sugar.

The potassium soaps are much more soluble than the sodium soaps, and as they are converted into the latter by sodium chloride, they cannot be salted out. The highly alkaline jelly obtained by evaporating the caustic solution is ordinary soft soap. It is usually made from train oil. It is only the alkali soaps which are soluble. The lead soap or plaster, for example, formed by boiling fat with litharge and water, is a soft, insoluble mass, and the magnesium and calcium soaps constitute the curdy scum which is formed when soap is used with hard water.

Soap was known to the Romans, who probably made the necessary caustic alkali by boiling seaweed ashes with lime. Its detergent action is due to its hydrolysis by a large excess of water to free alkali, which combines with and loosens the greasy dirt, and an insoluble acid salt, which forms the lather and envelopes and isolates the dirt thus loosened. Before soap was known, free caustic alkali and ammoniacal urine were used for cleaning.

Palmitic and Stearic Acids: Cetyl Alcohol.—The fat acids are set free in the normal manner by decomposing the soaps with dilute mineral acids, and stearic acid is readily obtained in this way from mutton suet soap. The soap is boiled with excess of dilute sulphuric acid, and the mixed oily acids rise to the surface and solidify to a cake on cooling. After thoroughly washing with water, each time re-melting and cooling, the stearic acid can be separated from the accompanying palmitic acid, by fractional crystallisation from hot alcohol, in which the latter is the more soluble. It is more readily purified, however, by adding to the hot alcoholic solution of the impure acids enough of a similar solution of magnesium acetate to precipitate about one-fourth of the acids present. The precipitate thus thrown down consists of magnesium stearate, which, after washing with alcohol, is pure. This is a general method of separating acids of this kind (Heintz, 1852). "Stearin" candles are made of the mixed stearic and palmitic acids obtained by hydrolysing tallow with superheated steam or dilute sulphuric acid.

Palmitic acid is best obtained from palm oil, which consists principally of palmitin and oleïn (Heintz). The soap is made and decomposed in the manner just described, and the palmitic acid is separated from the freely soluble oleïc acid (p. 137) by crystallisation from alcohol. The crystallisation is of course repeated until the melting point remains constant. Sodium palmitate is also obtained by fusing oleïc acid with caustic soda.

Palmitic acid, $C_{16}H_{31}O.OH$ (Chevreul, 1813), crystallises from alcohol or ether in white needles, and melts at 62°. Stearic acid, $C_{18}H_{35}O.OH$ (Chevreul; *στεάρ*=tallow), forms pearly plates, and melts at 69°. Both acids are inodorous and practically tasteless, but their alcoholic solutions redden litmus. They are decomposed when distilled under ordinary pressure, but they can be distilled unchanged under diminished pressure (p. 150), the boiling points being thus much reduced.

As already mentioned, the natural waxes are ethereal salts of the fatty acids with alcohols of the ethyl series. Spermaceti, for example, the wax which crystallises out from sperm oil when removed from the whale and cooled, is cetyl palmitate, $C_{16}H_{31}O.OC_{16}H_{33}$. The cetyl alcohol can be isolated by hydrolysing the wax with boiling alcoholic potash, and precipitating the palmitic acid from the resulting solution with barium chloride. The product is filtered from the barium soap, and the cetyl alcohol which separates on concentrating the solution is recrystallised from ordinary alcohol.

Cetyl alcohol, $C_{16}H_{33}.OH$ (Chevreul, 1823), is a white, crystalline, wax-like substance, melting at 49°, and is inodorous and tasteless. When fused with potash it is oxidised to potassium palmitate, hydrogen being evolved, and conversely, palmitic acid is reduced to cetyl alcohol when warmed with zinc dust and acetic acid. These are general reactions of the eleven-carbon and higher alcohols and acids.

Beeswax consists of myricyl palmitate, $C_{16}H_{31}O.OC_{30}H_{61}$, and ceryl cerotate, $C_{27}H_{53}O.OC_{27}H_{55}$.

Homologous Series: the Aliphatic Alcohols and Acids.—The alcohols and acids of which acetic acid and ethyl alcohol are the types, thus form two parallel series, which at the lower ends are physically and chemically very different, but at the higher ends physically very similar.

The lowermost members of the two series are liquids having marked and pleasant odours, and are freely soluble in water. As the series are ascended, the solubilities diminish, and the liquids become more viscous and oily, and at the same time their odours become unpleasant. The ten-carbon alcohol and acid are practically insoluble in water, but have only faint odours; and as already noted, the sixteen-carbon compounds, cetyl alcohol and palmitic acid, are wax-like, crystalline substances, which are quite insoluble in water, and odourless. The same gradation of properties is noticeable in the ethereal salts, although the odours of these, however powerful, are never actually unpleasant.

The acids of the acetic series are termed the fatty or aliphatic acids, from the origin of the higher members, and the whole group of compounds, from their relationship to the acids, the fatty or aliphatic group.

With respect to composition a very remarkable relationship exists amongst the individual members of the several series. It has been seen that the alcohols and acids, as organic hydroxides, bear a general analogy to the alkali hydroxides and inorganic hydroxyacids, and this analogy extends to the graduated increase in molecular weight; but instead of the increase being only approximately regular, as in the inorganic series, it is perfectly regular and constant.

THE ALIPHATIC ALCOHOLS AND ACIDS.

Methyl alcohol	$CH_3.OH$	⟷	Formic acid	$CHO.OH$
Ethyl alcohol	$C_2H_5.OH$	⟷	Acetic acid	$C_2H_3O.OH$
Propyl alcohol	$C_3H_7.OH$	⟷	Propionic acid	$C_3H_7O.OH$
Butyl alcohol	$C_4H_9.OH$	⟷	Butyric acid	$C_4H_7O.OH$
Amyl alcohol	$C_5H_{11}.OH$	⟷	Valeric acid	$C_5H_9O.OH$
. . . . . .	. . . .		. . . . .	. . . .
Cetyl alcohol	$C_{16}H_{33}.OH$	⟷	Palmitic acid	$C_{16}H_{31}O.OH$
Octodecyl alcohol	$C_{18}H_{37}.OH$	⟷	Stearic acid	$C_{18}H_{35}O.OH$
. . . . . .	. . . .		. . . . .	. . . .

The members of these series differ in formulæ uniformly by CH_2, or a multiple of this group, and in molecular weight by 14, or a multiple of this number (Schiel, Dumas, 1842)—

$$C_2H_5.OH - CH_3.OH = CH_2 = 14.$$

$$C_{18}H_{35}O.OH - CHO.OH = 17\ CH_2 = 17 \times 14.$$

This relationship, unknown amongst inorganic compounds, is termed homology (Gerhardt, 1844; *ὁμόλογος*, agreeing). The series are termed homologous series, and their members, homologous compounds, or homologues. Methyl alcohol is thus the lower homologue of ethyl and cetyl alcohols, and stearic acid the higher homologue of formic and valeric acids.

It is obvious that the homology extends to all the series of compounds. Methyl chloride, for example, is homologous with ethyl and propyl chlorides, and propyl hydrogen sulphate with the other alkyl sulphates.

Homologous compounds may be represented by general formulæ. The general formula of the alcohols is

$$C_nH_{2n+1}.OH \text{ or } C_nH_{2n+2}O,$$

and that of the acids.

$$C_nH_{2n-1}O.OH \text{ or } C_nH_{2n}O_2,$$

the alkyl and acidyl radicles being respectively represented by the formulæ—

$$C_nH_{2n+1} \text{ and } C_nH_{2n-1}O.$$

Isomerism and Metamerism.—Many of the oxides and hydroxides are related in another manner, which is likewise peculiar to organic compounds. It often happens in the varied combinations of the homologous radicles that compounds are formed, which although quite distinct from one another, have the same composition and formula. Thus:

Methyl propionate	$C_3H_5O.OCH_3$,
Ethyl acetate	$C_2H_3O.OC_2H_5$ and
Propyl formate	$CHO.OC_3H_7$

all have the same empirical formula, C_2H_4O. Methyl formate and acetic acid, and alcohol and methyl ether, form similar pairs.

Compounds such as these, which have the same composition and formulæ, but different properties, are termed isomeric compounds, or isomerides (Berzelius, 1838; *ἴσος*=equal, *μέρος*=a part), and the relationship between them, isomerism. As will be seen later, there are many forms of isomerism amongst organic compounds. Here it is due to the homology of the combined radicles, and is termed metamerism. Two compounds are metameric, when the sums of their radicles are equal—

$$C_3H_5O + CH_3 = C_2H_3O + C_2H_5 = CHO + C_3H_7 = C_4H_8O.$$

Synopsis.—The fats, waxes and soaps are ethereal or metallic salts of complex acids of the acetic series, and on this account the acetic and related series are collectively termed the fatty or aliphatic group. The members of the various series differ in composition by regular atomic increments, and are hence termed homologous. For the same reason many of them have the same composition, but different properties, and are termed isomeric.

SECTION II

SYNTHESIS AND MOLECULAR STRUCTURE

CHAPTER X

ACETAMIDE AND ETHYLAMINE

Acetamide.—The Organic compounds dealt with in the preceding chapters bear so far a decided analogy to the acids, alkalies and salts of Inorganic Chemistry, but a group of Organic nitrogen derivatives has now to be considered, which exhibits the mutual relations of these compounds in a different light. It has been seen that ethyl acetate is readily hydrolysed to its proximate constituents by alkalies, in the same way as a metallic salt, and it might be thought from analogy that ammonia would have the same action. But it is not so, for instead of ammonium acetate, acetamide, a dehydration product of this substance is obtained.

When ethyl acetate is added to an equal volume of concentrated ammonia, the liquids do not at first mix, but they become homogeneous after a day or two, if occasionally shaken. The action is more quickly brought about by heating in a sealed tube. On distilling the product, the excess of ammonia is first expelled, and then a solution of ammonia in dilute alcohol, followed by water alone. The alcohol can be separated and identified by distillation with dilute sulphuric acid. Finally the thermometer rises rapidly to over 200°, and an oily liquid passes over, which soon crystallises to a white solid. It is best to remove the condenser at this stage, and receive the distillate in a test tube cooled with wet filter paper.

The substance thus obtained usually melts at about 60°, but by removing the accompanying liquid by pressure between filter paper, the melting point (p. 27) is raised 10° or more, and on re-melting and repeating this fractional crystallisation eventually becomes constant.

Acetamide, $C_2H_3O.NH_2$ (Dumas, 1847), is a colourless, crystalline substance, which melts at 82°, and boils at 222°. It is freely soluble in water and alcohol. The crude product smells like mice, but this is due to an impurity, for after repeated recrystallisation from dry ether it becomes odourless.

Detection and Estimation of Nitrogen.—Acetamide contains nitrogen as well as carbon and hydrogen. The presence of nitrogen in an organic substance is proved by heating it either with soda-lime, when ammonia is evolved, and can be recognised by the usual tests, or with sodium or potassium, when the alkali cyanide is produced. The latter test is applicable to all substances. The bulb tube is broken by plunging the hot end into a little water, and the solution of cyanide filtered from carbonaceous matter, and examined by the Prussian blue test (p. 205).

Nitrogen is estimated as ammonia, or as the free gas. In the ammonia processes the substance is either heated to redness with soda-lime, when the ammonia is expelled directly, or it is boiled with concentrated sulphuric acid and a little permanganate or mercuric oxide, and the ammonia liberated by caustic alkali from the ammonium sulphate thus produced (Kjeldahl). In any case the gas is collected in dilute hydrochloric acid, and its amount estimated by means of the insoluble ammonium platinochloride, or volumetrically. Neither of the ammonia processes is quite satisfactory, as many substances do not yield the whole of their nitrogen under this treatment.

The best method of estimating nitrogen consists in burning the substance with copper oxide in a combustion tube, and measuring the liberated nitrogen (Dumas). It is termed the absolute method. The substance is mixed with part of the copper oxide, instead of resting in a boat as in the carbon combustion, and carbon dioxide is passed through the tube before and after the combustion, to expel the air and nitrogen. The gases, after passing over red-hot copper gauze, to decompose nitrogen oxides, are collected in a graduated tube over mercury, and the carbon dioxide is absorbed by strong caustic potash solution. The weight of nitrogen is then calculated from the volume of gas remaining.

Thus:

0·1096 gram of acetamide

yields approximately

22·6 cc. of moist nitrogen,

measured over water at 20° and 769 mm.

The weight of the gas is accordingly

0·0262 gram,*

and the percentage of nitrogen therefore

$(0{\cdot}0262/0{\cdot}1096) \times 100$ or 23·9.

In the estimation of carbon and hydrogen in nitrogenous substances a long roll of red-hot copper gauze is placed after the copper oxide, to decompose any oxides of nitrogen that may be formed.

Relation of Acetamide to Acetic Acid and Ammonia.—The empirical formula of acetamide determined from the analysis is

C_2H_5NO,

---

* $22{\cdot}6 \times (752/760) \times (273/293) \times 0{\cdot}001256$ ($0{\cdot}001256$ = weight of 1 cc. of nitrogen at 0° and 760 mm.; pressure of water vapour at 20° = 17 mm.).

and this is the molecular formula indicated by the vapour density. The formation of the substance from ethyl acetate is therefore represented by the equation

$$C_2H_3O.OEt+NH_3=C_2H_5NO+Et.OH,$$

which also accounts for the liberation of the alcohol.

Now when acetamide is boiled with caustic soda solution, it gives off the whole of its nitrogen as ammonia, and on distilling the residue with dilute sulphuric acid, acetic acid passes over. The decomposition is thus a simple hydrolysis. The same hydrolysis is effected by boiling the substance with dilute sulphuric acid—

$$C_2H_5NO+NaOH=C_2H_3O.ONa+NH_3.$$

As acetamide is both made from and convertible into acetic acid, it must contain the acetyl radicle, so that its rational formula is that stated above. It is therefore derived from acetic acid by the exchange of hydroxyl for amidogen, and the ammonia in its formation behaves as nitrogen hydride, and not as ammonium hydroxide as in most of its Inorganic actions.

The formula of acetamide is fully confirmed by other modes of formation. It is produced, for example, when acetic chloride is heated with ammonium carbonate, and can be separated from undecomposed material by fractional distillation (Gerhardt, 1853)—

$$C_2H_3O.Cl+NH_3=C_2H_3O.NH_2+HCl.$$

It is also formed by simply distilling ammonium acetate. Glacial acetic acid is neutralised with powdered ammonium carbonate, the action being completed on a water bath, and the dried product is at once distilled. Water and a little ammonia and acetic acid first pass over, but when the temperature reaches 180°, the distillate solidifies, and is purified in the manner already described. The lower fraction is neutralised with a further quantity of the carbonate and again distilled, the operation being repeated until the quantity is insignificant (Kündig, 1858)—

$$C_2H_3O.ONH_4=C_2H_3O.NH_2+H_2O.$$

The constitution of acetamide is further confirmed by the practically neutral character of the substance. It behaves both as a feeble acid and as a feeble base. Thus on warming its aqueous solution with mercuric oxide, the latter dissolves, and on cooling the solution, a crystalline mercury acetamide, $Hg(NHAc)_2$, separates. On the other hand, on passing dry hydrogen chloride into an ethereal solution of the amide, a crystalline hydrochloride, $AcNH_2, HCl$, is precipitated. The latter, however, is very acid and unstable, and at once decomposed by water.

But acetamide may also be regarded from another point of view, namely as ammonia, in which one of the hydrogen atoms is replaced by acetyl—

$$NH_2.Ac,$$

and this view is borne out by its behaviour with nitrous acid. The acid is conveniently generated in the solution. The cold aqueous solution of the acetamide is strongly acidified with dilute sulphuric acid, and a cold solution of sodium nitrite added to it, with constant stirring, until the presence of a slight excess of nitrous acid is shown by the blueing of a potassium-iodide-starch paper dipped into the liquid. On warming the product, or even before, a brisk effervescence sets in, and abundance of nitrogen is evolved, and finally on distilling the solution, acetic acid passes over. The acetamide here behaves in precisely the same way as ammonia itself—

$$Ac.NH_2 + NO.OH = Ac.OH + N_2 + H_2O\,;$$
$$H.NH_2 + NO.OH = H.OH + N_2 + H_2O.$$

Acetonitrile.—Acetamide can be still further dehydrated. When it is roughly mixed with twice its bulk of phosphorous pentoxide, and gently heated in a small flask or test tube connected with a condenser, a colourless liquid passes over, whilst phosphoric acid remains behind. After redistillation, the liquid boils at a fairly constant temperature, and is approximately pure. The same product can be directly obtained from ammonium acetate, though with the expenditure of a much larger quantity of the pentoxide.

Acetonitrile, C_2H_3N (Dumas, 1847), is a colourless volatile liquid, which boils at 82°. It has a sharp but agreeable odour, and burns readily with a characteristic purple-mantled flame. The empirical formula is that stated above, and this is also the molecular formula indicated by the vapour density. The nitrile thus bears the same relation to acetamide, as the latter to ammonium acetate, and it can, in fact, be reconverted into the amide by heating with water in a sealed tube at 180°—

$$C_2H_3O.NH_2 \longleftrightarrow C_2H_3N + H_2O.$$

Like acetamide, acetonitrile is hydrolysed by alkalies and acids to acetic acid and ammonia, and as will be seen presently, this reaction is of great importance. The liquid is simply boiled with caustic soda solution in a reflux apparatus, until ammonia ceases to be evolved, and on distilling the residual liquid with excess of dilute sulphuric acid the acetic acid passes over—

$$C_2H_3N + NaOH + H_2O = C_2H_3O.ONa + NH_3.$$

Ethylamine.—Acetonitrile not only takes up water, but it readily combines with an equivalent amount of hydrogen. When the nitrile is dissolved in dilute sulphuric acid, and zinc added in small quantities from time to time, its odour eventually disappears, and on distilling the product with excess of caustic soda, and collecting the distillate in a little water, an alkaline solution is obtained, which is strikingly like ammonia in odour and general actions.

But the hydrochloride obtained by neutralising the liquid and evaporating it to dryness on a water bath is soluble in alcohol, and the gas which is liberated on heating the hydrochloride with lime is inflammable. It is termed ethylamine.

A better yield is obtained by reducing the boiling alcoholic solution of the nitrile with metallic sodium. The operation is carried out in a reflux apparatus supplied with condensing water at about 50°, so that most of the alcohol returns, whilst the gas passes over and is collected in dilute hydrochloric acid.

The ethylamine hydrochloride made in either of these ways (Mendius, 1862) is always accompanied by some ammonium chloride, from which it is separated by extracting the evaporated residue with warm absolute alcohol, in which the inorganic chloride is insoluble. The solution is filtered and the alcohol distilled off on a water bath. The free ethylamine is prepared, as stated above, by heating the hydrochloride with lime, as in the preparation of ammonia, and after drying with quicklime is condensed in a freezing mixture.

Ethylamine, $C_2H_5.NH_2$ (Wurtz, 1848, see also p. 215), is a colourless volatile liquid, which boils at 18°, and has a specific gravity of 0·699 at 8°. Its odour is strongly ammoniacal, but at the same time recalls that of stale fish. The solution has most of the properties of aqueous ammonia. It fumes with hydrochloric acid, is strongly alkaline, absorbs carbon dioxide freely, and precipitates metallic hydroxides. The vapour is exceedingly soluble in water, but is heavier than air, and as already stated, it is inflammable, and can be condensed to a liquid at ordinary temperatures.

The presence of nitrogen in ethylamine is proved by the formation of cyanide when its vapour is passed over heated sodium, and the empirical and molecular formula deduced from the analysis, and vapour density is that indicated above. No oxygen is present, and the substance is therefore formed by direct addition of hydrogen to acetonitrile—

$$C_2H_3N + 4H = C_2H_7N.$$

Relation of Ethylamine to Alcohol and Ammonia.—From the mode of its preparation it is evident that unlike acetamide and acetonitrile, ethylamine is stable towards alkalies and acids. In this respect it resembles ammonia precisely. It forms stable additive salts also, similar to the ammonium salts. Ethylamine hydrochloride, for example, C_2H_7N, HCl, is a feathery crystalline substance.

Whilst, however, ethylamine differs from acetamide in its behaviour with acids and alkalies, it resembles it precisely in its action with nitrous acid. When a solution of the base in excess of dilute sulphuric acid is warmed with nitrous acid under the conditions already described, a similar action takes place. The whole of the nitrogen is evolved in the free state, and on distilling the product alcohol passes over (Hofmann, 1849). This reaction afforded the first method of converting acetic acid into alcohol, the reduction of acetyl chloride and of aldehyde (p. 69), having been effected subsequently to that of acetonitrile (Mendius, 1862).

Ethylamine thus bears the same relation to alcohol as acetamide to acetic acid, and is therefore represented by a rational formula analogous to that of acetamide. The amine may therefore, like the amide, be regarded as a derivative of ammonia, in which one of the hydrogen atoms is replaced by ethyl.

This view is confirmed by its preparation from ammonia and the ethyl haloids (Hofmann, 1849). Ethyl chloride, for example, is heated in a closed vessel at 100° with excess of alcohol which has been saturated with ammonia gas at 0°. After an hour the product is cooled and filtered from some ammonium chloride which crystallises out, and the excess of ammonia and part of the alcohol are distilled off on a water bath. The ethylamine hydrochloride separates on cooling—

$$C_2H_5Cl + NH_3 = C_2H_5.NH_2 + HCl = C_2H_5.NH_2,\ HCl.$$

Ethylamine may also be made in other ways. It was first prepared from ethyl cyanate (p. 214).

Besides ordinary salts, ethylamine, like ammonia, forms compounds with metallic salts. The most important of these is the platinochloride, an orange crystalline substance, resembling ammonium platinochloride. It is precipitated in the same way as the latter by adding platinum chloride to an aqueous solution of the hydrochloride, and is purified by washing with alcohol and ether. The aurochloride and mercuriodide are similar crystalline compounds.

Determination of Molecular Weight by the Platinum Method.—The molecular weight of basic ammonia derivatives, such as ethylamine, can be determined by analysis of the platinochlorides, for these, like ammonium platinochloride, are reduced to the metal when heated to redness; 0·3706 gram of ethylamine platinochloride yields, for example, approximately

0·1457 gram of platinum.

Now the formula of ammonium platinochloride being $2(NH_3 . HCl), PtCl_4$, that of the ethylamine compound, from analysis and analogy, is

$$2(NH_2Et,\ HCl),\ PtCl_4,$$

and its molecular weight is accordingly

$$2(M + 1 + 35{\cdot}4) + 198 + 4 \times 35{\cdot}4,$$

where M is the molecular weight of the base.

But the molecule contains an atom of platinum, the relative amount of which is therefore as

$$198 : [2(M + 1 + 35{\cdot}4) + 198 + 4 \times 35{\cdot}4].$$

Hence

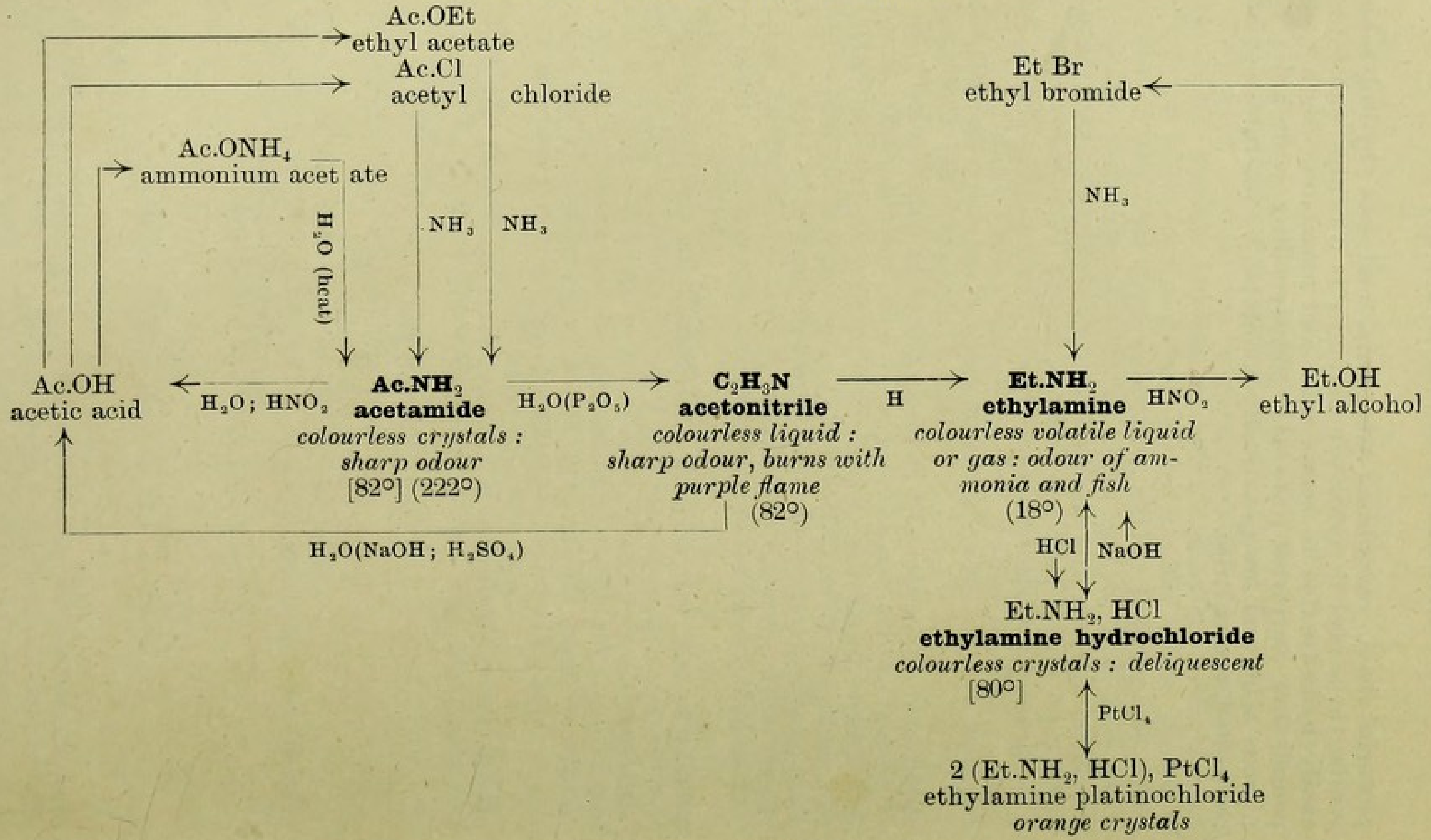
$$\frac{198}{2(M + 1 + 35{\cdot}4) + 198 + 4 \times 35{\cdot}4} = \frac{0{\cdot}1457}{0.3706},$$

from which

$$M = 45{\cdot}6.$$

Synopsis.—The ethyl and acetyl radicles form nitrogen compounds, which bear the same relation to ammonia as the alcohols and acids to water. The alkyl derivative, ethylamine, is a powerful base, resembling ammonia, and not hydrolysable, whilst the acidyl derivative, acetamide, is a neutral substance, easily hydrolysable to acetic acid and ammonia. Both compounds are converted into the corresponding hydroxides by nitrous acid, and are genetically connected by an intermediate compound, acetonitrile.

ACETAMIDE AND ETHYLAMINE.



CHAPTER XI

THE CYANIDE SYNTHESIS

Formonitrile or Hydrogen Cyanide.—Acetamide, acetonitrile and ethylamine are types of three great classes of compounds, to which they bear the same relation as ethyl alcohol and acetic acid to the aliphatic alcohols and acids. These amides and amines resemble their prototypes so closely, however, that it is unnecessary to discuss them in detail. Formamide, $CHO.NH_2$, for example, an oily liquid boiling at 192°, is made by the action of ammonia on ethyl formate. Like acetamide it is hydrolysed to ammonia and the acid when boiled with caustic soda, and with the exception that it does not solidify at ordinary temperatures, is very like its homologue—

$$CHO.OEt + NH_3 = CHO.NH_2 + Et.OH;$$
$$CHO.NH_2 + NaOH = CHO.ONa + NH_3.$$

But the nitriles are of great importance, for they are identical with the alkyl cyanides, and thus afford a means of transition from one alkyl series to another. The formonitrile, CHN, for example, obtained by distilling the amide with phosphorus pentoxide,

$$CHO.NH_2 = CHN + H_2O,$$

is none other than the hydrocyanic or prussic acid, HCN, prepared from the metallic cyanides. By distilling potassium cyanide or ferrocyanide (p. 205) with dilute sulphuric acid, dilute hydrocyanic acid is obtained—

$$KCN + H_2SO_4 = HCN + KHSO_4,$$

from which the concentrated acid can be prepared by quickly salting out with calcium chloride. The anhydrous substance is obtained by redistilling this product, and dehydrating the vapour with warm calcium chloride before condensing it.

Hydrogen cyanide, HCN (Scheele, 1782), whether prepared from metallic cyanides or formamide, is a mobile, volatile liquid, which freezes at –15°, boils at 26°, and burns with a purple-mantled flame. Its odour is faint but repulsive, and it is excessively poisonous, inhalation of the vapour even being dangerous.

Synthesis of Formic Acid and Methyl Alcohol from Carbon.—Hydrocyanic acid, being identical with formonitrile, is hydrolysed by alkalies to the alkali formate and ammonia, in the same way as acetonitrile to the acetate. The hydrolysis may, in fact, be effected by simply boiling an aqueous solution of potassium cyanide in a reflux apparatus. Ammonia is evolved in abundance, and eventually nothing but potassium formate remains—

$$KCN+2H_2O=[HCN+KOH+H_2O=]CHO.OK+NH_3.$$

The entire conversion requires some time, and the cyanide remaining after an hour's boiling is conveniently eliminated by gently boiling with dilute sulphuric acid in an open vessel until the product ceases to give the Prussian blue reaction. Some of the formic acid is, of course, volatilised, but on distilling the filtered liquid sufficient passes over for identification.

Now, potassium cyanide can be made in small amount by passing nitrogen over a red-hot mixture of charcoal and potassium carbonate, and barium cyanide is made in a similar manner, and on a manufacturing scale, by passing the gas over a mixture of barium carbonate and coke, heated in an electric furnace—

$$BaCO_3+4C+N_2=Ba(CN)_2+3CO,$$

and it follows, therefore, that formic acid may be made from its elements.

Further, hydrocyanic acid is reduced by zinc and dilute sulphuric acid in precisely the same way as acetonitrile—

$$CHN+4H=CH_3.NH_2,$$

and the methylamine thus formed (p. 215) is a gas, which resembles ethylamine in almost every respect, but condenses only at -6°. It resembles its homologue in all its chemical actions, and in particular, is converted by nitrous acid into methyl alcohol—

$$CH_3.NH_2+NO.OH=CH_3.OH+N_2+H_2O.$$

Methyl alcohol can therefore be made from its elements.

Methyl Cyanide: Conversion of Methyl Alcohol into Acetic Acid and Ethyl Alcohol: Third Rational Formulæ. — The synthesis of formic acid from hydrogen cyanide suggests that acetic acid may be made in the same way from methyl cyanide, and this is actually the case.

Methyl cyanide is readily made by dry-distilling a mixture of methyl potassium sulphate with potassium cyanide (Dumas, 1847)—

$$CH_3.KSO_4+KCN=K_2SO_4+CH_3.CN.$$

The finely powdered and intimately mixed substances are heated to redness in a hard glass tube, which is closed at one end, and opens at the other into a condenser (Fig. 8). The distillate consists of the cyanide mixed with an evil-smelling isomeric compound, most of which is removed by shaking with dilute sulphuric acid, in which the impurity is insoluble. To obtain the acetic acid the filtered solution is made strongly alkaline with caustic soda, and boiled in a reflux apparatus until ammonia ceases to be evolved, and on distilling the product with excess of dilute sulphuric acid, as in the synthesis of formic acid, the acetic acid passes over. It is accompanied by a little formic acid, however, formed from the residual isomeric compound, but this is eliminated by boiling with a little mercuric sulphate and redistilling.

The acetic acid thus obtained (Frankland and Kolbe, 1847), is in every respect identical with the natural product.

The identity of methyl cyanide with acetonitrile is obvious from its hydrolysis. The liquid can be obtained in a pure condition, however, by digesting the crude distillate with cold concentrated hydrochloric acid, which destroys the isomeric compound, and then neutralising it and salting out the cyanide with calcium chloride. After redistilling from a little phosphorus pentoxide, its properties are identical with those of the nitrile. The cyanide can also be made by heating methyl iodide in a sealed tube with an alcoholic solution of potassium cyanide, and fractionating the product—

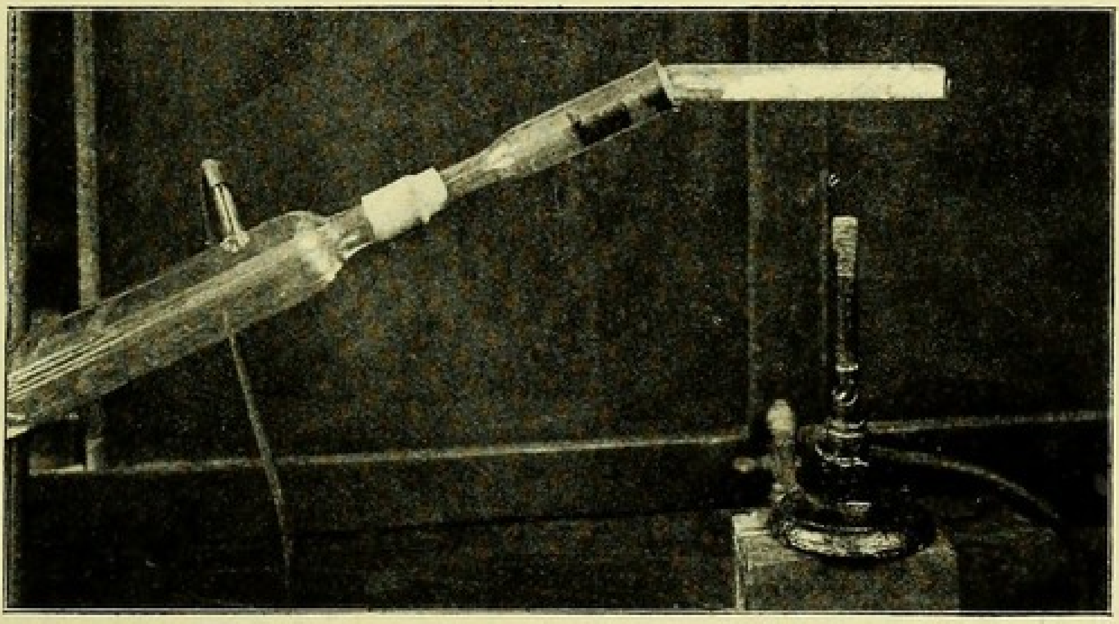


Fig. 8.—Dry or Destructive Distillation.

$$CH_3I + KCN = CH_3.CN + KI.$$

Since methyl cyanide is identical with acetonitrile, it is converted by reducing agents into ethylamine; and as the latter is transformed into alcohol by nitrous acid, it follows that both acetic acid and alcohol can be synthesised through methyl alcohol from their elements.

Since also acetonitrile is a methyl compound, it follows that acetic acid and alcohol are methyl compounds, and that the methyl group passes unchanged through the several transformations—

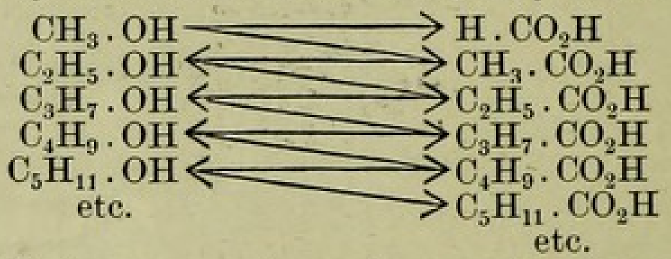
$$\begin{tikzcd}
\mathrm{CH_3.OH} \arrow[r, leftrightarrow] & \mathrm{CH_3.KSO_4} \arrow[r] & \mathrm{CH_3.CN} \arrow[r, leftrightarrow] \arrow[d] & \mathrm{CH_3.CO_2H} \\
& & \mathrm{CH_3.CH_2NH_2} \arrow[r] & \mathrm{CH_3.CH_2OH.} \arrow[u]
\end{tikzcd}$$

The acid and alcohol can therefore be represented by the third pair of rational formulæ—

$CH_3.CO_2H$ and $CH_3.CH_2OH$.

Synthesis of the Higher Alcohols and Acids.—The conversion of methyl alcohol into acetic acid (Frankland and Kolbe), is a typical instance of Organic Synthesis, or building up an organic radicle from others containing fewer carbon atoms.

The addition of a carbon atom to the ethyl and propyl radicles can be effected in the same way. Ethyl alcohol can thus be converted into propionic acid and propyl alcohol; propyl alcohol can be converted into butyric acid and butyl alcohol, and so on almost indefinitely; and by this and other methods, which will be considered later, practically all the compounds which have thus far been considered can be synthesised from their elements. The aliphatic acids and alcohols, for example, up to the nine-carbon members, can be made from methyl alcohol by this cyanide synthesis (Lieben and Rossi, 1871–1877). Above the two-carbon compounds the alcohols are made from the synthesised acids by reduction of the aldehydes (p. 73), propylamine and its higher homologues being converted by nitrous acid, not simply into the corresponding alcohols, but partly into isomeric compounds (p. 215). The synthesis, of course, is equally valid.

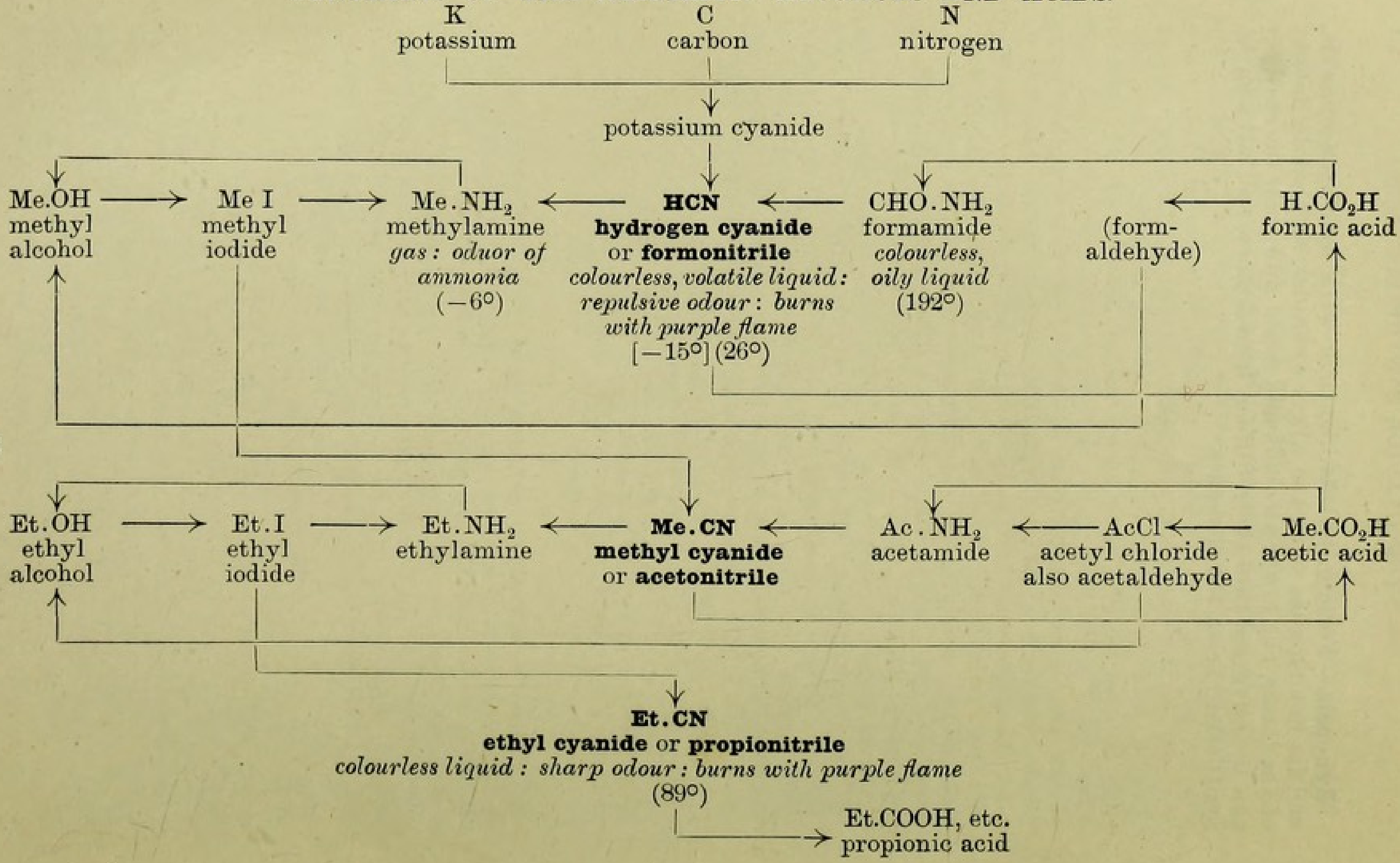


It is difficult to carry out work as extensive as this. The yield of product in Organic operations rarely approaches that indicated by the equations, for not only is loss inevitable in boiling, distillation, crystallisation, etc., but in many cases the action is diverted into secondary channels by comparatively slight alterations in conditions. In the preparation of the cyanides from the alcohols, for example, large quantities of the isomeric impurities are formed.

But the actual conversion of the substance at one end of a chain into that at the other end is not essential, provided that each link is established. Thus it is much easier in the above chain of syntheses to make ethyl alcohol from sugar than from methyl alcohol, and it is sufficient to prepare enough from the latter source to establish its identity, and then to proceed with the more accessible product. Similarly, butyric acid is easily made by fermentation. In this way, by testing the links separately, many chains of synthetic relations have been established that might not otherwise have been realised. The sugars afford a notable instance of this.

Synopsis.—Formonitrile is identical with hydrogen cyanide, and its homologues with the alkyl cyanides, so that by means of the latter, the lower alcohols and acids and their derivatives can be converted into their higher homologues, and all can be synthesised from the elements.

SYNTHESIS OF THE ALIPHATIC ALCOHOLS AND ACIDS.



CHAPTER XII

MOLECULAR STRUCTURE

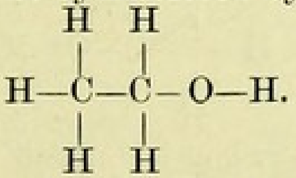
Constitution or Structure: Valency.—As a result of the cyanide synthesis, it follows that both alcohol and acetic acid are represented by no less than three rational formulæ, each of which indicates some chemical characteristic or relationship. Acetic acid, primarily an acid hydroxide, is also a methyl derivative, and in common with its homologues, a carboxyl compound, and alcohol is both a methyl and an ethyl derivative, as well as a basic hydroxide—

$$\mathrm{C_2H_5O.H \qquad C_2H_5.OH \qquad CH_3.CH_2OH}$$
$$\mathrm{C_2H_3O_2.H \qquad C_2H_3O.OH \qquad CH_3.COOH.}$$

The more diverse the relations of a substance, the more numerous its formulæ thus become, and from the cyanide synthesis alone it is obvious that the higher alcohols and acids contain all the lower radicles—

$$\mathrm{C_3H_7.OH \qquad C_2H_5.CH_2OH \qquad CH_3.C_2H_4OH}$$
$$\mathrm{C_3H_5O.OH \qquad C_2H_5.CO_2H \qquad CH_3.C_2H_3O_2.}$$

But as the number of atoms in a molecule is fixed, and the molecules of a pure substance all alike, it follows that all the radicles in the rational formulæ coexist in each of the molecules (Gerhardt), and that the atoms are grouped in some comprehensive arrangement or structure comprising all the smaller groups. The theory of structure (Kekulé, Couper, 1857), postulates that this is effected by actual linking, and that the atomic linkages may be symbolised by bonds (Couper)—



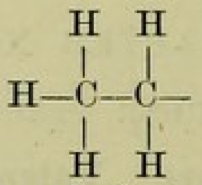
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O}-\mathrm{H}. \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Now it is known from Inorganic Chemistry that there are very definite limits to the combining powers of the elements (Frankland, Kekulé, 1857). Oxygen combines at the most with two other atoms, as in water, nitrogen with three, as in ammonia, and carbon with four, as in marsh gas. Hydrogen itself never combines with more than one atom of any kind, for no compound is known that is broken up by the simple removal of this element. With the aid of these rules of valency, the internal molecular structure of a substance can be determined from its chemical relations.

Structures of the Aliphatic Alcohols and Acids.—In alcohol the active hydrogen is always removed when the oxygen is taken away, and is therefore linked to the latter—

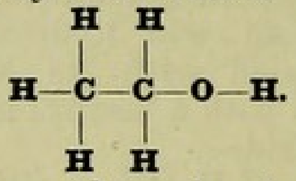
—O—H.

Since hydrogen cannot serve as a link, the carbon atoms must be directly united, and the five hydrogen atoms attached to them—



$$\begin{array}{ccccc} & & \mathrm{H} & & \mathrm{H} \\ & & | & & | \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C}- \\ & & | & & | \\ & & \mathrm{H} & & \mathrm{H} \end{array}$$

The remaining valency of the carbon is satisfied by the unattached valency of the oxygen and the complete structure is therefore represented by the formula

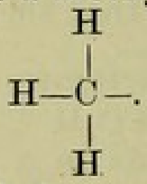


$$\begin{array}{ccccccccc} & & \mathbf{H} & & \mathbf{H} & & & & \\ & & | & & | & & & & \\ \mathbf{H} & - & \mathbf{C} & - & \mathbf{C} & - & \mathbf{O} & - & \mathbf{H}. \\ & & | & & | & & & & \\ & & \mathbf{H} & & \mathbf{H} & & & & \end{array}$$

Similarly the acetic acid molecule contains a hydroxyl group,

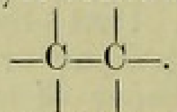
—O—H,

and as a methyl derivative a methyl group—



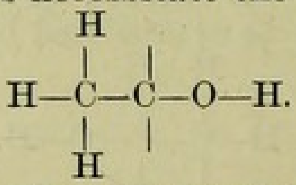
$$\begin{array}{ccc} & & \mathrm{H} \\ & & | \\ \mathrm{H} & - & \mathrm{C}-. \\ & & | \\ & & \mathrm{H} \end{array}$$

Further, as it can be made from and converted into alcohol and methyl cyanide (see below), it contains the nucleus



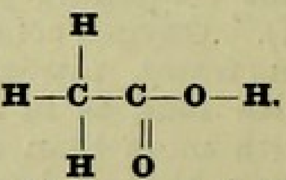
$$\begin{array}{ccccc} & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & -. \\ & | & & | & \end{array}$$

These three conditions necessitate the arrangement



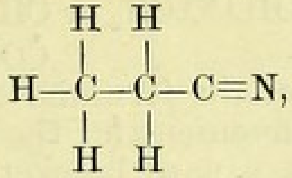
$$\begin{array}{ccccccccc} & & \mathrm{H} & & & & & & \\ & & | & & | & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H}. \\ & & | & & | & & & & \\ & & \mathrm{H} & & & & & & \end{array}$$

The two remaining valencies must therefore be satisfied by the second oxygen atom, and the structure of the acid represented by the formula



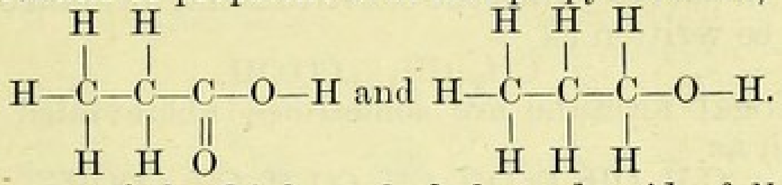
$$\begin{array}{ccccccccc} & & \mathbf{H} & & & & & & \\ & & | & & & & & & \\ \mathbf{H} & - & \mathbf{C} & - & \mathbf{C} & - & \mathbf{O} & - & \mathbf{H}. \\ & & | & & \| & & & & \\ & & \mathbf{H} & & \mathbf{O} & & & & \end{array}$$

The structures of the higher alcohols and acids follow also from the cyanide synthesis, for in the alkyl cyanides it is the nitrogen that is detached by hydrolysis, so that the cyanogen carbon atom must be directly linked to the alkyl. The structural formula of ethyl cyanide is thus



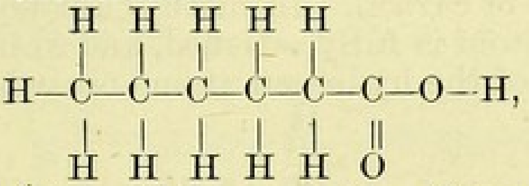
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C- & C\equiv N, \\ & | & | & \\ & H & H & \end{array}$$

and the formulæ of propionic acid and propyl alcohol,



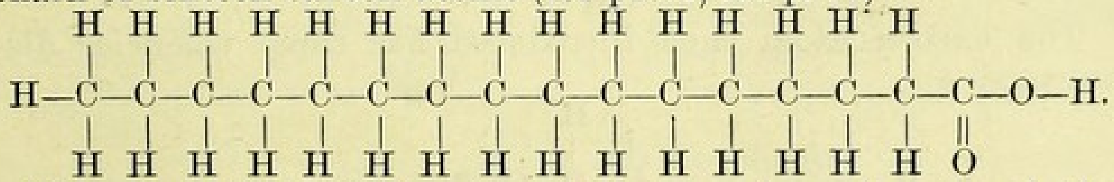
$$\begin{array}{ccccc} & H & H & & \\ & | & | & & \\ H- & C- & C- & C- & O-H \\ & | & | & \| & \\ & H & H & O & \end{array} \text{ and } \begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C- & O-H. \\ & | & | & | & \\ & H & H & H & \end{array}$$

The formulæ of the higher alcohols and acids follow in the same way, an additional carbon atom being attached to the carbon chain at each step. Thus the structure of caproïc acid is represented by the formula



$$\begin{array}{cccccccc} & H & H & H & H & H & & \\ & | & | & | & | & | & & \\ H- & C- & C- & C- & C- & C- & C- & O-H, \\ & | & | & | & | & | & \| & \\ & H & H & H & H & H & O & \end{array}$$

and that of palmitic acid by a similar formula containing a chain of sixteen carbon atoms (for proof, see p. 97)—



$$\begin{array}{cccccccccccccccccc} & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & & \\ & | & | & | & | & | & | & | & | & | & | & | & | & | & | & | & & \\ H- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & O-H. \\ & | & | & | & | & | & | & | & | & | & | & | & | & | & | & | & \| & \\ & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & O & \end{array}$$

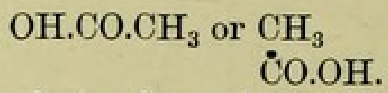
This capability of forming chains is characteristic of the atoms of carbon and in part accounts for the very large number of its compounds.

Structural and Constitutional Formulæ.—Formulæ, such as these, showing the arrangement of the atoms in a molecule, are termed structural formulæ. They epitomise the entire chemical behaviour of the substances they represent, and show at a glance their points of resemblance and difference. Thus the mobile hydrogen and hydroxyl of alcohol and acetic acid are marked. The synthesis of both compounds from methyl alcohol is accounted for. The mechanism of their oxidation and reduction is also apparent, the hydrogen of the non-methylic carbon being attacked, and the methyl remaining unaltered. The greater activity of the carboxylic hydrogen is also accounted for by the juxtaposition of the second oxygen atom. In fact, given a structural formula, it is generally possible to form an accurate idea of the chemical behaviour of the substance.

The full graphic or structural formulæ are cumbrous and are usually abbreviated into constitutional formulæ, such as

$$CH_3.CH_2.OH,\ CH_3-CH_2-OH \text{ or } CH_3.CO.OH.$$

These convey the same information if the valencies are taken into account. The actual position of the groups is immaterial, provided that the proper order and linking are maintained. The formula of acetic acid for instance may also be written as



$$\mathrm{OH.CO.CH_3} \text{ or } \begin{array}{l}\mathrm{CH_3}\\ \mathrm{CO.OH.}\end{array}$$

In the case of long chain formulæ containing a number of similar groups, it is convenient for the sake of brevity to place one of the groups, in a square bracket, indicating the actual number by a suffix. Thus the constitutional formula of palmitic acid may be written as

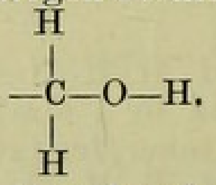
$$\mathrm{CH_3.[CH_2]_{14}.CO.OH.}$$

Constitutional formulæ are sometimes abbreviated into such forms such as

$$\mathrm{C_2H_5.OH,\ Et.OH,\ CH_3.CO_2H,\ CH_3.COOH.}$$

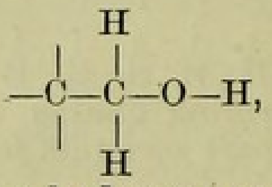
These are similar to the rational formulæ, but the dots represent linkages and are not mere marks of separation.

Cause of Homology and Metamerism.—Homology is due to the fixed valency of carbon. In methyl alcohol for example the valency of each atom is fully satisfied, and to introduce a second carbon atom one of the hydrogen atoms must be removed—



$$\begin{array}{ccccc} & \mathrm{H} & & & \\ & | & & & \\ - & \mathrm{C} & - \mathrm{O} - & \mathrm{H.} & \\ & | & & & \\ & \mathrm{H} & & & \end{array}$$

The carbon atom thus introduced has three valencies disengaged—



$$\begin{array}{cccccc} & & & \mathrm{H} & & \\ & | & & | & & \\ - & \mathrm{C} & - & \mathrm{C} & - \mathrm{O} - & \mathrm{H,} \\ & | & & | & & \\ & & & \mathrm{H} & & \end{array}$$

which require three more hydrogen atoms, and the net result is thus the introduction of $\mathrm{CH_2}$, the difference between $\mathrm{CH_3}$ and H.

If the methyl group replaces a methyl hydrogen atom, ethyl alcohol is the result—

$$\mathrm{H.CH_2.OH - H + CH_3 = CH_3.CH_2.OH,}$$

whilst if the hydroxylic hydrogen is displaced methyl ether is formed—

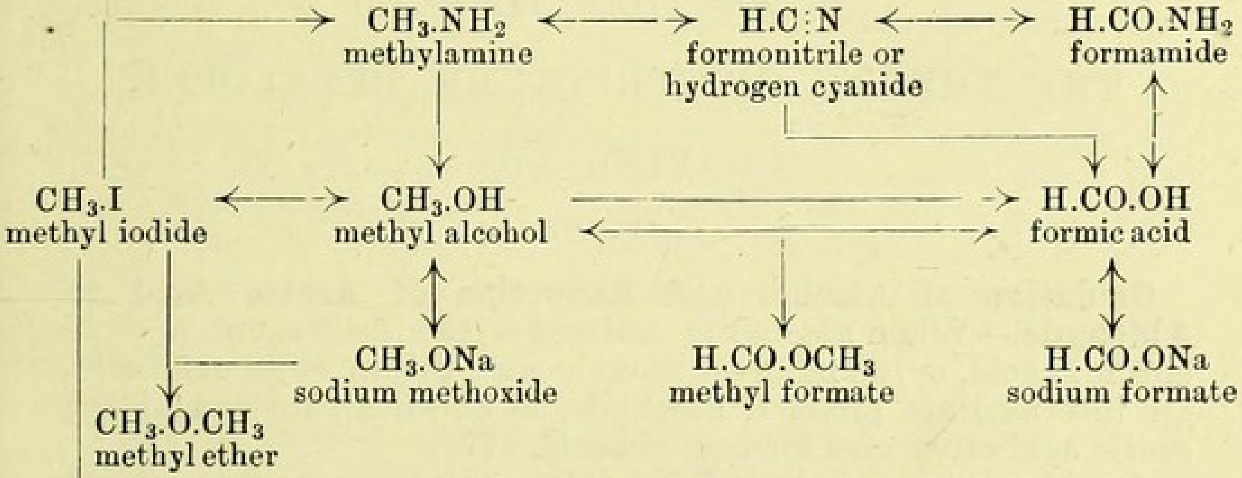
$$\mathrm{CH_3.O.H - H + CH_3 = CH_3.O.CH_3.}$$

Hence metamerism.

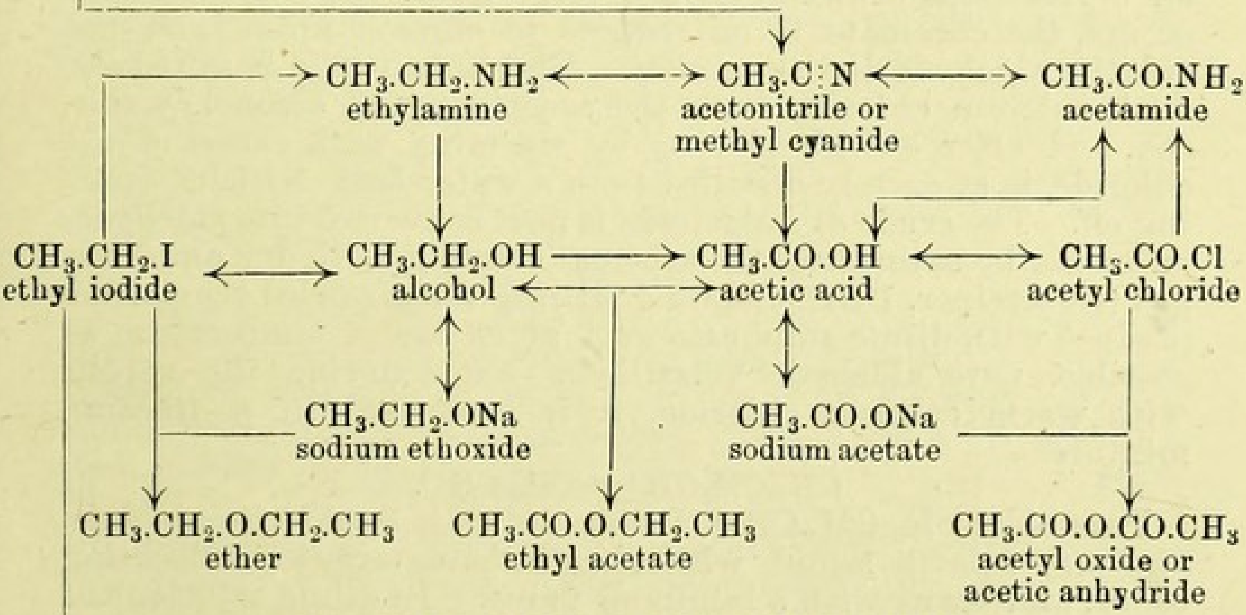
Synopsis.—The existence of several radicles in the same molecule leads to the assumption that the atoms are linked together in a definite arrangement, termed the structure or constitution of the substance. This arrangement is deduced from its reactions and the valency of its atoms, and the formulæ thus obtained are termed structural or constitutional formulæ. They not only symbolise the chemical actions and relations of the substances but also account for homology and isomerism.

EXPERIMENTAL BASIS OF STRUCTURAL FORMULÆ.

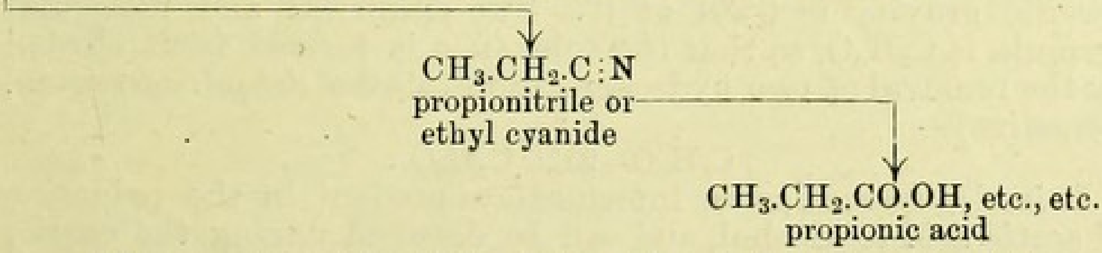
I. THE METHYL-FORMIC GROUP.



II. THE ETHYL-ACETIC GROUP.



III. THE PROPYL-PROPIONIC GROUP.



[For structure of the higher fatty acids and alcohols, see p. 97.]

SECTION III

THE THEORY OF STRUCTURE DEVELOPED

CHAPTER XIII

ALDEHYDE

Oxidation of Alcohol and Reduction of Acetic Acid to Aldehyde.—When alcohol is oxidised with a mild agent, such as chromic acid, or manganese dioxide and dilute sulphuric acid, an intermediate product, aldehyde, is obtained, instead of the acetic acid otherwise formed (Scheele, 1774).

A cold mixture of alcohol and dilute sulphuric acid is poured on crystallised bichromate in a large flask, and a brisk action occurs, the chromate being reduced to chrome alum, and the volatile aldehyde distilling over. The light liquid is salted out with calcium chloride from the accompanying alcohol, water, etc., and after quickly drying by warming with excess of the chloride, is at once re-distilled from a water-bath without pouring off. The crude dry aldehyde is next converted into aldehyde-ammonia by saturating the ethereal solution with dry ammonia gas (Döbereiner, 1821), and on distilling the air-dried crystalline product with dilute sulphuric acid at as low a temperature as possible, pure aldehyde volatilises. After drying the vapour with warm calcium chloride, it is condensed in a freezing mixture—

$$CH_3.CH_2OH \longrightarrow CH_3.CHO.$$

Pure aldehyde, $CH_3.CHO$ (Liebig, 1821), is a colourless, mobile, and very volatile liquid, which has a characteristic, suffocating odour, and burns with a luminous flame. In dilute solution the odour is not unlike that of stale apples. It boils at 21°, and its specific gravity is 0·801 at 0°. The empirical and molecular formula is C_2H_4O, so that the substance is formed from alcohol by the removal of two hydrogen atoms (*alcohol dehydrogenatum*, Berzelius)—

$$C_2H_6O - 2H = C_2H_4O.$$

It is also formed as an intermediate product in the reduction of acetic acid to alcohol, and can be detected during the earlier stages of the operation—

$$C_2H_3O.Cl + 2H = C_2H_3O.H + HCl.$$

It is produced also by reducing barium acetate with barium formate. The two salts are made from the acids and the carbonate. The weighed quantities are dissolved in water, and evaporated to dryness, and the intimate mixture thus obtained is distilled from a hard glass tube, as in the preparation of methyl cyanide, the distillate being collected in water. The residue consists of barium carbonate, produced by oxidation of the formate (Limpricht, 1856)—

$$Ba(O.CO.CH_3)_2+Ba(O.CO.H)_2=2CH_3.CHO+2BaCO_3.$$

Oxidation of Aldehyde to Acetic Acid and its Reduction to Alcohol.—Aldehyde is a very unstable substance. It is oxidised to acetic acid even by prolonged exposure to air, and by boiling with acid permanganate the oxidation is very rapidly effected. The aldehyde solution is cautiously poured down the condenser of a reflux apparatus containing the acid mixture, and after the violent action has moderated, more acid and permanganate are added, and the boiling continued until the agent ceases to be decolourised. The product is then filtered, and the acetic acid distilled off—

$$CH_3.CHO+O=CH_3.COOH.$$

Being so readily oxidisable, it has marked reducing power. When aldehyde is warmed with ammoniacal silver nitrate in a beaker of water, the metal is precipitated on the sides of the tube as a brilliant mirror (Liebig). The ammonia serves to neutralise the acetic and nitric acids—

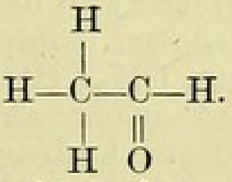
$$C_2H_4O+2AgNO_3+2NH_3+H_2O=2Ag+CH_3.COONH_4+NH_4.NO_3.$$

Conversely, it is reduced to alcohol by digestion with sodium amalgam and dilute sulphuric acid. After a few hours the characteristic odour disappears, and on distilling the product, dilute alcohol passes over (Wurtz, 1862)—

$$CH_3.CHO+2H=CH_3.CH_2OH.$$

On this account it can also act as a feeble oxidising agent. A solution of rosaniline—magenta—is bleached when a large excess of sulphurous acid is added to it, owing to the formation of a colourless compound, but on adding even a trace of aldehyde, this product is slowly oxidised, and a violet colour appears (Schiff).

Constitution of Aldehyde.—As aldehyde is intermediate to alcohol and acetic acid, it contains the nucleus $CH_3.C$, and as the remaining three valencies can only be satisfied by direct attachment of the remaining hydrogen and oxygen atoms, the structural formula is



$$\begin{array}{ccccccc} && \mathrm{H} &&&& \\ && | &&&& \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}. \\ && | && \| && \\ && \mathrm{H} && \mathrm{O} && \end{array}$$

The molecule thus consists of a methyl group linked to a monovalent radicle, CHO. This is known as the aldehyde group, and is identical with the formyl radicle. Formic acid, in fact, owes its reducing power to the presence of this group, and the formation of aldehyde from barium acetate and formate may thus be interpreted as the union of methyl with the formyl or aldehyde groups (Williamson, 1857)—

$$Ba(O.CO.CH_3)_2+Ba(O.CHO)_2=2BaCO_3+2CH_3.CHO.$$

The constitution of aldehyde is confirmed by the action of phosphorus pentachloride, which converts it into a dihalogen product, ethylidene chloride. The action is vigorous, and the dichloride is separated from the phosphorus compounds by washing with water and alkali.

Ethylidene chloride, $CH_3.CHCl_2$, is a heavy, colourless liquid, which boils at 60°, and has a sweet odour and taste. When heated in a sealed tube with dilute sulphuric acid, it is reconverted into aldehyde. Now the two chlorine atoms thus reciprocally interchangeable with the aldehyde oxygen are of course directly attached to carbon, and it follows therefore that this oxygen is attached to carbon by both its valencies—

$$C_2H_4O \longleftrightarrow C_2H_4Cl_2.$$

Phosphorus pentachloride behaves with ethers and ethereal salts in the same way as with alcohols and acids, and thus serves to differentiate singly-linked from doubly-linked oxygen—

$$R_1.O.R_2 \rightarrow R_1.Cl+R_2.Cl\,;\ R{:}O \rightarrow R{:}Cl_2.$$

Although aldehyde itself does not contain hydroxyl, certain derivatives are known in which it appears as a dihydroxy-compound. Thus, on heating it with alcohol, or ethylidene chloride with sodium ethoxide, a kind of double ether, acetal, is formed.

Acetal, $CH_3.CH(OEt)_2$ (Liebig, 1831), is a liquid, boiling at 104°. Its constitution is proved, not only by its formation from ethylidene chloride, but by its conversion by phosphorus pentachloride into ethylidene and ethyl chlorides. Now it is hydrolysed by dilute sulphuric acid to aldehyde and alcohol, and it would thus appear that the formation of aldehyde by oxidation is preceded by that of a dihydroxy-compound. In some cases such dihydroxy-compounds can actually be isolated (see Chloral)—

$$\begin{tikzcd}
CH_3.CH_2OH \arrow[r] & CH_3.CH(OH)_2 \arrow[r, leftrightarrow] \arrow[rr, leftrightarrow, bend right] & CH_3.CH(OEt)_2 \arrow[r, leftrightarrow] & CH_3.CHCl_2.
\end{tikzcd}$$

Additive Compounds, Polymerides, and Condensation Products of Aldehyde.—The crystalline aldehyde-ammonia, $CH_3.CHOH.NH_2$ (p. 143) used in the purification of aldehyde is formed by direct union of the two molecules, and is termed an additive compound. A second compound of the same class, aldehyde sodium sulphite, $CH_3.CHOH.SO_3Na$, also a crystalline substance, is formed when aldehyde is shaken with a saturated solution of sodium hydrogen sulphite, and like the ammonia compound is readily hydrolysed into its constituents by dilute acid or alkali carbonate. An additive compound of a different type, aldehyde hydrocyanide, $CH_3.CHOH.CN$, a liquid boiling at 183°, is formed when aldehyde is heated with concentrated hydrocyanic acid in a closed vessel at 100°. It differs from the preceding compounds in that only part of the added molecule, the nitrogen, is detached by hydrolytic agents, the cyanogen being converted into carboxyl in the normal manner (see Lactic Acid, p. 143). Alcohol and acetic acid themselves may of course be regarded as additive derivatives of aldehyde, since they are formed by direct addition of hydrogen and oxygen.

The tendency of aldehyde to form additive compounds is so marked that it will even combine with itself. When a drop of concentrated sulphuric acid is added to the pure liquid, contraction takes place, much heat is evolved, and the boiling point rises many degrees, whilst if the temperature is kept below 0°, the aldehyde is converted into a white crystalline solid.

Paraldehyde,  $\mathrm{CHMe}<\begin{matrix}\mathrm{O.CHMe}\\ \mathrm{O.CHMe}\end{matrix}>\mathrm{O}$, is a sparingly soluble liquid boiling at 124°. Its molecular formula $C_6H_{12}O_3$, follows from its vapour density, and its constitution from its reactions. Unlike aldehyde, it is a stable substance, and is oxidised and reduced only with difficulty. It does not reduce silver, for instance, nor does it colour bleached rosaniline. But it is converted into ethylidene chloride by phosphorus pentachloride, in in the same way as acetal into ethylidene and ethyl chlorides, and is thus a complex ether of the acetal type (Kekulé, 1870).

Metaldehyde, $(C_2H_4O)_x$, is a white crystalline substance, which at about 115° commences to sublime, and is partially reconverted into aldehyde, completely when heated in a sealed tube. Metaldehyde resembles paraldehyde in its actions, but its molecular weight is unknown. It is also formed by the prolonged action of calcium chloride, and this is why aldehyde must be dried quickly.

An internal additive compound of a different type is formed by digesting aldehyde with zinc chloride, or concentrated hydrochloric acid. Aldol, $C_4H_8O_2$, is a liquid of complex constitution (p. 152), resembling aldehyde in its general actions.

These internal compounds are necessarily isomeric with aldehyde, and their molecules are simple multiples of its own molecules. Such multiple isomerides are termed polymerides (Berzelius, 1831).

Aldehyde thus acts almost entirely by addition, but the additive compounds thus formed may undergo further change. Thus when the liquid is mixed with hydroxylamine hydrochloride solution, and the base set free by caustic soda, the two molecules unite, but at the same time lose water. The compound thus formed is isolated by shaking the product with ether. It is freely soluble in this liquid, but the ethereal solution is insoluble in water, and can thus be separated mechanically. The ether is then distilled off. This device is much used in organic work.

Aldoxime, $CH_3.CH{:}N.OH$, is a colourless liquid, boiling at 115°. It is reconverted into aldehyde and hydroxylamine by hydrochloric acid, and is dehydrated to acetonitrile by phosphorus pentachloride. It is useful in separating aldehyde from mixtures—

$$CH_3.CHO + NH_2.OH \leftrightarrow CH_3.CH{:}N.OH \rightarrow CH_3.CN.$$

An analogous compound, aldehyde-phenyl-hydrazone, $CH_3.CH{:}N.NH.C_6H_5$ (Fischer, 1885), an insoluble yellow liquid boiling at about 250°, is formed in a similar way from aldehyde and phenyl-hydrazine acetate (p. 257), and is reconvertible into its constituents in the same way—

$$CH_3.CHO + NH_2.NH.C_6H_5 \leftrightarrow CH_3.CH{:}N.NH.C_6H_5 + H_2O.$$

Compounds thus formed by the union of two molecules with elimination of water, or other simple product, are termed condensation products. When water itself is eliminated, as in these particular cases, condensation is the exact reverse of hydrolysis.

Aldehyde forms condensation products with itself. Crotonaldehyde, $C_3H_5.CHO$ (p. 138), for example, is formed by the further action of zinc chloride on aldol, or by simply distilling it, and an action which is possibly similar is brought about by warming aldehyde with strong caustic soda solution. Aldehyde resin (Döbereiner, 1821) thus formed is a sticky yellowish substance, having a characteristic soapy and resinous odour. Nothing is known of its chemical nature, as it cannot be crystallised or distilled.

The tendency of aldehyde to form these additive and condensation products is highly characteristic, and as will be seen later, it is probable that actions of this kind play a very important part in the natural synthesis of organic compounds in plants.

The Aldehydes.—Like alcohol and acetic acid, aldehyde is the type of a large class of compounds, each pair of alcohols and acids being connected by a similar product. These intermediate compounds are termed, generically, the aldehydes, and distinguished by reference to the acids.

The most conspicuous of them is formaldehyde, the product intermediate to methyl alcohol and formic acid. It is formed by dry distilling barium formate, but is best prepared by the oxidation of methyl alcohol. Dry air, charged with the vapour by passing through the liquid at 40°, is led over a short spiral of copper gauze, which is heated to dull redness in a short length of combustion tube. The product is carried through a train of well cooled flasks, a 40 per cent. solution of the aldehyde collecting in the first, and weaker solutions in the remainder. The pure aldehyde is obtained by warming the strong solution, and condensing the dried vapour in a freezing mixture.

Formaldehyde, $H.CHO$ (Hofmann, 1867), is a gas which condenses to a liquid at −21°. It is very pungent and acrid. Pure formaldehyde is very unstable, and when warmed to the ordinary temperature polymerises explosively with evolution of much heat. The 40 per cent. solution is quite stable, however, and is used as an antiseptic.

In its general actions, formaldehyde closely resembles acetaldehyde, and is readily oxidised and reduced. It reduces silver, and colours bleached rosaniline. With ammonia, however, it forms a condensation product, hexamethyleneamine, $N_4(CH_3)_6$, a crystalline substance, and it is not resinified by alkalies, but converted into methyl alcohol and the alkali formate—

$$2H.CHO + NaOH = CH_3.OH + H.COONa.$$

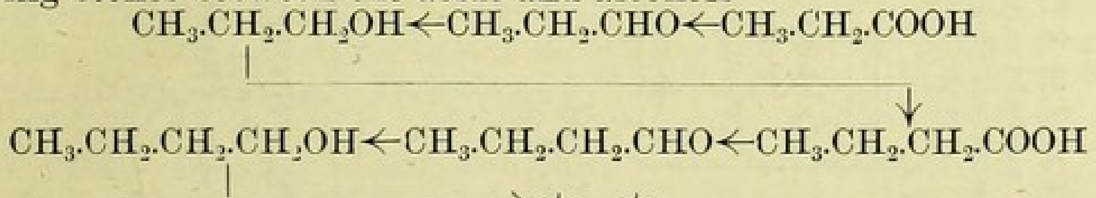
Formaldehyde polymerises much in the same way as its prototype; the metaformaldehyde or trioxymethylene, $C_3H_6O_3$, formed by spontaneous polymerisation, is a crystalline substance melting at 171°, which is dissociated into the mother substance when vaporised or heated with water at 130°. Formaldehyde is also directly polymerisable to *a*-acrose, $C_6H_{12}O_6$, a sugar isomeric, and synthetically connected with the natural sugars.

Of the higher aldehydes, propaldehyde, $C_2H_5.CHO$ (Chancel, 1869), is a suffocating, mobile liquid, boiling at 49°, and butaldehyde, a similar liquid boiling at about 75°. The former is best made from the alcohol, and the latter by reduction of the acid by the formate method. Both are much less soluble in water than their lower homologues, but resemble them precisely in their actions. As the series is ascended, the aldehydes become more oily and insoluble, and less volatile, and finally wax-like solids resembling the higher compounds of the other series. They all show the characteristic aldehyde actions, however, and are readily oxidised and reduced to the corresponding acids and alcohols. They also form additive and condensation products in the same way as their prototype.

Valeraldehyde and its higher homologues resembles formaldehyde in their action with caustic soda, one molecule being oxidised to the acid at the expense of a second which is reduced to the alcohol. Valeraldehyde itself thus yields amyl alcohol and the alkali valerate—

$$2C_4H_9.CHO + NaOH = C_4H_9.COONa + C_4H_9.CH_2OH.$$

The aldehydes are particularly useful in synthesis from their very instability, and as mentioned above are convenient stepping stones between the acids and alcohols—



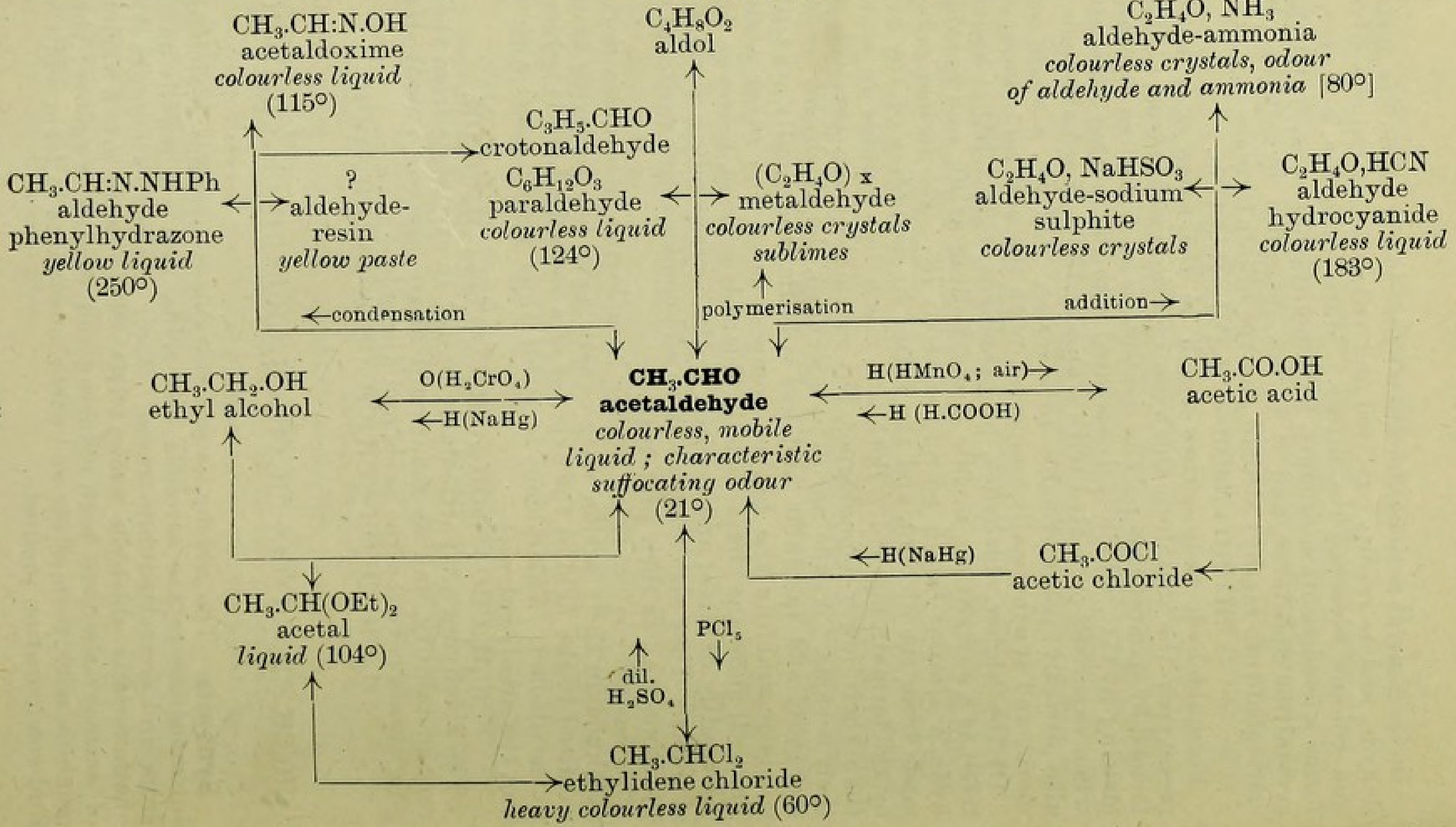
$$CH_3.CH_2.CH_2OH \leftarrow CH_3.CH_2.CHO \leftarrow CH_3.CH_2.COOH$$

$$CH_3.CH_2.CH_2.CH_2OH \leftarrow CH_3.CH_2.CH_2.CHO \leftarrow CH_3.CH_2.CH_2.COOH$$

$$\rightarrow \text{etc., etc.}$$

Synopsis.—The aldehydes are unstable compounds which are intermediate to the alcohols and acids, and are readily made from and converted into them. Their molecules contain the characteristic aldehyde group CHO. They enter into a variety of actions: they are both reducing and oxidising agents; they combine with themselves and other substances to form additive and condensation products.

ALDEHYDE.


$C_4H_8O_2$
aldol
$CH_3.CH:N.OH$
acetaldoxime
colourless liquid
(115°)
$C_3H_5.CHO$
crotonaldehyde
C_2H_4O, NH_3
aldehyde-ammonia
colourless crystals, odour of aldehyde and ammonia [80°]
$CH_3.CH:N.NHPh$
aldehyde
phenylhydrazone
yellow liquid
(250°)
?
aldehyde-
resin
yellow paste
$C_6H_{12}O_3$
paraldehyde
colourless liquid
(124°)
(C_2H_4O) x
metaldehyde
colourless crystals
sublimes
$C_2H_4O, NaHSO_3$
aldehyde-sodium
sulphite
colourless crystals
C_2H_4O,HCN
aldehyde
hydrocyanide
colourless liquid
(183°)
←condensation
polymerisation
addition→
$CH_3.CH_2.OH$
ethyl alcohol
$O(H_2CrO_4)$
←H(NaHg)
$CH_3.CHO$
acetaldehyde
colourless, mobile liquid ; characteristic suffocating odour
(21°)
$H(HMnO_4;\ air)$→
←H (H.COOH)
$CH_3.CO.OH$
acetic acid
←H(NaHg)
$CH_3.COCl$
acetic chloride
$CH_3.CH(OEt)_2$
acetal
liquid (104°)
PCl_5
dil.
H_2SO_4
$CH_3.CHCl_2$
ethylidene chloride
heavy colourless liquid (60°)

CHAPTER XIV

ACETONE AND SECONDARY PROPYL ALCOHOL

Acetone.—It has been known for several centuries that when sugar of lead is distilled, a volatile inflammable spirit passes over, but it was only recognised in the last century that this spirit is distinct from alcohol. It is termed acetone.

Acetone is readily made in the laboratory by distilling dry barium acetate. The operation is carried out in the same way as in the preparation of aldehyde, at as low a temperature as possible, and the crude product is purified by means of the crystalline bisulphite compound which it resembles aldehyde in forming. On shaking the distillate with sodium hydrogen sulphite solution, heat is evolved, and the mixture rapidly sets to a white crystalline mass. This is pressed and dried between filter paper, and on distillation with sodium carbonate solution, pure but dilute acetone passes over, whilst the sulphurous acid remains behind as normal sodium sulphite. The acetone is salted out from the distillate with calcium chloride, and is finally dried with the same agent and redistilled.

As already stated, acetone is also formed in considerable quantity in the distillation of hard wood, and is thus present in crude wood spirit. The spirit, after removal of the acid and water by distillation with lime, consists of a mixture of acetone and methyl alcohol, and these are fairly completely separable by fractional distillation. Commercial acetone is obtained in this way, and the pure substance prepared from it by the bisulphite method. Acetone is present naturally in diabetic urine in which it is probably formed by the decomposition of acetoacetic acid (p. 150).

Acetone, $CH_3.CO.CH_3$ (Lemery, 17th century), is a mobile, inflammable liquid, which has an ethereal odour somewhat akin to that of phosphorus. It boils at 57°, and has a specific gravity of 0·814 at 0°, and it is soluble in water and alcohol in all proportions. It is much used as a solvent in organic work.

The molecular formula of acetone is C_3H_6O, so that the substance is isomeric with propaldehyde, and is formed by direct resolution of the barium acetate into two simpler molecules—

$$Ba(O.CO.CH_3)_2 = BaCO_3 + C_3H_6O.$$

Additive Compounds and Condensation Products of Acetone.—The mode of formation of acetone is thus analogous to that of the aldehydes from barium formate and the barium salts of the fatty acids, and the resemblance extends in a general manner to its chemical actions. The compound is more closely allied to the aldehydes in fact than to any other of the groups thus far considered.

It does not reduce silver at all readily, nor does it colour bleached rosaniline, except slowly and imperfectly; and it does not form polymerides. But it gives rise to various additive compounds and condensation products, closely resembling those of the aldehydes.

Thus the sodium hydrogen sulphite compound, $C_3H_6O,NaHSO_3$ (Limpricht, 1855), is similar to aldehyde sodium sulphite. The hydrocyanide, C_3H_6O,HCN, also resembles that of aldehyde, and is converted by acids in a similar manner into a homologue of lactic acid. An additive compound with ammonia is not known, but several condensation products have been isolated.

Similarly acetone condenses with hydroxylamine and phenylhydrazine, forming products which are closely akin to the corresponding aldehyde compounds, and are made and decomposed in the same way. Acetoxime, $C_3H_6{:}N.OH$ (V. Meyer, 1883), is a crystalline solid, and acetone phenylhydrazone, $C_3H_6{:}N.NH.C_6H_5$, a liquid.

Like aldehyde, acetone also condenses with itself. Thus on saturating the liquid with hydrogen chloride gas two products are formed, mesityl oxide, $C_6H_{10}O$, a liquid of peppermint odour, which boils at 130°, and phorone, $C_9H_{14}O$, a yellowish crystalline solid. Further by the dehydrating action of concentrated sulphuric acid, mesitylene, C_9H_{12}, is formed, a fragrant, mobile liquid (p. 322).

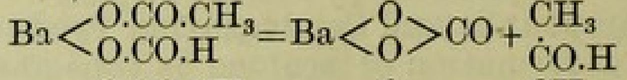
Oxidation of Acetone: its Constitution.—Acetone is thus distinctly akin to the aldehydes. When it is boiled in a reflux apparatus, however, with acid permanganate, carbon dioxide is evolved in abundance, and on distilling the product after the permanganate has ceased to be decolourised, acetic acid passes over—

$$C_3H_6O + 4O = CH_3.COOH + CO_2 + H_2O.$$

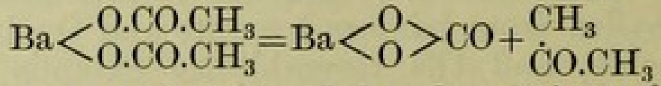
Although isomeric with propaldehyde, acetone thus differs from it in breaking up on oxidation. Now since it yields acetic acid, it must certainly contain the group $CH_3.C\equiv$, and in all probability the acetyl group, and if this is the case, its molecule must consist of methyl linked to acetyl—

$$CH_3.CO.CH_3.$$

This view is in complete harmony with its formation from barium acetate, for if the formula be written in this way, the formation of acetone becomes exactly parallel to that of aldehyde (Williamson, 1857)—



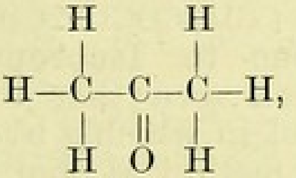
$$Ba{<}^{O.CO.CH_3}_{O.CO.H} = Ba{<}^{O}_{O}{>}CO + {}^{CH_3}_{CO.H}$$



$$Ba{<}^{O.CO.CH_3}_{O.CO.CH_3} = Ba{<}^{O}_{O}{>}CO + {}^{CH_3}_{CO.CH_3}$$

The constitution is confirmed by the action of phosphorus pentachloride, which converts the substance into acetone chloride, $C_3H_6Cl_2$, a colourless liquid resembling ethylidene chloride, but boiling at 70°. The oxygen of acetone is therefore present as carbonyl, as in the aldehydes, so that the three carbon atoms must be linked together. Now there are only two possible carbonyl formulæ for a three-carbon compound of this composition, namely, $CH_3.CH_2.CO.H$ and $CH_3.CO.CH_3$, and as the first of these has already been assigned to propaldehyde, the second must be that of acetone.

The structural formula of acetone is thus



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C & - & C & - & H, \\ & & | & & \| & & | & & \\ & & H & & O & & H & & \end{array}$$

and its molecule is built up of two methyl groups linked to carbonyl. In the aldehydes the carbonyl is linked to only one alkyl group, the other valency being satisfied by hydrogen.

Synthesis of Acetone from Methyl and Acetyl.—The presence of the two methyl groups in acetone is independently proved by a direct synthesis from two methyl compounds, acetic chloride and zinc methyl. The latter is made by boiling methyl iodide in a water-bath at 90° with a mixture of zinc dust and reduced copper. The reflux apparatus is provided with a mercury valve, and the air is replaced by dry carbon dioxide before the action is commenced, as the product is very oxidisable. When iodide ceases to run back from the condenser the solid product is distilled from an oil-bath at 160° and upwards, a stream of carbon dioxide being passed through the whole apparatus—

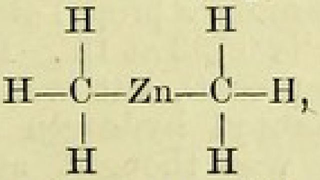
$$2Zn + MeI = 2ZnMeI = ZnMe_2 + ZnI_2.$$

Zinc methyl or methide, $ZnMe_2$ (Frankland, 1852), is a colourless liquid, which owing to the great oxidability of zinc is spontaneously inflammable in air, and is hence kept in sealed vessels. It boils at 46°, and freezes at $-40°$, and its specific gravity is 1·386 at 10°.

The molecular formula of zinc methyl is ZnC_2H_6, and as it is hydrolysed by water to zinc oxide and ordinary marsh gas—

$$ZnC_2H_6 + H_2O = ZnO + 2CH_4,$$

and zinc is divalent, its structure is represented by the formula



$$\begin{array}{ccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & Zn & - & C & - & H, \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

and its formation by the above equations.

Zinc methyl is of great use in synthesis, as it affords a means of exchanging methyl for halogen. When mixed with acetic chloride, for example, and the solid product of the action distilled with water, the chlorine is exchanged for methyl and acetone is generated (Freund, 1861)—

$$2CH_3.COCl + Zn(CH_3)_2 = 2CH_3.CO.CH_3 + ZnCl_2.$$

The mechanism of the action is not quite as simple however as would at first sight appear. The crystalline compound obtained in the first instance is formed by direct combination of the acetyl chloride with the zinc methyl—

$$CH_3.COCl + ZnMe_2 = CH_3.CMeCl.O.ZnMe,$$

and this interacts with a further quantity of the chloride, the water serving to decompose the excess of the latter—

$$CH_3.CMeCl.O.ZnMe + CH_3.COCl = 2CH_3.CO.CH_3 + ZnCl_2.$$

Reduction of Acetone to Isopropyl Alcohol: Position, Isomerism.—It has been seen that the higher alcohols are virtually methyl alcohol in which a hydrogen atom is replaced by alkyl. If therefore methyl alcohol be termed carbinol, the alcohols in general become alkyl-carbinols. Ordinary alcohol for example is methyl-carbinol, $CH_2Me.OH$.

From this point of view there should be carbinols, such as dimethyl-carbinol, $CHMe_2.OH$, and trimethyl-carbinol, $CMe_3.OH$, in which two or even three of the marsh-gas hydrogen atoms are replaced by alkyl (Kolbe, 1860).

Now on reducing acetone with sodium amalgam in acid solution in the same way as aldehyde, an alcohol is obtained, which can be purified in the ordinary manner by fractionation and dehydration with quicklime (Friedel, 1862). It has the same composition and vapour density as propyl alcohol, C_3H_8O, and is undoubtedly an alcohol, for it forms a sodium derivative, and is converted into an acetate by acetyl chloride. But its boiling point and specific gravity are much lower.

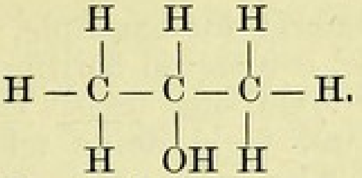
If this alcohol is the isomeride of propyl alcohol required by the above theoretical considerations, it should be reconverted by oxidising agents, not into an aldehyde and an acid containing the same number of carbon atoms, as is the case with the ordinary alcohols, but into acetone or the oxidation products of this substance (Kolbe, 1862)—

$$CHMe_2.OH \longleftrightarrow CMe_2{:}O.$$

This is actually the case, for when it is boiled with chromic acid mixture, acetone is formed, and may be isolated and identified by means of its bisulphite compound (Friedel, 1863).

Isopropyl alcohol, $CHMe_2.OH$ (Berthelot, 1855), is a colourless liquid which closely resembles propyl alcohol, but it boils at 83°, and its specific gravity is 0·792 at 15°. It is present in fusel oil to the extent of 15 per cent., but was first obtained by the hydrolysis of the isopropyl hydrogen sulphate formed from propylene (p. 105). It was thought at the time to be the analogue of ordinary alcohol required by the rule of homology.

The structural formula of isopropyl alcohol follows from the above theoretical considerations, and from its relation to acetone—



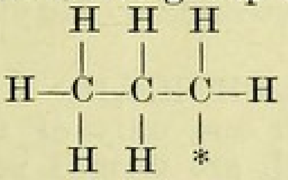
$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H.} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{OH} & & \mathrm{H} & & \end{array}$$

As already stated, the alcohol forms a series of salts, etc., which are distinct from the corresponding propyl compounds. The most important of these is the iodide.

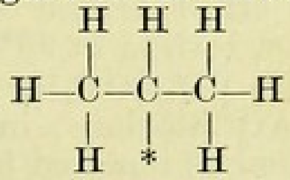
Isopropyl iodide, $CH_3.CHI.CH_3$ (Berthelot, 1857), is a colourless liquid which resembles ethyl and propyl iodides, but boils at 90°. It is best prepared by repeatedly distilling diluted glycerol with iodine and yellow phosphorus, and is purified in the same way as ethyl iodide.

Isopropyl iodide is converted by caustic alkalies, not into the alcohol, but into its dehydration product, propylene, and this is the case with most of the iodides higher than ethyl iodide. When boiled with lead oxide and water, however, it is readily hydrolysed, and the same transformation can be effected by heating it with silver acetate, and then hydrolysing the isopropyl acetate in the ordinary way. When isopropyl iodide is heated with silver oxide it is converted into isopropyl ether $(CHMe_2)_2O$, a liquid of peppermint odour, which boils at 82°, but resembles ordinary ether in its actions.

The isopropyl compounds are thus the derivatives of an alkylic radicle isopropyl, $CHMe_2$, which is isomeric with and analogous in function to the ordinary propyl radicle. The isomerism of the propyl and isopropyl compounds, and of propaldehyde and acetone is different from metamerism and polymerism. It is termed position isomerism, as it depends on the variation in the position of the active group with regard to the carbon chain—



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & * & & \end{array}$$



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & * & & \mathrm{H} & & \end{array}$$

The active group in the ordinary propyl compounds is attached to a carbon atom, which is united to only one other carbon atom, whilst in the isopropyl compounds this atom is directly linked to two others.

The Ketones and Secondary Alcohols.—By distilling the homologues of barium acetate, or by acting on the acid chlorides with the zinc alkyls, compounds are formed which are homologous with and analogous to acetone. They are termed on this account, ketones.

Propione, for example, $C_2H_5.CO.C_2H_5$, a pleasant-smelling liquid, boiling at 103°, is formed from barium propionate—

$$Ba\ (O.CO.C_2H_5)_2 = BaCO_3 + C_2H_5.CO.C_2H_5,$$

and butyrone, $C_3H_7.CO.C_3H_7$, a similar liquid, boiling at 144°, is formed by dry-distilling barium butyrate. By distilling mixtures of barium salts, mixed ketones are obtained. Methyl

ethyl ketone, $CH_3.CO.C_2H_5$, for example, obtained from barium acetate and propionate, is a liquid boiling at 81°.

In their action with oxidising agents the ketones also resemble their prototype, and yield acids whose molecules contain fewer carbon atoms. The molecule is always broken between the carbonyl and one of the alkyl groups, usually that which is least rich in carbon. Methyl ethyl ketone, for example, yields carbon dioxide and propionic acid—

$$CH_3.CO.C_2H_5 \rightarrow CO_2 + COOH.C_2H_5,$$

and diethyl ketone, a mixture of propionic and acetic acids—

$$CH_3.CH_2.CO.C_2H_5 \rightarrow CH_3.COOH + COOH.C_2H_5.$$

The ketones condense with hydroxylamine and phenylhydrazine in precisely the same way as acetone, and the compounds thus formed are useful in isolating and characterising them. The hydroxylamine compounds are known as ketoximes.

It is only those ketones which contain a methyl group which form crystalline bisulphite compounds, but most of them unite with hydrocyanic acid, and several important syntheses have been effected by means of this reaction. That of citric acid (p. 170) may be mentioned.

When reduced with sodium amalgam the ketones are converted into alcohols, which bear the same relation to isopropyl alcohol as the ordinary alcohols to normal propyl alcohol—

$$R_1.CO.R_2 \longleftrightarrow R_1.CH(OH).R_2,$$

and there is one of these alcohols for every ketone, just as there is an ordinary alcohol for every aldehyde. Propione for example is reducible to secondary amyl alcohol, a liquid of fusel odour, boiling at 117°—

$$C_2H_5.CO.C_2H_5 \longleftrightarrow C_2H_5.CHOH.C_2H_5,$$

and methyl ethyl ketone yields secondary butyl alcohol, a similar liquid, boiling at 99°—

$$CH_3.CO.C_2H_5 \longleftrightarrow CH_3.CHOH.C_2H_5.$$

The ordinary alcohols, in which one only of the carbinol hydrogen atoms is replaced by alkyl, are termed primary alcohols, and are distinguished by the presence of the primary alcohol group

$$CH_2OH.$$

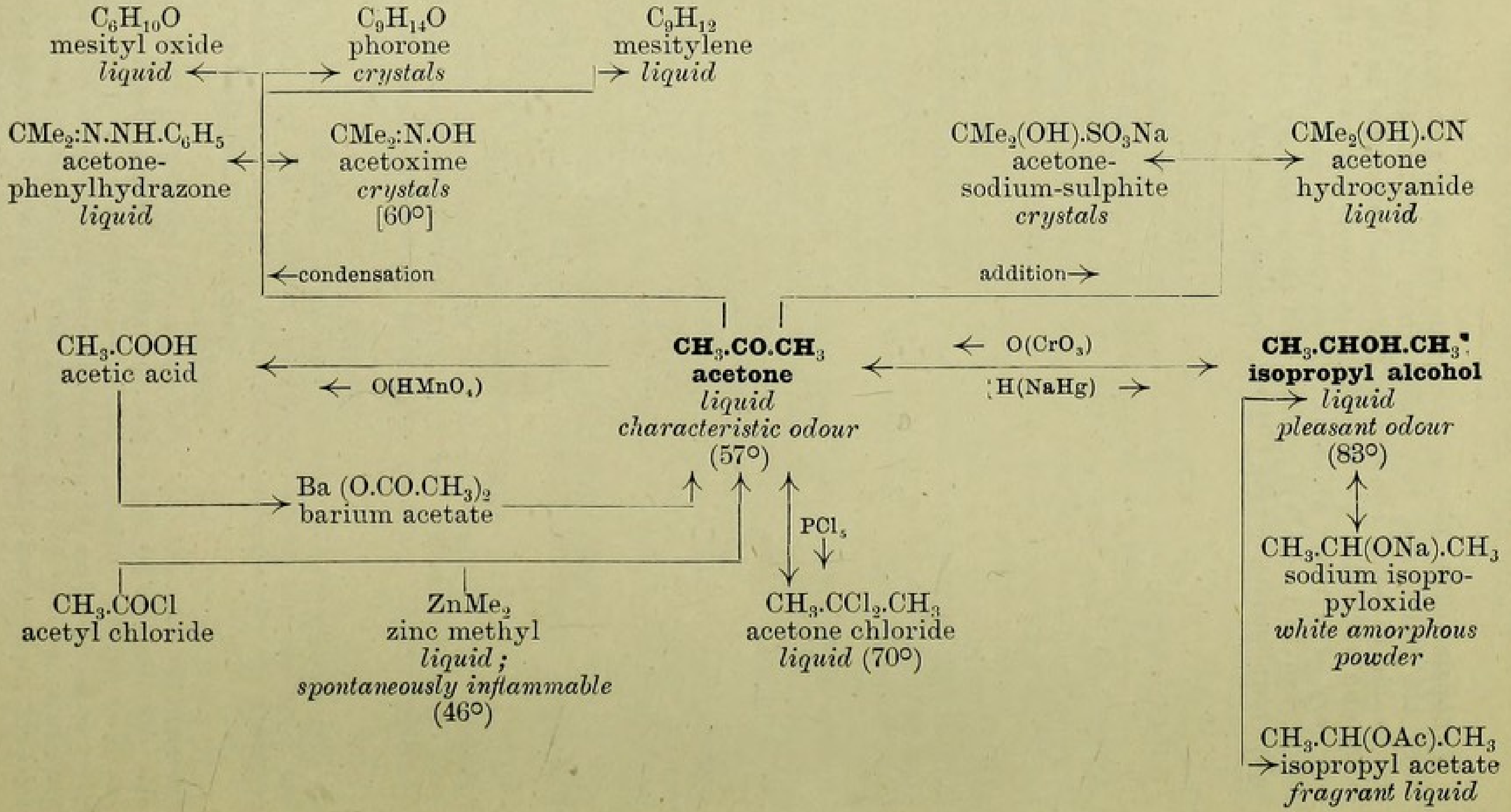
The isomeric alcohols, homologous with isopropyl alcohol, in which two of the carbinol hydrogen atoms are replaced, are termed secondary alcohols, and are characterised by the presence of the secondary alcohol group

$$CHOH.$$

Like their prototype, the secondary alcohols are reconverted into ketones by gentle oxidation, although of course they are broken up by more powerful oxidising agents. With this exception they resemble the ordinary alcohols, and form salts with acids in the same way. The boiling points of the secondary alkyl compounds are as a rule somewhat lower than those of their primary isomerides.

Synopsis.—The ketones are compounds which are isomeric with the aldehydes, but differ from them in that they are oxidisable to acids containing fewer carbon atoms in the molecule, and reducible to secondary alcohols isomeric with the ordinary or primary alcohols. They contain the ketonic group CO linked to two alkyl groups, and the secondary alcohols contain characteristic group CHOH, similarly linked.

ACETONE AND ISOPROPYL ALCOHOL.



CHAPTER XV

THE FOUR BUTYL ALCOHOLS

Isobutyl Alcohol and Isobutyric Acid: Chain or Nucleal Isomerism.—Whilst only one methyl and ethyl and two propyl alcohols are known, the isomerism of the higher alcohols is more complex, for there are four butyl, and no less than eight amyl alcohols.

It has been already mentioned that primary butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, is prepared by reduction of butaldehyde, and that secondary butyl alcohol, $CH_3.CH_2.CHOH.CH_3$, can be formed by reduction of methyl ethyl ketone. The secondary alcohol was first obtained from butylene and secondary-butyl hydrogen sulphate, in the same way as secondary propyl alcohol from propylene, and it is readily made from erythritol (p. 193), in the same way as secondary propyl alcohol from glycerol. The erythritol is converted into secondary-butyl iodide by distillation with iodine and phosphorus, and the iodide into the acetate and alcohol in the manner already mentioned (Luynes, 1863).

The first butyl alcohol that was known, however, was isolated from fusel oil, of which it constitutes about 6 per cent. It is roughly separated by fractionation, and then purified by conversion into the iodide in the manner already described.

Isobutyl alcohol, $C_3H_7.CH_2OH$ (Wurtz, 1852), is a liquid which boils at 108°, and resembles syringa flowers in odour. In its chemical behaviour it resembles ordinary alcohol. It forms a sodium derivative, and an acetate, etc., and it is oxidisable to an acid having the composition of butyric acid, and closely resembling it. The two acids, in fact, were at first thought to be identical, and isobutyl alcohol was deemed on this account the analogue of ordinary alcohol required by the rule of homology. But closer investigation showed that the properties of the acids are different.

Isobutyric acid, $C_3H_7.COOH$ (Redtenbacher, 1846), is an oily liquid, which resembles butyric acid in odour, but it boils at 154°, and is only sparingly soluble in water. The calcium salt, moreover, unlike calcium butyrate, is more soluble in hot than in cold water, and the acid itself, instead of being unaffected by chromic acid mixture, is readily oxidised to acetic acid and carbon dioxide. Isobutyric acid was first obtained from the carob bean.

Isobutyl alcohol can be converted moreover by cautious oxidation into an aldehyde, isobutaldehyde, $C_3H_7.CHO$, which may also be formed from isobutyric acid, and is readily converted into either. Isobutaldehyde is a liquid boiling at 61°, whilst ordinary butaldehyde boils at 74°; it has all the properties of an aldehyde.

Isobutyl alcohol is thus a primary alcohol, and there are therefore two primary alcohols of the constitution $C_3H_7.CH_2OH$, and two acids of the constitution $C_3H_7.COOH$.

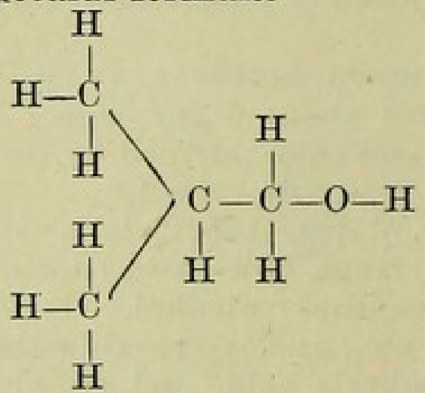
Now ordinary butyric acid may be regarded as propyl-formic acid, $CH_3.CH_2.CH_2-COOH$, and since there are two propyl radicles, there may be expected an isopropyl-formic acid of the constitution $CHMe_2-COOH$, which will be connected with an isopropyl-carbinol of the constitution $CHMe_2-CH_2OH$ (Kolbe, 1864). If isobutyric acid is this isopropyl-formic acid, it should be formed from isopropyl alcohol by the cyanide synthesis.

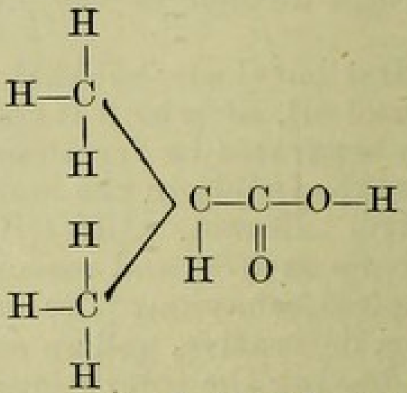
This is actually the case, for by boiling isopropyl iodide with alcoholic potassium cyanide and hydrolysing the resulting isopropyl cyanide, an acid is obtained which is identical with the fusel and carob acid (Erlenmeyer, 1867)—

$$CHMe_2.I \rightarrow CHMe_2.CN \rightarrow CHMe_2.COOH.$$

The constitution of isobutyric acid has been further confirmed by its synthesis by introduction of two methyl groups into the methyl of acetic acid (p. 150).

Isobutyl alcohol and isobutyric acid are thus represented by structural formulæ





which differ from those of all the compounds that have thus far been considered in that they contain a branching chain of carbon atoms. The isomerism is here due to a variation in the form of the carbon chain or nucleus, and is consequently termed chain or nucleal isomerism. The straight butyl chain, C—C—C—C, is termed a normal chain, and the corresponding compounds, normal compounds, whilst the isobutyl compounds, containing the isobutyl chain, $\genfrac{}{}{0pt}{}{C}{C}{>}C{-}C$, are termed branching chain compounds. The prefix iso- is applied to such compounds as contain the isopropyl group. It is noteworthy that the branching chain is associated in this, as in other similar cases, with lower boiling points than the corresponding normal chain.

Tertiary Butyl Alcohol.—The existence of the fourth butyl alcohol was foreshadowed by the same reasoning as led to the recognition of the secondary alcohols (Kolbe, 1860). As already indicated, the primary and secondary alcohols being mono- and di-alkyl-carbinols, there should be tri-alkyl-carbinols or tertiary alcohols, of which the simplest must be trimethyl-carbinol or tertiary butyl alcohol, $CMe_3.OH$.

This tertiary butyl alcohol can be prepared from acetyl chloride and zinc methyl by a modification of the acetone synthesis (p. 77). If a second equivalent of the zinc alkyl is added, and the product kept for some days before adding the water, the crystalline additive compound exchanges chlorine for methyl—

$$CMe_2Cl.ZnMe + ZnMe_2 = CMe_3.O.ZnMe + ZnMeCl,$$

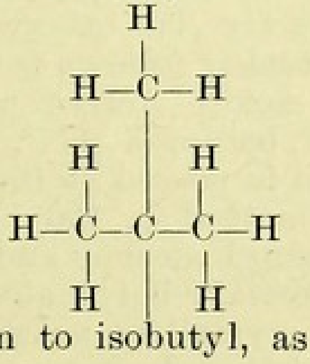
and this second product, which is also crystalline, is then hydrolysed by the water to the tertiary alcohol, zinc oxide and marsh gas. The alcohol can be distilled off and dehydrated with baryta—

$$CMe_3.O.ZnMe + H_2O = CMe_3.OH + ZnO + CH_4.$$

Tertiary butyl alcohol, $CMe_3.OH$ (Butlerow, 1864), crystallises in colourless prisms, and resembles camphor in odour. It melts at 25°, and boils at 83°, and is thus more volatile and more easily solidified than its isomerides with longer carbon chains. It forms a sodium derivative, and an acetate, etc., so that its alcoholic nature is undoubted, but when oxidised with chromic acid mixture it breaks up altogether, yielding carbon dioxide and acetone, together with acetic acid from the oxidation of the latter—

$$CMe_3.OH + 4O = COMe_2 + CO_2 + 2H_2O.$$

The tertiary butyl radicle CMe_3 or



bears the same relation to isobutyl, as the secondary to the normal butyl radicle.

The Amyl Alcohols and Valeric Acids.—On account of the rigid quadrivalence of carbon, no further radicles can be introduced into the methyl group of methyl alcohol, but by repeating the exchange of alkyl for hydrogen in the alkyl groups of the derived alcohols, it is obvious that radicles of very great complexity may be formed. It may be expected, therefore, that the isomerism of the amyl alcohols and valeric acids will be still more complex, and this is the case. There are four primary amyl alcohols and therefore four valeric acids, and in addition to these there are three secondary and one tertiary alcohol.

Normal amyl alcohol, $CH_3.CH_2.CH_2.CH_2.CH_2OH$, and normal valeric acid, $CH_3.CH_2.CH_2.CH_2.COOH$, do not occur in nature, and are prepared synthetically from normal butyl alcohol by the cyanide method (Lieben and Rossi, 1872).

The chief of the amyl alcohols, however, are two primary alcohols occurring in fusel oil (p. 40), of which they constitute about one-third by volume. The main fraction obtained from dry potato-spirit oil boils fairly constantly at 130-132°, and was thought for a long time to be a chemical individual, and termed amyl alcohol (Dumas, *amylum*=starch). But the specific rotatory power of this alcohol varies with different specimens, and as the rotatory power of a pure substance (p. 144), like any other property, is constant, it follows that the fusel alcohol is a mixture.

Commercial amyl alcohol is resolved into its two constituents by fractionally crystallising barium amyl sulphate from water. The less soluble salt yields on hydrolysis an alcohol, which is optically inactive, whilst the alcohol from the more soluble salt has a constant rotatory power (Pasteur, 1855).

Fermentation, inactive or isoamyl alcohol, $CHMe_2.CH_2.CH_2OH$, which constitutes about 25 per cent. of potato fusel oil, is a liquid of rank, penetrating odour, which boils at 131°. Its constitution follows from its oxidation to the corresponding acid. Isovaleric acid, $CHMe_2.CH_2.COOH$, is an oily liquid of very clinging and unpleasant odour, which occurs naturally in the root of the lesser valerian. It boils at 175°. Its constitution as an isobutyl derivative follows from its synthesis from isobutyl alcohol by the cyanide method.

Active amyl alcohol, or secondary-butyl-carbinol, $CHMeEt.CH_2OH$, is an optically active, but otherwise similar liquid, boiling at 131°; its constitution follows from its oxidation to the corresponding valeric acid. Active valeric acid, $CHMeEt.COOH$, is an oily liquid, boiling at 177°, and its constitution as methyl-ethyl-acetic acid is proved by its synthesis from acetic acid by the acetoacetic method (p. 150).

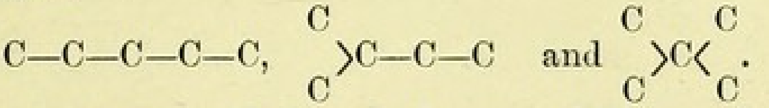
The fourth primary amyl alcohol and corresponding valeric acid are derived from tertiary butyl alcohol. Trimethyl-acetic acid, $CMe_3.COOH$, is a crystalline substance, which resembles acetic acid in odour, and is made from tertiary butyl iodide by the cyanide synthesis. Trimethyl-carbinol, $CMe_3.CH_2OH$, is a crystalline substance, which is formed by reducing the acid chloride with sodium amalgam.

The secondary amyl alcohols, which are all liquid substances, can be made by reducing the corresponding ketones, and in other ways. Their constitutional formulæ are

$$CH_3.CH_2.CH_2.CHOH.CH_3,\quad CH_3.CH_2.CHOH.CH_2.CH_3 \text{ and } CHMe_2.CHOH.CH_3.$$

Tertiary amyl alcohol or dimethyl-ethyl-carbinol, $CMe_2Et.OH$, is a liquid of camphor odour, boiling at 102°. It is formed from propionyl chloride and zinc methyl, in an analogous manner to tertiary butyl alcohol.

The amyl alcohols and their derivatives are thus built on the three nuclei—

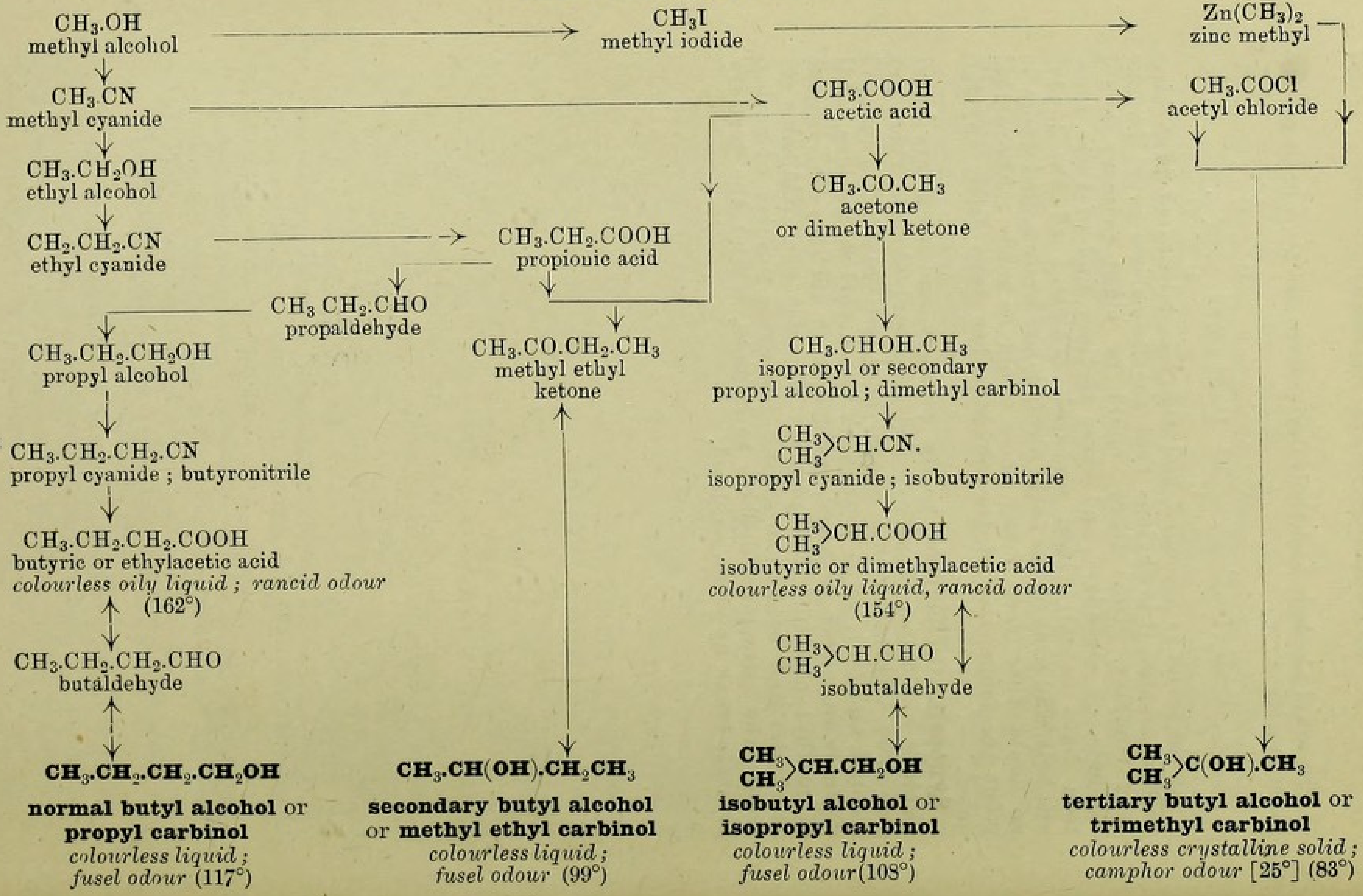


$$C-C-C-C-C,\quad \begin{matrix}C & \\ & >C-C-C \\ C & \end{matrix} \quad \text{and} \quad \begin{matrix}C & & C\\ & >C< & \\ C & & C\end{matrix}.$$

As the series is ascended, and the possibilities of branching become greater, it is obvious that the isomerism must become very complex. Thus there should be eight primary hexyl alcohols, six secondary, and three tertiary, and of these, fourteen have actually been prepared. Thirteen of the heptyl alcohols, and nine of the octyl alcohols are known, and there is no doubt that very many more could be made. Above this point the isomerism of the alcohols has been little investigated.

Synopsis.—In addition to the primary and secondary butyl alcohols analogous to propyl and isopropyl alcohol, there are two more, together with a related acid, derived from isopropyl alcohol, and built on a branching chain carbon nucleus. All alcohols are either primary, secondary, or tertiary derivatives of methyl alcohol. The primary alcohols are oxidisable to aldehydes and acids containing the same number of carbon atoms, the secondary alcohols to ketones, whilst the tertiary alcohols break up when oxidised.

THE BUTYL ALCOHOLS.



SECTION IV

THE HYDROCARBONS AND THE THEORY OF SUBSTITUTION

CHAPTER XVI

THE ETHANE HYDROCARBONS

Methane or Marsh-gas.—The Organic compounds thus far considered contain oxygen and other elements in addition to carbon and hydrogen, but a number of compounds have now to be dealt with, which contain carbon and hydrogen only. These are termed the hydrocarbons. They are of considerable importance in themselves, but their especial interest lies in their bearing on theory and classification.

The simplest of the hydrocarbons is methane, the marsh-gas which is formed in the mud of stagnant ponds, and which constitutes the explosive fire-damp that is given off in coal-mines. It occurs naturally also in the petroleum districts, and issues from the earth at Baku on the Caspian Sea, and in various places in the Pennsylvanian oil district. It is also formed by the dry-distillation of organic matter, and thus constitutes some 40 per cent. of ordinary coal gas.

Methane or marsh-gas, CH_4 (Volta, 1777), is a light insoluble gas, which is condensed by great cold and pressure to a light, colourless liquid, boiling at $-160°$. It burns with a blue, faintly luminous flame to carbon dioxide and water (Volta), and forms a highly explosive mixture with air or oxygen.

Gaseous organic compounds like methane are analysed by explosion with oxygen, a considerable excess of which must be used to diminish the force of the explosion. Thus when a mixture of

5 c.c. of methane
and 20 c.c. of oxygen

is exploded in a eudiometer tube over mercury, it yields under the same conditions of temperature and pressure:

10 c.c. of steam
and 5 c.c. of carbon dioxide,

whilst 10 c.c. of oxygen remains unconsumed. The volume of the steam is determined from the shrinkage of the gaseous product on cooling, that of the carbon dioxide by absorption with caustic alkali, and that of the residual oxygen by absorption with alkaline pyrogallol (p. 298).

Since by Avogadro's law the numbers of molecules in the various gases are proportional to their volumes, it follows that

$$5x + 10O_2 = 5CO_2 + 10H_2O$$
$$\text{or } x + 2O_2 = CO_2 + 2H_2O,$$

where x is a molecule of methane. Hence

$$x = CO_2 + 2H_2O - 2O_2 = CH_4.$$

The molecular weight thus found, 16, is confirmed by the density, 8, which is determined in the same way as that of an inorganic gas.

Synthesis of Methane.—Methane has been synthesised in many ways. The first synthesis (Dumas, 1830) was effected by heating an intimate mixture of fused sodium acetate and soda-lime, and affords a convenient method of making small quantities of the gas. The operation is carried out in a hard glass tube provided with delivery tube—

$$CH_3.COONa + NaOH = CH_4 + Na_2CO_3.$$

A direct synthesis from inorganic compounds can be effected by passing sulphuretted hydrogen saturated with carbon bisulphide vapour over red-hot copper turnings (Berthelot, 1856). The sulphur is taken up by the copper, whilst the hydrogen combines with the carbon. The gas is separated from sulphuretted hydrogen, etc., by shaking with alcohol, in which it is fairly soluble. The solution is then warmed and the methane washed with concentrated sulphuric acid—

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$

The formation of methane from zinc methyl and water has already been mentioned (p. 77). The zinc compound is best diluted with ether, as the action is violent—

$$Zn(CH_3)_2 + H_2O = ZnO + 2CH_4.$$

The formation and hydrolysis of the zinc methyl may be combined in one operation by heating methyl iodide with zinc and water in a sealed tube. The gas escapes in quantity on opening the cooled tube (Frankland, 1856)—

$$2CH_3I + 2Zn + H_2O = 2CH_4 + ZnI_2 + ZnO.$$

Methane can also be formed by direct reduction of the methyl halogen compounds by means of an electrolytic copper-zinc couple (Gladstone and Tribe, 1874). Granulated zinc, nearly filling a small flask, is washed with dilute sulphuric acid and water and then coated with a very thin layer of copper by filling the flask with dilute copper sulphate. After a few minutes the solution is washed away with water, and the flask completely filled with alcohol, and on now introducing a little methyl bromide or iodide, and warming slightly, a stream of methane is evolved, the action continuing for hours. The residual liquid contains zinc bromide, etc., the hydrogen being furnished by the alcohol—

$$CH_3Br + 2H = CH_4 + HBr.$$

Chlorination of Methane: Substitution.—Methane can not only be made from the methyl halogen compounds and methyl alcohol, but can also be converted into them. When it is mixed with an equal volume of chlorine and exposed to diffused daylight, action takes place, and the gas gradually becomes acid with hydrogen chloride; and on passing the washed and dried product through a U-tube immersed in a powerful freezing mixture, methyl chloride is condensed. It is identical in every respect with the methyl chloride prepared from methyl alcohol, and is convertible into the alcohol by the ordinary hydrolysis. This synthesis of methyl alcohol was the first to be effected (Berthelot, 1857)—

$$C \rightarrow CS_2 \rightarrow CH_4 \longleftrightarrow CH_3Cl \longleftrightarrow CH_3.OH.$$

It is thus evident that methane is methyl hydride, $CH_3.H$, and that methyl chloride may be regarded as derived from it by substitution of chlorine for hydrogen. The chloride is on this account termed a substitution product of the hydrocarbon. The replacement of hydrogen by chlorine is termed direct substitution, and that of chlorine by hydrogen inverse substitution.

It follows also that methyl alcohol is a hydroxy-substitution-product of methane. The importance of this will be seen presently.

Ethane.—The action of the copper-zinc couple on ethyl bromide is precisely similar to its action on the methyl halogen compounds, ethyl hydride or ethane being produced—

$$C_2H_5.Br + 2H = C_2H_5.H + HBr.$$

Ethane, C_2H_6 (Frankland, 1848), is a gas which resembles methane, but is slightly heavier than air, and is condensible to a colourless liquid by a pressure of 46 atmospheres at 4°. It burns with a slightly luminous flame to carbon dioxide and water, the greenish colour due to the ethyl bromide vapour in the crude product disappearing after washing the gas with caustic soda. Like its lower homologue, ethane occurs naturally in the oil districts. At the Delameter oil well at Pittsburg, for example, nearly pure ethane is given off in enormous quantities, and is used for heating blast furnaces, and for general domestic purposes.

Ethane may also be prepared from zinc ethyl in the same way as methane from zinc methyl (Frankland, 1856)—

$$ZnEt_2 + H_2O = 2Et.H + ZnO,$$

and by heating ethyl iodide with zinc and water in a sealed tube—

$$2EtI + 2Zn + 2H_2O = 2EtH + ZnI_2 + ZnO.$$

It is also formed by heating sodium propionate with soda-lime in the same way as methane from sodium acetate.

From all these points of view it must be regarded as ethyl hydride. Moreover it is attacked by chlorine in precisely the same way as methane, and the substitution product, chlorethane, thus formed is identical in every respect with ethyl chloride, and is hydrolysable in the ordinary manner to alcohol (Berthelot)—

$$C_2H_6 = EtH \leftrightarrow EtCl \leftrightarrow Et.OH.$$

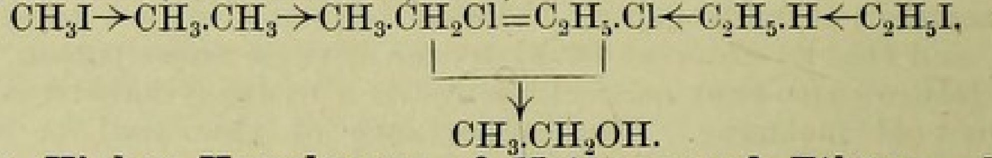
But the hydrocarbon may also be regarded as dimethyl, $CH_3.CH_3$, and it was first obtained in fact in an attempt to isolate the methyl radicle. It is thus formed also by heating methyl iodide with metallic zinc or sodium (Frankland, 1849)—

$$CH_3I + Na_2 + CH_3I = CH_3.CH_3 + 2NaI,$$

and by electrolysing a strong alcoholic solution of potassium acetate (Kolbe, 1849). Hydrogen of course appears at the anode—

$$\begin{array}{l} CH_3.\vdots COO \vdots K \\ CH_3.\vdots COO \vdots K \end{array} = \begin{array}{l} CH_3 \\ \dot{C}H_3 \end{array} + 2CO_2 + K_2.$$

The identity of ethyl hydride with dimethyl, however, is proved by the identity of the chlorination products of the two gases, and the convertibility of both into one and the same ethyl alcohol (Schorlemmer, 1862)—



$$\begin{tikzcd}[column sep=small] CH_3I \arrow[r] & CH_3.CH_3 \arrow[r] & CH_3.CH_2Cl = C_2H_5.Cl \arrow[d] & C_2H_5.H \arrow[l] & C_2H_5I, \arrow[l] \\ & & CH_3.CH_2OH. & & \end{tikzcd}$$

The Higher Homologues of Methane and Ethane.—The alkyl halogen compounds in general are reducible by copper-zinc or zinc-dust and water to hydrocarbons, homologous with methane and ethane.

Propane, C_3H_8 (Berthelot, 1867), obtained by reducing propyl iodide with copper-zinc is a gas which resembles ethane, but is readily condensible to a liquid boiling at −17°. It is also formed together with ethane and butane, by heating a mixture of methyl and ethyl iodides with zinc-dust—

$$CH_3I + Zn + C_2H_5I = CH_3.C_2H_5 + ZnI_2.$$

Propane was first obtained by heating acetone in a sealed tube with concentrated hydriodic acid and red phosphorus (Berthelot). This mixture acts as a powerful reducing agent, the hydrogen iodide being resolved at the high temperature into iodine and nascent hydrogen. The phosphorus combines with the iodine, and probably also starts the action by replacing oxygen or hydroxyl by halogen. Practically all alcoholic and ketonic substances are reducible in this manner, and many acids also—

$$CH_3.CO.CH_3 + 4HI = CH_3.CH_2.CH_3 + H_2O + 2I_2.$$

Propane is also easily obtained by reducing isopropyl iodide with zinc and dilute hydrochloric acid. The position isomerism of the iodides disappears when the atoms attached to the carbon nucleus become similar. As soon as chain isomerism appears, however, isomerism amongst the hydrocarbons becomes possible, and there are thus two butanes corresponding with the chain-isomeric butyl radicles.

Normal butane, $CH_3.CH_2.CH_2.CH_3$ (Frankland, 1849), a liquid boiling at 1°, is obtained, together with zinc ethyl, by heating dry ethyl iodide with excess of zinc in a sealed tube. On opening the ice-cooled tube some ethane and ethylene (p. 102) escape, but on allowing the temperature to rise slightly, a steady stream of the butane vapour is obtained—

$$EtI + Zn + EtI = Et.Et + ZnI_2.$$

Butane is also formed by reducing butyric and succinic acids with hydriodic acid and phosphorus (Berthelot)—

$$CH_3.CH_2.CH_2.COOH + 6HI = CH_3.CH_2.CH_2.CH_3 + 2H_2O + 3I_2.$$

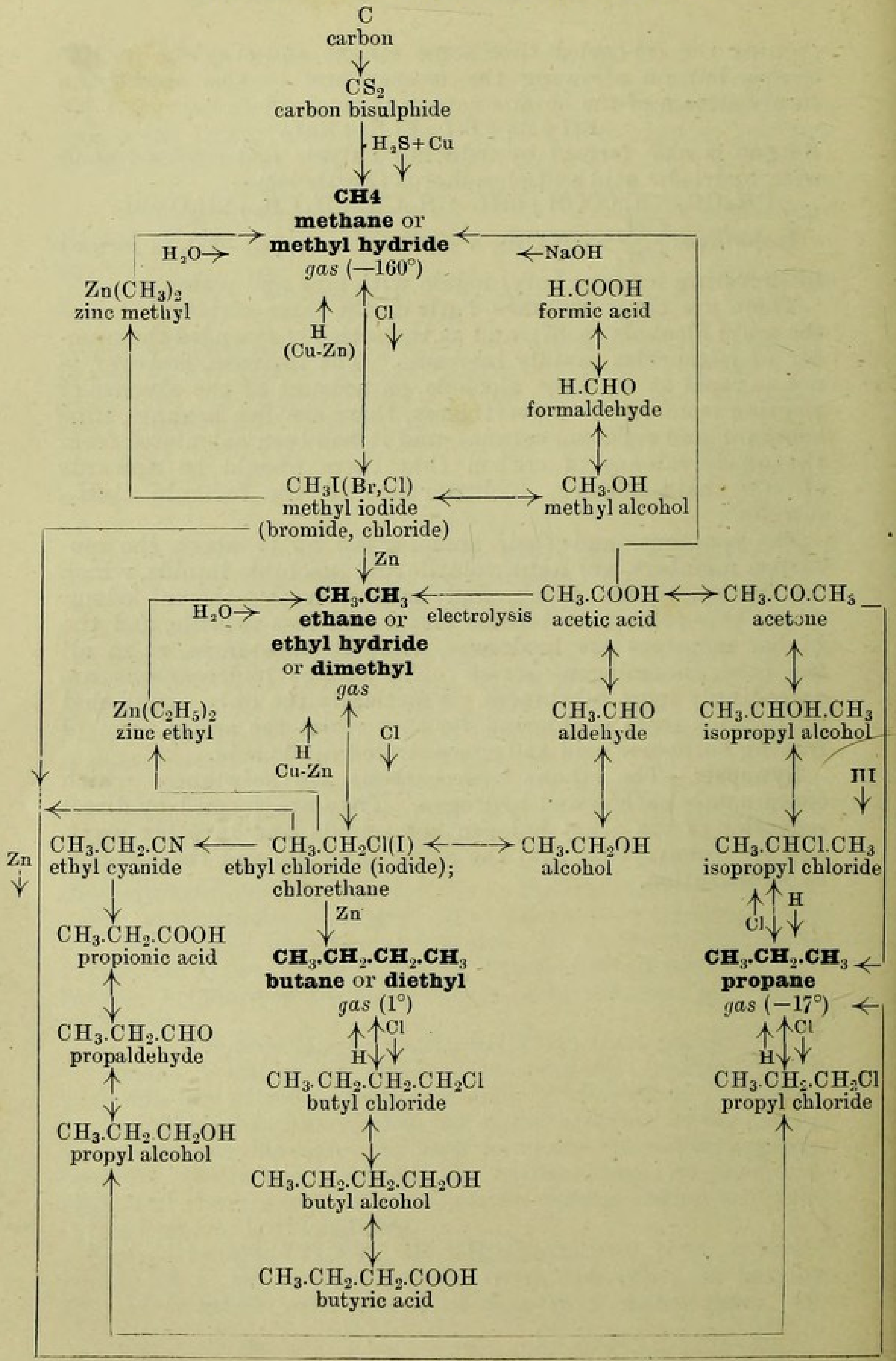
Isobutane, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.CH_3$, a gas condensing at -17°, is formed by digesting tertiary butyl iodide with zinc and water.

There are three pentanes, built on the three carbon chains of the amyl alcohols (p. 87), and as the series is ascended the number of isomerides rapidly increases. The increase, however, is not so rapid as with the alcohols, on account of the absence of position isomerism. Nevertheless, there are five hexanes, nine heptanes, and eighteen octanes, and it has been calculated from the quadrivalence of carbon that there should be upwards of 800 chain-isomeric hydrocarbons of the formula $C_{13}H_{28}$ (Cayley).

The pentanes, and their homologues, up to about the ten-carbon members, are light, volatile and insoluble liquids, which are greasy to the touch, and have a fresh ethereal odour. Above this point they become viscid and less volatile, and the higher members are inodorous, wax-like substances, as in all the other homologous series. The ethane hydrocarbons are exceedingly inert substances. Practically the only agent that will attack them is chlorine, for they resist the action even of fuming sulphuric acid and concentrated nitric acid.

Synopsis.—The ethane hydrocarbons are substances which contain only carbon and hydrogen. They are formed by direct reduction of the alkyl halogen compounds, and in other ways, and are reconvertible into the alkyl chlorides and the alcohols by substitution.

THE LOWER ETHANE HYDROCARBONS.



CHAPTER XVII

THE NATURAL PARAFFINS

Petroleum: Paraffin Oil and Wax.—It has been already stated that methane and ethane occur naturally in the petroleum districts, and petroleum itself, and the paraffin oil obtained by distilling cannel coal and shale are in fact mixtures of hydrocarbons of the ethane series (Pelouze, Greville Williams, Schorlemmer, 1857–1864).

Petroleum or rock oil has been known for ages, but only in small quantities. The oily scum which floats on the surface of wells in certain districts was used as a healing ointment by the Romans, and in later times by the North American Indians. The first discovery of petroleum in quantity was made in Derbyshire in the middle of the present century (Lyon Playfair, 1849), when a rich spring of dense oil was found in a disused mine. This spring was exhausted in a few years, however, and to supply the demand for the oil that had by this time arisen, various methods were tried of making it artificially. The most successful of these, which is still used, consists in distilling cannel coal or shale—slate-coal (Young, 1856).

Soon after this oil was struck in Pennsylvania, and in 1861 a well was bored, from which the crude oil flowed spontaneously at the rate of 100,000 gallons a day. Since then, petroleum has been found in various parts of the world. It is probable that natural petroleum, the supply of which in many districts seems inexhaustible, is formed by the action of infiltered water on hot metallic carbides at a great depth. Other hypotheses have been put forward, however.

As stated above, American petroleum, and shale and cannel oil, are complex mixtures of hydrocarbons of the ethane series. The crude oils are dark viscid liquids, having a very unpleasant odour, and must be roughly purified and fractionated before they are fit for use.

Shale oil, for example, is separated from the accompanying water, and then redistilled, coke remaining in the retort. The distillate is agitated with caustic soda to remove phenols (p. 251), and then with concentrated sulphuric acid to remove basic impurities and colouring matter. It is then washed and rectified. The more volatile portions (sp. gr. 0·77–0·79) are termed variously petroleum naphtha, light petroleum or benzoline, whilst the next but still mobile fractions (sp. gr. 0·82–0·83) form the ordinary paraffin oil used for lighting, heating, and motor purposes. These are followed by more or less viscid fractions, forming various grades of lubricating oil and vaseline. The tail fractions solidify on cooling, and after pressing and recrystallising from light petroleum, are known as paraffin wax.

Paraffin wax was first obtained from wood tar (Reichenbach, 1839) before the ethane hydrocarbons were known, and was given its name on account of its chemical inertness (*parum affinis*). The name was made generic, when the nature of the petroleum hydrocarbons was established (p. 97).

Constitution of the Petroleum Hydrocarbons: Paraffin Series.—The solid paraffins contain about 25 carbon atoms in the molecule, but are difficult to obtain in the pure state from the commercial wax. The liquids, however, are readily separable. Light petroleum or benzoline, for example, is shaken with concentrated sulphuric acid until the latter is no longer coloured, and is then digested with a mixture of concentrated sulphuric and nitric acids, until nitrous fumes cease to be evolved. The light oil, which has now completely lost the characteristic "petroleum" odour, is washed with water and dilute caustic soda, and roughly dried with solid caustic potash, and then completely dried by distilling two or three times from metallic sodium. By fractionating this product, pentane, hexane, and heptane can be obtained in a pure state (Greville Williams).

The natural paraffins are probably all normal compounds, and the constitutions of many of them have been definitely established. By passing chlorine through natural pentane, for example, for many hours in daylight, it is converted into a mixture of isomeric monochloropentanes or amyl chlorides. The gas is passed merely into the surface of the liquid, so that the chloro-compounds, which are less volatile than the hydrocarbons, and condense, may escape further chlorination. The amyl chlorides are converted into the corresponding alcohols by heating with silver acetate, and hydrolysing the resulting amyl acetates with alkali (compare p. 79). The alcohols are then separated by fractional distillation, and their constitution determined by oxidation with chromic acid mixture.

One of the fractions ultimately yields normal valeric acid, and the other a mixture of acetic and propionic acids. The latter acids can be separated by fractional neutralisation. Enough caustic soda is added to neutralise rather more than half the acids present, and on distilling the product, the propionic acid alone passes over, the more powerful acetic acid remaining in combination with the alkali. The acids are identified by analysing their silver salts.

Now the valeric acid can only be formed by the oxidation of normal amyl alcohol—

$$CH_3.CH_2.CH_2.CH_2.CH_2OH \rightarrow CH_3.CH_2.CH_2.CH_2.COOH,$$

whilst the other acids may result from the oxidation of either methyl-propyl-carbinol, or diethyl-carbinol—

$$\begin{array}{l} CH_3.CHOH.CH_2.CH_2.CH_3 \rightarrow CH_3.CO.CH_2.CH_2.CH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \rightarrow CH_3.COOH + COOH.CH_2.CH_3 \\ CH_3.CH_2.CHOH.CH_2CH_3 \rightarrow CH_3.CH_2.CO.CH_2.CH_3. \end{array}$$

The original chlorides are thus primary and secondary normal amyl chlorides—

$$CH_3.CH_2CH_2.CH_2.CH_2Cl$$

and

$$CH_3.CHCl.CH_2.CH_2.CH_3 \text{ or } CH_3.CH_2.CHCl.CH_2.CH_3,$$

and the hydrocarbon normal pentane :

$$CH_3.CH_2.CH_2.CH_2.CH_3$$

(Schorlemmer, 1863).

The natural paraffins being thus identical with the ethane hydrocarbons, the term paraffin is applied to the series in general (Watts). From their genetic connection with the paraffins, the alkyl or hydrocarbon radicles are sometimes termed paraffinoid radicles.

The normality of the higher paraffins has been established by a step-by-step process connecting them with the nine-carbon fatty acid, whose constitution is known from the cyanide synthesis. Thus by dry distilling a mixture of barium stearate and acetate, methyl-heptadecyl-ketone, $CH_3.CO.C_{17}H_{35}$, is formed, a wax-like substance, which is convertible by chromic acid mixture into acetic acid and margaric acid, $C_{16}H_{33}.COOH$, the next lower homologue of stearic acid. Margaric acid is convertible in turn into methyl-hexadecyl ketone and palmitic acid, the latter into methyl-pentadecyl-ketone and the fifteen-carbon fatty acid, and so on, until the nine-carbon acid is reached. It follows therefore that the fatty acids are all normal compounds (Krafft, 1882).

Now the acids and ketones are all reducible to the paraffins by the hydriodic acid method, stearic acid thus yielding octodecane, C_8H_{38}, margaric acid, heptadecane, $C_{17}H_{36}$, and so on, and these hydro-carbons are therefore also normal (Krafft).

In a few special cases the constitutions of paraffins have been established synthetically. Thus by heating butyl iodide with zinc-dust, dibutyl or normal octane is obtained—

$$2CH_3.[CH_2]_2.CH_2I \rightarrow CH_3.[CH_2]_2.CH_2.CH_2.[CH_2]_2CH_3 = CH_3[CH_2]_6CH_3$$

Similarly the primary octyl iodide derived from this octane is convertible into dioctyl or normal hexadecane—

$$2CH_3.[CH_2]_6.CH_2I \rightarrow CH_3.[CH_2]_6.CH_2.CH_2.[CH_2]_6.CH_3 = CH_3.[CH_2]_{14}.CH_3.$$

This hexadecane is in every respect identical with that obtained by reducing palmitic acid with hydriodic acid, and both the hydrocarbon and the fatty acid are therefore normal compounds (Zincke, 1869 ; Schorlemmer, 1872)—

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.COOH.$$

It is not as yet known how these long-chained carbon compounds are formed in nature. The longest chain that is known occurs in the normal hydrocarbon, $C_{64}H_{130}$, which is formed synthetically by the last method.

The Hydrocarbons as the Basis of Classification.—The paraffins form a very valuable link between the various classes of compounds. The isomerism of the butyl and amyl alcohols, for example, although accounted for by their relation to methyl alcohol, is much more concisely expressed by reference to the position of the hydroxyl group in the three pentane chains (p. 87). The modern system of classification is based on this principle, the alcohols and their derivatives being regarded as substitution products of the related hydrocarbons (p. 100).

Thus methyl alcohol, $CH_3.OH$, is hydroxy-methane; ethyl alcohol, $CH_3.CH_2OH$, hydroxy-ethane; normal propyl alcohol, $CH_3.CH_2.CH_2OH$, α-hydroxy-propane; and isopropyl alcohol, $CH_3.CHOH.CH_3$, β-hydroxy-propane. Similarly the four butyl alcohols are respectively α- and β-hydroxy-butane and α- and β-hydroxy-isobutane. Acetone may be termed keto-propane, and the two normal five-carbon ketones respectively α- and β-keto-pentane.

To provide names for all classes of compounds on this plan, an International system of nomenclature has been devised (Geneva Conference, 1892), in which the stems of the names represent the parent hydrocarbons, and the substituted groups are indicated by suffixes or prefixes. Thus alcohol is ethanol; aldehyde, ethanal; acetic acid, ethanoic acid; and ethyl chloride, chlorethane.

Position isomerides, such as the propyl alcohols, are distinguished by numerical prefixes. Thus normal propyl alcohol is 1-propanol, and its isomeride 2-propanol, the carbon atoms being numbered from the end of the chain—

$$\overset{(1)}{CH_3}.\overset{(2)}{CHOH}.\overset{(3)}{CH_3}.$$

The ketones are distinguished by the suffix *one*. Thus acetone, $CH_3.CO.CH_3$, is propanone; propione, $CH_3.CH_2.CO.CH_2.CH_3$, is 3-pentanone; whilst the metameric methyl-propylketone, $CH_3.CO.CH_2.CH_2.CH_3$, is 2-pentanone.

The chain isomerism of the butanes and their derivatives is indicated in a similar manner, the branching chain compounds being classed as alkyl derivatives of the longest carbon chain in the molecule. Isobutane is thus 2-methyl-propane, $CH_3.CHMe.CH_3$; isobutyl alcohol, 2-methyl-1-propanol, $CH_3.CHMe.CH_2OH$; and isobutyric acid, $CH_3.CHMe.COOH$, 2-methyl-propanoic acid. Similarly, tertiary butyl alcohol is 2-methyl-2-propanol, $CH_3.CMeOH.CH_3$.

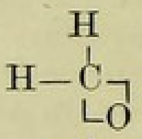
The amides, nitriles, and amines also take their names from the related hydrocarbons. Acetamide, for example, is ethanamide; acetonitrile, ethane-nitrile; and ethylamine, amino-ethane.

The operations involved in converting the natural paraffins into any of their derivatives are difficult and tedious (compare Benzene), but this does not lessen the value of the system, which lies in referring all types of compounds to the simplest. Its importance will be seen in the sequel.

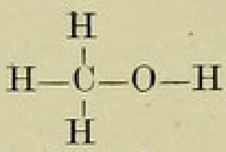
Synopsis.—The natural paraffins of petroleum and shale-oil are hydrocarbons of the ethane series. Their importance, from a chemical point of view, lies in their convertibility into the alcohols and their derivatives by substitution. The modern system of nomenclature is based on this fact.

THE HYDROCARBONS AS THE BASIS OF CLASSIFICATION.

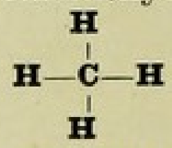
I. Derivatives of Methane.



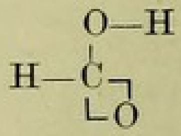
methanal
(formaldehyde)



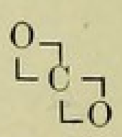
methanol
(methyl alcohol)



methane

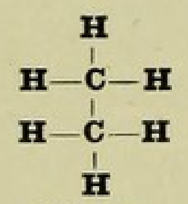


methanoic acid
(formic acid)

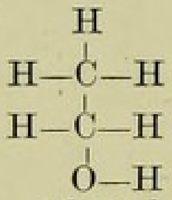


carbon dioxide

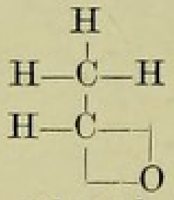
II. Derivatives of Ethane.



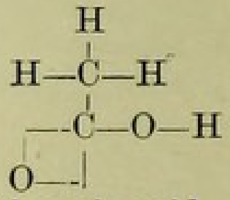
ethane



ethanol
(alcohol)

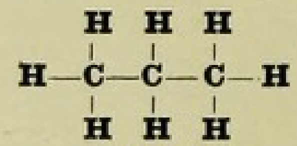


ethanal
(aldehyde)

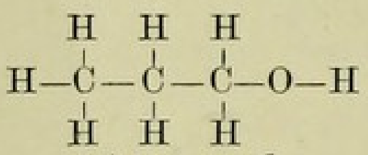


ethanoic acid
(acetic acid)

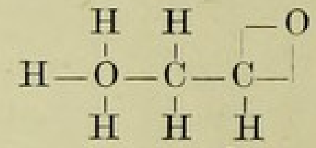
III. Derivatives of Propane.



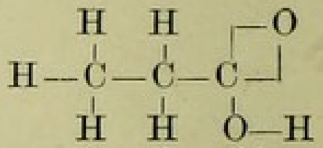
propane



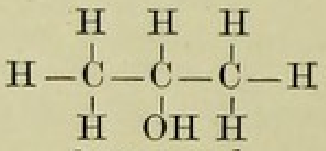
1-propanol
(propyl alcohol)



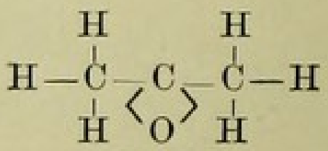
propanal
(propaldehyde)



propanoic acid
(propionic acid)

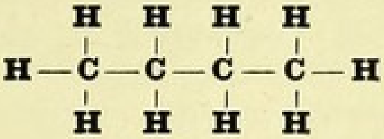


2-propanol
(isopropyl alcohol)



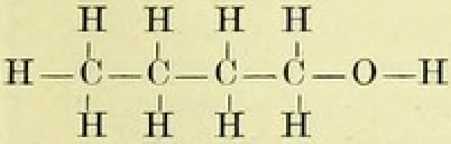
propanone
(acetone)

IV. DERIVATIVES OF BUTANE.



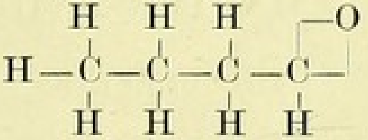
$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

butane



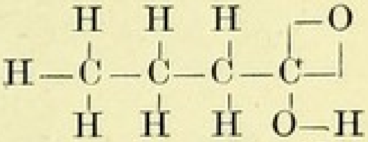
$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -O-H \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

1-butanol or α-hydroxybutane
(normal butyl alcohol)



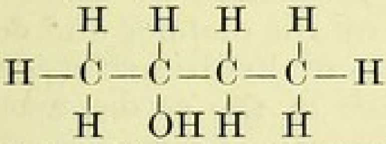
$$\begin{array}{ccccccccc} & H & & H & & H & & O & \\ & | & & | & & | & & \| & \\ H- & C & - & C & - & C & - & C & \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

butanal
(butaldehyde)



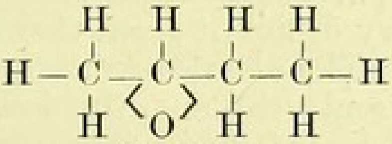
$$\begin{array}{ccccccccc} & H & & H & & H & & O & \\ & | & & | & & | & & \| & \\ H- & C & - & C & - & C & - & C & \\ & | & & | & & | & & | & \\ & H & & H & & H & & O-H & \end{array}$$

butanoic acid
(butyric acid)



$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H \\ & | & & | & & | & & | & \\ & H & & OH & & H & & H & \end{array}$$

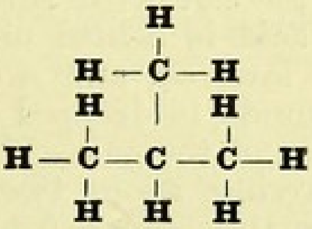
2-butanol or β-hydroxybutane
(secondary butyl alcohol)



$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H \\ & | & & & & | & & | & \\ & H & & \langle O \rangle & & H & & H & \end{array}$$

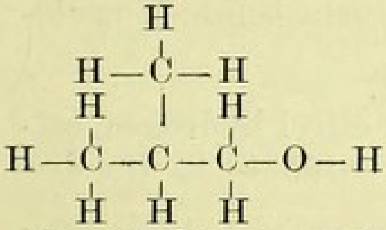
butanone
(methyl ethyl ketone)

V. DERIVATIVES OF ISOBUTANE.



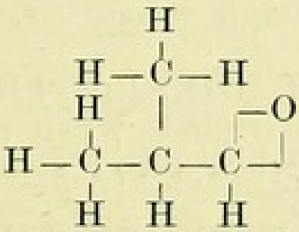
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & H- & C & -H & \\ & H & | & H & \\ & | & | & | & \\ H- & C & -C- & C & -H \\ & | & | & | & \\ & H & H & H & \end{array}$$

methylpropane
(isobutane)



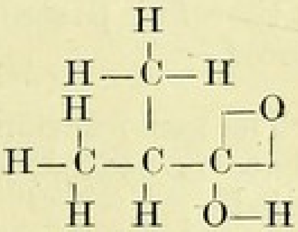
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & H- & C & -H & \\ & H & | & H & \\ & | & | & | & \\ H- & C & -C- & C & -O-H \\ & | & | & | & \\ & H & H & H & \end{array}$$

2-methyl-1-propanol
or α-hydroxyisobutane
(isobutyl alcohol)



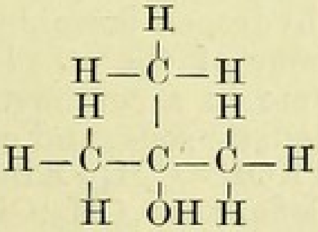
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & H- & C & -H & \\ & H & | & O & \\ & | & | & \| & \\ H- & C & -C- & C & \\ & | & | & | & \\ & H & H & H & \end{array}$$

methylpropanal
(isobutaldehyde)



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & H- & C & -H & \\ & H & | & O & \\ & | & | & \| & \\ H- & C & -C- & C & \\ & | & | & | & \\ & H & H & O-H & \end{array}$$

methylpropanoic
acid
(isobutyric acid)



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & H- & C & -H & \\ & H & | & H & \\ & | & | & | & \\ H- & C & -C- & C & -H \\ & | & | & | & \\ & H & OH & H & \end{array}$$

2-methyl-2-propanol
or β-hydroxyisobutane
(tertiary butyl alcohol)

CHAPTER XVIII

THE OLEFINES

Ethylene.—Before proceeding to the more complex derivatives of the paraffins, two series of hydrocarbons must be considered, which, although intimately related to the ethane hydrocarbons, are very different from them. These are the olefines and acetylenes. The olefines were the first series of hydrocarbons recognised, and ethylene, the lowest member of the series, was the second hydrocarbon prepared.

Ethylene is readily made by heating alcohol with concentrated sulphuric acid at about 180° (Deiman, 1795), the ethyl hydrogen sulphate that is first formed being resolved into sulphuric acid and the hydrocarbon. To obtain the gas in quantity, a mixture of alcohol with three times its volume of concentrated sulphuric acid is heated until a brisk action sets in. The flame is then lowered, and a cold mixture of equal volumes of the same liquids is dropped in at such a rate as to maintain a steady stream of the gas. If care be taken to avoid much frothing and charring, about twelve times the original volume of alcohol can be thus converted. A certain amount of charring is unavoidable, however, and the sulphuric acid is in consequence partly reduced to sulphur dioxide. The ethylene is therefore passed through strong caustic soda before it is collected—

$$C_2H_5.HSO_4=C_2H_4+H_2SO_4.$$

The same action takes place when pure ethyl hydrogen sulphate is heated, and when ethyl sodium sulphate is dry-distilled—

$$C_2H_5.NaSO_4=C_2H_4+NaHSO_4.$$

The hydrocarbon is also formed when ethyl bromide or iodide is heated with alcoholic instead of with aqueous potash, the organic molecule under these conditions losing the elements of the halogen acid. The hydrogen bromide is also easily abstracted by passing the vapour of the ethyl bromide over a short layer of red-hot soda-lime in a combustion tube. The gas is washed as before with caustic soda, and collected over water—

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

Ethylene, ethene, or olefiant gas, $CH_2:CH_2$(Deiman and others, 1795), is a colourless, insoluble gas, having a sweet odour and taste. It is condensible to a liquid which boils at −104°, and freezes at −165°. The molecular formula follows from the analysis and density, and the ethylene molecule thus contains two hydrogen atoms less than that of ethane.

Additive Compounds of Ethylene.—With the exception of the aldehydes and cyanides, the substances thus far studied do not combine directly with other substances. The paraffins in particular only enter into action by substitution of their hydrogen, and do not even form molecular compounds. But there are large numbers of organic compounds which, like aldehyde, combine directly with others and with elements, and of these ethylene is the typical representative.

Ethylene, for example, combines directly with hydrogen when a mixture of the two gases is passed over spongy platinum, and is thus converted into ethane—

$$C_2H_4 + H_2 = C_2H_6.$$

Similarly, with hydrogen chloride gas, it forms ethyl chloride—

$$C_2H_4 + HCl = C_2H_5Cl.$$

It combines also with concentrated sulphuric acid at 170°, and with the fuming acid at the ordinary temperature, and in this way is easily reconverted into alcohol (Faraday, Hennell 1826)—

$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5.HSO_4 \rightarrow C_2H_5.OH.$$

Unlike the paraffins also it is readily oxidisable, and is converted into aldehyde, acetic acid, and even oxalic acid (p. 124) by chromic acid mixture, and into glycol (p. 122) by permanganate—

$$C_2H_4 \rightarrow CH_3.CHO \rightarrow CH_3.COOH \rightarrow COOH.COOH.$$

But the most characteristic action of ethylene is found in its direct combination with chlorine and bromine. When the gas is shaken with bromine water, the latter is at once decolourised, and the solution acquires a sweet odour resembling that of chloroform. The product is readily prepared in quantity. Ethylene, well washed with caustic soda, and with concentrated sulphuric acid, to remove alcohol vapour, is passed into a layer of bromine at the bottom of a tall cylinder of cold water. Heat is evolved, and the bromine is gradually converted into a heavy, colourless liquid. This is purified by shaking successively with dilute alkali and water, and after drying with calcium chloride is distilled.

Ethylene bromide, $CH_2Br.CH_2Br$ (Balard, 1827), is a liquid resembling chloroform. It boils at 130°, and freezes at 9°, and its specific gravity is 2·19 at 11°. Ethylene chloride, $CH_2Cl . CH_2Cl$ (Deiman, 1795), the first compound of this class prepared, is a similar liquid, boiling at 84°, which collects in oily drops —Dutch liquid—when the two constituent gases are mixed in a large flask. Hence the original name of the hydrocarbon—olefiant gas.

The molecular formulæ of these halogen compounds not only follow from their vapour densities, but can also be deduced from their composition with the aid of the valency hypothesis. If the molecular formula of ethylene were CH_2, that of the bromide would be CH_2Br_2, or carbon would not be tetravalent. But this formula does not agree with the analysis, and that of the hydrocarbon must therefore be at least C_2H_4. For the same reason it cannot be greater than this.

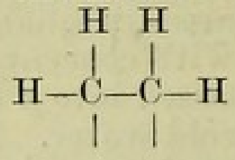
Ethylene bromide and chloride are thus formed by the direct addition of bromine to the hydrocarbon, and are additive compounds, like aldehyde-ammonia. The ethylene behaves as a divalent radicle, and combines with the halogen in the same way as a divalent metal such as mercury. Conversely, when ethylene bromide vapour is passed over hot zinc dust, it loses its bromine, and is reconverted into the hydrocarbon, in much the same way as mercury is precipitated from mercuric salts—

$$CH_2Br.CH_2Br + Zn = CH_2{:}CH_2 + ZnBr_2.$$

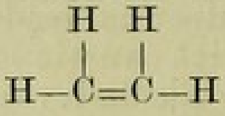
Constitution of Ethylene: Saturated and Unsaturated Compounds.—Ethylene bromide is isomeric with the ethylidene bromide formed by the action of phosphorus pentabromide on aldehyde. Now, according to the theory of structure and valency, there are only two possible compounds of the formula $C_2H_4Br_2$, and the constitutional formulæ of these are $CH_3.CHBr_2$ and $CH_2Br.CH_2Br$. But the first formula is that of ethylidene bromide, and the second is therefore that of the isomeric ethylene bromide.

Compounds such as ethylene and aldehyde, which combine directly with others, are termed unsaturated compounds, whilst such as ethane and alcohol, from which one or more subsidiary atoms must be displaced before action can occur, are termed saturated compounds.

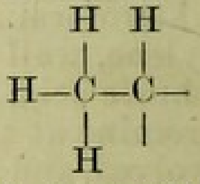
Several structural formulæ can be devised which adequately represent this unsaturated character of the hydrocarbon—



$$\begin{array}{ccccccc} & & \text{H} & & \text{H} & & \\ & & | & & | & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & | & & | & & \end{array}$$



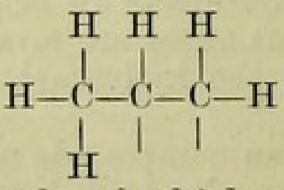
$$\begin{array}{ccccccc} & & \text{H} & & \text{H} & & \\ & & | & & | & & \\ \text{H} & - & \text{C} & = & \text{C} & - & \text{H} \end{array}$$



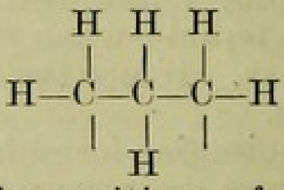
$$\begin{array}{cccccc} & & \text{H} & & \text{H} & \\ & & | & & | & \\ \text{H} & - & \text{C} & - & \text{C} & - \\ & & | & & | & \\ & & \text{H} & & & \end{array}$$

but a study of its homologues shows that only the symmetrical are available. There is only one methyl-ethylene and one ethyl-ethylene, whereas, according to the third or unsymmetrical formula, there should be two sets of such derivatives.

Further, the first formula, in which the two unsaturated valencies are free, cannot be adopted, for, according to this methyl-ethylene or propylene should exist in two isomeric forms—



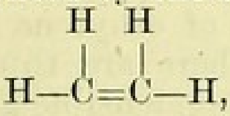
$$\begin{array}{ccccccccc} & & \text{H} & & \text{H} & & \text{H} & & \\ & & | & & | & & | & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & | & & | & & | & & \\ & & \text{H} & & & & & & \end{array}$$



$$\begin{array}{ccccccccc} & & \text{H} & & \text{H} & & \text{H} & & \\ & & | & & | & & | & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & | & & | & & | & & \\ & & & & \text{H} & & & & \end{array}$$

the formulæ of which would differ in the positions of the free unsaturated valencies. But only one propylene is known. As will be seen later also, there is abundant evidence that in the compounds formed by the addition of bromine to the homologues and analogues of ethylene, the bromine is always added to adjacent carbon atoms.

Ethylene is thus represented by the structural formula



$$\begin{array}{c} \overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}} \\ \end{array}$$

$$H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H,$$

in which the carbon atoms are connected by a double linkage (see Acetylene, p. 110).

The Olefines.—The first homologue of ethylene is methyl-ethylene or propylene. The lower compound, methylene, CH_2, which might be expected, is unknown. When, for example, methylene iodide, CH_2I_2, is heated with metallic zinc or copper, ethylene itself is formed, just as ethane is obtained on attempting to prepare free methyl—

$$2CH_2I_2 + 2Cu = CH_2{:}CH_2 + Cu_2I_2.$$

In a similar manner, by the action of sodium on ethylidene chloride, ethylene itself is produced, instead of the isomeric ethylidene, $CH_3.CH=$ which might be expected. The failure of all attempts to prepare such compounds with free valencies is strong confirmatory evidence of the validity of the doubly-linked formula for ethylene.

Propylene or methyl-ethylene is made in much the same way as ethylene, but both from propyl and from isopropyl compounds. It is most conveniently prepared by boiling a saturated solution of zinc chloride in isopropyl alcohol—

$$CH_3.CHOH.CH_3 = CH_3.CH{:}CH_2 + H_2O,$$

but it can also be made by boiling propyl or isopropyl iodide with alcoholic potash—

$$CH_3.CH_2.CH_2I \rightarrow CH_3.CH{:}CH_2 \rightarrow CH_3.CHI.CH_3$$

Propylene or propene, $CH_3.CH{:}CH_2$ (Reynolds, 1851), is a gas which resembles ethylene, but compresses to a colourless liquid at −40°. It combines with bromine in precisely the same way, and the propylene bromide thus formed is a liquid resembling ethylene bromide. The hydrocarbon also combines with sulphuric and hydrochloric acids, but instead of forming primary propyl compounds, the secondary derivatives are produced. Propyl alcohol may in this way therefore be converted into secondary propyl alcohol—

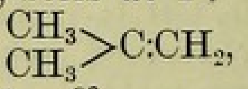
$$CH_3.CH_2.CH_2OH \rightarrow CH_3.CH{:}CH_2 \rightarrow CH_3.CH(O.SO_3H).CH_3 \rightarrow \\ CH_3.CHOH.CH_3.$$

Isobutyl can be converted into tertiary butyl alcohol in a similar manner, and the same action occurs with the higher homologues of ethylene, primary compounds being thus converted into secondary, and secondary into tertiary compounds.

When for instance hydrogen chloride gas is passed into boiling amyl alcohol in presence of zinc chloride, a quantity of secondary amyl chloride is formed along with the primary chloride, from the intermediate formation of propylene, and the office of the zinc chloride in the preparation of ethyl chloride would thus seem to be, in part at all events, to induce the formation of ethylene.

Owing to the recurrence of position isomerism, the isomerism of the higher homologues of ethylene is more complicated than that of the paraffins. There are thus three butylenes, and a mixture of these easily condensible gases can be isolated from the liquid which condenses on compressing oil-gas (Faraday, 1825).

Ethyl-ethylene, $CH_3.CH_2.CH{:}CH_2$, from normal butyl alcohol, boils at $-5°$. Symmetrical dimethyl-ethylene, $CH_3.CH{:}CH.CH_3$, from secondary butyl alcohol, boils at 1°. Isobutylene or unsymmetrical dimethyl-ethylene,



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C{:}CH_2$, from isobutyl and tertiary butyl alcohols, boils at $-6°$.

The butylenes readily form dibromides, and are converted by sulphuric acid, etc., into secondary and tertiary butyl compounds, in the same way as propylene into the secondary propyl compounds.

Apart from their unsaturated character and consequent chemical activity, the higher homologues of ethylene are physically like the paraffins, and either greasy liquids or wax-like solids according to their molecular weight. They occur in small amount in petroleum and coal-tar oil (p. 95), and are readily separated from the paraffins and other hydrocarbons by shaking with fuming sulphuric acid. Like ethylene, they combine with this, forming alkyl hydrogen sulphates, from which they are set free by heating.

The ethylene series of hydrocarbons are known as the olefines, from their characteristic power of forming oily dichlorides and dibromides (Guthrie, 1860). They are necessarily all polymeric with the unknown methylene, and can in consequence be represented by the general formula C_nH_{2n}.

Substitution Products of the Olefines.—Besides the additive compounds, which are saturated, and paraffin derivatives, the olefines form a variety of substitution products, although rarely by direct action. Thus when ethylene bromide is boiled with a solution of caustic soda in moderately strong alcohol it loses one equivalent of hydrogen bromide per molecule, and is converted into an unsaturated compound, monobrom-ethylene. The vapour of the product is passed into ice-cold alcohol, and on pouring the solution into a large volume of ice-water the brom-ethylene separates as a heavy colourless liquid, which can be purified in the same way as ethyl bromide (Regnault, 1834)—

$$CH_2Br.CH_2Br + NaOH = CH_2{:}CHBr + NaBr + H_2O.$$

Brom-ethylene or vinyl bromide, $CH_2{:}CHBr$, is a volatile liquid, which resembles ethyl bromide, but boils at 23°. It differs from the paraffin derivative however in that, like ethylene, it combines directly with bromine, at once decolourising it. The additive compound thus formed, bromethylene bromide, or 1-1-3-tribromethane, $CH_2Br.CHBr_2$, is a liquid resembling ethylene bromide and chloroform, and boiling at 188°.

The hydroxy-compound corresponding with vinyl bromide is unknown in the pure state, and cannot be prepared by the usual reactions. When, for example, vinyl bromide is heated with silver oxide and water, an agent which usually effects the replacement of halogen by hydroxyl, the isomeric acetaldehyde is formed, doubtless by molecular rearrangement of the transiently formed hydroxide—

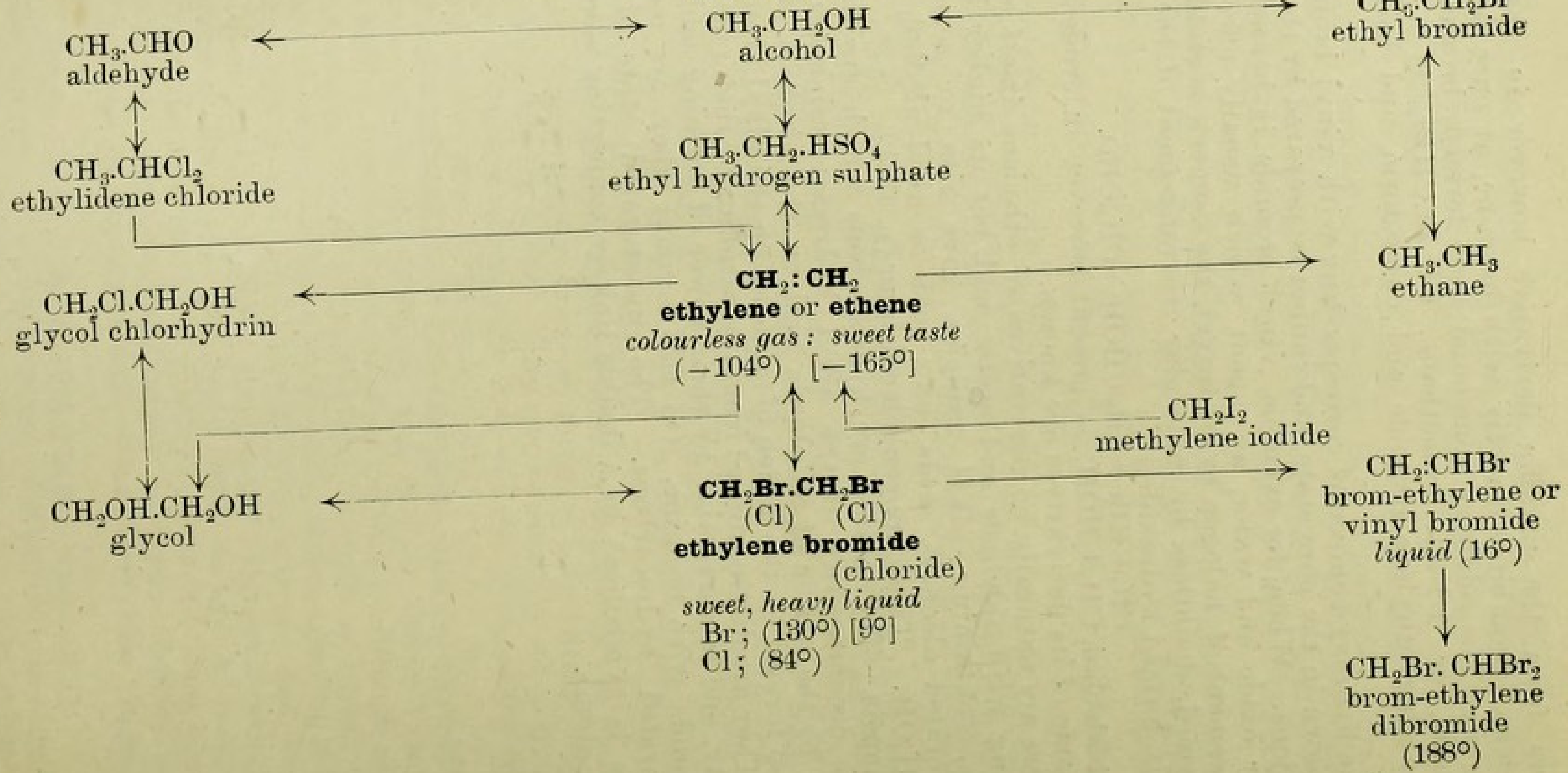
$$CH_2{:}CHBr \rightarrow CH_2{:}CHOH \rightarrow CH_3.CHO.$$

Vinyl alcohol, $CH_2{:}CHOH$, is present however in crude ether, and some of its derivatives are known.

There are naturally no derivatives of ethylene itself corresponding with aldehyde and acetic acid, but its higher homologues, containing alkyl radicles, give rise to series of unsaturated alcohols, acids, etc., such as allyl alcohol, $CH_2{:}CH.CH_2OH$. These are considered later (p. 135).

Synopsis.—The olefines are hydrocarbons which are formed by the decomposition of the alkyl hydrogen sulphates, and hence by the action of sulphuric acid on the alcohols. They are also formed by the action of alkalies on the alkyl bromides, etc. They are distinguished from the paraffins by their chemical activity, and in particular by their power of forming additive compounds with bromine. On this account they are termed unsaturated hydrocarbons. The unsaturated state of the olefines is symbolised by a double linkage connecting adjacent carbon atoms.

ETHYLENE.


$CH_3.CH_2OH$
alcohol
$CH_3.CHO$
aldehyde
$CH_3.CH_2Br$
ethyl bromide
$CH_3.CH_2.HSO_4$
ethyl hydrogen sulphate
$CH_3.CHCl_2$
ethylidene chloride
$CH_2:CH_2$
ethylene or **ethene**
colourless gas : sweet taste
(−104°) [−165°]
$CH_3.CH_3$
ethane
$CH_2Cl.CH_2OH$
glycol chlorhydrin
CH_2I_2
methylene iodide
$CH_2OH.CH_2OH$
glycol
$CH_2Br.CH_2Br$
(Cl) (Cl)
ethylene bromide
(chloride)
sweet, heavy liquid
Br ; (130°) [9°]
Cl ; (84°)
$CH_2:CHBr$
brom-ethylene or
vinyl bromide
liquid (16°)
$CH_2Br.CHBr_2$
brom-ethylene
dibromide
(188°)

CHAPTER XIX

THE ACETYLENES

Acetylene.—It has been seen that by the action of alcoholic alkali on ethylene bromide, hydrogen bromide is removed, and the unsaturated compound vinyl bromide formed. By the action of a concentrated solution of sodium ethoxide in absolute alcohol the whole of the bromine is removed in this way, and a hydrocarbon, acetylene, is produced, which is still more unsaturated than ethylene.

The ethylene bromide is simply slowly dropped into a reflux apparatus containing absolute alcohol in which the maximum amount of sodium has been dissolved consistent with clearness, and a brisk action at once takes place, which requires assisting by heat only towards the end of the operation. The gaseous hydrocarbon passes from the upper end of the condenser, and after washing with ice-cold alcohol to remove vinyl bromide, is collected over water. It may be more quickly prepared by passing the vapour of the dibromide over red-hot soda-lime, as in making ethylene from ethyl bromide—

$$CH_2Br.CH_2Br+2NaOH=CH\vdots CH+2NaBr+2H_2O.$$

Acetylene or ethine, $CH\vdots CH$ (E. Davy, 1839), is a colourless, insoluble gas, of sour, oppressive odour. It is condensed to a liquid by a pressure of 48 atmospheres at 1°. The molecular formula follows from the analysis and density, and the gas bears the same relation to ethylene therefore as the latter to ethane. It can be converted into either of these gases by direct addition of hydrogen. Ethane is formed when a mixture of acetylene and hydrogen is left in contact with platinum black, and ethylene when copper acetylide (see below) is warmed with zinc dust and strong ammonia—

$$CH_2{:}CH_2\leftarrow CH\vdots CH\rightarrow CH_3.CH_3$$

Acetylene is formed in various other ways. It is produced for instance when iodoform (p. 116) is heated with a mixture of reduced copper and zinc dust, and is formed by direct synthesis from its elements when an electric arc is maintained between carbon terminals in an atmosphere of hydrogen (Berthelot, 1868)—

$$2C+H_2=C_2H_2.$$

Acetylene is also produced by the imperfect combustion of hydrocarbons such as are present in coal gas, and is thus formed in considerable quantities when a Bunsen flame is allowed to burn at the bottom of the air tube.

The best way of making the hydrocarbon, however, is by synthesis from coke and water. When coke is fused with lime in an electric furnace, calcium carbide is formed, a grey semi-crystalline solid (Moissan, 1890). This is hydrolysed by water, at the ordinary temperature, and with great energy, into acetylene and slaked lime. The water is simply allowed to drop slowly on lumps of the carbide in a suitable generating vessel—

$$CaO + 3C \rightarrow CaC_2 \rightarrow C_2H_2 + Ca(OH)_2.$$

Acetylene thus manufactured is used as an illuminating agent. It burns with an intensely luminous flame when led through a suitable jet, although when burned from an open vessel the flame is very smoky. As acetylene can be converted into ethylene, and ethylene into ethyl hydrogen sulphate and alcohol, the latter can be made from coke.

Derivatives of Acetylene: its Constitution.—From its formation from and conversion into ethylene, acetylene is represented by the constitutional formula

$$CH \vdots CH,$$

the two carbon atoms being connected by three valencies—a triple linkage.

The symbolic nature of these linkages must be borne in mind, for the stability of a linkage does not increase with the number of valencies. The reverse is the case. Ethylene is much more readily attacked by agents than ethane, and acetylene is endothermic, and so unstable that it decomposes explosively into its elements when a detonator is fired in it. Liquid acetylene appears to be a dangerous explosive. The same is true of the various derivatives, those of ethane being stable, and many of the acetylene compounds explosive—

$$C_2H_2 = C_2 + H_2.$$

The hydrogen of acetylene is mobile to metals. When sodium is gently heated in the gas, sodium acetylide, $CH \vdots CNa$, is formed, a white solid from which the hydrocarbon is explosively regenerated by water. Similarly when acetylene is passed into a solution of ammonio-silver nitrate, a yellowish precipitate of silver acetylide, C_2Ag_2, is thrown down; and in the same way ammonio-cuprous chloride yields reddish-brown copper acetylide, C_2Cu_2. Both the latter compounds are explosive when dry, the copper compound exploding when simply heated at 120°.

Copper acetylide forms a very sensitive test for acetylene. When, for instance, a beaker wetted with a solution of cuprous chloride in ammonia is inverted over a Bunsen burner in which the flame is burning below, the presence of acetylene, evident from the odour, is confirmed by the precipitation of the red cetylide. It also affords a convenient means of separating the hydrocarbon from other gases, as it is quantitatively decomposed into acetylene and cuprous chloride when warmed with concentrated hydrochloric acid; the precipitate must not have been allowed to become dry. In the absence of calcium carbide, copper acetylide, and thus pure acetylene, may be made in considerable quantity by aspirating the products of combustion of air in coal gas through the cuprous solution.

Although acetylene is more unsaturated than ethylene, it forms additive compounds much less readily, and may be shaken with bromine water for some time without decolourising it. When passed into cold bromine, however, it is converted into acetylene tetrabromide, $CHBr_2.CHBr_2$, a liquid resembling ethylene bromide, but boiling at 137°, whilst by adding the halogen to an alcoholic solution of the hydrocarbon, the intermediate dibromethylene, $CHBr{:}CHBr$, is formed, a liquid resembling vinyl bromide. Acetylene also takes up a molecule of hydrogen bromide when heated with the concentrated acid at 100°, and is converted into vinyl bromide.

Like ethylene, the hydrocarbon is slowly absorbed by concentrated sulphuric acid, and when the resulting solution is diluted and distilled with water, acetaldehyde is obtained—

$$CH\vdots CH + H_2O = CH_3.CHO.$$

Similarly when the gas is passed into chromic acid mixture, it is oxidised to acetic acid, whilst with alkaline permanganate, the alkali oxalate is formed.

Acetylene combines with nitrogen when electric sparks are passed through the mixed gases, forming hydrogen cyanide by direct addition—

$$C_2H_2 + N_2 = 2HCN.$$

and it readily polymerises, forming benzene, C_6H_6, and other compounds, when passed through a red-hot combustion tube. It is thus an important synthetic agent.

Homologues of Acetylene.—Several homologues of acetylene of the general formula C_nH_{2n-2} are known.

Allylene or propine, $CH_3.C\vdots CH$ (Markownikoff, 1861), is an easily condensible gas, which is formed by heating propylene bromide, $CH_3.CHBr.CH_2Br$, with alcoholic potash, whence its constitution. It is very soluble in concentrated sulphuric acid, and the solution when diluted and distilled yields acetone and mesitylene. Allylene resembles acetylene in almost every respect, forms metallic compounds for instance, and is oxidised to propionic acid by chromic acid.

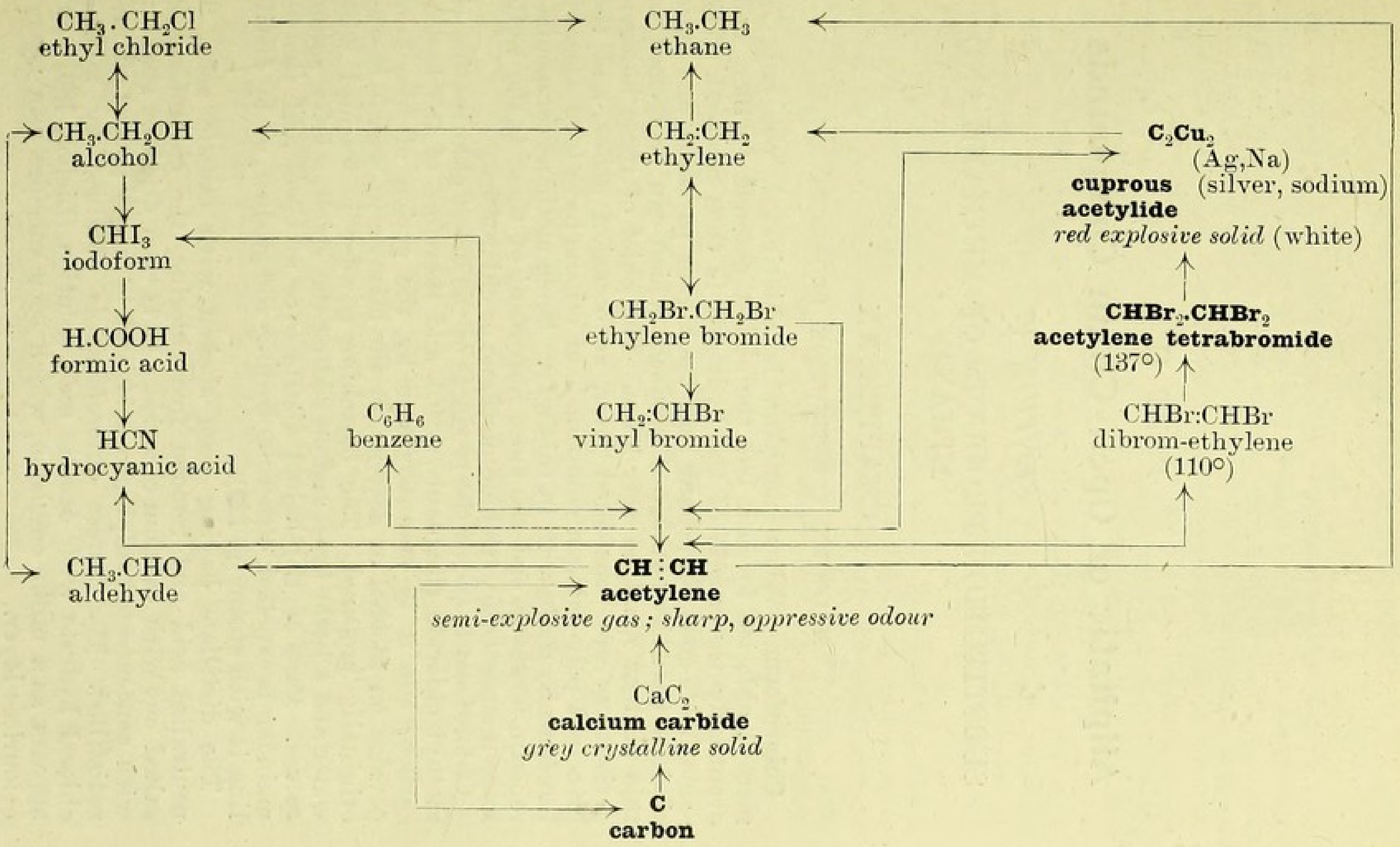
There is, however, a second hydrocarbon of the formula C_3H_4. Allene, or isoallylene, $CH_2{:}C{:}CH_2$ is a gas, which, like allylene, is hydrolysed by sulphuric acid and water to acetone; but it does not form metallic compounds, and, on the other hand, it forms additive compounds with much greater readiness. The tetrabromide, for instance, $CH_2Br.CBr_2.CH_2Br$, is a liquid resembling ethylene bromide, but boiling at 220°. Allene must therefore be regarded as propadiene, $CH_2{:}C{:}CH_2$, a diolefine. The suffix *-ene* denotes the presence of one or more ethylene linkages in distinction to the suffixes *-ine* and *-ane*, which respectively indicate acetylene and paraffin linkages.

In the four-carbon and higher acetylenes and diolefines, position isomerism is possible, as in the higher olefines, and the formation of metallic derivatives is dependent on the presence of the mobile hydrogen of the CH or methine group. Thus ethylacetylene or 1-butine, $CH \vdots C.CH_2.CH_3$, a liquid boiling at 18°, forms such derivatives, whilst dimethylacetylene or 2-butine, $CH_3.C \vdots C.CH_3$ does not do so.

As in all the homologous series, the higher acetylenes are oily liquids or wax-like solids. Like propylene and the higher olefines, they give rise to a series of alcohols, acids, etc., such as propargyl alcohol (p. 139).

Synopsis.—By removing hydrogen bromide from ethylene bromide, acetylene is eventually formed, a doubly unsaturated hydrocarbon, the state of which is symbolised by a triple linkage in its formula. Acetylene and certain of its homologues are distinguished from the olefines and paraffins by forming explosive compounds with metals.

ACETYLENE.


$CH_3 . CH_2Cl$
ethyl chloride
$CH_3.CH_3$
ethane
$CH_3.CH_2OH$
alcohol
$CH_2{:}CH_2$
ethylene
C_2Cu_2
(Ag_2,Na)
(silver, sodium)
cuprous acetylide
red explosive solid (white)
CHI_3
iodoform
$CH_2Br.CH_2Br$
ethylene bromide
$CHBr_2.CHBr_2$
acetylene tetrabromide
(137°)
H.COOH
formic acid
C_6H_6
benzene
$CH_2{:}CHBr$
vinyl bromide
CHBr:CHBr
dibrom-ethylene
(110°)
HCN
hydrocyanic acid
$CH_3.CHO$
aldehyde
CH ⋮ CH
acetylene
semi-explosive gas ; sharp, oppressive odour
CaC_2
calcium carbide
grey crystalline solid
C
carbon

PART II

Aliphatic or Open-Chain Compounds

SECTION V

SUBSTITUTION PRODUCTS OF METHANE AND ETHANE

CHAPTER XX

HALOGEN SUBSTITUTION PRODUCTS

Chloroform.—When methane is chlorinated, not only is methyl chloride formed, but the action extends further, and eventually the whole of the hydrogen is thus replaced. The same holds good for ethane and the higher paraffins, and it is obvious that the number of products which can be formed in this manner must be very large. The chief of these halogen derivatives are considered later, as occasion arises, and the principal poly-halogen compounds of ethane have been already incidentally dealt with in this way. Some methane compounds remain, however, and the most important of these is the well-known anæsthetic, trichloromethane or chloroform.

Chloroform is one of the products of the direct chlorination of methyl chloride (Regnault, 1840), and therefore of the hydrocarbon, but it is manufactured by the action of bleaching powder on alcohol or acetone, in the manner in which it was originally prepared. The bleaching powder is warmed with water and a little lime, and on adding the spirit, a brisk action occurs. Part of the haloid distils over at once, and the remainder is expelled, either by boiling the product, or by distilling it with steam (p. 129).

The distillate having been shaken with caustic soda, to neutralise acid and remove free chlorine, the chloroform is salted out with calcium chloride. It is then dried by shaking with concentrated sulphuric acid, and is finally poured off and redistilled. The purest chloroform is obtained by mixing chloral hydrate with caustic soda solution (Liebig, 1831). It appears as a milky emulsion, which soon subsides as a heavy, colourless layer.

Chloroform, $CHCl_3$ (Liebig, Souberain, 1831), is a colourless liquid having a powerful but not unpleasant odour, and a very sweet taste. It boils at 61° and freezes at –70°, and its specific gravity is 1·53 at 0°. It is extensively used as an anæsthetic (Simpson, 1848). The liquid itself is not inflammable, but its alcoholic solution burns with a green-mantled flame, like the alkyl chlorides, and also precipitates silver chloride when warmed with silver nitrate. Chloroform further resembles the simple chlorides in that it is hydrolysed by alkalies, the ultimate products being the alkali chloride and the formate.

The hydrolysis is most readily effected in alcoholic solution, however, and in this case, especially when an alcoholic solution of sodium ethoxide is used, an intermediate product can be isolated, analogous to acetal. It rises to the surface as an oily layer.

Ethyl orthoformate, $H.C(OEt)_3$ (Williamson, 1854), is a liquid which boils at 146°, and is easily hydrolysed by aqueous alkali to formic acid and alcohol. The homologous ethyl orthoacetate, $CH_3.C(OEt)_3$ is prepared in the same way from trichlorethane, $CH_3.CCl_3$, a liquid obtained by chlorinating ethyl chloride, and is hydrolysed in the same way to alcohol and acetic acid. It thus appears that the acids, like the aldehydes, are dehydration products of hydroxy-paraffins—

$$H.CCl_3 \rightarrow H.C(OEt)_3 \rightarrow [H.C(OH)_3 \rightarrow] H.COOH + H_2O.$$

In presence of alkali, chloroform condenses with ammonia, forming the alkali cyanide. The action is readily brought about by adding solid caustic soda to an alcoholic solution of chloroform and concentrated ammonia. On evaporating the product to dryness, the alkali cyanide and chloride remain—

$$CHCl_3 + NH_3 + 4NaOH = NaCN + 3NaCl + 4H_2O.$$

Amines have a similar action (p. 208), and the reaction with phenylamine or aniline serves as a convenient means of detecting small quantities of chloroform. It is carried out in the same way as with ammonia, and the volatile product, phenyl isocyanide (p. 253) is recognisable, even in small quantities, by its peculiarly unpleasant odour.

Chloroform is oxidised by chromic acid mixture to the poisonous carbonyl chloride or phosgene gas (p. 196) and hydrochloric acid; the same change is slowly effected by air in daylight, and the liquid must therefore be kept in well-stoppered bottles, and in a cool, dark place—

$$CHCl_3 + O = COCl_2 + HCl.$$

On further chlorinating chloroform in presence of iodine (p. 117), it is converted into carbon tetrachloride, or tetrachlormethane, the end product in the chlorination of the hydrocarbon. Carbon tetrachloride, CCl_4 (Regnault, 1840), is a colourless liquid which boils at 77°, but otherwise resembles chloroform. It is hydrolysed by alkalies in the same way as the latter, the end product, obtained by boiling it with alcoholic potash, being the alkali carbonate. The chloromethanes thus form a connecting link between the organic compounds and the mineral compound, carbonic acid—

$$CCl_4 + 6KOH = K_2CO_3 + 4KCl + 3H_2O.$$

Iodoform.—The iodine compound corresponding with chloroform is made in an analogous manner by the action of iodine and alkali on alcohol or acetone. The iodine is added to a solution of sodium carbonate containing alcohol, and the whole is warmed gently, and the addition of the halogen continued until the colour ceases to be discharged. A relatively large quantity is required. On cooling the product the yellow iodoform crystallises out, and is washed with a little cold water and dried between filter paper.

Iodoform, CHI_3 (Serullas, 1822), is a bright yellow crystalline substance, melting at 119°. It has a clinging and characteristic odour, and is used in surgery as an antiseptic. Iodoform is hydrolysed by alcoholic alkali in precisely the same way as chloroform, and similarly, when heated with zinc dust and water, it is reduced to methane—

$$2CHI_3 + 6Zn + 3H_2O = 2CH_4 + 3ZnI_2 + 3ZnO.$$

When heated with dry zinc dust, however, it is converted into the hydrocarbon acetylene. This proves that iodoform contains hydrogen, the very low percentage of which (0·25) falls within the limits of error of an ordinary combustion—

$$2CHI_3 + 3Zn = 3ZnI_2 + C_2H_2.$$

The Chloracetic Acids.—Not only does chlorine substitute in the paraffins, but it also replaces the hydrogen of the acids, and, indirectly, that of the alcohols and aldehydes. The first well-defined substitution product prepared was, in fact, trichloracetic acid.

Trichloracetic acid is deposited in small crystals when a mixture of acetic acid vapour and chlorine is exposed to direct sunlight (Dumas, 1838); but it is more readily obtained by oxidising its aldehyde, chloral, with nitric acid (Kolbe, 1845). Molten chloral hydrate is mixed with an excess of "fuming" nitric acid, and after the violent action has subsided, the solution is heated until nitrous fumes cease to be evolved. The product is then fractionated, and the fraction, distilling within two or three degrees of 193°, purified by repeated crystallisation. The middle fraction of the distillate yields a further quantity on retreatment with nitric acid—

$$CCl_3.CHO + O = CCl_3.COOH.$$

Trichloracetic acid, $CCl_3.COOH$ (Dumas, 1838), is a crystalline substance, melting at 55°. It resembles acetic acid in all its actions, and forms metallic salts, such as potassium trichloracetate, $CCl_3.COOK$ and alkylic salts, such as ethyl trichloracetate, $CCl_3.COOEt$. The presence of hydroxyl is shown by the conversion of the substance into an acid chloride, $CCl_3.COCl$ by phosphorus trichloride, and the ready hydrolysis of this chloride by water. It is thus the three methyl hydrogen atoms of the acetic acid which are substituted. This is confirmed, moreover, by the reduction of trichloracetic to acetic acid by sodium amalgam (Melsens, 1842), and by its resolution into chloroform and carbon dioxide when boiled with water (Dumas)—

$$CH_3.COOH \leftarrow CCl_3.COOH \rightarrow CHCl_3 + CO_2.$$

Trichloracetic acid can also be synthesised from carbon bisulphide, and the method is of interest, as it afforded the first synthesis of acetic acid (Kolbe, 1844)—

$$C \rightarrow CS_2 \rightarrow CCl_4 \rightarrow C_2Cl_4 \rightarrow CCl_3.CCl_3 \rightarrow CCl_3.COOH \rightarrow CH_3.COOH.$$

The intermediate monochloracetic and dichloracetic acids can also be prepared, the latter by boiling chloral with aqueous potassium cyanide, and fractionating the product—

$$CCl_3.CHO + KCN = CHCl_2.COOH + HCN + KCl,$$

and the former by chlorinating glacial acetic acid or acetic anhydride—

$$HCl \leftarrow CH_3\,COOH + Cl_2 \rightarrow CH_2Cl.COOH \leftarrow (CH_3.CO)_2O + Cl_2$$

$$\hookrightarrow CH_3.COCl.$$

In making chloracetic acid from the anhydride, the latter is simply heated on a water-bath while the chlorine is passed into it. The bye-product acetic chloride distils over, leaving the nearly pure chloracetic acid behind.

In chlorinating acetic acid itself, however, a carrier must be used, such as iodine, sulphur or phosphorus, which acts in much the same way as the nitric oxide in the manufacture of sulphuric acid. The iodine chloride, for example, formed by the direct combination of the elements, acts quite violently on the acid, and as it is at once regenerated from the resulting hydriodic acid by the further action of the chlorine, the process is continuous (Müller, 1862).

The chlorination is carried on in a reflux apparatus until the necessary increase in weight is observed, and the product, which readily crystallises on being cooled in ice and stirred, is purified by fractionation. The tail fraction, distilling above 180° is melted, crystallised, and drained, in the same way as acetamide, until the melting point is constant. The lower fractions are worked up again. A purer product is obtained with sulphur as a carrier, and the chlorination is in this case effected more quickly—

$$CH_3.COOH + ICl = CH_2Cl.COOH + HI.$$

Chloracetic acid, $CH_2Cl.COOH$, is a crystalline solid, melting at 62°. Dichloracetic acid, $CHCl_2.COOH$ is an oily liquid, boiling at 191°. Both acids resemble trichloracetic acid in forming metallic and alkylic salts, and in their convertibility into acid chlorides by phosphorus trichloride, but they behave with alkalies in the same way as the mono- and di-chloro-paraffins, and are hydrolysed to alcoholic and aldehydic derivatives (pp. 121, 123).

Chloral and Chloral Hydrate.—Trichloraldehyde or chloral, the aldehyde of trichloracetic acid, is formed when aldehyde is chlorinated in presence of marble. The marble serves to take up the hydrochloric acid, which otherwise brings about condensation (p. 119). It is more readily made, however, by chlorinating alcohol. Chlorine is passed into alcohol in a reflux apparatus, the spirit at first being kept cool, but afterwards heated at 60°. The chlorination is continued for many hours until ethyl chloride ceases to be evolved. The product is then heated with concentrated sulphuric acid for several hours at the same temperature, and the oily layer of chloral which separates is removed and redistilled from calcium carbonate. The chloral is finally converted into the crystalline hydrate by mixing it with an equimolecular proportion of water.

Chloral, $CCl_3.CHO$ (Liebig, 1831), is a pungent, heavy liquid, boiling at 97°, and its hydrate, $CCl_3.CH(OH)_2$, is a crystalline substance melting at 57°. The latter has a peculiar sweetish odour, resembling that of stale apples, and an acrid, unpleasant taste. It is much used as a hypnotic (Liebreich, 1869).

Both chloral and chloral hydrate show the usual properties of aldehydes. Their aqueous solutions reduce ammoniacal silver nitrate, and colour bleached rosaniline, and chloral itself forms additive compounds with ammonia, hydrogen cyanide, and sodium bisulphite. The hydrate is one of the few examples of hydroxy-compounds in which two hydroxyl groups are linked to the same carbon atom, and completely justifies the view that aldehydes are dihydroxy-derivatives of the hydrocarbons.

When volatilised, chloral hydrate is dissociated into chloral and steam, for its boiling point is about the same as that of water or chloral, and its vapour density is the mean, instead of the sum, of the vapour densities of its constituents. Nevertheless, it is an actual chemical compound when solid, for it is converted into a diacetate, $CCl_3.CH(OAc)_2$, by acetyl chloride. Chloral forms a similar crystalline alcoholate, closely resembling the hydrate.

Although oxidisable to trichloracetic acid in the normal manner, chloral is converted into ordinary alcohol when reduced with sodium amalgam, the chlorine appearing to be replaced before the aldehyde group is affected; and as already noted, when it is mixed with cold caustic alkali, it is hydrolysed to chloroform and the alkali formate, just as the acid is resolved into the haloid and the carbonate—

$$\begin{tikzcd} CH_3.CH_2OH \arrow[r, leftrightarrow] & CCl_3.CHO \arrow[r] \arrow[rr, bend right] & CCl_3.COOH \arrow[r] & CHCl_3. \end{tikzcd}$$

The formation of chloral from alcohol is somewhat complex, but may be summarised by saying that the alcohol is first oxidised to aldehyde, and the latter then chlorinated. Several stages intervene, however, between the aldehyde and the final product. The aldehyde combines at once with some of the unchanged alcohol, forming acetal, and the latter is chlorinated to dichloracetal—

$$CH_3.CH_2OH \rightarrow CH_3.CHO \rightarrow CH_3.CH(OEt)_2 \rightarrow CHCl_2.CH(OEt)_2.$$

This, by further chlorination, at the higher temperature, is resolved into chloral alcoholate and ethyl chloride, and finally, the alcoholate is resolved by the sulphuric acid into ethyl hydrogen sulphate and chloral—

$$CHCl_2.CH(OEt)_2 \rightarrow CCl_3.CHOH.OEt \rightarrow CCl_3.CHO.$$

The formation of chloroform from alcohol and bleaching powder is probably parallel, the chloral first formed being hydrolysed by the lime; and the formation of iodoform is also probably analogous, although the iodal corresponding with the chloral is unknown. It is quite possible, however, that it is transiently formed in the action.

Butyl Chloral.—The condensation product which is formed when aldehyde is chlorinated alone is a homologue of chloral, and has much the same properties. The chlorine is passed into cold paraldehyde, and after the action has moderated, the liquid is heated at 100°, and the chlorination continued until action ceases. The product is poured into alcohol and neutralised with calcium carbonate, and the alcoholate which is thus formed is fractionated and decomposed with concentrated hydrochloric acid.

The action is again complex. Probably chloraldehyde is first formed, and then, under the influence of the liberated hydrochloric acid, a condensation product of this with a second molecule of aldehyde (Pinner, 1875)—

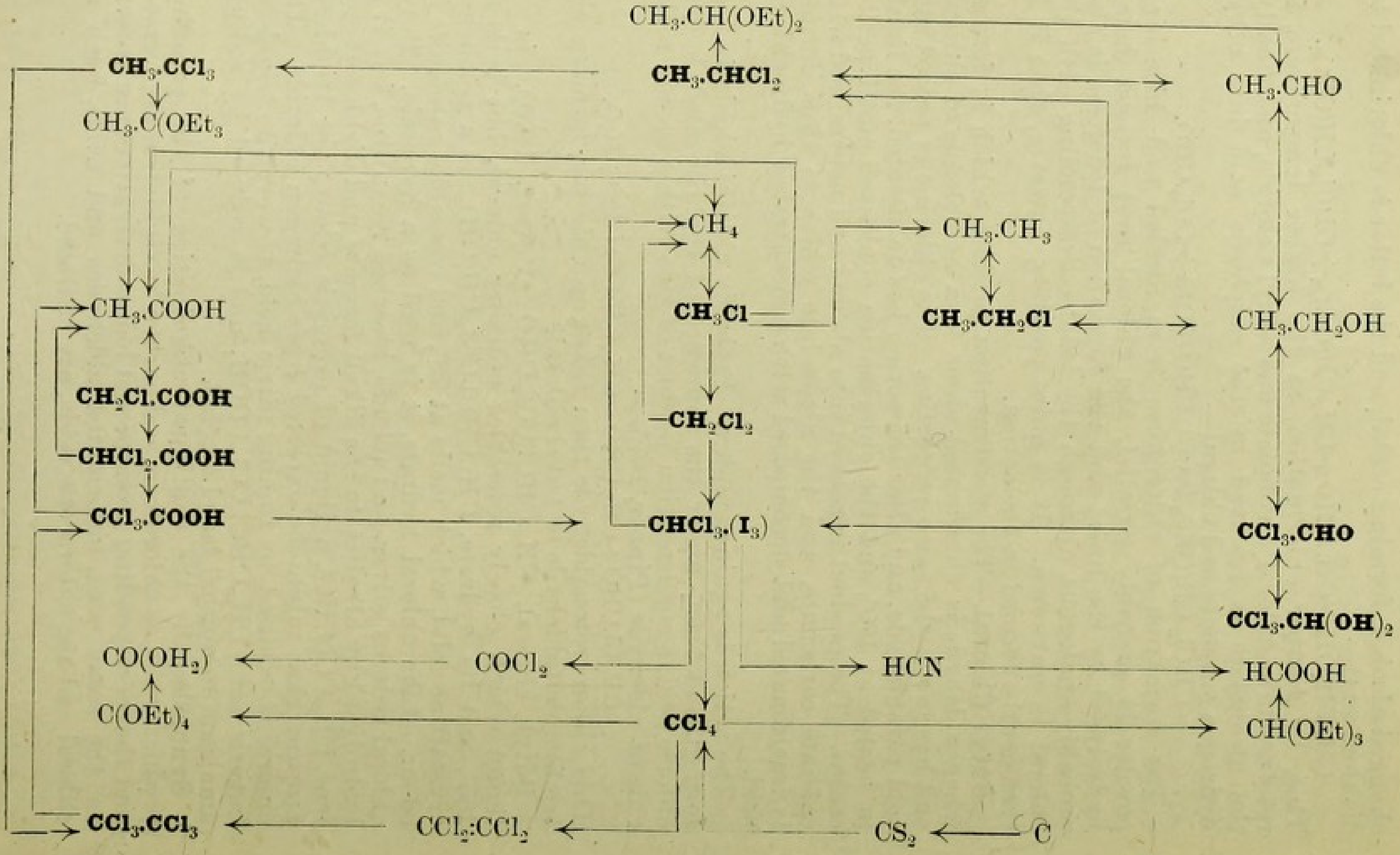
$$CH_2Cl.CHO + CH_3.CHO = CH_3.CH{:}CCl.CHO + H_2O.$$

This chlorocrotonaldehyde then takes up chlorine, forming the trichlorobutaldehyde or butyl chloral.

Butyl chloral, $CH_3.CHCl.CCl_2.CHO$ (Pinner, 1870), is a liquid which closely resembles ordinary chloral, but boils at 165°, and its hydrate, $CH_3.CHCl.CCl_2.CH(OH)_2$, is a colourless crystalline solid, which melts at 78°, and resembles camomile in odour. Like chloral hydrate, it is used as a hypnotic. Butyl chloral reduces silver, and colours bleached rosaniline, but it is hydrolysed by alkalies to the alkali formate and dichloropropylene, $CH_3.CCl{:}CHCl$, a liquid of aromatic odour; the trichloropropane that might be expected loses hydrogen chloride. The chloral is oxidised by fuming nitric acid, however, to trichlorobutyric acid, $CH_3.CHCl.CCl_2.COOH$, and is reduced by sodium amalgam to normal butyl alcohol.

Synopsis.—By the continued chlorination of the paraffins, products such as chloroform and carbon hexachloride are formed, and the corresponding bromine and iodine derivatives are known. In the same way, chlorinated aldehydes and acids, such as chloral and the chloracetic acids, are produced.

THE MONO- AND DI-CARBON HALOGEN SUBSTITUTION PRODUCTS.



CHAPTER XXI

HYDROXY-SUBSTITUTION PRODUCTS: THE GLYCOL-OXALIC SERIES

Glycollic Acid.—Since alcohol, aldehyde, and acetic acid are derived from ethane by successive oxidation of the methyl hydrogen atoms, compounds may be expected, in which the second methyl group is thus oxidised. These compounds are known. They are more complex than the compounds of simple constitution which have thus far been under consideration, for they behave in a dual manner. The hydroxy-compound corresponding with chloracetic acid, for example, is a primary alcohol, as well as an acid, and has a set of derivatives in each of these capacities, and in the remaining members of the series, the alcohol, aldehyde and acid groups are combined with each other in every conceivable way.

Glycollic or hydroxy-acetic acid can be made in various ways. It is formed when a solution of chloracetic acid is heated in a sealed tube at 150°, and crystallises out on concentrating the product. The action is hydrolytic, and parallel to the hydrolysis of the alkyl chlorides (Hofmann, 1858)—

$$CH_2Cl.COOH + H_2O = CH_2OH.COOH + HCl.$$

The acid is produced when formaldehyde hydrocyanide is digested with concentrated hydrochloric acid, in the same way as lactic acid from aldehyde hydrocyanide (p. 143)—

$$CH_2OH.CN + HCl + 2H_2O = CH_2OH.COOH + NH_4Cl,$$

and it occurs naturally in unripe fruit. It can also be made by oxidising ordinary alcohol with nitric acid, and can be prepared fairly readily by gently oxidising invert sugar (p. 175). Cane sugar is boiled for an hour with dilute sulphuric acid, and the product, invert sugar, after neutralisation with barium carbonate, is warmed with a mixture of calcium carbonate and freshly precipitated silver oxide. The sugar is converted partly into carbon dioxide and oxalic acid, which remain in combination with the lime, and partly into silver glycollate, which can be dissolved out with water. On precipitating the silver with hydrochloric acid, the glycollic acid remains in solution, and crystallises out on concentration. It was first obtained from glycocoll (p. 222).

Glycollic acid, $CH_2OH.COOH$ (Strecker, 1851), is a deliquescent, crystalline substance, which melts at about 80°. That it is hydroxyacetic acid is proved by various reactions. As an acid, it forms various metallic salts, such as ethyl glycollate, whilst as an alcohol it forms with acids such salts as acetylglycollic acid, $CH_2(OAc).COOH$. The presence of alkylic and oxylic hydroxyl groups is confirmed by the action of phosphorus pentachloride. In the cold, this agent yields glycollic chloride, $CH_2OH.COCl$. This is a liquid which is reconverted into the acid by simple digestion with water, and is therefore an acid chloride. On heating the phosphorus chloride with the acid, however, chloracetic chloride, $CH_2Cl.COCl$, is formed, a liquid identical with that formed directly from chloracetic acid, and convertible into the latter acid by hydrolysis with cold water.

Glycollic acid can not only be made from formaldehyde, but can also be converted into it, for when it is heated with concentrated sulphuric acid at 150°, a brisk effervescence sets in, and carbon monoxide escapes, whilst paraformaldehyde sublimes into the cooler parts of the vessel—

$$3CH_2OH.COOH = (CH_2O)_3 + 3CO + 3H_2O.$$

Glycol.—From its dual character the oxidation and reduction products of glycollic acid are numerous. Thus, not only as an acid is it connected with an aldehyde and alcohol—

$$CH_2OH.COOH \leftarrow CH_2OH.CHO \leftarrow CH_2OH.CH_2OH,$$

but as a primary alcohol it is oxidisable to a second aldehyde and acid—

$$CH_2OH.COOH \rightarrow CHO.COOH \rightarrow COOH.COOH\ ;$$

whilst in its dual capacity it is related to a third, a double aldehyde—

$$CH_2OH.COOH \leftarrow CHO.CHO.$$

The double or diprimary alcohol, glycol, is made by hydrolysis of ethylene bromide. The dibromide is boiled with potassium carbonate solution in a reflux apparatus, until it is all dissolved, an operation requiring many hours. The product is concentrated, and after separating the potassium bromide which crystallises out, is extracted with alcohol, in which the residual bromide is insoluble. The clear extract is then fractionated. After the alcohol has passed over, the temperature rises slowly, and fairly pure glycol distils at 170-200°. Much of the dibromide is converted into vinyl bromide and lost.

Glycol or ethylene alcohol, $CH_2OH.CH_2OH$ (Wurtz, 1856), is a sweet syrupy liquid, which boils at 197°, and freezes at a low temperature to a crystalline solid, melting at 11°. Its constitution follows from its molecular formula and actions. Thus there are two sodium derivatives, and the two hydroxyl groups are successively replaceable by halogen. The alkylic character of the hydroxyl groups is proved by the formation of two acetyl derivatives when the liquid is boiled with acetic acid, and the primary character of these alcohol groups is demonstrated by the successive oxidation of the substance by nitric acid to the corresponding aldehyde and acid, glyoxylic and oxalic acids. The name glycol registers the double analogy to glycerine (p. 129) and alcohol.

The dichloro-derivative of glycol, formed by the action of phosphorus pentachloride, is identical with ethylene dichloride, whilst the monochloro-compound, or glycol chlorhydrin, may be regarded as chlorethyl alcohol. It is best formed by the action of sulphur dichloride on glycol. The two liquids are heated at 100° until hydrogen chloride ceases to be evolved, and the chlorhydrin is extracted from the product with ether, and fractionated, after neutralising any acid with moist potassium carbonate.

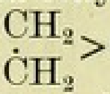
Glycol chlorhydrin, or chlorethyl alcohol, $CH_2Cl.CH_2OH$ (Wurtz, 1859), is a sweet tasting liquid, boiling at 128°. It is reduced by sodium amalgam to ethyl alcohol, and oxidised by chromic acid mixture to chloracetic acid, whilst it is hydrolysed by dilute sulphuric acid to glycol—

$$\begin{tikzcd} CH_2OH.CH_2OH \arrow[r, leftrightarrow] & CH_2Cl.CH_2OH \arrow[r] \arrow[dr] & CH_2Cl.COOH \\ & & CH_3.CH_2OH. \end{tikzcd}$$

Both glycol and its chlorhydrin may be directly prepared from ethylene. When the hydrocarbon is shaken with aqueous hypochlorous acid it is converted into the chlorhydrin, whilst with strong potassium permanganate solution glycol is produced. Either substance is extracted from the product with ether. Glycol and its chlorhydrin are on this account termed ethylene glycol and chlorhydrin. As will be seen later, all ethylene derivatives behave in this manner—

$$CH_2Cl.CH_2OH \leftarrow CH_2{:}CH_2 \rightarrow CH_2OH.CH_2OH.$$

Ethylene chlorhydrin can be deprived of its halogen in the same way as the dibromide, but the product thus formed is of a different type to vinyl bromide. On mixing the chlorhydrin with concentrated aqueous potash, a violent action sets in, and a gas passes off, which after drying with calcium chloride can be condensed in a freezing mixture. It is isomeric with aldehyde, and is termed ethylene oxide.

Ethylene oxide,  $\genfrac{}{}{0pt}{}{CH_2}{CH_2}{>}O$, is a mobile liquid, boiling at 14°, but differing entirely from aldehyde. It is a strong base, and neutralises hydrochloric acid almost as readily as ammonia, being reconverted into ethylene chlorhydrin. Like the chlorhydrin and aldehyde, however, it is reduced to alcohol by sodium amalgam. It may be regarded as a kind of internal ether of glycol.

Glyoxylic Acid and Glyoxal.—Of the three aldehydic derivatives of glycol, one is an alcohol-aldehyde, another an aldehyde-acid, and the third a double aldehyde.

The first product, glycollic aldehyde, $CH_2OH.CHO$, a sweet, syrupy substance, is obtained by the hydrolysis of bromacetaldehyde with baryta water, or better, by a simple decomposition of dihydroxymaleic acid (p. 165). The others, glyoxylic acid and glyoxal, were originally prepared by oxidation of alcohol with nitric acid (compare Glyceric Acid, p. 132).

Glyoxylic acid, CHO.COOH (Debus, 1856), is conveniently obtained by hydrolysis of dibromacetic acid, to which it bears the same relation as aldehyde to ethylidene bromide. It is a syrup which crystallises only with difficulty. As an acid, it forms the usual metallic salts, but the ethereal salts are unknown. As an aldehyde, it is oxidised by nitric acid to the corresponding acid, oxalic acid, and reduced by zinc dust and water to the corresponding primary alcohol, glycollic acid. It is reconverted into dibromacetic acid by phosphorus pentabromide—

$$CH_2OH.COOH \leftarrow CHO.COOH \rightarrow COOH.COOH.$$

Glyoxylic acid gives the usual aldehyde reactions, but with caustic soda, it resembles valeraldehyde and formaldehyde, and is converted into glycollic and oxalic acids—

$$2CHO.COOH + 3NaOH = CH_2OH.COONa + COONa.COONa + 2H_2O.$$

Glyoxal or glyoxylic aldehyde, CHO.CHO (Debus, 1856), is conveniently made by oxidising aldehyde with nitric acid at the ordinary temperature, and is separated from the product as the bisulphite compound. It is an amorphous solid, or when not quite free from water, a syrupy liquid. Glyoxal gives the usual aldehyde reactions, and is oxidised by nitric acid to glyoxylic or oxalic acid, according to the concentration. With alkalis it resembles glyoxylic acid, and is converted into the alkali glycollate, one of the aldehyde groups being oxidised at the expense of the other—

$$CHO.CHO + NaOH = CH_2OH.COONa.$$

Oxalic Acid.—The end product of the oxidation of all these substances, short of carbon dioxide, is oxalic acid, which also results from the oxidation of many other Organic compounds. As already noted, for example, it is formed from acetic acid by the action of alkaline permanganate. The acid occurs naturally in the common sorrel (*oxalis*), and in rhubarb and other plants. It was at one time thought to be a kind of acetic acid, and was only recognised as distinct in the latter part of the eighteenth century.

Most of the oxalic acid used is made from sawdust (cellulose, p. 181) by oxidation with air and caustic alkali. The sawdust is made into a paste with caustic potash and soda, and heated in open vessels at about 240°, and on extracting the product with cold water, the potash is dissolved out, and the sparingly soluble sodium oxalate left (Dale, 1856). The function of the potash is not quite clear, but it is indispensable to the action The sodium oxalate is boiled with milk of lime, by which it is converted into the insoluble calcium oxalate, and the alkali regenerated, and the calcium oxalate, after washing, is decomposed with dilute sulphuric acid, and the oxalic acid recrystallised.

In the laboratory, oxalic acid is conveniently made by oxidising sugar, starch, etc., with nitric acid (Scheele, 1776). When cane sugar, for instance, is warmed with a considerable excess of moderately concentrated nitric acid, a violent action sets in, and dense nitrous fumes are evolved, and on concentrating the product and allowing it to cool, oxalic acid crystallises out. The success of the operation depends on stopping the concentration, and therefore the action, at the right point. If the oxidation is not carried far enough, a syrupy intermediate product, saccharic acid (p. 185), remains, whilst if it is carried too far, the oxalic acid is converted into carbon dioxide and lost. It is generally necessary in this and similar cases to start the crystallisation by adding a small crystal of the substance, or if this is not available, by rubbing the sides of the vessel with a glass rod to afford nuclei for the crystals.

Pure oxalic acid, $COOH.COOH+2H_2O$ (Scheele, 1776), crystallises from water in colourless, well-defined prisms, which lose their water of crystallisation at 100°. The anhydrous acid is slightly volatile, and sublimes slowly in slender needles when heated at 100°. It is soluble in concentrated sulphuric acid, and crystallises from this solvent in large prisms.

The molecular formula of oxalic acid follows from the composition of the two classes of metallic oxalates, and from the vapour densities of its ethereal salts. Its constitution as the simplest dicarboxylic acid is necessitated by considerations of valency, but is also established by its relation to glycol and glycollic acid, from which, as previously stated, it is formed by oxidation, and into the latter of which it is converted by reduction with zinc and dilute hydrochloric acid—

$$CH_2OH.COOH \longleftrightarrow COOH.COOH.$$

Further, the acid chloride, oxalyl chloride, $COCl.COCl$, a fuming liquid, boiling at 70°, is formed when ethyl oxalate is distilled with phosphorus pentachloride. On distilling the acid itself with either of the phosphorus chlorides, it is resolved into a mixture of hydrogen chloride and the oxides of carbon. An analogous result is obtained by heating it with concentrated sulphuric acid, affording the well-known method of preparing carbon monoxide—

$$COOH.COOH=CO+CO_2+H_2O.$$

The similar decomposition into carbon dioxide and formic acid has been already noted. The acid probably forms an unstable ethereal salt with the glycerol, which immediately splits up into carbon dioxide and monoformin (p. 131), the formate of glycerol analogous to glycol acetate. The monoformin is then hydrolysed by the water of crystallisation of the acid to formic acid and glycerol, or decomposed by a further quantity of oxalic acid into formic acid and glycerol oxalate—

$$\begin{array}{l} C_3H_7O_2.O.CO.COOH \rightarrow C_3H_7O_2.O.CO.H+CO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \hookrightarrow C_3H_8O_3+H.COOH. \end{array}$$

Oxalic acid, as the end product of the hydroxy-ethane series, cannot be further oxidised without breaking up its molecule, so that when it is warmed with acid permanganate, it is resolved into carbon dioxide and water, the permanganate being decolourised. The action is rapid and quantitative, and the amount of the acid in a solution may be estimated in this manner.

The Oxalates.—Of the metallic oxalates, potassium hydrogen oxalate occurs in plants, and is very sparingly soluble in water; ferrous oxalate is bright yellow in colour; calcium oxalate is insoluble in acetic acid, and hence serves for the detection and estimation both of the metal and of the acid; and silver oxalate is somewhat explosive.

The alkali salts are made directly from the acid and the caustic or carbonated alkalies. Ammonium oxalate, $COONH_4.COONH_4$, for example, is prepared by simply neutralising a solution of the acid with ammonia and evaporating to crystallisation, whilst the acid salt, ammonium hydrogen oxalate, $COONH_4.COOH$, is made by neutralising only half the solution, and adding the other half before evaporating—

$$COONH_4.COONH_4 + COOH.COOH = 2COONH_4.COOH$$

Sodium oxalate also results, together with pure hydrogen, when sodium formate is heated, and is directly synthesised from carbon dioxide by heating metallic sodium in that gas—

$$2H.COONa \rightarrow COONa.COONa \leftarrow Na_2 + 2CO_2.$$

Of the ethereal salts, ethyl oxalate, $COOEt.COOEt$, is readily prepared by heating the anhydrous acid with absolute alcohol in a distilling flask at 100°, while a stream of alcohol vapour is passed in from a second flask, to remove the liberated water. The temperature being gradually raised to 130°, the excess of alcohol and the water distil over, and when the distillation has ceased, the residue is fractionated.

Ethyl oxalate is a colourless liquid, boiling at 186°, and having a specific gravity of 1·079 at 20°. When boiled with caustic soda solution in a reflux apparatus, it is hydrolysed in the usual manner to alcohol and sodium oxalate. Methyl oxalate, which is formed in the same way, is a colourless, crystalline solid, which melts at 54°. It is often the case that methyl salts are solid when their homologues are liquid.

Some ethyl hydrogen oxalate, $COOEt.COOH$, is formed in the preparation of the diethyl salt. It is a heavy, colourless liquid, which is decomposed when distilled under ordinary pressure, but can be distilled unchanged by diminishing the pressure (p. 150); under 15 mm. pressure it boils at 117°.

Oxamide and Oxamic Acid: Oxalonitrile.—When ethyl oxalate is shaken with aqueous ammonia, oxamide is precipitated. The action is the same as with ethyl acetate, and alcohol can be separated from the filtrate by distilling it with excess of dilute sulphuric acid—

$$COOEt.COOEt + 2NH_3 = CONH_2.CONH_2 + 2EtOH.$$

The amide is also formed by heating normal ammonium oxalate, in the same way as acetamide from ammonium acetate—

$$COONH_4.COONH_4 = CONH_2.CONH_2 + 2H_2O.$$

Oxamide, $CONH_2.CONH_2$ (Bauhof, 1817), is an insoluble crystalline powder. Like all the amides it is hydrolysed by boiling alkali to ammonia and the alkali salt of the acid—

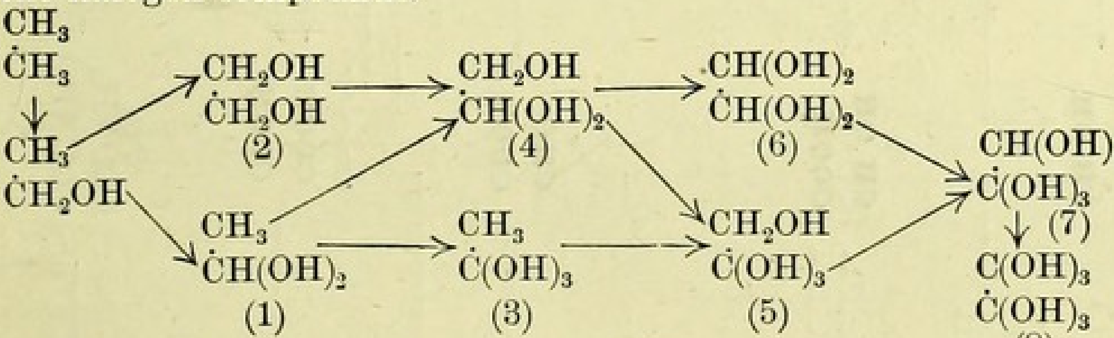
$$CONH_2.CONH_2+2NaOH=COONa.COONa+2NH_3.$$

It is a diamide, however, and contains two amido-groups, so that when ammonium hydrogen oxalate is heated, an intermediate product is formed, which is both an amide and an acid. Oxamic acid, $CONH_2.COOH$, is a crystalline powder, which melts and decomposes at 210°, and is hydrolysed by alkalies in the same way as oxamide. Its ethyl salt, ethyl oxamate, $CONH_2.COOEt$ (Boullay and Dumas, 1828), a crystalline substance melting at 115°, is formed by passing ammonia gas into ethyl oxalate.

The oxalonitrile, CN.CN, obtained by heating oxamide with phosphorus pentoxide, is a gas, which is identical with the cyanogen formed by heating mercuric cyanide (p. 207). Similarly, from ethyl oxamate, ethyl cyanoformate, CN.COOEt, is produced. Both compounds are hydrolysed by alkalies and acids to oxalic acid and ammonia in the manner characteristic of nitriles—

$$CN.CN+2KOH+2H_2O=COOK.COOK+2NH_3.$$

Relation of the Glycol-Oxalic Series to Ethane.—The members of the glycol-oxalic series are thus the hydroxyethanes, or their dehydration products, corresponding with the chlorethanes, and the more stable of them can be made by direct hydrolysis of the halogen compounds.

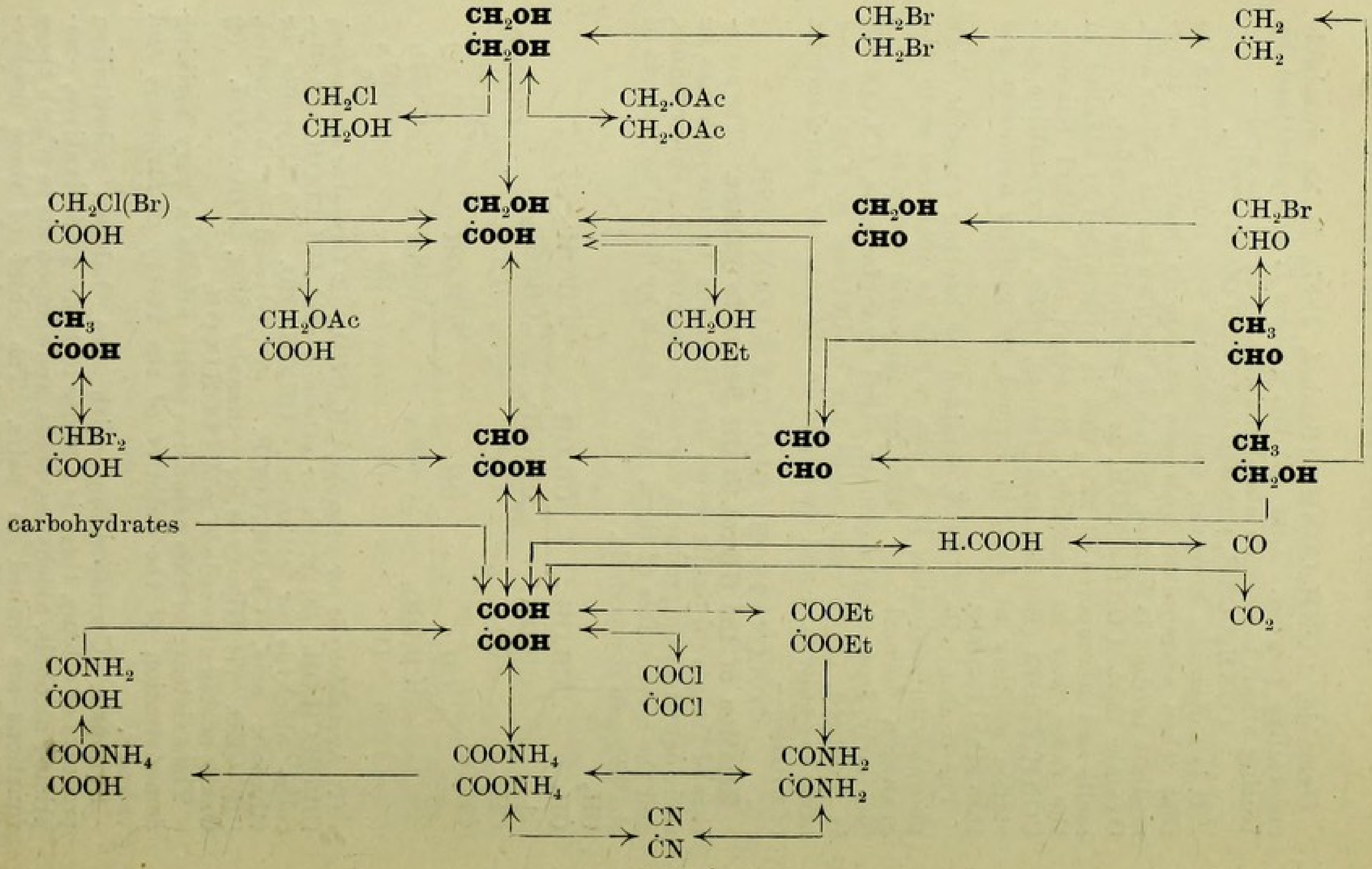


(1) Acetaldehyde or ethanal, $CH_3.CHO$. (2) Glycol or ethanediol, $CH_2OH.CH_2OH$. (3) Acetic or ethanoic acid, $CH_3.COOH$. (4) Glycollic aldehyde or ethanolal, $CH_2OH.CHO$. (5) Glycollic or ethanolic acid, $CH_2OH.COOH$. (6) Glyoxal or ethanedial, CHO.CHO. (7) Glyoxylic or ethanalic acid, CHO.COOH. (8) Oxalic acid or ethanedioic acid, COOH.COOH.

The existence of this extensive series affords a very striking demonstration of the validity of the theory of structure and valency.

Synopsis.—Corresponding with the halogen substitution products of ethane, there is a series of hydroxy-derivatives, comprising alcohols, aldehydes, acids, and compounds in which these functions are united in pairs. The chief of these doubly-functioned compounds are the diprimary alcohol, glycol, and the dicarboxylic acid, oxalic acid.

THE HYDROXY-ETHANES.



SECTION VI

THREE-CARBON DERIVATIVES

CHAPTER XXII

THE GLYCEROL-MESOXALIC SERIES

Glycerol.—The alcohol, glycerol, with which the acids are combined in the natural fats is a trihydroxy-propane, analogous to glycol. It is obtained by distilling with steam the alkaline lye which remains after the saponification of fat. The solution is boiled in a distilling flask while a brisk current of steam is passed through it (p. 241). The glycerol vapour mixes with the steam, and is carried over and condensed with it, and on evaporating the distillate on a water-bath, is left as a syrupy liquid. This is dried by simply heating in an open vessel at about 175°.

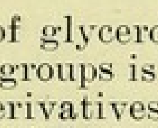
The hydrolysis is also readily effected by boiling the fat with litharge and water, the resulting solution being simply filtered from the insoluble lead soap. Glycerol was originally obtained in this way from olive oil. On a large scale the alcohol is prepared by direct hydrolysis of fat with superheated steam or dilute sulphuric acid—

$$C_3H_5(O.CO.C_{17}H_{35})_3 + 3H_2O = C_3H_5(OH)_3 + 3C_{17}H_{35}.COOH.$$

Glycerol, glycerine, or propane-triol, $CH_2OH.CHOH.CH_2OH$ (Scheele, 1779; γλυκυς = sweet, κηρος = wax), is a sweet, viscid liquid, which boils at 290°, without undergoing decomposition when pure. It freezes at a low temperature to a crystalline solid, melting at 20°. The specific gravity of the liquid is 1·28 at 20°.

The molecular formula of glycerol is $C_3H_8O_3$. The presence of three alkylic hydroxyl groups is shown by the formation of mono-, di- and tri-acetyl derivatives, and it is thus a tribasic alcohol of the formula $C_3H_5(OH)_3$. By heating with hydriodic acid and phosphorus it is reduced to propane, of which it is thus the trihydroxide (Berthelot, 1854), and as it is a stable compound, the three hydroxyl groups must be attached to separate carbon atoms.

Glycerol is, therefore, propane-triol, and is represented by the constitutional formula



$$\begin{array}{c} CH_2OH \\ \dot{C}HOH \\ \dot{C}H_2OH. \end{array}$$

This is confirmed by its behaviour on oxidation (see below), and by its synthesis from isopropyl alcohol. The latter alcohol is converted into propylene and propylene dichloride in the manner already described, and the dichloride is converted into trichloropropane by energetic chlorination in presence of iodine, hydrogen being replaced by chlorine. This chloro-paraffin is identical with trichlorhydrin, $CH_2Cl.CHCl.CH_2Cl$, the trichloro-derivative of glycerol (see below), and is readily hydrolysed to the latter by heating with silver oxide and water (Friedel and Silva, 1873). As isopropyl alcohol can be made from acetone, and thus from acetic acid and carbon, this constitutes a complete synthesis of the glycerol—

$$C \rightarrow CH_3.CHOH.CH_3 \rightarrow CH_3\,CH : CH_2 \rightarrow CH_3.CHCl.CH_2Cl$$

$$\rightarrow CH_2Cl.CHCl.CH_2Cl \rightarrow CH_2OH.CHOH.CH_2OH.$$

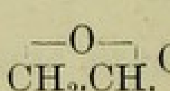
Ethereal Salts of Glycerol: the Glycerides.—The ethereal salts of glycerol are sometimes distinguished by the suffix *-in*. The hydrochloric acid salts or chlorhydrins are viscid or mobile liquids, according to the proportion of chlorine, and like the acetates are readily hydrolysed to glycerol.

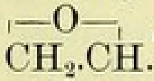
Mono- and di-chlorhydrin each exist in two isomeric forms, differing in the position of the chlorine. The α-modifications, in which the secondary alcohol group is unaltered, may be formed by direct action of hydrochloric acid, but α-dichlorhydrin is best made by the action of sulphur "monochloride." The perfectly dry glycerol is heated on a water-bath with the monochloride until hydrochloric acid ceases to be evolved. The dichlorhydrin is extracted from the product with ether, in which it is freely soluble, and the insoluble ethereal solution is fractionated, the fairly pure product passing over within a few degrees of its boiling point—

$$C_3H_6O(OH)_2 + 2S_2Cl_2 = C_3H_6OCl_2 + 3S + SO_2 + 2HCl.$$

α-Dichlorhydrin, $CH_2Cl.CHOH.CH_2Cl$ (Berthelot, 1854), is a colourless ethereal liquid, boiling at 176°. It is reduced to isopropyl alcohol by sodium amalgam, and is oxidised by chromic acid to dichloracetone, $CH_2Cl.CO.CH_2Cl$; hence its constitution. It is an important stepping-stone in the synthesis of citric acid (p. 169). By the action of phosphorus pentachloride, both the dichlorhydrins are converted into the corresponding trichloro-compound. Trichlorhydrin, $CH_2Cl.CHCl.CH_2Cl$, or 1-2-3-trichloropropane, is a mobile liquid resembling chloroform, and boiling at 158°.

The chlorhydrins form internal ethers analogous to ethylene oxide. When, for example, α-dichlorhydrin is slowly poured into concentrated caustic soda, a vigorous action takes place in the same way as with glycol chlorhydrin, and epichlorhydrin passes over.



Epichlorhydrin, $\overset{—O—}{CH_2.CH}.CH_2Cl$ (Berthelot), is an oily ethereal liquid, boiling at 117°. Like ethylene oxide, it readily unites with hydrochloric acid, and is reconverted into the dichlorhydrin. The corresponding alcohol, glycide alcohol,  $\overset{\overline{\quad O \quad}}{CH_2.CH}CH_2OH$, a liquid boiling at 162°, is obtained by the action of potash on α-monochlorhydrin. It resembles glycerol, and is easily hydrated to it.

Glycerol nitrate, formed by adding glycerol slowly to a mixture of concentrated nitric and sulphuric acids, is the well-known explosive nitroglycerine. On pouring the solution thus obtained into a quantity of cold water, the nitrate separates as a heavy oil. This is washed until free from acid, and dried with calcium chloride.

Glycerol trinitrate or trinitrin, $C_3H_5(O.NO_2)_3$ (Sobrero, 1847), is a colourless oil, which is sweet in taste, but poisonous, even when absorbed through the skin. Although it burns quietly in an open vessel, it explodes with great violence when struck or suddenly heated. On account of its uncertain behaviour, and for convenience of transport and handling, nitroglycerine is usually mixed with an absorbent siliceous earth, and in this form is known as dynamite (Nobel). Highly explosive substances, such as glycerol trinitrate, cannot be analysed by the usual methods. As a general rule, the compound is sealed up in a hard glass tube with excess of copper oxide, and the tube embedded in plaster of Paris and heated to redness. The explosion is thus confined to the tube, so that the gaseous products, thus fully oxidised, can be drawn off and analysed.

As an ethereal salt, glycerol trinitrate is hydrolysed by alkalies to glycerol and the alkali nitrate, so that the name nitroglycerine is inappropriate (see Nitrobenzene)—

$$C_3H_5(O.NO_2)_3+3NaOH=C_3H_5(OH)_3+3NaNO_3.$$

The salts of glycerol with Organic acids are sometimes termed the glycerides. The three acetates or acetins already mentioned are viscid liquids of high boiling point. They are formed by heating glycerol with glacial acetic acid, the number of acetyl groups entering into combination depending on the temperature and proportions. Mono- and di-formin are similar substances. The tributyrate or tributyrin is the ethereal salt in which the butyric acid exists in butter fat.

As already stated, the common fats are ethereal salts of glycerol with the fatty and related acids[*], and they can in some cases be made by direct synthesis. Thus the stearin, or glycerol tristearate—

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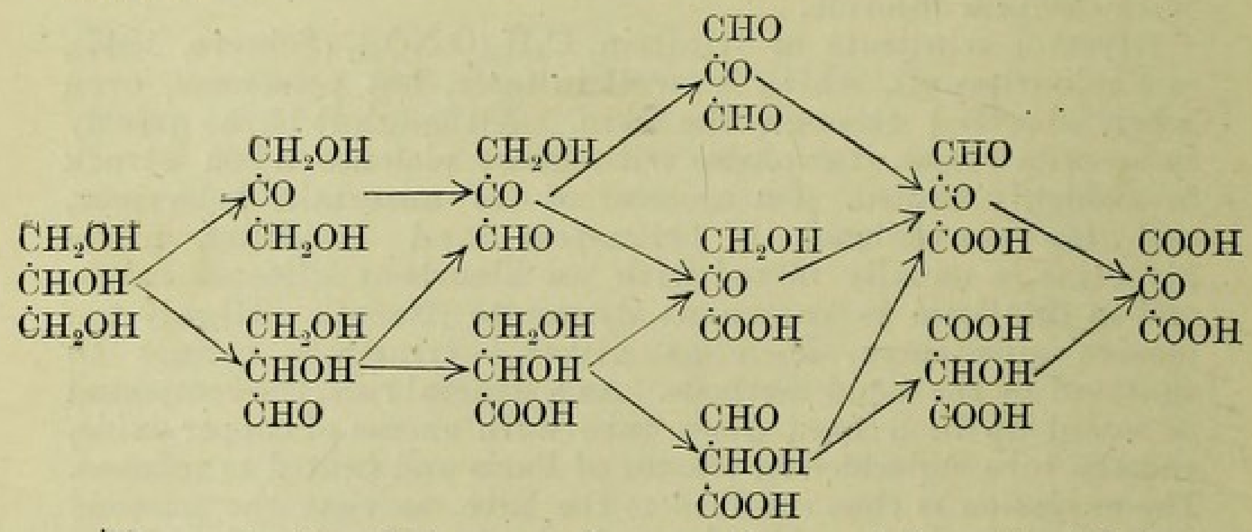
[*] Lanolin, or wool fat, however, which is distinguished by its property of passing through the skin, is a mixture of the fatty acid ethereal salts of cholesterol, $C_{26}H_{43}.OH$, a crystalline alcohol of unknown constitution, which also occurs free in the red blood corpuscles.

$$\begin{array}{l} CH_2.O.CO.C_{17}H_{35} \\ \dot{C}H.O.CO.C_{17}H_{35} \\ \dot{C}H_2.O.CO.C_{17}H_{35}, \end{array}$$

which can be isolated from mutton fat by fractional crystallisation from ether, is also formed by heating stearic acid with glycerol at a high temperature. The product from either source crystallises in lustrous plates, melting at 66°. All three palmitins and trioleïn have been synthesised in the same way.

Oxidation Products of Glycerol.—As glycerol contains a secondary alcohol group in addition to the two primary groups of glycol, it is obvious that its oxidation products must be moie complex—



The majority of these are known, the most important being glyceric aldehyde and acid, and mesoxalic acid.

Glyceric aldehyde, or glycerose, $CH_2OH.CHOH.CHO$, is a sweet syrupy liquid, which resembles glycollic aldehyde, and is formed by oxidising glycerol with cold bromine water. It is analogous in constitution and behaviour to the sugars, and is convertible into certain of them by polymerisation (p. 191). Like all aldehydes, glyceraldehyde is oxidised by silver oxide to the corresponding acid, but the latter is better prepared by direct oxidation of glycerol with nitric acid. A mixture of glycerol and water is placed in a tall narrow cylinder, and a layer of fuming nitric acid introduced beneath it by means of a thistle funnel. At the end of a week the nitric acid has inter-diffused with and oxidised the glycerol, and the product is evaporated on a water bath to a syrup. The crude glyceric acid is diluted and boiled with lead carbonate, and the recrystallised lead salt suspended in water and decomposed with hydrogen sulphide; On evaporating the clear liquid the glyceric acid remains as a syrup.

Glyceric acid, $CH_2OH.CHOH.COOH$ (Debus, 1858) is a syrupy acid liquid which has not been made to crystallise. It is converted by phosphorus diiodide into β-iodopropionic acid (p. 137).

The theoretical end product of the limited oxidation of glycerol, mesoxalic acid, can only be obtained from it by indirect processes, as it is not stable. It is prepared by hydrolysis of alloxan, an oxidation product of uric acid, with baryta water, the resulting barium mesoxalate being decomposed with dilute sulphuric acid.

Mesoxalic acid, $COOH.CO.COOH + H_2O$ (Liebig and Wöhler, 1838) is a crystalline substance, melting at 119°. It loses its water only with difficulty, so that the latter is possibly combined in hydroxylic form with the ketonic group in the same way as in chloral hydrate. As a ketone the acid is reduced by sodium amalgam to the corresponding secondary alcohol, tartronic acid, $COOH.CHOH.COOH$, a similar crystalline substance.

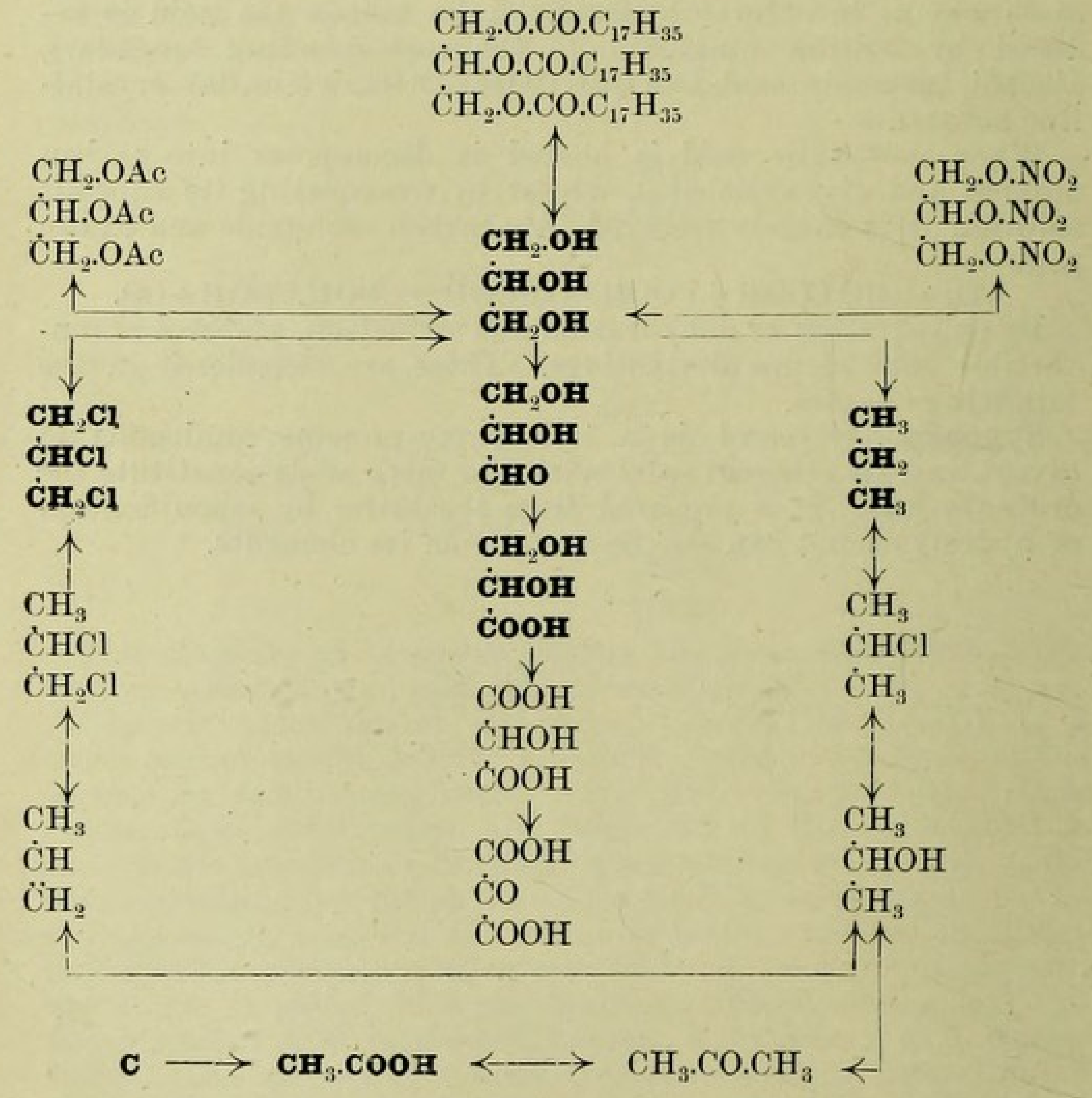
When mesoxalic acid is heated it decomposes into carbon dioxide and glyoxylic acid, whilst by evaporating its aqueous solution it is largely resolved into carbon monoxide and oxalic acid—

$$CO_2 + CHO.COOH \leftarrow COOH.CO.COOH \rightarrow COOH.COOH + CO.$$

By dehydration or dehydration and reduction, glycerol is convertible into olefine derivatives. These are considered in the following chapter.

Synopsis.—Glycerol is a trihydroxy-propane analogous to glycol, and its ethereal salts with the fatty acids constitute the ordinary fats. It is prepared from the latter by saponification or hydrolysis, but can also be made from its elements,

GLYCEROL.


$CH_2.O.CO.C_{17}H_{35}$
$\dot{C}H.O.CO.C_{17}H_{35}$
$\dot{C}H_2.O.CO.C_{17}H_{35}$
$CH_2.OAc$
$\dot{C}H.OAc$
$\dot{C}H_2.OAc$
$CH_2.O.NO_2$
$\dot{C}H.O.NO_2$
$\dot{C}H_2.O.NO_2$
$\mathbf{CH_2.OH}$
$\mathbf{\dot{C}H.OH}$
$\mathbf{\dot{C}H_2OH}$
$\mathbf{CH_2OH}$
$\mathbf{\dot{C}HOH}$
$\mathbf{\dot{C}HO}$
$\mathbf{CH_2OH}$
$\mathbf{\dot{C}HOH}$
$\mathbf{\dot{C}OOH}$
$COOH$
$\dot{C}HOH$
$\dot{C}OOH$
$COOH$
$\dot{C}O$
$\dot{C}OOH$
$\mathbf{CH_2Cl}$
$\mathbf{\dot{C}HCl}$
$\mathbf{\dot{C}H_2Cl}$
CH_3
$\dot{C}HCl$
$\dot{C}H_2Cl$
CH_3
$\dot{C}H$
$\dot{C}H_2$
$\mathbf{CH_3}$
$\mathbf{\dot{C}H_2}$
$\mathbf{\dot{C}H_3}$
CH_3
$\dot{C}HCl$
$\dot{C}H_3$
CH_3
$\dot{C}HOH$
$\dot{C}H_3$
$\mathbf{C}$
$\mathbf{CH_3.COOH}$
$CH_3.CO.CH_3$

CHAPTER XXIII

THE UNSATURATED ALCOHOLS AND ACIDS

Allyl Alcohol and its Derivatives.—Before passing on to the remaining oxygenated derivatives of propane, some compounds related to propylene and the other unsaturated hydrocarbons must be considered. It has been already noticed that there are no substitution products of ethylene and acetylene corresponding with aldehyde and acetic acid, and that although there is an alcoholic derivative of the former hydrocarbon, this compound is very unstable. With the addition of a third carbon atom, however, the matter is different, for in both propylene and allylene there is a methyl group which is convertible into an alcoholic and acid group. Many compounds thus derived from the unsaturated hydrocarbons have been made, although not by direct substitution, and these derivatives share the unsaturated character of the parent substances.

The primary alcohol, $CH_2{:}CH.CH_2OH$, derived from propylene, is termed allyl alcohol, its sulphide being identical with the oil obtained by distilling garlic (*allium*) with steam (Wertheim, 1844). The corresponding iodide is readily prepared from glycerol by the action of iodine and phosphorus.

Yellow phosphorus, in small pieces, is slowly added to a mixture of dry glycerol and powdered iodine, air being excluded by a slow stream of carbon dioxide. There is a brisk action after each addition, and the iodide and water at once distil off, heat being applied if necessary. Isopropyl iodide is formed if the action is allowed to proceed further. On redistilling the dried heavy layer of allyl iodide, it passes over within two or three degrees of its boiling point, and is fairly pure. To completely eliminate the isopropyl iodide, however, the product is shaken with alcohol and metallic mercury, with which the unsaturated iodide forms a crystalline additive compound C_3H_5HgI. This is recrystallised from hot alcohol, and decomposed by shaking the still moist crystals with the exact amount of iodine required to combine with the mercury—

$$CH_2OH.CHOH.CH_2OH \rightarrow [CH_2I.CHI.CH_2I] \rightarrow CH_2{:}CH.CH_2I + I_2.$$

Allyl iodide, $CH_2{:}CH.CH_2I$ (Berthelot, 1854), is a heavy colourless liquid, which boils at 101°, and has a pronounced odour of garlic. Its constitution is established by its relation to allyl alcohol, into which it is converted by warming with lead oxide and water, and from which it is formed by the action of phosphorus and iodine. When warmed with hydriodic acid, it is converted into isopropyl iodide, owing probably to the intermediate formation of propylene—

$$CH_3.CHI.CH_3 \leftarrow [CH_2{:}CH.CH_3] \leftarrow CH_2{:}CH.CH_2I \longleftrightarrow CH_2{:}CH.CH_2OH.$$

Allyl alcohol was originally prepared by the action of ammonia on allyl oxalate, formed by heating the iodide with silver oxalate, but it is more easily made by the reduction of glycerol with formic acid (Tollens, 1870). If in the preparation of this acid the heating is continued after distillation has ceased, the evolution of carbon dioxide recommences, and oily drops of the unsaturated alcohol begin to run down the sides of the flask, and presently distil over. The yield is much increased by adding a trace of ammonium chloride to convert the small quantity of sodium oxalate, which is always present, into the ammonium salt.

The portion of the liquid which distils whilst the temperature of the reacting mass is rising from 190° to 260° is partially purified by fractionation, and then boiled with solid potash, to eliminate the accompanying acroleïn. Finally it is dehydrated with baryta, and redistilled. The addition of oxalic acid may be continued until the glycerol is used up.

Allyl alcohol or propenol, $CH_2{:}CH.CH_2OH$ (Cahours and Hofmann, 1857), is a colourless pungent liquid, which boils at 97°, and has a specific gravity of 0·871 at 0°. The presence of alkylic hydroxyl is proved by the formation of an acetate, when the liquid is heated with acetyl chloride, and that of the primary alcohol group by its oxidation to an aldehyde and acid containing the same number of carbon atoms. Finally the presence of an ethylene linkage is established by the rapid decolorisation of bromine water, and formation of an additive compound with bromine. Allyl alcohol is thus hydroxypropylene or propenol, and bears the same relation to propyl alcohol as propylene to propane. This is confirmed by the direct oxidation of the alcohol to glycerol by alkaline permanganate in the same way as ethylene to glycol—

$$CH_2{:}CH.CH_2OH \longleftrightarrow CH_2OH.CHOH.CH_2OH.$$

The first allyl compound obtained was the isothiocyanate or oil of mustard (Lefebvre, 1660, p. 211).

Acroleïn and Acrylic Acid.—The aldehyde formed by oxidising allyl alcohol with chromic acid is more conveniently prepared by direct dehydration of glycerol. The latter is heated with twice its weight of potassium hydrogen sulphate. The impure aldehyde which distils over is kept in contact with litharge and calcium chloride for some time to purify and dry it, and is then rectified—

$$CH_2OH.CHOH.CH_2OH = CH_2{:}CH.CHO + 2H_2O.$$

Acrylic aldehyde or acroleïn, $CH_2{:}CH.CHO$ (Redtenbacher, 1843), is a mobile liquid, which boils at 52°, and is intolerably pungent and irritating in odour. As an aldehyde, it shows the usual reactions, reduces silver, colours bleached rosaniline, is resinified by caustic soda, etc. It is easily reduced to allyl alcohol by zinc and dilute hydrochloric acid, and is oxidised by silver oxide to the corresponding acrylic acid. As an ethylene derivative it combines directly with bromine. and the additive compound, acroleïn dibromide, $CH_2Br.CHBr.CHO$, thus formed, is converted by ice-cold baryta water into a sugar, α-acrose (p. 191), which is closely related and convertible into some of the natural sugars.

When acroleïn-ammonia is distilled with phosphorus pentoxide, it is converted into picoline (p. 389), a basic substance closely related to the vegetable alkaloids.

As stated above, acroleïn is readily oxidised to acrylic acid. The aqueous solution is digested with silver oxide in the dark, and the product is boiled and the silver precipitated from the resulting silver acrylate with sodium carbonate. The sodium acrylate is distilled with dilute sulphuric acid, and the pure acid obtained by decomposing the dry lead salt, which is formed in the same way as lead formate, with hydrogen sulphide—

$$CH_2{:}CH.CH_2OH \rightarrow CH_2{:}CH.CHO \rightarrow CH_2{:}CH.COOH.$$

Acrylic or propenic acid, $CH_2{:}CH.COOH$ (Redtenbacher, 1843), is a liquid which closely resembles acetic acid in appearance and odour. It boils at 140°, and readily freezes to an ice-like solid, melting at 7°. As an acid, acrylic acid forms the usual salts, but the ethereal salts can only be formed indirectly. As an ethylene derivative it unites directly with bromine, forming the additive compound, dibromopropionic acid, $CH_2Br.CHBr.COOH$, a crystalline solid. When boiled with zinc and dilute hydrochloric acid, acrylic acid takes up hydrogen and is reduced to propionic acid.

Acrylic acid also unites with hydriodic acid, forming β-iodopropionic acid, $CH_2I.CH_2.COOH$, a crystalline substance which is reconverted into the unsaturated acid by distillation with litharge. β-Iodopropionic acid is also formed when phosphorus diiodide is mixed with glyceric acid. There is a violent action, and on heating the product it clears to a liquid which crystallises on cooling. The crude acid is recrystallised from hot light petroleum—

$$CH_2OH.CHOH.COOH \rightarrow CH_2I.CH_2.COOH \leftrightarrow CH_2{:}CH.COOH.$$

When acrylic acid is fused with caustic potash, it is oxidised to potassium formate and acetate, the molecule being broken at the ethylene linkage, as is usually the case with ethylene derivatives—

$$CH_2{:}CH.COOH + 2KOH = H.COOK + CH_3.COOK + H_2.$$

The Acrylic Series: Oleïc Acid.—It has been already noted that one of the condensation products of acetaldehyde is a similar aldehydic substance, crotonaldehyde. This is readily formed by heating aldehyde with zinc chloride and a few drops of water, for a day or two, at 150°, and is purified by fractionating the product. It is also obtained by distilling aldol (p. 152)—

$$CH_3.CHOH+CH_2.CHO \rightarrow CH_3.CHOH.CH_2.CHO \rightarrow CH_3.CH{:}CH.CHO+H_2O.$$

Crotonaldehyde, $CH_3.CH{:}CH.CHO$, is a liquid which resembles acroleïn, but boils at 105°. It is converted by silver oxide into the corresponding crotonic or methyl-acrylic acid, $CH_3.CH{:}CH.COOH$, and the constitution of this as 2-butenic acid follows from its reduction to normal butyric acid by zinc and hydrochloric acid, and its oxidation to acetic acid alone by fusion with potash—

$$CH_3.CH_2.CH_2.COOH \leftarrow CH_3.CH{:}CH.COOH \rightarrow CH_3.COOK+CH_3.COOK.$$

There is a second crotonic acid of precisely the same constitution, the existence of which, and other similar compounds, has led to a further development of the theory of structure (p. 160).

The most important of the higher members of the acrylic series is oleïc acid, a compound which bears the same relation to stearic acid as acrylic to propionic acid. Its glycerol salt, trioleïn, is readily separated from olive oil by cooling it with ice, the bulk of the accompanying stearin and palmitin at once crystallising out. The remainder separates on diluting the oil with alcohol and again cooling. The alcohol is then distilled off, and the oleïn washed with water, and fractionated under low pressure. Almond oil, the non-volatile oil obtained by pressing sweet or bitter almonds, is almost pure oleïn. Oleïc acid itself is prepared from trioleïn by boiling the crude oleïn with lead oxide and water, and extracting the lead oleate from the mixed lead soaps with ether, in which it is freely soluble. The lead is precipitated from the ethereal solution with hydrochloric acid, and the acid is left in a fairly pure state on evaporating the filtrate.

Oleïc acid, $CH_3.CH{:}CH.[CH_2]_{14}.COOH$ (Chevreul, 1811), is a colourless oil, which solidifies at a low temperature to a crystalline solid melting at 14°. It is reduced by hydriodic acid and phosphorus at 200° to stearic acid, whence its normal constitution. It is oxidised by fusion with potash to potassium palmitate and acetate, so that the ethylene linkage is between the second and third carbon atoms from the end of the chain. Palmitic acid is conveniently prepared in this way—

$$CH_3.[CH_2]_{16}.COOH \leftarrow CH_3.CH{:}CH.[CH_2]_{14}.COOH \rightarrow CH_3.COOK+CH_3.[CH_2]_{14}.COOK.$$

As an ethylene derivative, oleïc acid decolorises bromine, forming an oily additive compound, dibromostearic acid, $CH_3.CHBr.CHBr.[CH_2]_{14}.COOH$, and it is oxidised by weak alkaline permanganate in the normal manner to the corresponding hydroxy-compound or glycol, dihydroxy-stearic acid, $CH_3.CHOH.CHOH.[CH_2]_{14}.COOH$.

Propargyl Alcohol and Propiolic Acid.—The alcohols and acids of the acetylene series are of comparatively little importance. Only one alcohol is known, propargyl alcohol, which is formed by heating bromallyl alcohol, $CHBr:CH.CH_2OH$, with caustic potash solution, much in the same way as acetylene from vinyl bromide. The bromallyl alcohol is made by heating tribromhydrin with alkali—

$$CH_2Br.CHBr.CH_2Br \rightarrow CHBr:CH.CH_2OH \rightarrow CH \vdots C.CH_2OH.$$

Propargyl alcohol or propinol, $CH \vdots C.CH_2OH$ (Henry, 1878), is a mobile liquid of pleasant odour, boiling at 115°. As an alcohol, it forms ethereal salts, such as the bromide, $CH \vdots C.CH_2Br$, and the acetate, and as an acetylene derivative, it forms metallic compounds such as the cuprous compound, $Cu_2(C \vdots C.CH_2OH)_2$, an explosive yellow solid. The salts of propargyl alcohol also form metallic compounds.

The aldehyde corresponding with propargyl alcohol has not been prepared, but the corresponding acid is known.

Propiolic or propinic acid, $CH \vdots C.COOH$ (Bandrowski, 1880), is a liquid resembling acrylic and acetic acids. It boils at 144°, and solidifies in the cold to silky crystals, melting at 6°. Its potassium salt is formed when the acid potassium salt of acetylene-dicarboxylic acid, $COOH.C \vdots C.COOH$ (p. 161), is heated with water, and by prolonged treatment with the same agent is converted into carbon dioxide and acetylene—

$$COOH.C \vdots C.COOK \rightarrow CH \vdots C.COOK \rightarrow CH \vdots CH.$$

As an acid, propiolic acid forms ethereal salts, such as ethyl propiolate, $CH \vdots C.COOEt$, a liquid boiling at 112°, and as an acetylene derivative it gives rise to explosive silver and copper compounds. It is reduced to propionic acid by sodium amalgam.

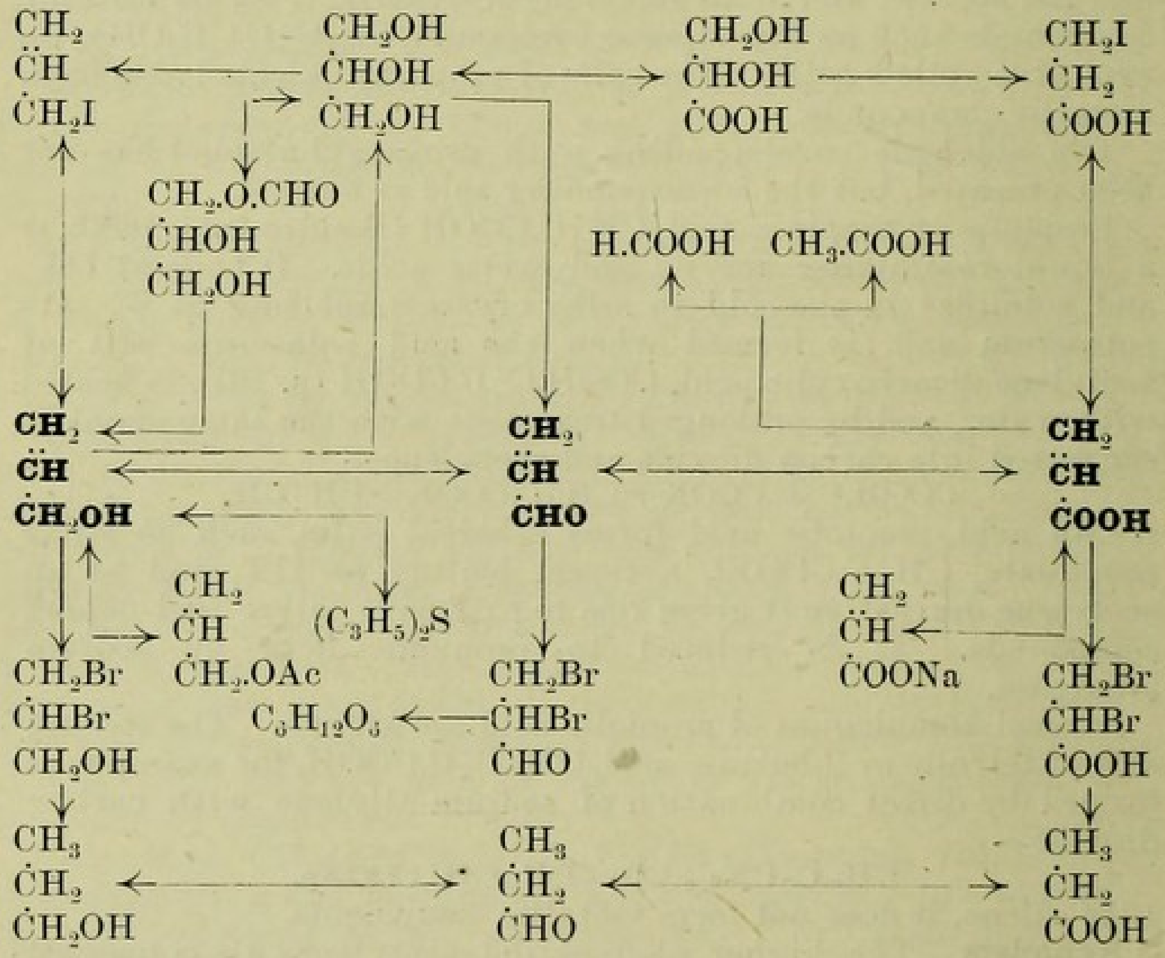
Several homologues of propiolic acid are known. The sodium salt of tetrolic or 2-butinic acid, $CH_3.C \vdots C.COOH$, for example, is formed by direct combination of sodium-allylene with carbon dioxide—

$$CH_3.C \vdots CNa + CO_2 = CH_3.C \vdots C.COONa.$$

Like allene, it does not form metallic compounds.

Synopsis.—The higher olefines and acetylenes are connected with alcohols and acids, which are similar to the paraffin alcohols and acids, but unsaturated. Allyl alcohol and acrylic acid are typical members of the first class, and propargyl alcohol and propiolic acid of the second.

THE ALLYL COMPOUNDS.



CHAPTER XXIV

THE FOUR LACTIC ACIDS: STEREOISOMERISM

Fermentation Lactic Acid.—In addition to the oxidation products of the propyl alcohols and glycerol, which have been fully dealt with, there should be, according to the theory of substitution, two series of mixed compounds, analogous to those of the glycol-oxalic series, and derived from the isomeric propane-glycols. These dihydroxy-propanes are known, and two of their oxidation products are of importance. The ultimate product of the oxidation of β-propylene or trimethylene glycol, $CH_2OH.CH_2.CH_2OH$, is malonic acid, $COOH.CH_2.COOH$, a dibasic acid used in synthesis (p. 152), whilst the first product from α-propylene glycol, $CH_3.CHOH.CH_2OH$, is identical with the lactic acid of sour milk.

In the souring of milk, the milk-sugar is converted by a microscopic fungus, bacillus lacti, into this lactic acid, which bears the same relation to propionic acid as glycollic to acetic acid. Lactic acid is conveniently prepared from cane-sugar. The sugar is dissolved in water and acidified with tartaric acid, and after a few days sour skim milk and a little putrid cheese are added, to provide and nourish the ferment. At the same time, zinc carbonate is stirred in to neutralise the acid as it is formed, which would otherwise stop the action. The mixture is kept warm for a week, and frequently stirred, and on boiling and filtering the semi-solid product, zinc lactate crystallises out.* The free acid is obtained by decomposing the zinc salt, suspended in water, with sulphuretted hydrogen. The filtered solution is concentrated, and the lactic acid separated from admixed mannitol (p. 186) by extraction with ether, in which the mannitol is insoluble.

Lactic acid is also formed by heating various sugars with caustic alkali. Thus when invert sugar (p. 175) is heated with strong caustic soda solution for some hours at a moderate temperature, the solution loses the characteristic reducing properties

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* If the fermentation is continued, the lactate is converted by a second ferment into the butyrate, with evolution of hydrogen and carbon dioxide. For this purpose calcium carbonate is better than the zinc salt. The mass eventually becomes liquid, and as soon as the evolution of gas has ceased, the lime is precipitated with washing soda solution and the sodium butyrate decomposed with dilute sulphuric acid.

due to the sugar, and after neutralising the alkali, lactic acid can be separated as the zinc salt (Hoppe-Seyler, 1871)—

$$C_6H_{12}O_6=2C_3H_6O_3.$$

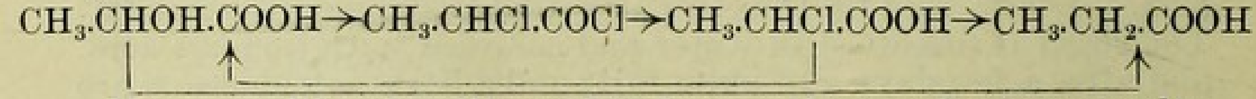
It is also formed synthetically in various ways (see below).

Fermentation or inactive lactic acid, $CH_3.CHOH.COOH$ (Scheele, 1780), is a syrupy liquid, which is decomposed when distilled, and has not been solidified. Its specific gravity is 1·248 at 15°.

Constitution of Lactic Acid.—From the composition of its metallic salts, such as zinc lactate, $Zn(C_3H_5O_3)_2+3H_2O$, the acid is a monobasic acid, whilst as hydrogen is displaced from its sodium salt by metallic sodium, and from the acid itself by acetyl chloride, it is also an alcohol.

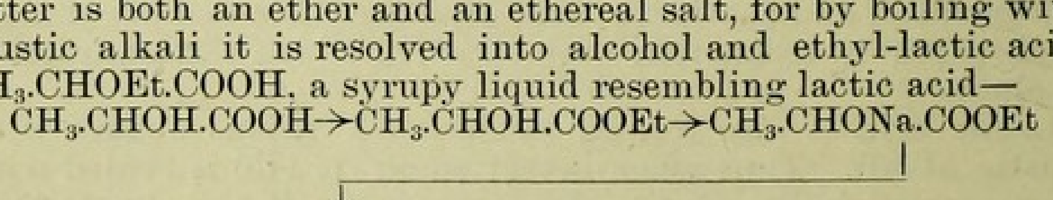
Lactic acid was in fact the first compound which was recognised as belonging to two classes. Its duality, like that of glycollic acid, is made clear by the action of phosphorus pentachloride, which converts it into *α*-chloropropionyl chloride, $CH_3.CHCl.COCl$. This liquid is identical with that obtained by chlorinating propionyl chloride. It is hydrolysed by water to *α*-chloropropionic acid, $CH_3.CHCl.COOH$, and is thus an acid chloride, and it is hydrolysed by alkalies to the alkali lactate, so that it is also an alkylic compound (Wurtz, Kolbe, 1859).

Further, lactic acid is converted into *α*-bromopropionic acid by heating with hydrobromic acid, and into the fatty acid itself by heating with hydriodic acid and red phosphorus—



$$CH_3.CHOH.COOH \rightarrow CH_3.CHCl.COCl \rightarrow CH_3.CHCl.COOH \rightarrow CH_3.CH_2.COOH$$

Moreover, like glycollic acid, it forms ethers and ethereal salts both as an alcohol and as an acid, as well as internal ethereal salts. Ethyl lactate, $CH_3.CHOH.COOEt$, for example, a liquid which is formed by saturating an alcoholic solution of the acid with hydrogen chloride, contains alkylic hydroxyl, for it is converted by sodium and ethyl iodide into ethylic ethyl-lactate, $CH_3.CHOEt.COOEt$, an insoluble liquid, boiling at 154°. The latter is both an ether and an ethereal salt, for by boiling with caustic alkali it is resolved into alcohol and ethyl-lactic acid, $CH_3.CHOEt.COOH$, a syrupy liquid resembling lactic acid—



$$CH_3.CHOH.COOH \rightarrow CH_3.CHOH.COOEt \rightarrow CH_3.CHONa.COOEt$$

$$\rightarrow CH_3.CH(OEt).COOEt \rightarrow CH_3.CH(OEt).COOH.$$

The double ethereal salt, lactide, $O{<}\begin{matrix}CHMe.CO\\CO.CHMe\end{matrix}{>}O$, a crystalline substance, melting at 124°, is obtained by heating the acid.

There are, however, two hydroxy-propionic acids possible, namely *α*-hydroxy- or 2-propanolic acid, $CH_3.CHOH.COOH$, and *β*-hydroxy- or 3-propanolic acid, $CH_2OH.CH_2.COOH$. Lactic acid is the first of these, for it can be converted into and synthesised from aldehyde, and thus contains the ethylidene group, $CH_3.CH$. When the acid is heated with dilute sulphuric acid at 120°, it is hydrolysed to aldehyde and formic acid—

$$CH_3.CHOH.COOH \rightarrow CH_3.CHO[(OH)_2] + H.COOH,$$

and conversely, as previously stated, it is formed when aldehyde hydrocyanide is mixed with strong hydrochloric acid. It is unnecessary to isolate the nitrile. A mixture of aldehyde with strong hydrocyanic and hydrochloric acids is simply kept until ammonium chloride ceases to separate, and the lactic acid extracted from the product with ether (Wislicenus, 1863). The constitution of the additive compounds of aldehyde follows from this synthesis. Lactic acid was first synthesised by the action of nitrous acid on alanine (Strecker, 1848, p. 223).

$$\begin{tikzcd}CH_3.CHO \arrow[r] & CH_3.CHOH.CN \arrow[r] & CH_3.CHOH.COOH. \arrow[ll, bend left]\end{tikzcd}$$

The constitution of lactic acid as a secondary alcohol is further proved by its oxidation by dilute potassium permanganate to the corresponding ketone or ketonic acid, pyroracemic acid, $CH_3.CO.COOH$, and by its formation from this acid by reduction with sodium amalgam. Pyroracemic acid is readily prepared by distilling racemic or tartaric acid with twice its weight of potassium hydrogen sulphate. The mass swells up and darkens, and the liquid ketonic acid passes over. The product is fractionated to separate acetic and pyrotartaric acids—

$$C_4H_4O_6 = C_3H_4O_3 + CO_2 + H_2O.$$

Pyroracemic acid, $CH_3.CO.COOH$, is a highly acid liquid, boiling at 168°. As a ketone, it forms with phenyl-hydrazine a hydrazone, $CH_3.C(:N.NHPh).COOH$, a crystalline substance, melting at 169°, and its constitution is further established by its formation from acetyl chloride by the cyanide synthesis—

$$CH_3.COCl \rightarrow CH_3.COCN \rightarrow CH_3.CO.COOH \rightarrow CH_3.CHOH.COOH.$$

As already stated lactic acid is formed by oxidation of propylene glycol. The glycol is a syrupy liquid resembling ordinary glycol. It is made from propylene bromide in precisely the same way, and when mixed with platinum black and exposed to the air, is gradually converted into lactic acid (Wurtz, 1857). The molecular weight of the acid was first established by this reaction—

$$CH_3.CHBr.CH_2Br \rightarrow CH_3.CHOH.CH_2OH \rightarrow CH_3.CHOH.COOH.$$

Hydracrylic Acid.—The second hydroxy-propionic acid or ethylene-lactic acid, $CH_2OH.CH_2.COOH$, is prepared by warming β-iodopropionic acid with silver oxide and water, and evaporating the filtered product in a vacuum over sulphuric acid—

$$CH_2I.CH_2.COOH \rightarrow CH_2OH.CH_2.COOH.$$

It is also formed by the oxidation of β-propylene or trimethylene glycol. The glycol is made from the trimethylene bromide formed by direct union of allyl bromide with hydrobromic acid—

$$CH_2:CH.CH_2Br \rightarrow CH_2Br.CH_2.CH_2Br \rightarrow CH_2OH.CH_2.CH_2OH.$$

Hydracrylic or ethylene-lactic acid, $CH_2OH.CH_2.COOH$ (Wislicenus, 1863), is a syrupy liquid resembling ordinary lactic acid. As an alcohol-acid, it is converted by phosphorus pentachloride into an alkyl-acid chloride, β-chloropropionyl chloride, $CH_2Cl.CH_2.COCl$, but it differs from ethylidene-lactic acid in that it is converted by oxidising agents into carbon dioxide and oxalic acid. It resolved moreover by distillation, not into an internal ethereal salt, but into acrylic acid and water, and conversely the latter is converted into sodium β-lactate by simply boiling with aqueous caustic soda—

$$CH_2OH.CH_2.COOH \longleftrightarrow CH_2{:}CH.COOH + H_2O.$$

The constitution of β-lactic acid is fully established by its formation from ethylene chlorhydrin by the cyanide synthesis—

$$CH_2{:}CH_2 \rightarrow CH_2OH.CH_2Cl \rightarrow CH_2OH.CH_2.CN \rightarrow CH_2OH.CH_2.COOH.$$

The Active Lactic Acids: Optical Activity.—According to the theory of structure there should be two hydroxypropionic acids, and only two. But there are actually four. The third, sarcolactic acid, is found in muscle, and therefore in extract of meat. It is best isolated from the solution of the latter by precipitating the albumen, etc. with alcohol, and extracting the acidified and alcohol-free residue with ether (Liebig, 1847).

Sarcolactic acid, $CH_3.CHOH.COOH$ (Berzelius, 1808), is a syrup which resembles fermentation lactic acid in almost every respect, and all its reactions show that it is α-hydroxypropionic acid. With the exception of the solubilities of the salts, in fact, the zinc salt, for example, being more soluble than the zinc salt of fermentation lactic acid, the two acids are chemically identical, and for a long time were thought to be absolutely identical.

Physically, however, they differ widely, for whilst fermentation lactic acid is without action on polarised light, sarcolactic acid rotates the plane of polarisation of such light in a clockwise or positive direction, or, as it is termed, is optically active, and dextrogyrate.

The rotation of the plane of polarisation by an optically active substance is proportional to the thickness of the layer traversed by the light, and to the strength of the solution, and is usually expressed in terms of the specific rotatory power, *i.e.* the rotation which would be caused by a layer 10 cm. thick of a solution containing 1 gram of the substance per c.c. The specific rotatory power is denoted by the symbol $[\alpha]_D$, sodium light being used, and is constant for each substance, provided the temperature and concentration are constant. The specific rotatory power of sarcolactic acid is $[\alpha]_D = +3{\cdot}5^\circ$.

Sarcolactic acid can also be made by fermentation. When, for instance, common mould, penicillium glaucum, is allowed to grow on a solution of ammonium lactate, ammonium sarcolactate is formed, and by means of a special ferment, micrococcus paralacti, grape sugar is directly convertible into sarcolactic acid. But, however prepared, the optical activity is constant.

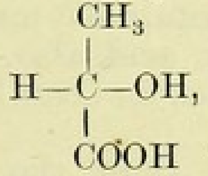
The fourth lactic acid (Schardinger, 1890) is formed by the action of bacillus lævolacti on cane-sugar. It resembles sarcolactic acid in every respect, with the exception that it is lævogyrate, the specific rotatory power being $[\alpha]_D = -3{\cdot}5^\circ$. It is therefore termed lævolactic acid, or l-lactic acid, as distinguished from dextrolactic, d-lactic, or sarcolactic acid, and inactive, i-lactic, or fermentation lactic acid.

Now, when dextrolactic and lævolactic acids are mixed in equal proportions, a product is obtained, which is not only inactive, but is identical with fermentation lactic acid, and similarly, when equal weights of the easily soluble zinc salts of the optically active acids are dissolved in water and the solutions mixed, the sparingly soluble inactive zinc lactate is precipitated (Purdie, 1892).

Conversely, when a solution of the strychnine salt of inactive lactic acid is concentrated, the crystals which first appear consist of strychnine lævolactate, whilst the more soluble salt remaining in the solution is the corresponding dextrolactate (Purdie, 1892).

It is thus evident that fermentation lactic acid is either a mixture or a molecular compound of dextro- and lævo-lactic acids, and that all three have precisely the same constitution.

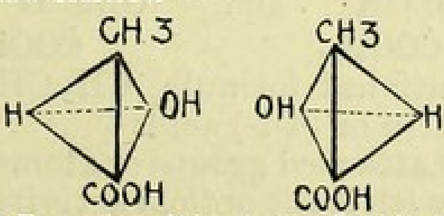
The Asymmetric Carbon Atom: Solid Formulæ.—The difference between the three ethylidene lactic acids cannot be represented by means of structural formulæ, and a further development is necessary. It will be noticed that the common formula of the three acids differs from that of hydracrylic acid, not only in the position of the hydroxyl group, but in that the carbon atom, to which this group is attached, is linked to four different groups or atoms, or is asymmetrically placed in the molecule—



$$\begin{array}{c} CH_3 \\ | \\ H-C-OH, \\ | \\ COOH \end{array}$$

and by assuming that the four valencies of this atom are distributed round this central atom at equal angles in space, instead of in a plane, two different solid formulæ become possible (Le Bel, Van't Hoff, 1874).

The postulate is geometrically equivalent to representing the atom as a regular tetrahedron to the apices of which the four groups and atoms are linked *—



Solid Formulæ of the Active Lactic Acids.

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* These formulæ are best studied with the aid of models. See Appendix I.

In both formulæ the four groups are linked to the central carbon atom, as in the plane formula, so that the structures are identical, but, nevertheless, the formulæ are not identical. If the right hand formula be imagined superposed on the left hand formula in such manner that the two methyl groups and the two carboxyl groups coincide, then the hydroxyl of the right hand formula falls over the hydrogen of the left hand formula, and vice versâ. The two formulæ are, in fact, mirror images of each other. They are related, moreover, in the same way as the rotatory powers of the two acids, for, looking from above, the sequence, H, OH, COOH is clockwise in the left-hand formula and anticlockwise in the right-hand formula.

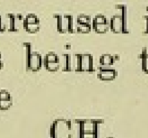
There is a further analogy, which although not yet proven in the case of the lactic acids, has been fully established in other similar cases (see Tartaric acid). The crystals of optical isomerides are usually hemihedral, that is to say, only their alternate faces are developed, and the faces which are developed in the crystals of the one active modification, are those which are suppressed in the other; the two kinds of crystals, therefore, like the two formulæ, are mirror images of each other.

The active lactic acids are thus adequately represented by the single solid formulæ, and the inactive acid by the two together.

Stereoisomerism.—Such isomerism, representable only by solid formulæ, is termed stereoisomerism (στερεος = solid). All optically active substances contain asymmetric carbon atoms, and there is every reason to believe that all compounds containing asymmetric carbon atoms are either optically active, or capable of resolution into optically active stereoisomerides.

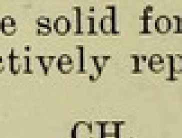
Thus secondary-butyl carbinol, $\mathbf{C}HMeEt.CH_2OH$, or active amyl alcohol, and methylethylacetic acid, $\mathbf{C}HMeEt.COOH$, or active valeric acid, both contain asymmetric carbon, and are both optically active. Glyceric acid also, $CH_2(OH).\mathbf{C}H(OH).COOH$, contains asymmetric carbon, and can be resolved into optically active constituents.

Stereoisomerides have thus the same constitution and structure, and are said to differ in configuration. As the perspective views of the solid formulæ are rather cumbrous, their plane projections are used instead, the solid formulæ of l-lactic and d-lactic acids being thus respectively represented by the projection formulæ



$$\begin{array}{c}CH_3\\ H.\dot{C}.OH\\ \dot{C}OOH\end{array}$$

and



$$\begin{array}{c}CH_3\\ OH.\dot{C}.H\\ \dot{C}OOH\end{array}$$

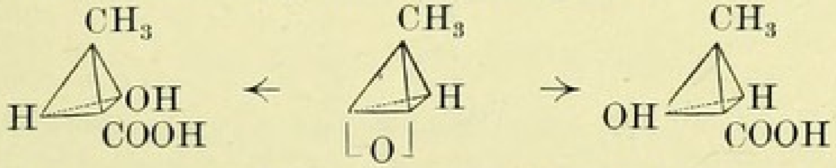
the ordinary constitutional formula, $CH_3.CHOH.COOH$, being reserved for the inactive or (d-l-) acid.

Directly two of the attached groups or atoms become identical, the asymmetry, and with it the optical activity, vanishes. Thus the lactic acids and glyceric acid are convertible into propionic acid, but the two projection formulæ

$$\begin{array}{c} CH_3 \\ H.\dot{C}.H \\ \dot{C}OOH \end{array} \qquad \begin{array}{c} CH_3 \\ H.\dot{C}.H \\ \dot{C}OOH \end{array}$$

are identical, the corresponding solid formulæ superposable, and the products identical and inactive. The essential condition both for asymmetry and optical activity is the linking of four dissimilar groups to the central carbon atom.

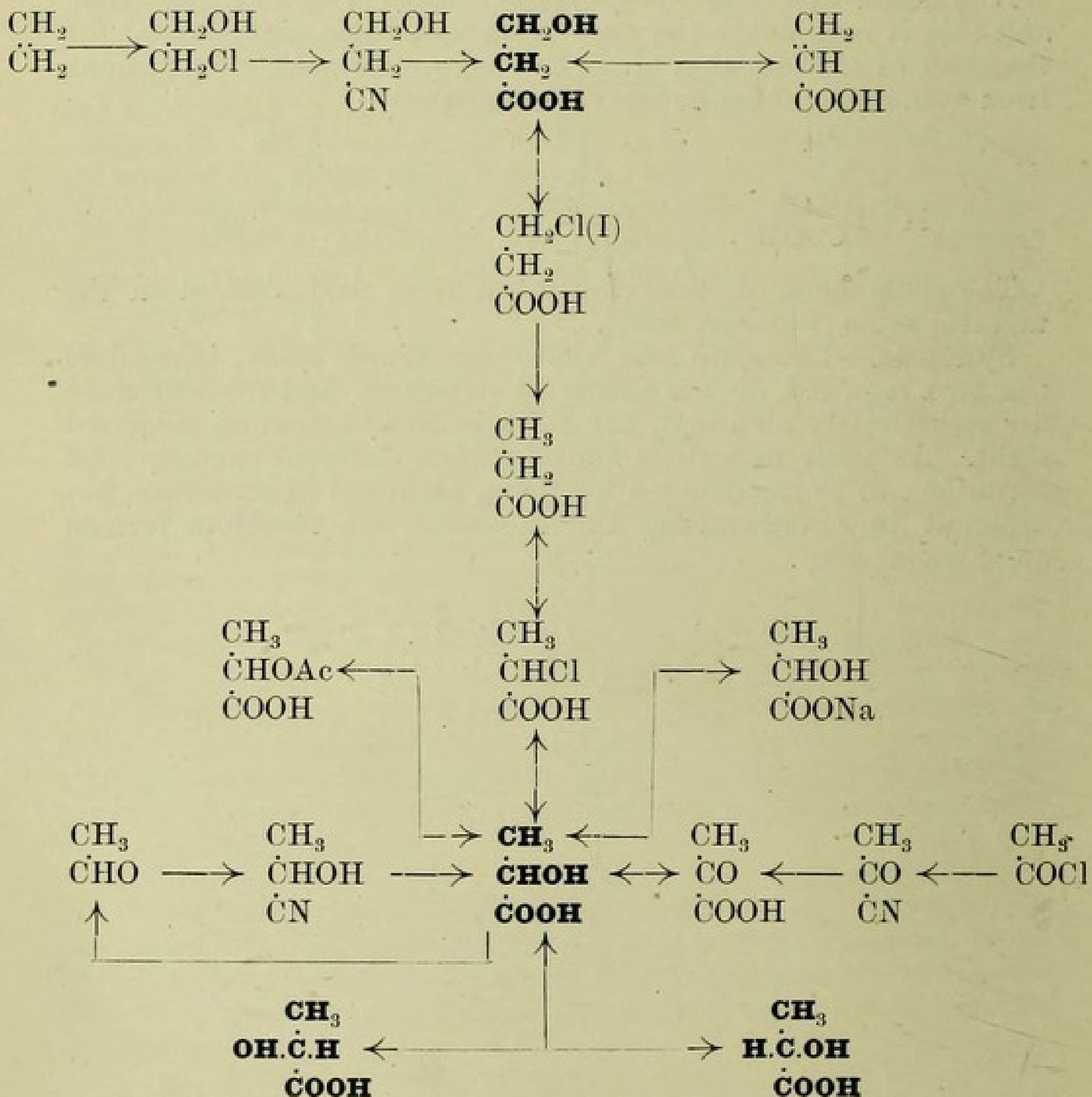
It is noteworthy that synthetic lactic acid is optically inactive, and this is invariably the case with synthetic compounds, for the chances of formation of the two asymmetrical configurations from symmetrical configurations are equal—



The phenomena of stereoisomerism were first studied in the tartaric acids (Pasteur, 1853).

Synopsis.—There are four hydroxypropionic acids, instead of the two required by the theory of structure, and three of these are structurally identical, but differ in their action on polarised light. As their molecules contain asymmetrical carbon, solid formulæ can be constructed for them, identical in structure, but different in configuration, and the acids are therefore termed stereoisomerides.

THE FOUR LACTIC ACIDS.



SECTION VII

FOUR-CARBON DERIVATIVES

CHAPTER XXV

THE ACETOACETIC SYNTHESIS

Ethyl Acetoacetate and Acetoacetic Acid.—The four-carbon hydrocarbons give rise to many derivatives, which differ from their three-carbon analogues, as might be expected, mainly in the complexity of their isomerism, and of course in their physical properties. With the addition of another carbon atom, however, types appear which are not possible in the lower series, and certain others come into prominence which were previously unimportant.

The most conspicuous example of this last class is acetoacetic acid, the next homologue of pyroracemic or acetoformic acid. The ethyl salt of this acid is an agent of great utility in synthesis. It is formed by the condensation of ethyl acetate in a manner somewhat analogous to that of aldehyde to aldol. An excess of the well-dried acetate is poured on sodium shavings in a reflux apparatus, and the action which soon sets in is continued on a water-bath until the whole of the metal has dissolved. The warm product is acidified with moderately strong acetic acid, and the ethyl acetoacetate thus set free is salted out with brine, with the addition of water if necessary.

The crude acetoacetate is fractionated on a water-bath, first under ordinary pressure, when the excess of ethyl acetate passes over, and then under very low pressure (Fig. 9). A little more ethyl acetate first passes over, followed by some water and acetic acid, and finally, the ethyl acetoacetate distils at an almost constant temperature—

$$2CH_3.COOEt \rightarrow CH_3.CO.CHNa.COOEt \rightarrow CH_3.CO.CH_2.COOEt.$$

By cautious hydrolysis of the ethereal salt the acid itself may be obtained. The acetoacetate is digested for a day or two with cold dilute potash, by which it is converted into the potassium salt, and the acid is liberated by excess of dilute sulphuric acid, and extracted from the solution with ether. It is separated from the solvent by evaporation at a low temperature.

Ethyl acetoacetate, $CH_3.CO.CH_2.COOEt$ (Geuther, 1863; Frankland and Duppa, 1865), is a light, colourless liquid, having a faint, but pleasant, fruity odour. It boils at 181° under ordinary pressure, and at 74° under 15 mm. pressure. The boiling point at very low pressures changes about 1° per mm. Acetoacetic acid, or 3-butanonic acid, $CH_3.CO.CH_2.COOH$, is an unstable syrupy liquid, having a peculiar and characteristic odour. Both acid and salt form a violet coloration with ferric chloride, and the acid itself may be detected in diabetic urine by this means, and by its odour.

The Acetoacetic Synthesis.—Ethyl acetoacetate is readily resolved into acetone and acetic acid, and is as readily converted into alkyl derivatives, which are resolvable in a similar manner. Its synthetic importance lies in these transformations. When the ethereal salt is distilled with dilute caustic soda, sodium carbonate is formed and acetone passes over, whilst when it is heated with concentrated alcoholic potash, it is hydrolysed to potassium acetate. On treating its alkyl derivatives in this way, alkyl derivatives of acetone and acetic acid are obtained—

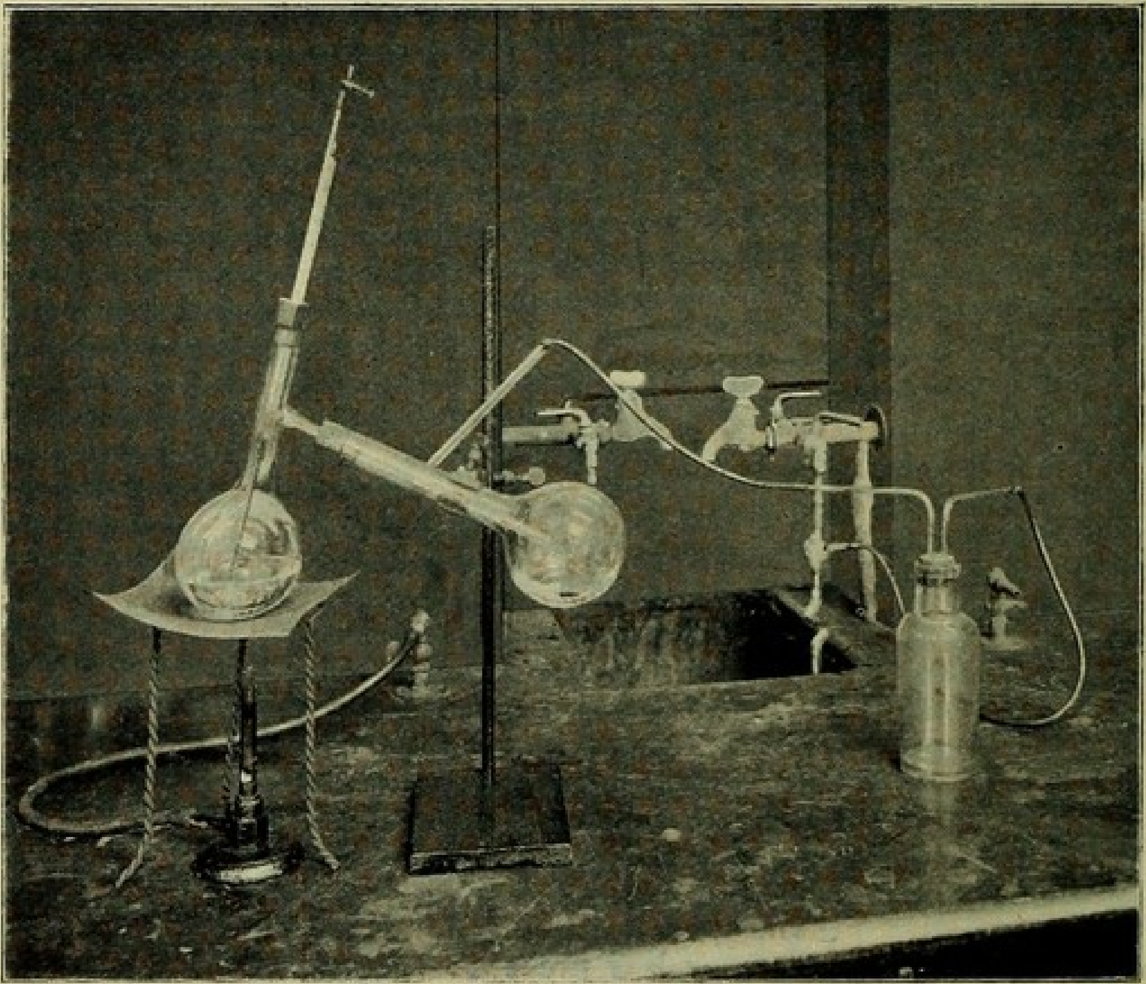


Fig. 9.—Distillation under Reduced Pressure.

$$2CH_3.COOH + EtOH \rightarrow CH_3.CO.CH_2.COOEt$$
$$\rightarrow CH_3.CO.CH_3 + CO_2 + EtOH.$$

The convertibility of ethyl acetoacetate into homologous alkyl derivatives is due to the mobility of its methylene hydrogen, which is influenced by the adjacent carbonyl groups, in the same way as the hydroxyl hydrogen of acetic acid. Metallic sodium dissolves in the ethereal salt just as in alcohol, and the replacement of hydrogen by sodium is even effected by sodium ethoxide.

Ethyl sodacetoacetate, $CH_3.CO.CHNa.COOEt$, is a crystalline substance, which is reconverted into the acetoacetate by acetic acid, and is the initial product in the preparation of the latter—

$$CH_3.CO.CH_2.COOEt \rightarrow CH_3.CO.CHNa.COOEt.$$

On boiling this sodium compound with ethyl iodide, the sodium is replaced by the alkyl, and the ethereal salt of ethyl-acetoacetic acid is formed. The action is precisely parallel to that of ethyl iodide on sodium ethoxide, and the product is isolated in the same way as the original ethyl acetoacetate—

$$CH_3.CO.CHNa.COOEt \rightarrow CH_3.CO.CHEt.COOEt.$$

Ethylic ethyl-acetoacetate, $CH_3.CO.CHEt.COOEt$, is a liquid which boils at 198°, and resembles the simple acetoacetate in every respect. When boiled with dilute caustic soda, it is resolved into carbon dioxide and ethyl-acetone or methyl propyl ketone, $CH_3.CO.CH_2.CH_2.CH_3$, whilst with concentrated alcoholic potash it is converted into the potassium salt of ethyl-acetic or normal butyric acid (Frankland and Duppa, 1865)—

$$CH_3.COOH + CH_2Et.COOH + EtOH \leftarrow CH_3CO.CHEt.COOEt \rightarrow CH_3.CO.CH_2Et + EtOH.$$

The synthetic process can be carried still further, for the resemblance of the derived salt extends to the mobility of the hydrogen. It is thus converted into ethylic ethyl-sodacetoacetate by the action of sodium ethoxide, $CH_3.CO.CNaEt.COOEt$, and this in turn interacts with alkyl iodides, forming compounds containing two substituted alkyl groups.

Ethylic methyl-ethyl-acetoacetate, $CH_3.CO.CMeEt.COOEt$, for example, is a liquid which resembles the original acetoacetate, and is resolvable in a precisely similar manner into methyl-ethyl-acetone, or 3-methyl-2-pentanone, $CH_3.CO.CHMe.CH_2.CH_3$, and methyl-ethyl-acetic or active valeric acid, $CH_3.CH_2.CHMe.COOH$ (Frankland and Duppa)—

$$\begin{tikzcd}
CH_3.CO.CHEt.COOEt \arrow[r] & CH_3.CO.CNaEt.COOEt \arrow[d] \\
CH_3.COOH + CHMeEt.COOH + EtOH & CH_3.CO.CMeEt.COOEt \arrow[l] \arrow[d] \\
 & CH_3.CO.CHMeEt + CO_2 + EtOH.
\end{tikzcd}$$

The acetoacetic synthesis is thus of peculiar importance, as by its means any monalkyl or dialkyl substitution product of acetic acid or acetone can be formed, of perfectly determinate constitution. As will be seen later, also, practically any molecule containing alkylic halogen can be linked on in this manner (Wislicenus), and other important syntheses can also be effected.

It is unnecessary to isolate the intermediate compounds.

Thus, in the preparation of methyl-ethyl-acetic acid, the sodium required to replace one equivalent of hydrogen is dissolved in alcohol, and mixed with the ethyl acetoacetate, and the mixture is boiled in a reflux apparatus with the calculated amount of ethyl iodide until the solution becomes neutral. The operation is then repeated with sodium and methyl iodide, and the product boiled with alcoholic potash. Finally the acetic and methyl-ethyl-acetic acids are set free with dilute sulphuric acid, and distilled off, and separated by fractional neutralisation. If the ketone is required, the ethereal salt is boiled with dilute aqueous potash, and the product salted out, and purified by means of its bisulphite compound.

The decompositions by alkali are not quite quantitative. In the "acid" decomposition, for example, a certain amount of ketone is always formed, and vice versâ, in the "ketonic" decomposition, a certain proportion of acid.

The mechanism of the formation of the acetoacetate is rather obscure. The presence of a little alcohol is essential, sodium having no action on the pure ethyl acetate. Probably a derivative of ortho-acetic acid is formed with the sodium ethoxide, and subsequently decomposed by a further quantity of the ethyl acetate—

$$\begin{tikzcd}
CH_3.COOEt + NaOEt \arrow[r] \arrow[rr, bend right] & CH_3.C(OEt)_2.ONa \arrow[r] & CH_3.CO.CHNa.COOEt + 2EtOH.
\end{tikzcd}$$

As a ketone, ethyl acetoacetate is reduced by sodium amalgam to the secondary alcohol, ethyl 3-butanolate, $CH_3.CHOH.CH_2.COOEt$. The corresponding acid is a syrupy substance, which is identical with that formed from aldol by oxidation with silver oxide. The latter is therefore β-hydroxy-butyric aldehyde $CH_3.CHOH.CH_2.CHO$. As a ketone, also, ethyl acetoacetate forms a crystalline bisulphite compound, which may be used in its purification.

The Malonic Acid Synthesis.—A synthesis very similar to the acetoacetic synthesis is effected by means of malonic acid, $COOH.CH_2.COOH$, the next homologue of oxalic acid. This substance, although a three-carbon compound, is considered here, as it behaves in the same manner as acetoacetic acid in the ketonic synthesis, and is, moreover, the type of an important series of dibasic acids derived from the four-carbon and higher paraffins.

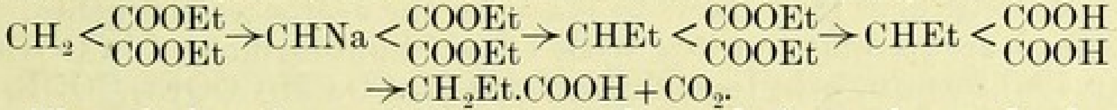
Malonic acid was originally obtained by oxidation of malic acid (p. 163) with chromic acid mixture, whence its name, but it is more conveniently made from acetic acid by the cyanide synthesis. Warm chloracetic acid solution is neutralised with sodium carbonate, and heated with the calculated amount of pure potassium cyanide until the vigorous action has quite subsided, and the cyanide has dissolved. The sodium cyanacetate thus formed is hydrolysed by boiling with concentrated hydrochloric acid, and the malonic acid extracted with ether and crystallised (Kolbe, Müller, 1864)—

$$CH_2Cl.COONa \rightarrow CH_2(CN).COONa \rightarrow CH_2(COOH).COOH.$$

Malonic or propanedioic acid, $COOH.CH_2.COOH$ (Dessaignes, 1858), forms long colourless crystals, and melts at 132°. Its constitution follows from its synthesis from acetic acid, and from its direct resolution into carbon dioxide and the fatty acid when heated a few degrees above its melting point—

$$COOH.CH_2.COOH = CH_3.COOH + CO_2.$$

The utility of the acid in synthesis depends on this decomposition, and on the circumstance that the methylene hydrogen of its ethyl salt is replaceable by metallic and alkyl radicles in the same way as that of ethyl acetoacetate (Conrad, 1880)—



$$CH_2 < \genfrac{}{}{0pt}{}{COOEt}{COOEt} \rightarrow CHNa < \genfrac{}{}{0pt}{}{COOEt}{COOEt} \rightarrow CHEt < \genfrac{}{}{0pt}{}{COOEt}{COOEt} \rightarrow CHEt < \genfrac{}{}{0pt}{}{COOH}{COOH}$$
$$\rightarrow CH_2Et.COOH + CO_2.$$

The ethyl malonate is conveniently made from the crude, dry cyanacetate, a mixture of which with absolute alcohol is saturated with dry hydrogen chloride gas. The cooled product is poured into ice-water, and the ethyl malonate extracted with ether, and fractionated in the usual manner—

$$CH_2(CN).COONa + 2EtOH + 2HCl = CH_2(COOEt)_2 + NaCl + NH_4Cl.$$

Ethyl malonate, $CH_2(COOEt)_2$, is a heavy, colourless liquid, which has a pleasant aromatic odour, and boils at 198°. It is converted without much difficulty into the alkyl-acetic acids.

On mixing the malonate with sodium ethoxide in alcoholic solution, it is converted into ethyl sodiomalonate, $CHNa(COOEt)_2$, a white crystalline substance resembling ethyl sodacetoacetate, and on boiling this substance with an alkyl iodide, such as ethyl iodide, an ethylic alkyl-malonate is obtained. The ethyl iodide is poured into the crude sodium derivative. and the whole boiled on a water-bath until neutral, in the same way as in the acetoacetic synthesis, the ethereal salt being extracted with ether and fractionated.

Ethylic ethyl-malonate, $CHEt(COOEt)_2$ is a liquid boiling at 207°.

To obtain the ethyl-acetic acid, the ethyl-malonic acid must be isolated. The alkyl-malonate is first converted into the sodium salt by boiling with strong caustic soda solution, and from this the sparingly soluble calcium salt is precipitated by the addition of concentrated calcium chloride. Enough dilute sulphuric acid to exactly combine with the calcium is now added, and the ethyl-malonic acid thus set free is extracted with ether, and recrystallised from water—

$$CHEt(COOEt)_2 \rightarrow CHEt(COONa)_2 \rightarrow CHEt(COO)_2Ca \rightarrow CHEt(COOH)_2.$$

Ethyl-malonic acid is a crystalline substance, melting at 111°, which resembles malonic acid in every respect, and when heated at 160° is resolved into carbon dioxide and ethyl-acetic acid. The ethyl-acetic acid thus prepared boils at 163°, and is in every respect identical with normal butyric acid, a further synthesis of which is thus afforded—

$$CH_3.CH_2.CH(COOH)_2 = CH_3.CH_2.CH_2.COOH + CO_2.$$

Dialkyl-acetic acids, such as active valeric acid, can be synthesised in the same way, the dialkyl-malonates being prepared in precisely the same manner as the dialkyl-acetoacetates, and converted into the corresponding malonic acids by the method just described—

$$CH_2(COOEt)_2 \rightarrow CMeEt(COOEt)_2 \rightarrow CMeEt(COOH)_2 \rightarrow CHMeEt.COOH + CO_2.$$

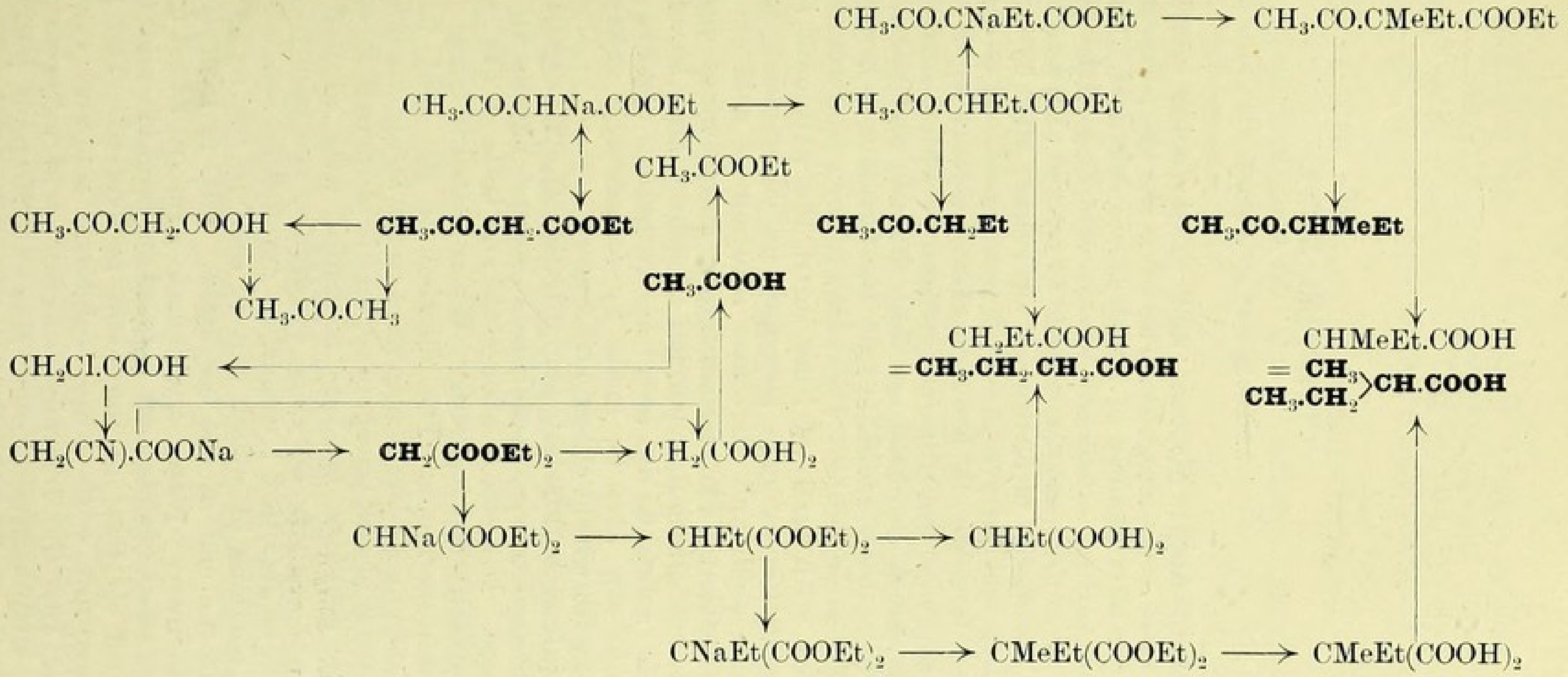
The malonic synthesis is in some respects preferable to the aceto-acetic synthesis. The yields are better, and the resulting acids do not need purification.

Malonic acid may itself be made by the acetoacetic synthesis. Ethyl acetoacetate unites with ethyl chloroformate, $Cl.COOEt$ (p. 196), forming ethyl acetomalonate, $CH_3.CO.CH(COOEt).COOEt$, a liquid which is converted into potassium acetate and malonate by boiling with alcoholic potash—

$$CH_3.CO.CH(COOEt).COOEt[=CH(CO.CH_3)(COOEt)_2] \rightarrow CH_3.COOK + CH_2(COOK)_2.$$

Synopsis.—By the action of sodium on ethyl acetate, ethyl acetoacetate is formed, a ketonic ethereal salt which is directly convertible both into acetone and acetic acid. It is semi-acid and forms alkyl derivatives, which are similarly convertible into alkyl-acetones and alkyl-acetic acids. An analogous semi-acid ethereal salt, ethyl malonate, made from cyanacetic acid, is convertible in a similar manner into substituted acetic acids alone.

THE ACETOACETIC AND MALONIC SYNTHESES.



CHAPTER XXVI

THE DIBASIC ACIDS

Succinic Acid.—Malonic and oxalic acids are the lowest members of a homologous series of acids, the succinic or oxalic series, the next member of which is succinic acid. Succinic acid is a crystalline substance which was originally obtained by distilling amber (*succinum*), and is formed also as a bye-product in the alcoholic fermentation of sugar, and by oxidation of many fats and fatty acids with nitric acid. It is conveniently prepared, however, by fermentation of tartaric acid.

A solution of ammonium tartrate, to which small quantities of magnesium sulphate, calcium chloride and potassium phosphate have been added, to feed the ferment, is kept in a warm place for some weeks. The ammonium succinate thus formed is boiled with milk of lime until the ammonia is expelled, the resulting calcium succinate is decomposed with dilute sulphuric acid, and the clear solution of acid evaporated to crystallisation. The fermentation starts more quickly in a very dilute solution, a portion of which may be added to the stronger solution as soon as turbidity appears. Calcium succinate can also be made by fermenting calcium malate (p. 163) with putrid cheese and water.

Succinic or butanedioic acid, $COOH.CH_2.CH_2.COOH$ (Agricola, 1550), is a colourless crystalline substance, having an unpleasant acid taste. It melts at about 185° and boils at 235°, at the same time partially decomposing. When heated it burns with a blue non-luminous flame. The relation of the acid to butane is established by its direct reduction to the latter when heated with hydriodic acid and phosphorus, and is confirmed by synthesis.

When ethylene bromide is boiled with alcohol and pure potassium cyanide, ethylene cyanide or succinonitrile, $CN.CH_2.CH_2.CN$, is obtained, a colourless crystalline substance melting at 54°, portions of which can be seen in the reflux condenser towards the end of the operation. This is hydrolysed in the usual manner. Water and caustic soda are added to the crude product, after filtering off potassium bromide, and the boiling continued as long as ammonia is evolved. The product is then acidified with dilute sulphuric acid and evaporated to dryness, and the liberated succinic acid extracted from the residue with boiling alcohol (Maxwell Simpson, 1861)—

$$CH_2Br.CH_2Br \rightarrow CN.CH_2.CH_2.CN \rightarrow COOH.CH_2.CH_2.COOH.$$

Succinic acid can thus be prepared from ethylene. Conversely, it is converted into the unsaturated hydrocarbon by simply electrolysing a strong solution of its potassium salt. Hydrogen is set free at the kathode, and ethylene at the anode—

$$\begin{array}{l}CH_2.COOK\\ \dot{C}H_2.COOK\end{array} = \begin{array}{l}CH_2\\ \dot{C}H_2\end{array} + 2CO_2 + K_2(2KHCO_3 + H_2).$$

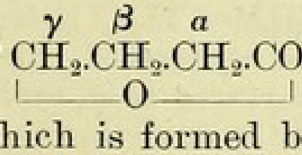
Derivatives of Succinic Acid: Butyrolactone.—Succinic acid is a dibasic acid, and its derivatives are analogous to those of oxalic acid. The alkali salts, however, are very soluble, and even calcium succinate is soluble in water, and can only be precipitated in presence of alcoholic ammonia. The basic ferric salt, formed by adding ferric chloride to a neutral solution of a succinate, is a brown gelatinous precipitate.

On the other hand, ethyl succinate is an oily liquid boiling at 216°, and closely resembling the oxalate. It is formed by warming the acid and alcohol with a little concentrated sulphuric acid, and isolated by extraction with ether. Like the oxalate, it is converted by aqueous ammonia into the corresponding diamide, succinamide, $C_2H_4(CONH_2)_2$, an insoluble crystalline powder. On heating ammonium succinate, however, or succinamide itself, ammonia is given off and a product of a new type formed.

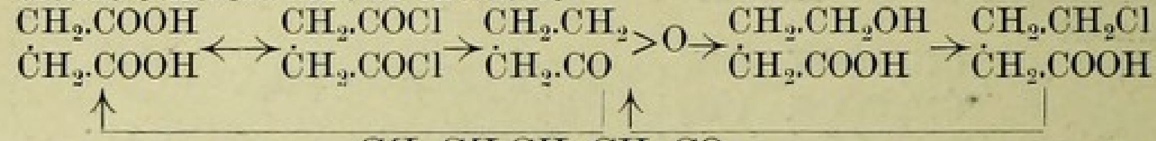
Succinimide, $\begin{array}{l}CH_2.CO\\ \dot{C}H_2.CO\end{array}\!\!>NH$ (Fehling, 1844), a crystalline substance melting at 126°, is a weak acid, and forms salts, such as potassium succinimide, $C_2H_4{:}(CO)_2{:}NK$, in which the imido-hydrogen, rendered mobile by the carbonyl groups, is replaced by the metal.

Similarly, when succinic acid is distilled, either alone, or with a little phosphorus pentachloride, it loses water, and not carbon dioxide, like malonic acid. The succinic anhydride, $\begin{array}{l}CH_2.CO\\ \dot{C}H_2.CO\end{array}\!\!>O$, thus formed, is a crystalline substance, whose vapour is very suffocating.

The succinyl chloride, $COCl.CH_2.CH_2.COCl$, formed by the action of phosphorus pentachloride on ethyl succinate is a liquid which resembles oxalyl chloride, and is hydrolysed by water in the normal manner to succinic and hydrochloric acids. On reduction, however, it is converted, not into succinic dialdehyde, as might be expected, but into an isomeric derivative of butyric acid.



γ-Butyrolactone, $\underbrace{\overset{\gamma}{C}H_2.\overset{\beta}{C}H_2.\overset{a}{C}H_2.CO}_{O}$ (Saytzeff, 1873), is a liquid boiling at 206°, which is formed both by reducing an ethereal solution of succinyl chloride with sodium amalgam and glacial acetic acid, and by distilling γ-chloro-butyric acid. It is reconverted into succinic acid by oxidation with chromic acid, but when warmed with caustic baryta solution, is hydrolysed to the barium salt of γ-hydroxy-butyric acid. It is thus an internal ethereal salt of the latter—



$$\begin{matrix} CH_2.COOH \\ \dot{C}H_2.COOH \end{matrix} \longleftrightarrow \begin{matrix} CH_2.COCl \\ \dot{C}H_2.COCl \end{matrix} \rightarrow \begin{matrix} CH_2.CH_2 \\ \dot{C}H_2.CO \end{matrix}\!\!>\!O \rightarrow \begin{matrix} CH_2.CH_2OH \\ \dot{C}H_2.COOH \end{matrix} \rightarrow \begin{matrix} CH_2.CH_2Cl \\ \dot{C}H_2.COOH \end{matrix}$$

γ-Valerolactone, $\underbrace{CH_3.CH.CH_2.CH_2.CO}_{O}$, the next homologue of butyrolactone, is formed by reducing levulinic or aceto-propionic acid, an easily crystallisable liquid obtained by distilling levulose (p. 174) and other carbohydrates with hydrochloric acid. It is only hydroxyl groups in the γ- and more remote positions, which interact in this manner to form lactones, α- and β-hydroxy-acids scarcely ever forming such compounds. Hydracrylic acid, for example, is converted into the unsaturated compound acrylic acid, and although glycollic and lactic acids form internal ethereal salts, two molecules enter into the action.

The Succinic Series of Acids.—Succinic acid is derived from normal butane and ethylene, and there is an isomeric acid similarly related to isobutane and ethylidene. This acid is formed from both α-chloropropionic acid and ethylidene chloride by the cyanide synthesis, and from malonic acid by the malonic synthesis—

$$\left.\begin{array}{ll} CH_3.CHCl.COONa \rightarrow CH_3.CH(CN).COONa & \rightarrow \\ CH_3.CHCl_2 \rightarrow CH_3.CH(CN)_2 & \rightarrow \\ CHNa(COOEt)_2 \rightarrow CHMe(COOEt)_2 & \rightarrow \end{array}\right\} CH_3.CH(COOH)_2$$

Isosuccinic or ethylidene-succinic acid, $CH_3.CH(COOH)_2$ (Wichelhaus, 1867), is a crystalline substance, melting at 130°. As a malonic acid, it is resolved by heat, not into water and an anhydride, but into carbon dioxide and the corresponding monacid, propionic acid. It is a general rule, that when the carboxyl groups of dicarboxylic acids are attached to adjacent carbon atoms, the acids are resolved into anhydrides by heat, but that when the groups are attached to the same carbon atom, monocarboxylic acids and carbon dioxide are formed. Succinic acid is the type of the first class of compounds, and malonic of the second—

$$CH_3.CH(COOH)_2 = CH_3.CH_2.COOH + CO_2.$$

The isomerism of the higher members of the succinic series is naturally very complex. In the first place, in addition to the alkyl derivatives of malonic acid, which have already been considered, there are similar derivatives of succinic acid.

Pyrotartaric acid $COOH.CHMe.CH_2.COOH$, for example, is a crystalline substance, which is formed, together with pyroracemic acid, by distilling tartaric acid, and can also be made from propylene bromide by the cyanide synthesis.

But in addition to these, there are a number of acids in which the carboxyl groups are attached to non-adjacent carbon atoms.

The most prominent of these is adipic acid, a crystalline substance which is formed by the oxidation of the higher fats and fatty acids with nitric acid, and is closely related to the sugars.

Adipic or hexanedioic acid, $COOH.CH_2.CH_2.CH_2.CH_2.COOH$ (Laurent, 1839), is a crystalline substance, melting at 149°. It can be synthesised by heating β-iodopropionic acid with reduced silver in the same way as butane from ethyl iodide and sodium—

$$COOH.CH_2.CH_2I + Ag_2 + CH_2I.CH_2.COOH = COOH.[CH_2]_4.COOH + 2AgI,$$

and its ethyl salt is formed when ethyl potassium succinate is electrolysed (Brown and Walker, 1892)—

$$\begin{array}{l} COOEt.CH_2.CH_2.COOK \\ COOEt.CH_2.CH_2.COOK \end{array} = \begin{array}{l} COOEt.CH_2.\dot{C}H_2 \\ COOEt.CH_2.\dot{C}H_2 \end{array} + 2CO_2 + K_2(2KOH + H_2).$$

The principal members of the oxalic-succinic series are tabulated below—

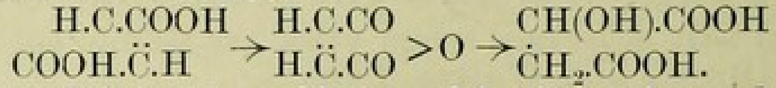
Oxalic acid	$\begin{array}{l} COOH \\ \dot{C}OOH \end{array}$
Malonic acid	$CH_2 < \begin{array}{l} COOH \\ COOH \end{array}$
Succinic acid	$\begin{array}{l} CH_2.COOH \\ \dot{C}H_2.COOH \end{array}$
Glutaric acid	$CH_2 < \begin{array}{l} CH_2.COOH \\ CH_2.COOH \end{array}$
Adipic acid	$\begin{array}{l} CH_2.CH_2.COOH \\ \dot{C}H_2.CH_2.COOH \end{array}$
Pimelic acid	$CH_2 < \begin{array}{l} CH_2.CH_2.COOH \\ CH_2.CH_2.COOH \end{array}$

The Unsaturated Dibasic Acids: Maleïc and Fumaric Acids.—Corresponding with the succinic series of acids, there are a number of dibasic acids similarly related to the higher olefines and acetylenes. The chief of the olefine acids are maleïc and fumaric acids.

When malic or hydroxy-succinic acid (p. 163) is distilled, it loses water, in the same way as hydracrylic acid; but instead of a single unsaturated acid being formed, two isomeric compounds are produced. Maleïc acid and its anhydride pass over, whilst fumaric acid remains behind. By heating the malic acid cautiously at 130–140°, the fumaric acid is formed alone.

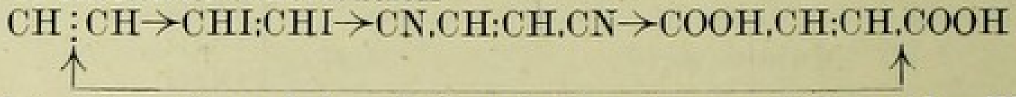
Maleïc or cis-butenedioic acid, $\begin{array}{l} H.C.COOH \\ H.\ddot{C}.COOH \end{array}$ (Lassaigne, 1819), is a crystalline substance of disagreeable acid taste, and is very soluble, even in cold water. It melts at 130°, and boils at 160°, at the same time partially decomposing into water and its anhydride. Maleïc anhydride, $\begin{array}{l} H.C.CO \\ H.\ddot{C}.CO \end{array} > O$, is a crystalline substance, melting at 60°.

Fumaric or trans-butenedioic acid, $\begin{array}{r} H.C.COOH \\ COOH.\ddot{C}.H \end{array}$ (Lassaigne, 1819), is also a crystalline substance, but of agreeable acid taste, and is practically insoluble in cold water. It occurs also in the common fumitory (*fumaria*). Fumaric acid melts only with difficulty, but sublimes to some extent at about 200°, and at the same time is partially converted into maleïc anhydride and water. This decomposition becomes quantitative when the acid is heated with phosphorus pentoxide. Conversely, when maleïc acid is heated at 130°, it is gradually converted into fumaric acid. Both acids are reconverted into malic acid when heated with water at 200°—



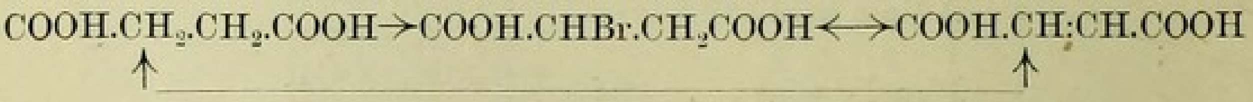
$$\begin{array}{l}H.C.COOH\\ COOH.\ddot{C}.H\end{array} \rightarrow \begin{array}{l}H.C.CO\\ H.\ddot{C}.CO\end{array}\!>\!O \rightarrow \begin{array}{l}CH(OH).COOH\\ \dot{C}H_2.COOH.\end{array}$$

Maleïc and fumaric acids are dibasic acids, and both yield acetylene when the aqueous solutions of their alkali salts are electrolysed. Fumaric acid can also be made from acetylene iodide, CHI:CHI (from acetylene and iodine) by the cyanide synthesis. They are both, therefore, ethylene-dicarboxylic acids, and of identical constitution—



$$CH\vdots CH \rightarrow CHI{:}CHI \rightarrow CN.CH{:}CH.CN \rightarrow COOH.CH{:}CH.COOH$$

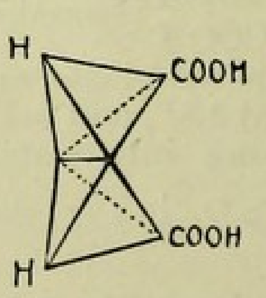
This is confirmed by their relation to succinic acid. They are reduced to this acid by sodium amalgam or hydriodic acid, and fumaric acid is formed by heating monobromo-succinic acid with alcoholic potash—

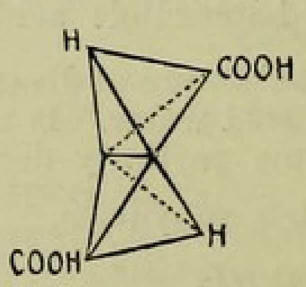


$$COOH.CH_2.CH_2.COOH \rightarrow COOH.CHBr.CH_2COOH \longleftrightarrow COOH.CH{:}CH.COOH$$

Further, both acids, as ethylene derivatives, combine with hydrogen bromide, forming bromosuccinic acid, and with bromine, forming dibromo-succinic acid, COOH.CHBr.CHBr.COOH.

This undoubted structural identity of maleïc and fumaric acids (Wislicenus, 1887) necessitates a further development of the conception of stereo-isomerism. If carbon atoms be represented as regular tetrahedra, the nucleal tetrahedra in ethylene derivatives must be linked edge to edge, and formulæ thus become possible for compounds of the maleïc and fumaric type, which are structurally identical but stereometrically different. The pairs of groups which are on the same side of the tetrahedra in the one formula are on opposite sides in the other (Van't Hoff)—





In the case of these dicarboxylic acids, that in which the two carboxyl groups are nearest, termed the plane-symmetrical or *cis* modification, will obviously form an anhydride the more readily, and is therefore maleïc acid, whilst the axial-symmetrical or *trans* modification is fumaric acid. Maleïc acid is thus cisbutene diacid, and fumaric acid transbutene diacid.

As in the case of the optically active compounds, it is convenient to use the plane projections of the formulæ—

$$\begin{array}{ll} H.C.COOH & H.C.COOH \\ H.\ddot{C}.COOH & COOH.\ddot{C}.H \end{array}$$

The two crotonic acids are represented by similar formulæ, and many such pairs of stereoisomerides are known—

$$\begin{array}{ll} CH_3.C.H & CH_3.C.H \\ COOH.\ddot{C}.H & H.\ddot{C}.COOH \end{array}$$

The Unsaturated Dibasic Acids: Acetylene-dicarboxylic Acid.—The acetylene derivative corresponding with maleïc and fumaric acids is formed by boiling dibromo-succinic acid with alcoholic potash, in the same way as acetylene itself from ethylene dibromide—

$$COOH.CHBr.CHBrCOOH = COOH.C\vdots C.COOH + 2HBr.$$

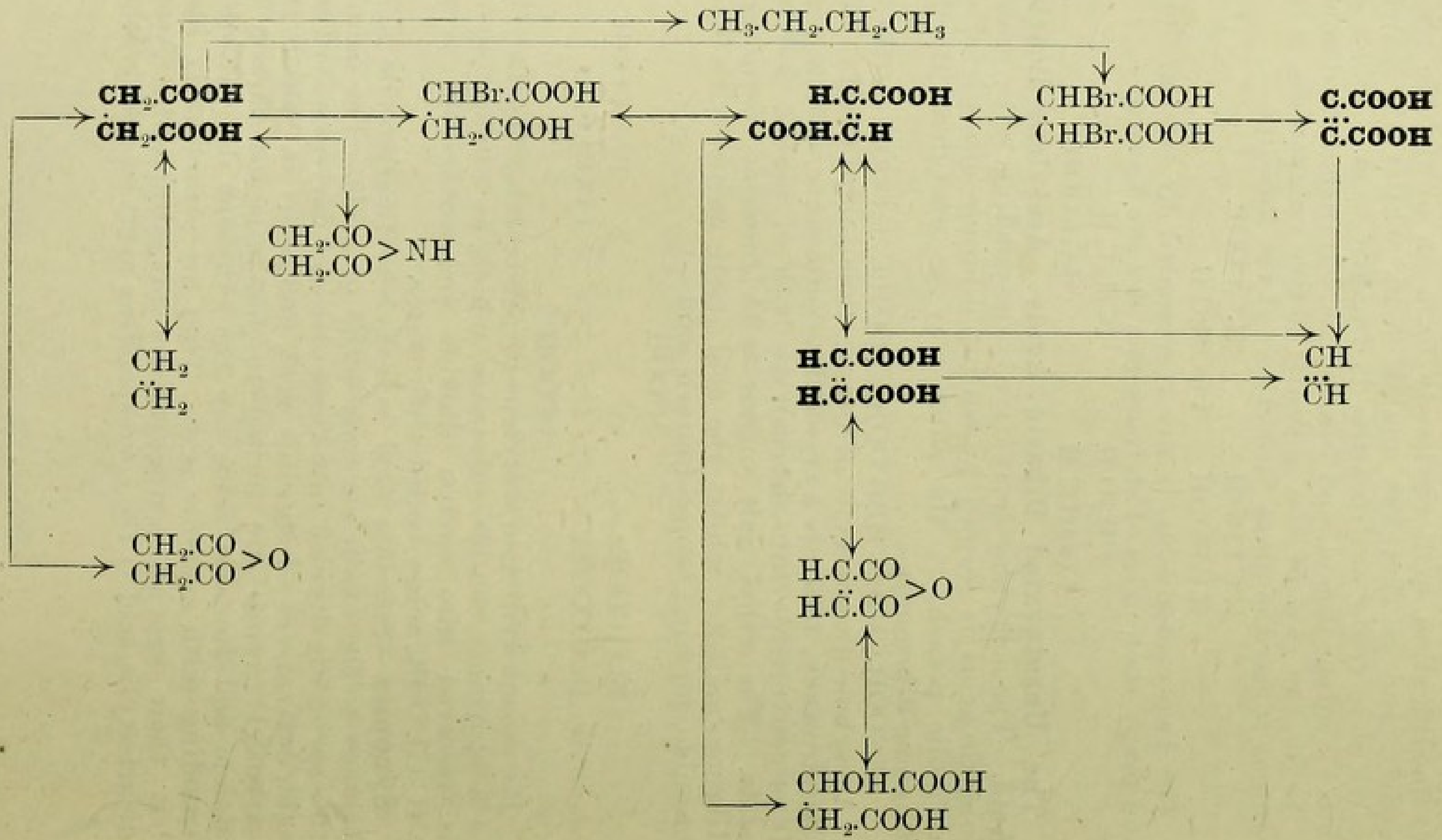
Acetylene-dicarboxylic or butine-dioic acid, $COOH.C\vdots C.COOH$ (Bandrowsky, 1887), is a crystalline substance, melting at 179°. It is convertible into derivatives both of maleïc and fumaric acids. The ethyl salt unites with bromine, forming ethyl dibromo-maleate, whilst the acid itself unites with hydrogen bromide, forming bromo-fumaric acid—


$$\begin{array}{ccccc} & & COOH & & \\ Br.C.COOEt & & \dot{C} & & Br.C.COOH \\ Br.\ddot{C}.COOEt & \leftarrow & \vdots & \rightarrow & COOH.\ddot{C}.H \\ & & C & & \\ & & \dot{C}OOH & & \end{array}$$

Potassium hydrogen acetylene-dicarboxylate, $COOH.C\vdots C.COOK$ is a sparingly soluble substance, which, as already mentioned, is resolved into carbon dioxide and potassium propiolate, $CH\vdots C.COOK$, when boiled with water.

Synopsis.—Succinic acid is ethylene-dicarboxylic acid, and belongs to the oxalic-succinic series of acids. The members of this series are divided into three classes—derivatives of malonic acid, derivatives of succinic acid, and acids in which the two carboxyl groups are united to non-adjacent carbon atoms. Maleïc and fumaric acids are the ethylene derivatives corresponding with succinic acid. They are structurally identical, but their spacial configurations are different. Acetylene-dicarboxylic acid is the corresponding acetylene derivative.

THE FOUR-CARBON DIACIDS.



CHAPTER XXVII

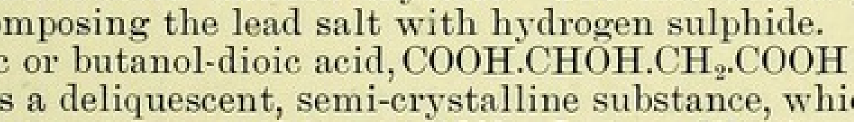
THE VEGETABLE ACIDS

The Malic Acids.—The sourness of unripe fruit is almost always due to tartaric, citric, or malic acids, which together with oxalic acid and a few others, may be termed the vegetable acids. Malic and tartaric acids are hydroxy-derivatives of succinic acid. Sour apples contain a considerable quantity of malic acid, but the substance is most economically obtained from rhubarb, or unripe mountain ash berries.

The juice expressed from the stalks or berries is concentrated, and the acid neutralised with boiling milk of lime. The normal calcium malate thus precipitated is dissolved in hot dilute nitric acid, and recrystallised as the acid salt, which forms much better defined crystals. The free acid is prepared by decomposing the lead salt with hydrogen sulphide.

Malic or butanol-dioic acid, $COOH.CHOH.CH_2.COOH$ (Scheele, 1785), is a deliquescent, semi-crystalline substance, which forms soft, warty masses, melting at 100°. It is a dibasic acid, as it forms two classes of salts, such as the calcium salts mentioned above. The lead salt, precipitated by lead acetate from a neutral solution of a malate, is characteristic, as it is insoluble in ammonia, and melts to a sticky paste when boiled with water.

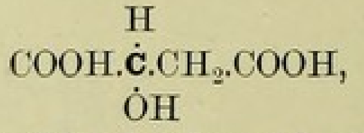
Malic acid is an alcohol, for, by the action of acetyl chloride, ethyl malate is converted into ethylic acetyl-malate, $COOEt.CH(OAc).CH_2.COOEt$, a liquid boiling at 258°. Its constitution as hydroxy-succinic acid is fully proved by analysis and synthesis. It is reduced to succinic acid when heated with hydriodic acid, and its inactive modification (see below) is formed when monobromo-succinic acid is heated with silver oxide and water. The latter is made by heating succinic acid in a sealed tube with bromine and water—



$$\begin{array}{l}CH_2.COOH\\ CH_2.COOH\end{array} \longrightarrow \begin{array}{l}CHBr.COOH\\ CH_2.COOH\end{array} \longrightarrow \begin{array}{l}CHOH.COOH\\ CH_2.COOH\end{array}$$

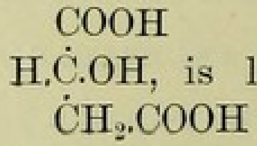
Like oxalic acid, malic acid forms two amides, namely, malamide, $C_2H_3(OH)(CONH_2)_2$, and malamic acid, $CONH_2.C_2H_3(OH).COOH$. They are both crystalline substances.

The malic acid molecule contains an asymmetrical carbon atom—

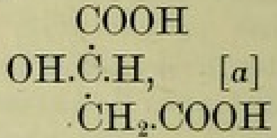


$$COOH.\overset{H}{\underset{\dot{O}H}{\mathbf{C}}}.CH_2.COOH,$$

and the acid, therefore, like lactic acid, assumes three stereoisomeric forms, in two of which it is optically active; and similarly with the exception of differences in the solubilities of their salts, the three acids are chemically identical.



Natural malic acid, $\begin{array}{l} COOH \\ H.\dot{C}.OH, \\ \dot{C}H_2.COOH \end{array}$ is lævogyrate, $[\alpha]_D = -3{\cdot}3°$.

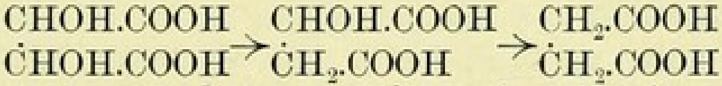


The complementary dextromalic acid, $\begin{array}{l} COOH \\ OH.\dot{C}.H, \\ \dot{C}H_2.COOH \end{array}$ $[\alpha] = +3{\cdot}3°$, is formed by the partial reduction of tartaric acid, and by the action of nitrous acid on aspartic acid (p. 224). The inactive

acid, $\begin{array}{l} CHOH.COOH \\ \dot{C}H_2.COOH \end{array}$, formed by mixing the solutions of equal weights of the active acids, is formed, not only synthetically, but also by the partial reduction of racemic acid, and as already stated, from fumaric and maleïc acids. Like inactive lactic acid, it can be resolved into its components by fractional crystallisation of its cinchonine salt.

Tartaric Acid.—Ordinary tartaric acid is a dihydroxy-derivative of succinic acid. Its chief source is argol, or potassium hydrogen tartrate, which is a constituent of grape juice, and separates as a crystalline "crust" in the preparation of wine, as it is insoluble in alcohol. The brownish argol is decolourised by digesting its hot solution with animal charcoal, and recrystallised from hot water. The colourless product, termed cream of tartar, is boiled with water and chalk, and is thus converted, half into the insoluble calcium tartrate, and half into the soluble potassium tartrate. The filtered solution of the latter is mixed with calcium chloride solution, and the second moiety of the acid thus precipitated, and finally the washed calcium tartrate is decomposed with the calculated amount of dilute sulphuric acid, and the clear solution of tartaric acid recrystallised until pure.

Tartaric or butane-diol-dioic acid, COOH.CHOH.CHOH.COOH (Scheele, 1769), crystallises in large colourless prisms, of pure and agreeable acid taste. It melts at 170°, but at a slightly higher temperature, chars, giving off fumes resembling those of burnt sugar. Tartaric acid is a dibasic acid, for it forms a diethyl salt, ethyl tartrate, $Et_2C_4H_4O_6$, the molecular weight of which follows from its vapour density. The molecule contains two alkylic hydroxyl groups, for the ethyl salt is converted by acetyl chloride into a crystalline ethyl diacetyltartrate, COOEt.CH(OAc).CH(OAc).COOEt, melting at 67°. Finally, that the acid is dihydroxy-succinic acid is proved by its successive reduction to malic and succinic acids, when heated with hydriodic acid, and by various syntheses (see Racemic Acid)—



$$\begin{array}{l}\text{CHOH.COOH}\\ \dot{\text{C}}\text{HOH.COOH}\end{array} \rightarrow \begin{array}{l}\text{CHOH.COOH}\\ \dot{\text{C}}\text{H}_2\text{.COOH}\end{array} \rightarrow \begin{array}{l}\text{CH}_2\text{.COOH}\\ \dot{\text{C}}\text{H}_2\text{.COOH}\end{array}$$

The tartrates are substances of great antiquity. Cream of tartar was known to the ancient Greeks, and tartar emetic, $K(SbO)C_4H_4O_6$, a basic, but soluble antimony salt, made by boiling cream of tartar with antimonious oxide and water, was used in the middle ages. Sodium potassium tartrate or Rochelle salt, $KNaC_4H_4O_6 + 4H_2O$ (Seignette, 1672), is a well-defined crystalline substance, formed by dissolving cream of tartar in sodium carbonate solution.

Tartaric acid is best isolated and identified by means of the calcium salt, which, as stated above, is thrown down when calcium chloride is well stirred with a neutral solution of a tartrate. It is soluble in acetic acid, and in caustic soda, and is thus easily distinguished from calcium oxalate. It is reprecipitated on warming the alkaline solution.

The tartrates are further distinguished by two other properties. They are readily oxidisable, and thus reduce silver in the same manner as formic acid; and like other poly-hydroxy-compounds, they prevent the precipitation of copper and iron by alkalies. When a neutral solution of a tartrate is warmed with ammoniacal silver nitrate, a silver mirror is deposited on the sides of the vessel, the acid being oxidised to carbonic and oxalic acids, and on adding caustic soda to a solution of copper sulphate containing Rochelle salt, a deep blue alkaline solution is obtained (Fehling, 1849). This is very valuable in the detection and estimation of substances, such as the sugars, which reduce copper only in alkaline solution.

When a strong solution of Rochelle salt is mixed with a little ferrous salt, and exposed in an open dish to direct sunlight, it is rapidly oxidised to dihydroxy-maleic acid, $\begin{array}{l}\text{OH.C.COOH}\\ \text{OH.}\ddot{\text{C}}\text{.COOH}\end{array}$, a yellow substance, which is coloured violet by caustic alkalies. This is resolved into glycollic aldehyde and carbon dioxide when heated with water—

$$\text{COOH.C(OH):C(OH).COOH} \rightarrow [\text{CH(OH):CH(OH)} \rightarrow]\text{CH}_2\text{OH.CHO}.$$

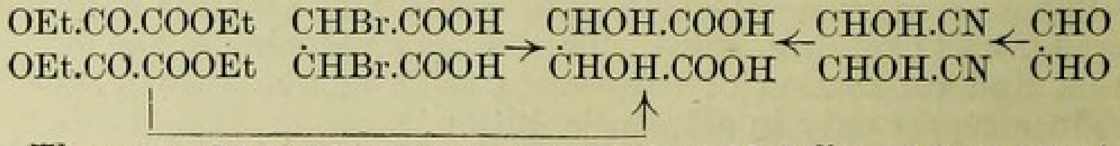
Racemic and Meso-Tartaric Acids.—Ordinary tartaric acid is optically active and dextrogyrate $[\alpha]_D = +14°$, its formula containing asymmetric carbon. But as there are two asymmetric carbon atoms, there are four stereo-isomeric acids, namely, dextro- and lævo-tartaric, and racemic and meso-tartaric acids, the last two being optically inactive.

Racemic acid, the inactive acid corresponding with inactive malic and lactic acids, is formed when tartaric acid is heated, and was first obtained from tartaric mother liquor. The liquor is boiled with chalk, and the insoluble racemic acid liberated from its calcium salt with dilute sulphuric acid. The racemic acid crystals are readily picked out from the accompanying crystals of tartaric acid, as they are efflorescent. The best way of making the acid is to heat tartaric acid with a little water in a sealed tube at 175°, for a day or two. The product is simply recrystallised to separate the small quantity of the more soluble meso-tartaric acid which is formed at the same time.

Racemic acid, $\begin{array}{l}\mathrm{CHOH.COOH} \\ \dot{\mathrm{C}}\mathrm{HOH.COOH}\end{array}$ (Kestner, 1822), crystallises with water, which it slowly loses, even at the ordinary temperature. The anhydrous acid melts at 206°.

Racemic and tartaric acid were the first isomeric compounds recognised (Berzelius, 1829). The metallic racemates differ from the tartrates much in the same way as the inactive from the active lactates. Calcium racemate, for example, is insoluble in acetic acid. The chemical relations of the acid, however, are practically identical with those of tartaric acid, and its constitution is therefore the same.

Racemic acid and the second inactive acid, mesotartaric acid, are the products obtained in all syntheses of the tartaric acids. Thus calcium racemate is formed when calcium dibromosuccinate is boiled with lime water (Kekulé and Perkin, 1861). Ethyl racemate is obtained when ethyl oxalate is reduced with sodium amalgam (Debus, 1872), and racemic and mesotartaric acids themselves can be made from glyoxal by the cyanhydrin synthesis—



$$\begin{array}{lclclcl}\mathrm{OEt.CO.COOEt} & & \mathrm{CHBr.COOH} & & \mathrm{CHOH.COOH} & & \mathrm{CHOH.CN} & & \mathrm{CHO} \\ \mathrm{OEt.CO.COOEt} & & \dot{\mathrm{C}}\mathrm{HBr.COOH} & \rightarrow & \dot{\mathrm{C}}\mathrm{HOH.COOH} & \leftarrow & \mathrm{CHOH.CN} & \leftarrow & \dot{\mathrm{C}}\mathrm{HO}\end{array}$$

The second inactive or meso-tartaric acid differs from racemic acid in that it cannot be resolved into active isomerides. It is made by heating racemic acid with water, and conversely, is converted into the latter by the same process, the direction of the action depending on the temperature. The two acids are separated by fractional crystallisation.

Mesotartaric acid, $\begin{array}{c}\mathrm{COOH} \\ \mathrm{H.\dot{C}.OH} \\ \mathrm{H.C.OH} \\ \dot{\mathrm{C}}\mathrm{OOH}\end{array}$ (Pasteur, 1851), is a crystalline substance, melting at 143°, or at a lower temperature than racemic acid. As already noted, it is much more soluble in water, and the same applies to its salts, potassium hydrogen mesotartrate, for example, being freely soluble.

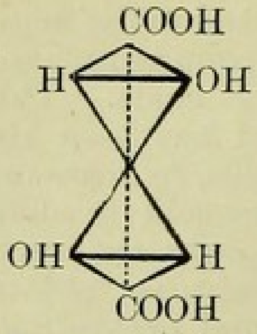
Lævo-Tartaric Acid.—Just as inactive lactic and malic acids can be resolved into the corresponding active compounds, racemic can be resolved into dextro- and lævo-tartaric acids. This separation was the first of the kind effected, and has been the model for all similar work (Pasteur, 1851). Thus, by growing mould on a solution of racemic acid, the dextro-acid is alone destroyed, and the solution eventually contains only the lævo-acid. Similarly, cinchonine racemate, like strychnine lactate, can be separated into its components by fractional crystallisation.

The most interesting method of separating the two acids is based on the asymmetry of the crystals. On evaporating a solution of sodium ammonium racemate, prepared by saturating a cooled solution of sodium racemate with ammonia gas, two kinds of crystals separate, which are recognisable as mirror images of each other, and can be picked out by hand (Pasteur). The separation is effected with less trouble by introducing a crystal of either salt into the super-saturated solution, when the crystals of that particular kind alone appear.

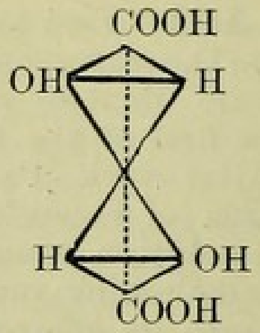
The crystals are hemihedral, that is to say, only their alternate faces are developed, and the faces which are developed in the crystals of the one kind, are those which are suppressed in the other. Moreover, the crystals of the dextro-gyrate acid are dextro-hemihedral, and those of the lævogyrate acid, lævo-hemihedral. It was this actual asymmetrical structure of the salts, which first led to the suggestion that their molecules are asymmetrical (Pasteur), and thus, eventually, to the theory of stereoisomerism.

Lævo-tartaric acid (Pasteur, 1851) resembles ordinary tartaric acid in every respect, with the exception that it is lævogyrate $[\alpha]_D = -14^\circ$, and that its crystals are the mirror images of those of the dextro-acid. By mixing its solution with that of ordinary active tartaric acid racemic acid is reproduced, and as the action is exothermic, much heat being evolved, the inactive acid is an actual compound of the active modifications.

The Isomerism of the Tartaric Acids.—The isomerism of racemic acid and its constituents is analogous to that of the lactic acids, but more complex, owing to the presence of two asymmetric carbon atoms in the molecule. In the active acids, the groups are similarly arranged around these two atoms, in the dextro-acid in one cyclic sense, and in the lævo-acid in the opposite sense, and racemic acid is represented in the same way as inactive lactic acid, by the two formulæ together, or simply by the ordinary structural formula, COOH.CHOH.CHOH.COOH. The solid formulæ are again conveniently represented by their plane projections—

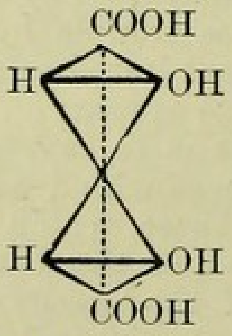


$$\text{or}\quad\begin{array}{r}\mathrm{COOH}\\ \mathrm{H.\dot{C}.OH}\\ \mathrm{OH.\dot{C}.H}\\ \mathrm{\dot{C}OOH}\end{array}$$



$$\text{or}\quad\begin{array}{r}\mathrm{COOH}\\ \mathrm{OH.\dot{C}.H}\\ \mathrm{H.\dot{C}.OH}\\ \mathrm{\dot{C}OOH}\end{array}$$

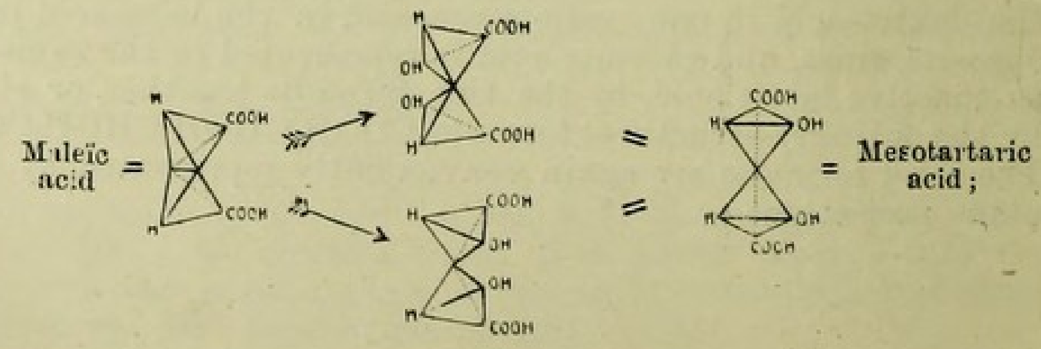
In mesotartaric acid, however, the groups must be assumed to be arranged round the two tetrahedra in cyclically opposite directions, so that the effect of the one set of groups is neutralised by that of the other. Mesotartaric acid is thus an internally compensated compound, and it is evident that a substance having a simple formula of this kind cannot be converted into isomerides without actual chemical change—

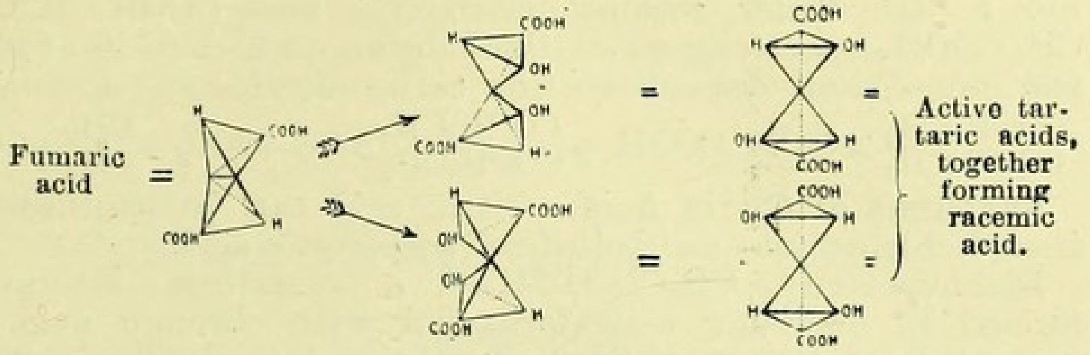


$$\text{or}\quad\begin{array}{r}\mathrm{COOH}\\ \mathrm{H.\dot{C}.OH}\\ \mathrm{H.\dot{C}.OH}\\ \mathrm{\dot{C}OOH}\end{array}$$

These configurations are confirmed by the chemical relationships of the acids. All four are reduced by hydriodic acid, first to malic acid, and ultimately to succinic acid; but whilst in every case the same succinic acid is produced, the active acids yield the active malic acids, and the inactive acids, inactive malic acid. Similarly, the acids formed by synthetic methods are invariably inactive, the chances of formation of the two active varieties being equal, as already indicated.

The formulæ, moreover, are in agreement with those of maleic and fumaric acids. These acids, as ethylene derivatives, are oxidised by dilute permanganate to the corresponding dihydroxy-compounds, as might be expected. But whilst maleic acid is converted into mesotartaric acid, fumaric acid yields only racemic acid, *i.e.* equal quantities of the two active acids (Kekulé, 1880)—





Citric Acid.—The acid of lemons and sour gooseberries is a hydroxy-polybasic acid, which bears to glycerol a relation somewhat analogous to that of malic acid to glycol, and may be conveniently considered in this place. The acid is readily obtained from lemons. The juice having been boiled, and filtered from the coagulated albumen, is neutralised with chalk and milk of lime, and again boiled, and the insoluble calcium citrate thus precipitated is decomposed with dilute sulphuric acid, as in the isolation of tartaric acid.

Citric or 3-methyl-3-pentanol-trioic acid,

$$\begin{array}{l}CH_2.COOH\\ \dot{C}(OH).COOH + H_2O\\ \dot{C}H_2.COOH\end{array}$$

(Scheele, 1784), forms large crystals, of pure and very agreeable acid taste. The hydrated acid melts at 100°, and the anhydrous acid at 153°. The acid is tribasic, as it forms three classes of salts, such as the mono-, di- and tri-potassium citrates, which are prepared in the same way as the ammonium oxalates (Liebig, 1838), and its molecular weight further follows from the vapour density of its triethyl salt. That the acid contains alkylic hydroxyl, is proved by the conversion of this salt by acetyl chloride into triethylic acetyl-citrate, $C_3H_4(OAc)(COOEt)_3$, a crystalline substance, resembling the corresponding tartrate.

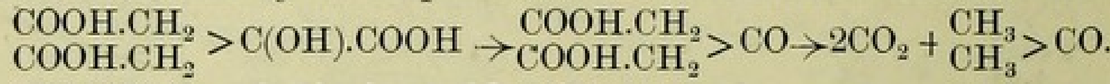
As regards nucleal constitution, citric acid is a derivative of glycerol, for it is reduced by hydriodic acid to tricarballylic acid, $C_3H_5(COOH)_3$, a crystalline substance, which can be made from tribromhydrin by the cyanide synthesis (Simpson, 1863)—

$$C_3H_5Br_3 \rightarrow C_3H_5(CN)_3 \rightarrow C_3H_5(COOH)_3.$$

Citric acid is therefore represented by one of the two constitutional formulæ—

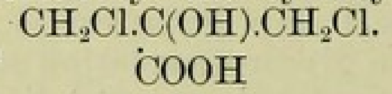
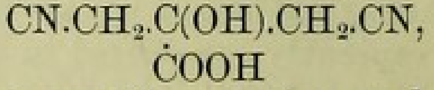
$$\begin{array}{lcl}CH_2.COOH & & CHOH.COOH\\ \dot{C}(OH).COOH & \text{or} & \dot{C}H_2.COOH\\ \dot{C}H_2.COOH & & \dot{C}H_2.COOH.\end{array}$$

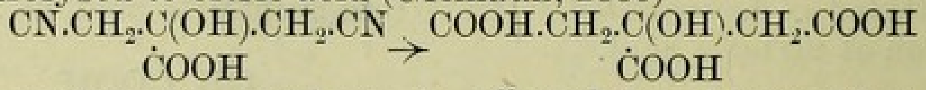
The first formula must be chosen, for the acid is readily converted into acetone by distillation with manganese dioxide and dilute sulphuric acid, carbon dioxide being evolved. Further, when it is heated with concentrated sulphuric acid on a water-bath, carbon monoxide is evolved, and on pouring the product into a little water, acetone dicarboxylic acid, $\mathrm{COOH.CH_2.CO.CH_2.COOH}$, separates, a crystalline substance which melts at 130°, and immediately decomposes into carbon dioxide and acetone—



$$\begin{matrix}\mathrm{COOH.CH_2}\\ \mathrm{COOH.CH_2}\end{matrix}>\mathrm{C(OH).COOH}\rightarrow\begin{matrix}\mathrm{COOH.CH_2}\\ \mathrm{COOH.CH_2}\end{matrix}>\mathrm{CO}\rightarrow\mathrm{2CO_2}+\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}>\mathrm{CO.}$$

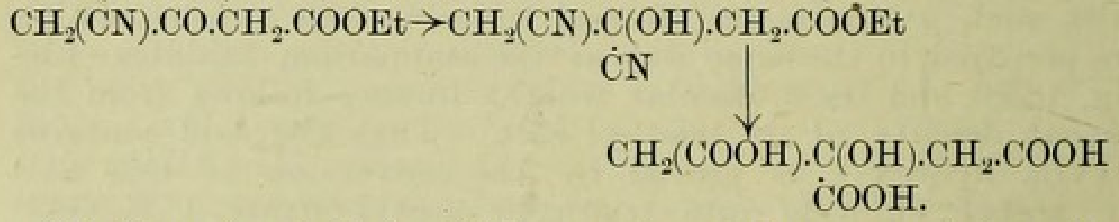
Synthesis of Citric Acid.—Citric acid can be synthesised from dichloracetone and both from acetoacetic acid.

Dichloracetone, $\mathrm{CH_2Cl.CO.CH_2Cl}$, a crystalline substance formed by oxidising α-dichlorhydrin with chromic acid, is converted by the cyanhydrin synthesis into dichloracetonic acid,  $\mathrm{CH_2Cl.}\underset{\mathrm{COOH}}{\mathrm{C}}\mathrm{(OH).CH_2Cl.}$ This substance is converted into the corresponding dicyanacetonic acid,  $\mathrm{CN.CH_2.}\underset{\mathrm{COOH}}{\mathrm{C}}\mathrm{(OH).CH_2.CN}$, by boiling with concentrated potassium cyanide solution, and on saturating the product with hydrogen chloride, the cyanide is hydrolysed to citric acid (Grimaux, 1880)—



$$\mathrm{CN.CH_2.}\underset{\mathrm{COOH}}{\mathrm{C}}\mathrm{(OH).CH_2.CN}\rightarrow\mathrm{COOH.CH_2.}\underset{\mathrm{COOH}}{\mathrm{C}}\mathrm{(OH).CH_2.COOH}$$

The acetoacetic synthesis is effected by chlorinating ethyl acetoacetate, and heating the γ-chloro-compound, $\mathrm{CH_2Cl.CO.CH_2.COOEt}$, with potassium cyanide solution. On digesting the γ-cyanoacetoacetate, $\mathrm{CH_2(CN).CO.CH_2.COOEt}$, thus formed, with hydrocyanic and hydrochloric acids, it is converted into citric acid (Haller, 1891)—



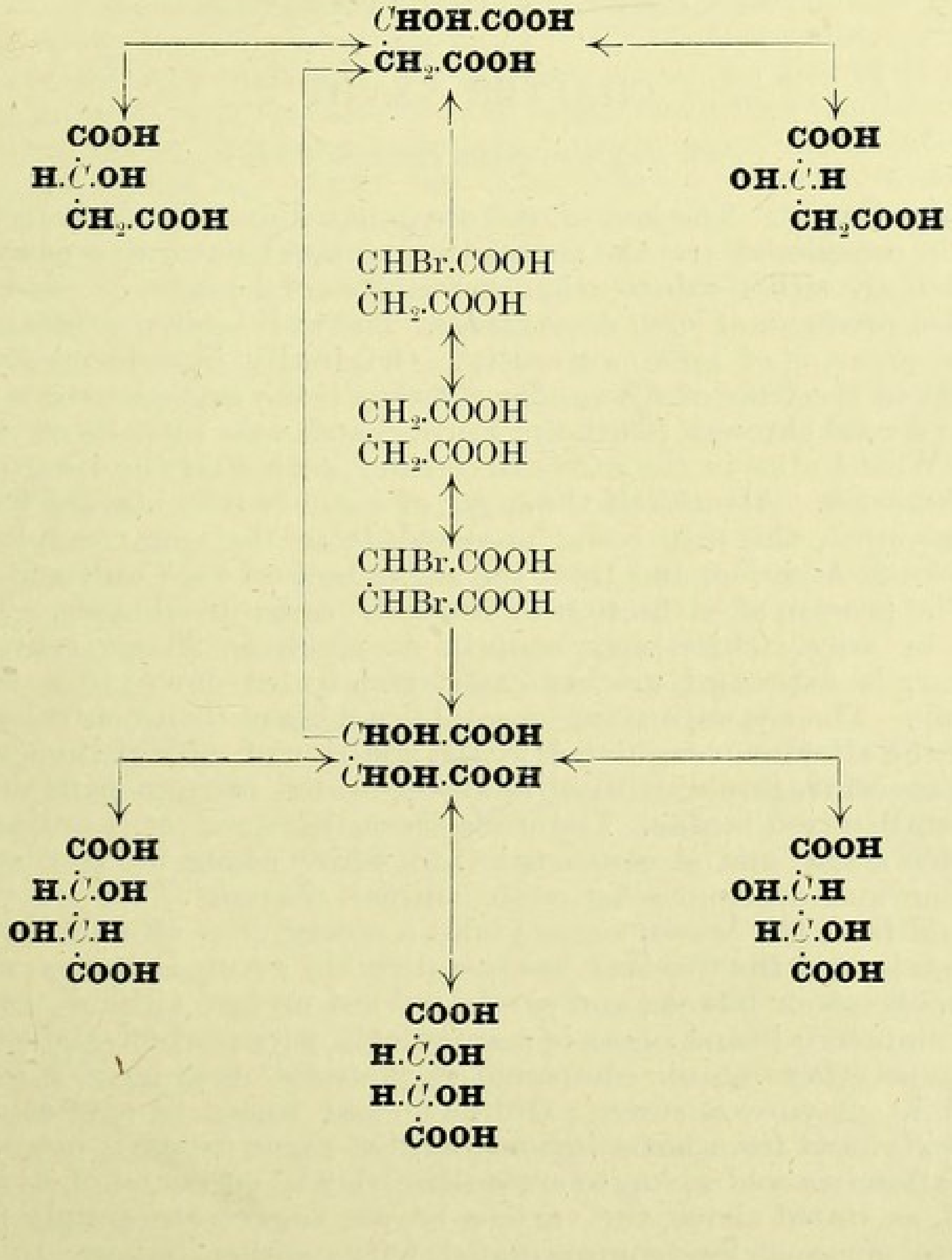
$$\mathrm{CH_2(CN).CO.CH_2.COOEt}\rightarrow\mathrm{CH_2(CN).}\underset{\mathrm{CN}}{\mathrm{C}}\mathrm{(OH).CH_2.COOEt}$$
$$\downarrow$$
$$\mathrm{CH_2(COOH).}\underset{\mathrm{COOH.}}{\mathrm{C}}\mathrm{(OH).CH_2.COOH}$$

The formula of citric acid does not contain asymmetric carbon, and the acid, therefore, unlike the other hydroxy-acids, is optically inactive, and cannot be resolved into active constituents.

As a tertiary alcohol, it is broken up by oxidising agents, acetic and oxalic acids being formed.

Synopsis.—The vegetable acids, malic and tartaric acid, are hydroxy-succinic acids. They are optically active compounds, but whilst there is only one inactive malic acid, there are two inactive tartaric acids, the second of which is accounted for by the mutually compensating action of the two asymmetric carbon atoms. Citric acid is a hydroxy-tricarboxylic derivative of glycerol.

THE FOUR-CARBON ALCOHOLIC DIACIDS.



SECTION VIII

SIX-CARBON DERIVATIVES

CHAPTER XXVIII

THE CARBOHYDRATES: SUGARS

Cane Sugar.—The last of the oxygenated paraffin derivatives to be considered are the sugars, and related natural products, which are either substitution derivatives of hexane, or condensation products of such derivatives. The well known substance, cane sugar, is of great antiquity. Originally introduced from India in the time of Alexander the Great, the sugar-cane gradually spread through Southern Europe, and was introduced into the West Indies in the fifteenth century, soon after the discovery of America. About half the sugar of commerce is obtained from this source, the rest being prepared from the sugar maple in in North America, and from the sugar beet on the Continent.

The process of extraction is much the same in all cases. The sap or juice, which may contain as much as 20 per cent. of sugar, is expressed mechanically, and boiled down to a thin syrup. The accompanying vegetable acids are then neutralised, and the albumen coagulated, by the addition of milk of lime, and the concentration continued in steam-heated vacuum pans until crystallisation begins. The crude crystalline product is ordinary brown sugar, and is converted into white sugar by recrystallising and decolourising with animal charcoal. The mother liquid from the brown sugar yields a second crop of still darker crystals, and the residual uncrystallisable syrup is partly used as molasses or treacle, and partly worked up into alcohol—rum.

Commercial cane sugar is a singularly pure product, and probably no other organic compound is prepared on so large a scale and in so pure a state. Ordinary loaf sugar is crystallised quickly, and from hot solutions, whilst sugar candy is prepared by allowing cold syrup to crystallise slowly on nuclei of string, and, as stated above, the various brown sugars are simply products more or less contaminated with mother liquor. In the laboratory, sugar is readily extracted from cane or beet by boiling with moderately strong alcohol.

Cane sugar or sucrose, $C_{12}H_{22}O_{11}$, by cryoscopic method, forms transparent, hard crystals, melting at 160° (*saccharum*, from Sanscrit = sandy). The colourless melt does not at once recrystallise on cooling, but remains for a time in a transparent, amorphous condition—barley sugar. At a somewhat higher temperature the sugar is converted into caramel, a dark brown, permanently amorphous substance, which is still soluble in water. Sugar itself is very soluble, forming the well-known sweet syrup, but it is practically insoluble in absolute alcohol. The aqueous solution is dextrogyrate, $[\alpha]_D = +66°$.

When sugar is heated to redness, it swells up and blackens, giving off the characteristic fumes of burnt sugar, and it eventually loses most of its hydrogen and oxygen as water, and is converted into charcoal. The elements are, in fact, in exactly the proportion to form water, and sugar and other similar compounds are on this account termed carbohydrates. Concentrated sulphuric acid has partly the same effect, a mixture of strong syrup and the acid blackening and swelling up enormously. Cane sugar is also distinguished from the other sugars by the action of sulphuric acid, and by the absence of action with caustic alkalies, alkaline copper tartrate, yeast, and phenylhydrazine.

When oxidised with nitric acid, sugar yields principally oxalic acid, as already noted, but tartaric and saccharic acids (p. 185) are also formed.

Glucose.—There are many sugars besides that of the cane and beet. Honey, for example, which was known long before cane sugar, slowly deposits, when kept, a sweet crystalline substance which is quite distinct from that of the sugar-cane. The same substance is obtained by concentrating the juice of ripe grapes, and can be prepared by hydrolysis of cane sugar and starch with dilute acids.

On dissolving powdered cane sugar in warm spirit acidified with hydrochloric acid, a clear syrup is obtained, which after a week or two deposits crystals of this glucose. The crystallisation can be effected in twenty-four hours if the syrup is sown with a ready-formed crystal of the product.

Similarly, on digesting starch on a water bath with very dilute sulphuric acid, it is dissolved, and after a time entirely converted into glucose. On removing the acid with powdered chalk, and concentrating the clear solution, the glucose eventually separates (Kirchhoff, 1811). As in all such cases, the crystallisation is hastened by introducing a ready-formed crystal into the syrup. If anhydrous glucose crystallised from alcoholic solution be used, and the syrup is warmed, anhydrous crystals at once separate.

Glucose is also formed in diabetes, and is excreted in relatively enormous quantities, sometimes as much as half a kilogram a day, in the urine of persons suffering from that disease.

Glucose, dextrose, or grape-sugar, $C_6H_{12}O_6$ (Glauber, 1660), is a colourless substance, which crystallises from cold solutions with 1 mol. of water of crystallisation, but from hot solutions in the anhydrous state. It melts at 146°, and like cane sugar is dextrogyrate, $[\alpha]_D = +53°$.

Glucose differs, however, in many respects from the more complex sugar. It is soluble in alcohol, and is not charred by sulphuric acid. It is coloured brown when warmed with caustic soda solution, and strongly reduces ammoniacal silver nitrate, and alkaline copper tartrate (p. 165) when warmed with these agents. In the first case metallic silver is deposited in mirror form, and in the second, the cupric salt is reduced to red cuprous oxide. The latter action is quantitative as well as qualitative, one molecule of glucose reducing five atoms of copper. The amount of glucose in a solution such as urine may thus be estimated by running the liquid into a known amount of the boiling copper solution until the colour is just discharged (Fehling, 1849). An emulsion of bismuth hydroxide in caustic soda is similarly reduced to black metallic bismuth when heated with glucose.

Glucose is further distinguished from cane sugar in that it is readily fermentable by yeast (p. 176), and that when heated on a water-bath with phenyl-hydrazine acetate it is converted into golden-yellow crystalline compound, glucosazone (p. 189). The microscopic appearance of the crystals is very characteristic, and their formation affords a conclusive proof of the presence of glucose in liquids such as urine (Fischer, 1884).

Fructose.—Besides glucose, honey and grape-juice contain an isomeric sugar, fructose or levulose, which is much more difficult to crystallise. It is also formed, in equal amount with glucose, in the hydrolysis of cane-sugar. The sugar is hydrolysed by heating on a water bath with dilute sulphuric acid, and the acid is removed with powdered chalk. Slaked lime is now slowly stirred into the ice-cold product without allowing the temperature to rise, and the resulting precipitate of the insoluble lime compound of fructose is filtered off and washed. The precipitate is suspended in water, and washed carbon dioxide passed in until the lime is converted into calcium carbonate; and on evaporating the clear solution, the fructose remains as a syrup (Dubrunfaut, 1848). After dehydrating by shaking with cold absolute alcohol it slowly crystallises, and can then be recrystallised from hot alcohol.

Fructose is also readily obtained in a pure state from inulin or dahlia starch (p. 180), in the same way as glucose from ordinary starch.

Fructose, levulose or fruit sugar, $C_6H_{12}O_6$ (Lowitz, 1802), is a colourless crystalline substance melting at 95°. Like cane sugar and glucose, it is optically active, but lævogyrate, $[\alpha]_D = -71°$. Fructose reduces metallic salts in the same way as glucose, but more slowly, and it is less easily fermentable by yeast. But it is converted by phenyl-hydrazine into the same yellow osazone.

The products of the hydrolysis of cane sugar are simply glucose and fructose. The equimolecular mixture, which is obtained in semi-crystalline form on evaporating the product after elimination of the acid, is known as invert sugar, as owing to the higher optical activity of the fructose it is lævogyrate. The cane sugar, or more correctly, its rotatory power, is said to be inverted. Invert sugar is of course not a chemical individual—

$$C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6.$$

Milk Sugar and Malt Sugar: Galactose.—The sweetness of milk is due to a sugar, milk sugar or lactose, which is isomeric with cane sugar. It is obtained by evaporating clear, fresh whey.

Lactose, $C_{12}H_{22}O_{11}$ (Bartoletti, 1619), is a somewhat gritty, microcrystalline substance, which melts when anhydrous at 205°. It is less sweet and less soluble than cane sugar, but like the latter, is dextrogyrate. It differs from cane sugar, however, in that it reduces metallic solutions even in the cold, and forms a yellow osazone. It is not fermentable by yeast, but is converted by the lactic ferment into lactic acid. Sodium lactate is formed also by fusing lactose with caustic soda.

Like cane sugar, however, lactose is hydrolysed by dilute mineral acids into two simpler sugars, one of which is glucose, and the other a third isomeride, galactose. The lactose is boiled with dilute sulphuric acid, and the acid eliminated in the manner already described, the new sugar crystallising out from the resulting syrup on adding a crystal of glucose. It is washed with cold alcohol and recrystallised from boiling alcohol.

Galactose, $C_6H_{12}O_6$ (Erdmann, 1855), is a sweet crystalline substance melting at 144°. It closely resembles glucose, and easily reduces alkaline metallic solutions. Its specific rotatory power is greater, however, and its osazone melts at a lower temperature than that of its isomeride.

The conversion of starch into glucose is preceded by the formation of a third isomeride of cane sugar, which is readily prepared by the action of malt extract. A mixture of the extract with 20 per cent. starch paste is heated at 60° for an hour, and then boiled and filtered. The solution is evaporated to a syrup, and the sugar crystallised from hot alcohol.

Maltose or starch sugar, $C_{12}H_{22}O_{11}+H_2O$ (Kirchhoff, 1811), is a crystalline substance somewhat resembling glucose. The anhydrous substance, obtained by drying the hydrated sugar at 100°, is very hygroscopic. Maltose is strongly dextrogyrate, $[\alpha]_D=+141°$, but it is less easily soluble in alcohol, and reduces alkaline metallic solutions less easily than glucose. It forms a characteristic osazone, however, and is directly fermentable by yeast. When boiled with dilute sulphuric acid, it is hydrolysed

$$O=2C_6H_{12}O_6.$$

A fourth complex sugar of the type of cane sugar and lactose is found in eucalyptus manna, and in beet molasses. Raffinose, $C_{18}H_{32}O_{16}$, is a crystalline substance, which is hydrolysed by dilute sulphuric acid to glucose, fructose and galactose.

The Glucosides.—A variety of crystalline substances occur in plants, which are hydrolysed by accompanying enzymes (p. 177) to glucose and various products, and are termed on this account the glucosides. Amygdalin, $C_{20}H_{27}NO_{11}$, for example, a soluble crystalline substance, melting at 200°, found in bitter almonds, is hydrolysed by the enzyme emulsin, or by dilute sulphuric acid, to grape sugar, benzaldehyde (p. 267) and hydrocyanic acid. It is on account of the formation of the latter that bitter almonds are poisonous. Phloridzin, $C_{21}H_{24}O_{10}$, a similar crystalline substance, is formed in the root bark of apple and other trees of the same order, and is hydrolysed by acids to glucose, phloretic acid and phloroglucinol (p. 297). It is of interest as producing artificial diabetes in animals. Potassium myronate, $C_{10}H_{18}KO_{10}NS_2$, the crystalline glucoside of black mustard seed, is hydrolysed by alkalies, or the accompanying enzyme myrosin, to glucose, allyl mustard oil (p. 211), and potassium hydrogen sulphate.

Some of the glucosides can be made synthetically. Thus helicin, $C_{13}H_{16}O_6$, a glucoside obtained by the oxidation of salicin, the natural glucoside of the willow, can be made from salicylic aldehyde (p. 303) and glucose. Analogous but simpler compounds, such as methyl-glucose, $C_6H_{11}O_5.OMe$, have been formed by saturating alcoholic solutions of glucose with hydrogen chloride.

Fermentation.—The various processes of fermentation, which are so frequently used in preparing organic substances, consist essentially in decomposing them with the aid of microscopic fungi. The alcoholic fermentation of glucose, fructose and maltose, for example, is induced by the yeast fungus, saccharomyces cerevisiæ, an oval unicellular organism about 0.01 mm in diameter, propagated by budding. The action only proceeds within certain limits of temperature, 4–34°, and most quickly within much narrower limits, 25–30°, and in solutions of appropriate concentration. It stops as soon as a certain percentage of alcohol is formed, the fungus being killed by strong alcohol, as well as by heat and acids, and the ordinary antiseptics. Certain mineral and ammonium salts must also be present to afford food for the ferment.

The greater part of the sugar (95 per cent.) is converted into alcohol and carbon dioxide, the latter gas being evolved in abundance. The decomposition is apparently simple, and is of historical interest, as the equation of weight between the sugar and the resulting products afforded the first instance of the law of conversation of mass (Lavoisier, 1790)—

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

The residue of the sugar is converted into glycerol (3 per cent.), succinic acid (0·5 per cent.), and fusel oil, the constituents of which, as already incidentally stated, are mainly isopropyl, isobutyl, isoamyl, and active amyl alcohols, together with normal propyl and butyl and higher alcohols. The formation of the fusel oil, at all events, is due to the presence of foreign organisms, as its amount diminishes as the yeast is freed from such impurities by bacteriological methods. It is probable that each organism has but one action on any particular substance.

The lactic fermentation of sugar and the destruction of tartaric acid by mould are effected by similar organisms, and the natural oxidation of alcohol to acetic acid is brought about by a fungus, mycoderma aceti, which will thrive even in a 14 per cent. solution of alcohol. Similarly urea in urine (p. 196) is hydrolysed by micrococcus ureæ, and putrefaction itself is due to the action of such ferments, the ptomaïnes being formed in this manner from albumen and proteids in general.

Very little is known of the mechanism of fermentation by micro-organisms. It cannot be a mere breaking down process, for butyric acid is formed from lactic acid, the chain of which is shorter, and the amyl alcohols in fusel oil are actually branching-chain compounds, whilst, as will be seen presently, the glucose from which they are formed is a derivative of a normal hydrocarbon. The ferments do not simply act as carriers or "catalysts," for they increase in number enormously during the process. Possibly the fermenting substance is digested by the organism, and the fermented products excreted.

Besides these actions, however, due to organised and living ferments, there are many similar decompositions, chiefly hydrolytic, which are brought about by chemical ferments or enzymes. These substances are complex compounds of albuminoid character, which usually occur in plants in proximity to the substances that it is their function to hydrolyse. Germinating seeds, for example, contain an enzyme, diastase, which is present in large quantity in malt, and can be precipitated from malt infusion by alcohol. When a little diastase is added to some warm starch emulsion, the latter clears up with great rapidity, and is hydrolysed to maltose, even when the diastase has been precipitated by alcohol and dried. The starch of food is hydrolysed in a similar manner by the ptyalin of saliva, an enzyme which resembles diastase in function.

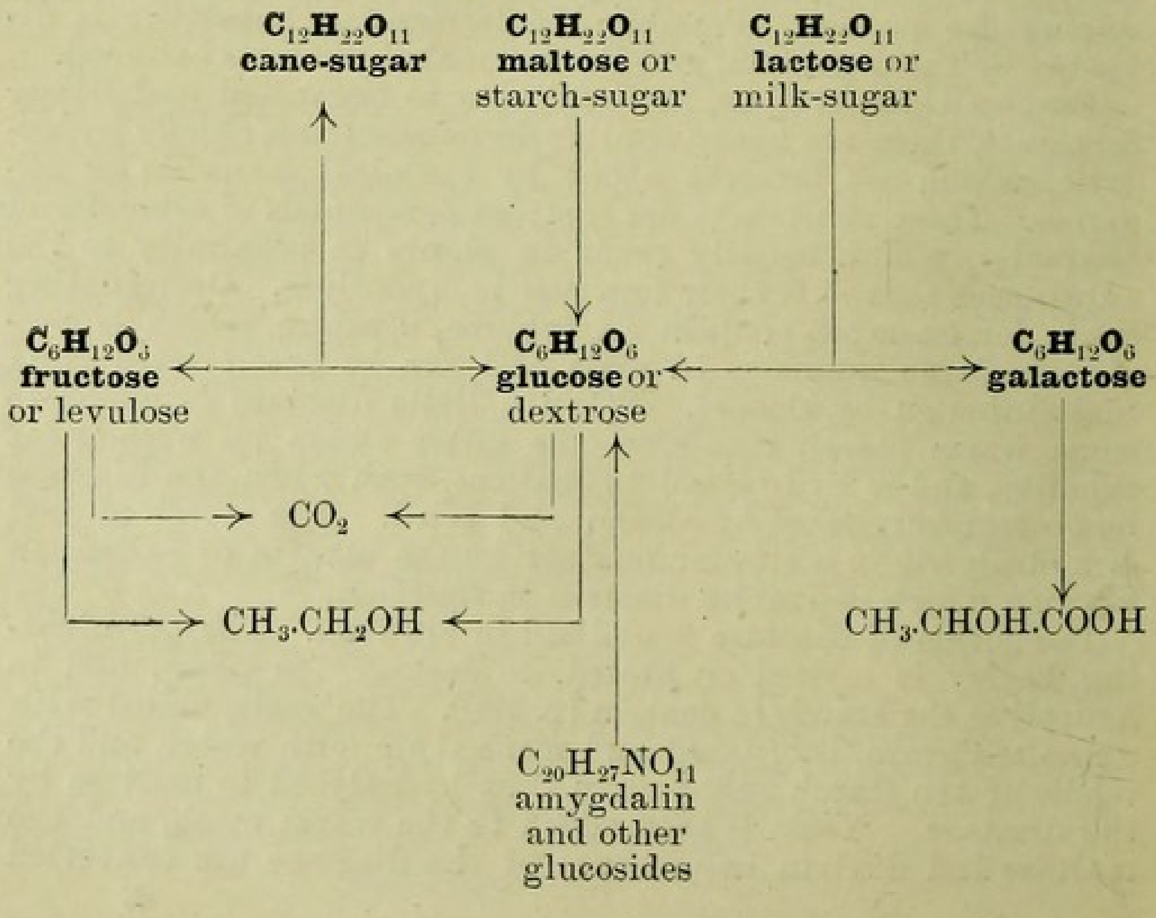
The action of diastase is utilised in brewing. The germinating barley is malted or heated, to destroy the germ, and to hydrolyse the starch to dextrin (p. 180). The malt, mixed with unmalted grain, is crushed and mashed up with water, and the whole of the starch and dextrin thus hydrolysed to maltose by the diastase. Yeast is then added to the warm mash, and the maltose and dextrin in presence of the diastase are converted into alcohol and carbon dioxide, the yeast being separated mechanically as soon as enough alcohol is formed. The product is then flavoured with hops and coloured with charred malt. Beer rarely contains more than 5 per cent. of alcohol.

In the manufacture of grain spirits, such as whisky, the product is of course distilled without the addition of hops or colouring matter. In the preparation of potato spirit much the same procedure is followed, but the hydrolysis of the starch is partially effected by steaming the potatoes under pressure at 150°, before adding the water and malt. Pure cultivated yeast is usually used in making potato spirit.

Another enzyme of practical importance is the invertase of yeast, which hydrolyses cane sugar, and thus allows of its direct fermentation by the yeast, after the lapse of sufficient time for the hydrolysis. The enzymes mentioned in connection with the glucosides are substances of similar character.

Synopsis.—The natural sugars are six-carbon or twelve-carbon saturated compounds. They are termed carbohydrates as they contain hydrogen and oxygen in the proportion to form water. The twelve-carbon sugars are hydrolysed by enzymes and dilute acids to the six-carbon sugars, and the latter are split up by living ferments in various ways. The most important decomposition of this class is that of glucose and fructose into alcohol and carbon dioxide by the yeast fungus.

THE NATURAL SUGARS.



CHAPTER XXIX

THE CARBOHYDRATES: STARCH AND CELLULOSE

The Starches.—From the ready manner in which glucose and maltose are prepared from ordinary starch, and fructose from inulin, it is obvious that the starches are very closely related to the sugars. Like the latter, in fact, they are carbohydrates.

The starches are the reserve material of plants, and are probably formed from the sugars when the amounts of the latter synthesised by the plant are in excess of immediate requirements. Bulbs and tubers contain very large quantities of starch, and this is why bulbous plants can grow and mature at a much earlier period of the year than others. Seeds, as a rule, contain only enough for the development of the seed-leaves.

Starch is usually obtained from grain or potatoes. When a stiff paste of wheaten flour, for example, is tied up in a cotton bag, and kneaded under cold water, the finely divided starch passes through the fabric, leaving the gluten and other constituents of the flour behind, and on keeping the milky liquid the starch gradually subsides, and may be dried at the ordinary temperature. It is separated on a manufacturing scale on much the same plan, the interstitial material being previously softened and disintegrated by allowing the coarsely-crushed and moistened grain to ferment.

Starch or amylum $(C_{12}H_{20}O_{10})_x$, is a white, pulverulent substance, which has been known from very early times (*αμυλον* =unground [flour]). It consists of amorphous, microscopic granules, of characteristic oval or circular shape. These granules are composed of concentric layers, showing organised structure, and vary in size from 0·002mm. in rice to as much as 0·1mm. in sago and potato starch. They are quite insoluble in cold water, but are converted by boiling water into an opalescent and sticky paste or emulsion. The starch is, in fact, resolved into two constituents, an insoluble starch cellulose, which constitutes the outer layers of the granules, and a soluble starch or granulose, which forms the nuclei (Naegeli, 1864). The granulose is precipitated on the addition of alcohol to the clear filtered solution.

The empirical formula of starch of all kinds is $C_6H_{10}O_5$, but the molecular formula must at least be double this, for the substance forms a hexacetate when heated with acetic anhydride and sodium acetate. From the manner in which it is hydrolysed (see below), it is probable that its molecular formula of granulose is $C_{120}H_{200}O_{100}$, and this is roughly confirmed by the cryoscopic method.

Soluble starch is blackened by concentrated sulphuric acid, but it does not give any other of the sugar reactions, except, of course, after hydrolysis. Most forms of starch, however, are characterised by the formation of an intensely blue additive compound with iodine, the colour of which is temporarily discharged by heating.

Other starches are known, but all have the same empirical formula. Glycogen or animal starch (Bernard, 1857) is found in the livers of animals, and is probably stored there as a reserve material for use in periods of fasting. It is converted by ferments into maltose, and by dilute acids directly into dextrose. It differs from the ordinary starches in that it coloured red by iodine. Inulin, the starch of dahlia and like tubers, is coloured yellow by iodine, and, as already stated, is quantitatively hydrolysed to fructose by dilute acids.

The Dextrins and Gums.—As already stated, the ultimate product of the hydrolysis of starch is either glucose or maltose, according as the hydrolytic agent is malt or a dilute acid. A number of intermediate compounds, the dextrins, are formed however when starch is heated at 200°, either alone or with a little dilute sulphuric acid.

The dextrins $(C_6H_{10}O_5)_x$, which are isomeric with starch, are transparent, amorphous substances, devoid of taste or odour. They are freely soluble in water, to sticky gummy solutions—British gum—and are dextrogyrate, whence the name. They are all precipitable by alcohol. Like starch, they are not fermentable by yeast except in presence of diastase, nor do they reduce alkaline copper solutions until after hydrolysis with dilute acid.

The various dextrins are distinguished by their behaviour with iodine. Amylodextrin, the first and most complex product, still forms a blue compound with iodine. The next, erythrodextrin, formed by the partial hydrolysis of the amylodextrin, gives a red colour. The succeeding compounds, the achroodextrins, give no colour at all. γ-Achroo-dextrin or maltodextrin, is the product immediately preceding maltose. The dextrins are probably formed by the gradual hydrolysis of the granulose, a molecule of maltose being detached at each stage—

$$(C_{12}H_{20}O_{10})_{10}+H_2O=(C_{12}H_{20}O_{10})_9+C_{12}H_{22}O_{11}$$
$$(C_{12}H_{20}O_{10})_9+H_2O=(C_{12}H_{20}O_{10})_8+C_{12}H_{22}O_{11}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$(C_{12}H_{20}O_{10})_2+H_2O=C_{10}H_{20}O_{10}+C_{12}H_{22}O_{11}$$
$$C_{12}H_{20}O_{10}+H_2O=C_{12}H_{22}O_{11}$$

The natural gums are probably sugar condensation products allied to the dextrins. The principal constituent of gum arabic, for example, is the calcium salt of arabic acid, $C_6H_{10}O_5$, an acid which is isomeric with starch and the dextrins, and yields galactose on hydrolysis. Other gums are hydrolysable to five-carbon sugars (p. 193). Cherry gum, for example, yields arabinose, and beech gum, xylose.

The Celluloses.—The cell walls of plants are composed of a carbohydrate termed cellulose, isomeric with starch, and closely related to the sugars. Simple cell aggregates, such as cotton and flax, consist almost entirely of this substance, whilst even in complex structures, such as wood, in which the chains of cells are cemented together by interstitial material, it forms the chief constituent.

The isolation of cellulose from cotton and the like is simple. The Swedish filter paper, for example, made from linen rags, is almost pure cellulose, and after dissolving out the small amount of iron and lime salts and silica, with hydrochloric and hydrofluoric acids, leaves practically no ash.

Wood cellulose is more difficult to isolate, the interstitial material having to be dissolved out. In the manufacture of wood pulp, the chopped wood is digested with caustic soda solution, at a high temperature and under pressure. In some processes, to avoid loss by oxidation, acid sulphites are used, such as those of lime or magnesia. By the end of the operation the wood is reduced to a soft grey pulp, which, after washing with water and bleaching with ordinary bleaching solution without addition of acid, is fairly pure cellulose.

Cellulose, $(C_{12}H_{20}O_{10})_x$, is a white substance which is insoluble in all ordinary solvents. It dissolves freely, however, in an ammoniacal solution of copper oxide (Schweizer). When simply isolated from cotton or wood it retains the tubular structure of the cell, the product from coniferous wood, for example, showing the characteristic pits; but when reprecipitated from the copper solution with dilute acids, it forms a colourless jelly, which dries to a horny amorphous mass.

When cellulose is immersed in concentrated sulphuric acid it quickly swells up and becomes transparent, and is eventually disintegrated; but if paper thus treated is quickly washed, before disintegration has commenced, it is converted into a tough substance, vegetable parchment. By diluting the sulphuric acid solution of the cellulose immediately after disintegration, a gelatinous isomeric substance is obtained which forms a blue iodide, and is hence termed amyloid. By longer digestion with the acid, however, the cellulose is converted into sulphuric acid derivatives, and these are hydrolysed to glucose on boiling with water. Cellulose is thus a derivative of glucose, and it is therefore possible to make alcohol from wood and from rags (Braconnot, 1811).

It will be seen later that the carbohydrates are complex alcoholic substances, and form salts with acids in much the same way as glycerol. The cellulose nitrates, formed by digesting cellulose with a mixture of nitric and sulphuric acids, in the same way as glycerol nitrate, are of great practical importance.

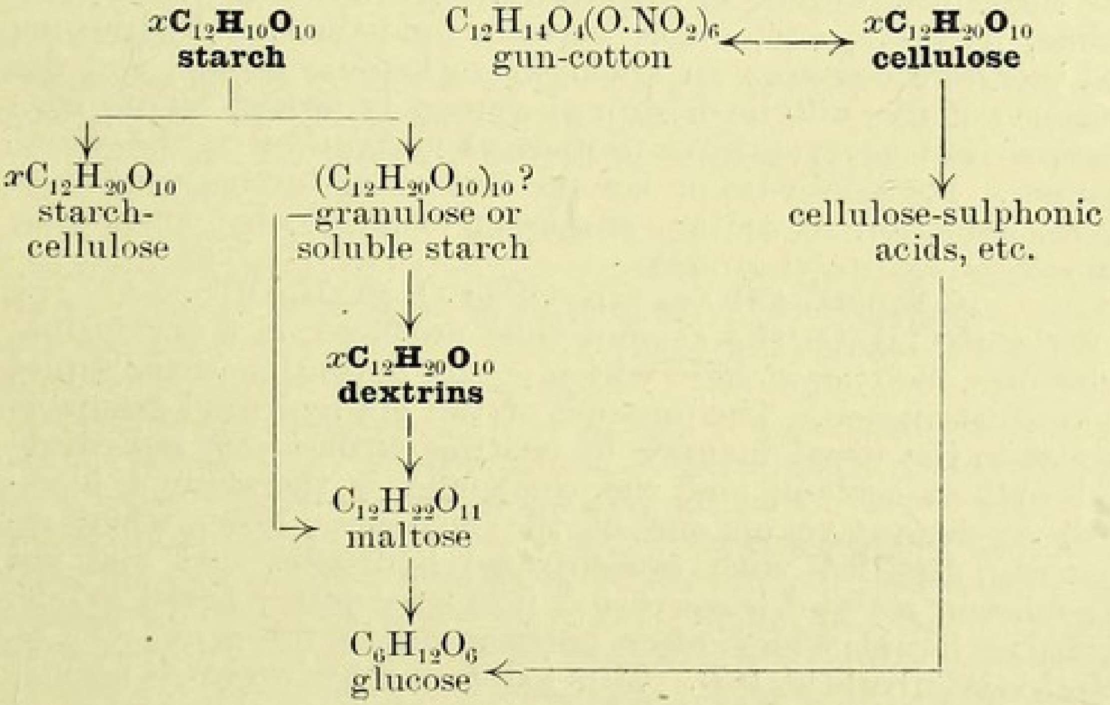
Cellulose hexanitrate or gun-cotton, $C_{12}H_{14}O_4(O.NO_2)_6$ (Schönbein, 1846), is made by immersing dry çotton wool, previously washed with potassium carbonate solution and water, in a mixture of nitric acid with three times its volume of concentrated sulphuric acid for a few minutes. The product, which retains the form and appearance of the cotton, is thoroughly washed with water—on the large scale, in a pulp-washing engine—and dried in air.

Gun-cotton burns quickly but quietly in the open-air, but when detonated in a confined space explodes with great violence. It partially dissolves in nitro-glycerine to a gelatinous mass, which, when mixed with castor-oil as a moderant, or with vaseline as a lubricant, forms a valuable "high" explosive—maximite, cordite. It is used instead of gunpowder in quick-firing guns, as it is smokeless.

Cellulose hexanitrate is insoluble in alcohol-ether, but by digesting the cellulose for many hours with a large excess of the mixed acids, a soluble pentanitrate is formed. The solution of this, which is termed collodion, is used in photography and surgery, as it leaves a thin waterproof film of the nitrate on any surface to which it is applied. A mixture of camphor and collodion-cotton is the "celluloid," of which imitations of starched linen, ivory, and tortoiseshell are made. It burns with almost explosive violence when ignited.

Synopsis.—The starches and celluloses are insoluble or partially soluble carbohydrates, which are ultimately converted into glucose by hydrolytic agents. The gums are probably intermediate products. The nitrates of cellulose are used as explosives, and in photography.

STARCH AND CELLULOSE.



CHAPTER XXX

THE CONSTITUTION OF THE SUGARS

Reduction of Glucose to Sorbitol and Hexane.—In its power of reducing metals, glucose resembles the aldehydes and hydroxy-acids, but although it forms compounds with metallic oxides, such as calcium oxide glucose, $C_6H_{12}O_6,CaO$, it is not an acid, for these compounds are additive. It forms a crystalline oxime, however, and, under certain conditions, a hydrazone, and therefore contains an aldehydic or ketonic group; and the presence of five alkylic hydroxyl groups is proved by its conversion into a crystalline pentacetyl derivative in the usual manner. Its aldehydic or ketonic nature is further confirmed by its reduction by sodium amalgam to an alcohol containing six alkylic hydroxyl groups—

$$C_5H_6(OH)_5.CHO[\text{or } C_5H_7(OH)_5{:}CO] \rightarrow C_6H_8(OH)_6.$$

Sorbitol, $C_6H_{14}O_6$, the alcohol thus produced, is a crystalline substance, melting at 108°, which occurs naturally in the sap of the mountain ash. The presence of the six hydroxyl groups is proved in the usual manner by heating with acetic anhydride and sodium acetate, and the compound is therefore a hexahydroxy-derivative of one of the hexanes. Now, when repeatedly distilled with concentrated hydriodic acid and red phosphorus, sorbitol is converted into a secondary hexyl iodide, $C_6H_{13}I$, a liquid which, after purification in the same way as ethyl iodide, boils at 167°. This iodide is a derivative of normal hexane, $CH_3.[CH_2]_4.CH_3$, for it is reduced to this hydrocarbon by simple digestion with zinc and hydrochloric acid. The hexane is identical with that which can be isolated from light petroleum, or made synthetically by the action of sodium on normal propyl iodide.

Sorbitol is thus a normal hexahydroxy-hexane, or hexane-hexol, and as it is a stable compound, and can even be distilled unchanged under very low pressure, it follows that the six hydroxyl groups are attached to six different carbon atoms. It is thus the six-carbon analogue of glycerol, and its conversion into secondary hexyl iodide is parallel to that of glycerol into secondary propyl iodide—

$$CH_2OH.CHOH.CHOH.CHOH.CHOH.CH_2OH$$
$$\longrightarrow CH_3.CH_2.CH_2.CH_2.CHI.CH_3.$$

Oxidation of Glucose: its Constitution.—Glucose is thus either the aldehyde or one of the two possible ketonic derivatives of sorbitol. Now on oxidising it in the cold with bromine water, it is converted into an acid containing the same number of carbon atoms, from which it may again be formed by reduction, and the first view must therefore be adopted.

Gluconic acid, $CH_2OH.[CHOH]_4.COOH$, is a syrupy substance, which, like sorbitol, and unlike glucose, does not reduce metallic solutions. It cannot itself be crystallised, as on concentrating its solution its lactone separates, a crystalline substance melting at 135°, in the same way as butyrolactone from a solution of γ-hydroxy-butyric acid (p. 158). But its salts can be crystallised and analysed, and it is readily separated from other substances by means of its phenyl-hydrazide.

Gluconic phenyl-hydrazide, $CH_2OH.[CHOH]_4.CO.NH.NHPh$ (Fischer, 1889), is a crystalline substance of amide character, which is prepared by heating the acid with phenyl-hydrazine and dilute acetic acid on a water-bath. When heated with strong baryta water on a water-bath, it is hydrolysed, as an amide, into phenyl-hydrazine, which can be extracted with ether, and barium gluconate, from which the acid is set free by dilute sulphuric acid.

On reducing gluconic lactone with sodium amalgam in slightly acid solution it is reconverted into glucose (Fischer, 1889). This is an action of great synthetic importance. The acid itself is not reduced in this manner, nor are acids like tartaric, which do not form lactones.

On oxidising gluconic acid with dilute nitric acid, it is converted into saccharic acid, which is identical with that formed in the same way from cane sugar and glucose. Either sugar is warmed with excess of moderately concentrated nitric acid, not above 60°, until fumes cease to be evolved. The solution is slightly diluted, the accompanying oxalic acid allowed to crystallise out, and the product neutralised with potassium carbonate, and strongly acidified with acetic acid. After some days, potassium hydrogen saccharate separates.

Saccharic acid, $COOH.[CHOH]_4.COOH$, is a deliquescent, gummy substance, which like gluconic acid readily forms a lactone. It is a dibasic acid, and its constitution is further proved by its reduction to adipic acid, $COOH.[CH_2]_4.COOH$ (p. 159), when heated with hydriodic acid and red phosphorus. By further oxidation with nitric acid it is converted into tartaric and oxalic acids.

These actions clearly indicate that glucose is the aldehyde corresponding with sorbitol and gluconic acid-hexane-pentolal—

$$CH_2OH.[CHOH]_4.CH_2OH \leftarrow CH_2OH.[CHOH]_4.CHO$$
$$\longrightarrow CH_2OH.[CHOH]_4.COOH.$$

This conclusion is completely confirmed by the action of hydrocyanic acid. When a mixture of glucose syrup with the calculated amount of concentrated hydrocyanic acid is kept for some days, and finally gently warmed, the odour of the acid disappears. On boiling the product with baryta water, ammonia is to be evolved, and on eliminating the barium with dilute sulphuric acid, a crystalline substance can be isolated.

Analysis indicates that this may be the lactone of a glucose carboxylic acid, $C_6H_7(OH)_6.COOH$, analogous to gluconic acid, and that this is so, and that the acid is normal, is proved by its reduction to normal heptylic acid, $CH_3.[CH_2]_5.COOH$, when boiled with hydriodic acid and red phosphorus. The cyanogen carbon is therefore linked to the end of the hexane chain, and as the end group of a chain cannot of course be ketonic, it follows that glucose is an aldehydic derivative of normal hexane (Kiliani, 1886)—

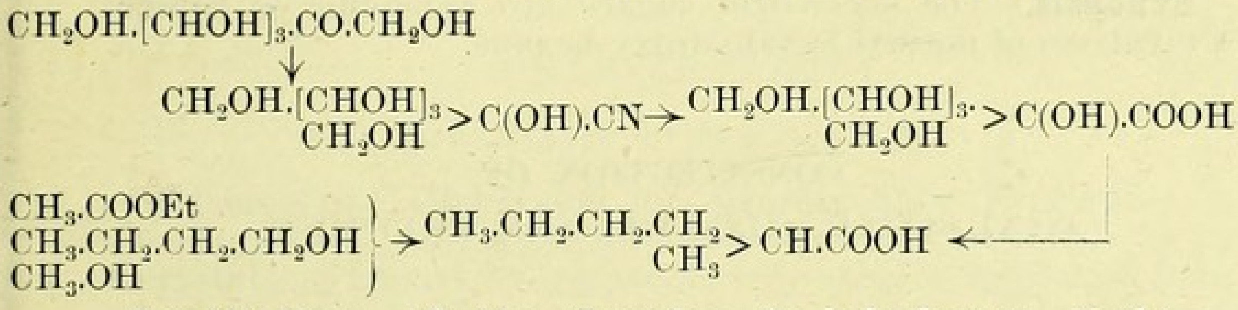
$$\begin{tikzcd} CH_2OH.[CHOH]_4.CHO \arrow[r] & CH_2OH.[CHOH]_4.CHOH.CN \arrow[dl] \\ CH_2OH.[CHOH]_5.COOH \arrow[r] & CH_3.CH_2.CH_2.CH_2CH_2.CH_2.COOH. \end{tikzcd}$$

Constitution of Fructose: Mannitol.—Like glucose, fructose reduces alkaline metallic solutions, and forms compounds with metallic oxides. It also forms an oxime and a crystalline pentacetyl derivative, and that it is an alcohol or ketone is confirmed by its reduction to an alcohol, mannitol, stereoisomeric with sorbitol. Mannitol, like sorbitol, is also a natural product, and is the principal constituent of the common manna of the manna ash, from which it is readily obtained in a pure state by recrystallisation from hot dilute alcohol. The hexahydroxy-hexanes contain four asymmetric carbon atoms, and their isomerism is therefore very complicated. Six optically active and seven inactive compounds are possible, and the majority of them are known.

Mannitol, $CH_2OH.[CHOH]_4.CH_2OH$ (Proust, 1806), is a very sweet substance, which forms large crystals, melting at 166°. It forms a hexacetate, and is converted by hydriodic acid, etc., into a hexyl iodide and hexane identical with those obtained from sorbitol. Until recently, in fact, it was thought that the reduction product of glucose was identical with mannitol, but its melting point and oxidation products are different.

Thus far, the actions of fructose are similar to those of glucose. But its behaviour on oxidation is very different. It is broken up even by mild oxidising agents, and oxalic and mesotartaric acids are the first products that can be isolated. Now a ketone of the constitution, $CH_2OH.[CHOH]_3.CO.CH_2OH$, might be expected to break up in this manner, in the same way as methyl butyl ketone into acetic and butyric acids, and that fructose is this ketone is proved by the cyanhydrin synthesis, in precisely the same way as with glucose.

Fructose cyanhydrin, a crystalline substance, melting at 115°, is converted by hydrolytic agents into a lactone, in the same way as glucose cyanhydrin, but this lactone is reduced by hydriodic acid and phosphorus to a heptylic acid, whose boiling point and salts are identical with those of methyl-normal-butyl-acetic acid, CHMeBu.COOH, made by the acetoacetic synthesis. Fructose or levulose is thus a ketone corresponding with the hexatomic alcohol mannitol—hexane-pentolone (Kiliani, 1886)—



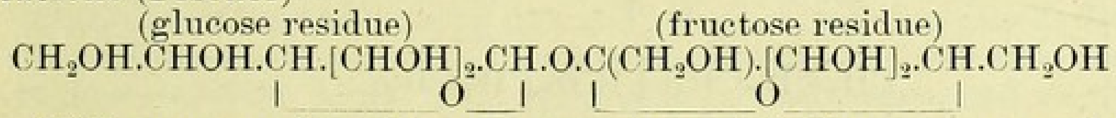
$$\begin{array}{l} CH_2OH.[CHOH]_3.CO.CH_2OH \\ \qquad\downarrow \\ \qquad \genfrac{}{}{0pt}{}{CH_2OH.[CHOH]_3}{CH_2OH}\!>C(OH).CN \rightarrow \genfrac{}{}{0pt}{}{CH_2OH.[CHOH]_3.}{CH_2OH}\!>C(OH).COOH \end{array}$$

$$\left.\begin{array}{l} CH_3.COOEt \\ CH_3.CH_2.CH_2.CH_2OH \\ CH_3.OH \end{array}\right\} \rightarrow \genfrac{}{}{0pt}{}{CH_3.CH_2.CH_2.CH_2}{CH_3}\!>CH.COOH \leftarrow\!\!-\!\!-\!\!-$$

Constitutions of the Complex Carbohydrates.—Nothing definite is yet known of the constitutions of the starches and cellulose, but the constitutions of cane sugar and its isomerides are fairly well established. With one exception, the complex carbohydrates have not yet been synthesised. Cane sugar, however, can be made artificially by digesting potassium fructose in alcoholic solution with acetyl-chlorhydrose, a compound which is formed by the action of acetylchloride on glucose (Marchlewski, 1896); and, as will be seen in the next chapter, both glucose and fructose can be made synthetically—

$$C_6H_7OCl(OAc)_4 + C_6H_7O(OH)_4.OK + 4EtOH = C_6H_7O(OH)_4.O.C_6H_7O(OH)_4 + KCl + 4EtOAc.$$

Cane sugar forms an octacetyl derivative, and as it does not reduce metallic solutions, or form a osazone, the remaining three oxygen atoms can only function in ethereal combination. The following formula, amongst others, epitomises these relations (Fischer)—

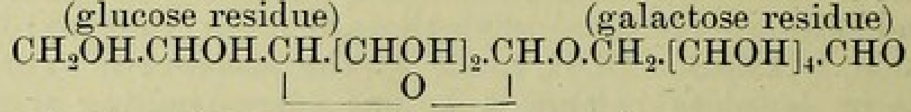


$$\overset{\text{(glucose residue)}}{CH_2OH.CHOH.\underbrace{CH.[CHOH]_2.CH}_{O}.O}.\overset{\text{(fructose residue)}}{\underbrace{C(CH_2OH).[CHOH]_2.CH}_{O}.CH_2OH}$$

Milk sugar and malt sugar are also octohydroxy-compounds, but they reduce metals and form osazones. That they are aldehydic and not ketonic is proved by their oxidation by bromine water to mono-carboxylic acids containing the same number of carbon atoms. Lactobionic acid, $C_{12}H_{21}O_{10}.COOH$, the first oxidation product of lactose, is hydrolysed by acids to glucose and galactonic acid, an acid stereoisomeric with gluconic acid, and formed by the oxidation of galactose.

Galactose is an aldose stereoisomeric with glucose. It is reducible to an alcohol, dulcitol, stereoisomeric with mannitol and sorbitol, and the galactonic acid formed from it by oxidation with bromine water, is further oxidised by nitric acid to mucic acid, a stereoisomeride of saccharic acid. Mucic acid, like saccharic acid, is reduced to adipic acid when heated with hydriodic acid and phosphorus.

The constitution of lactose is thus probably represented by the formula—

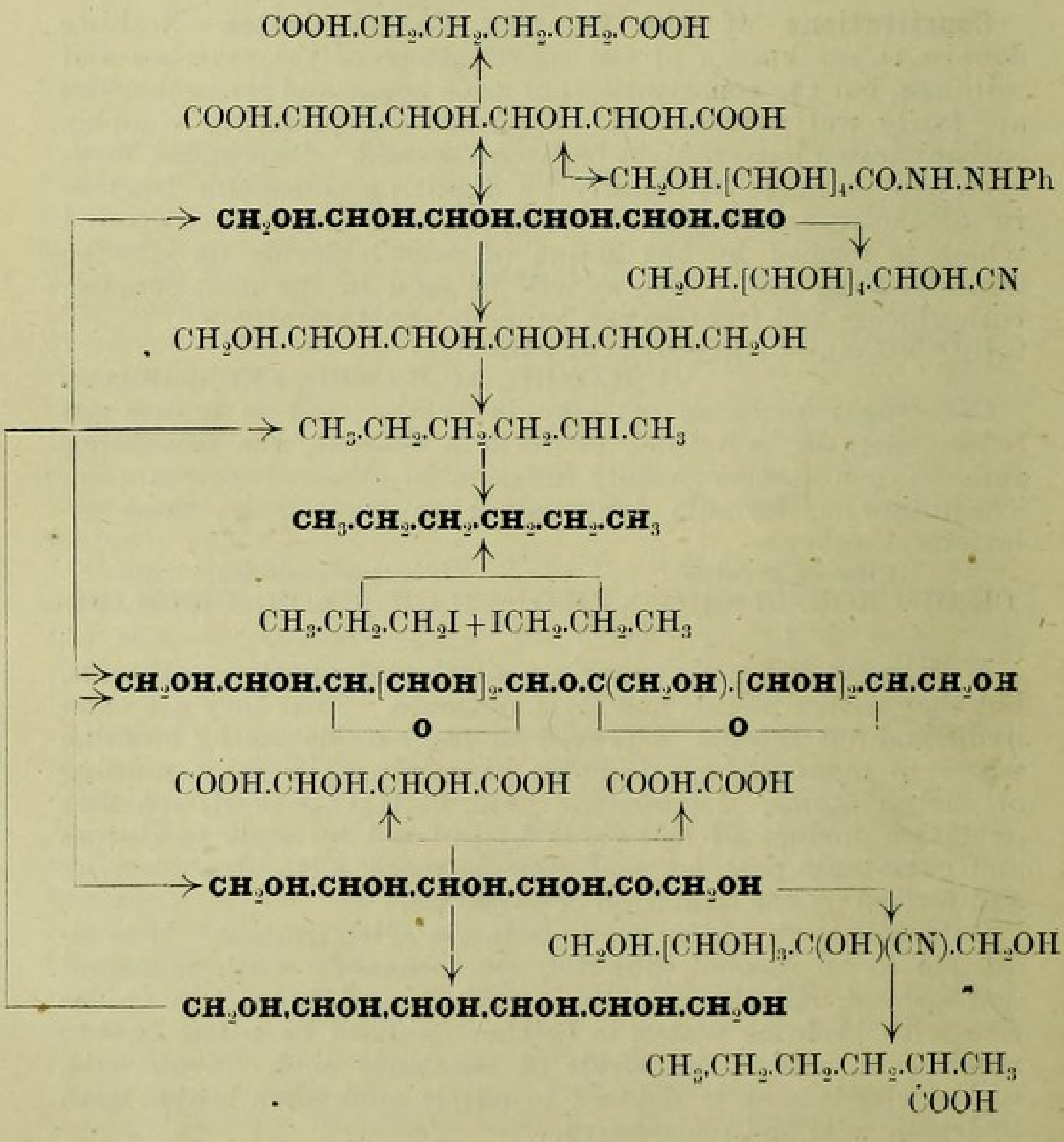


$$\overset{\text{(glucose residue)}}{\mathrm{CH_2OH.CHOH.}}\underbrace{\mathrm{CH.[CHOH]_2.CH}}_{\mathrm{O}}\mathrm{.O.}\overset{\text{(galactose residue)}}{\mathrm{CH_2.[CHOH]_4.CHO}}$$

Maltose is stereoisomeric with lactose.

Synopsis.—The six-carbon sugars are aldehydic or ketonic derivatives of normal hexahydroxy-hexane.

CONSTITUTION OF
CANE-SUGAR, GLUCOSE, AND FRUCTOSE.



CHAPTER XXXI

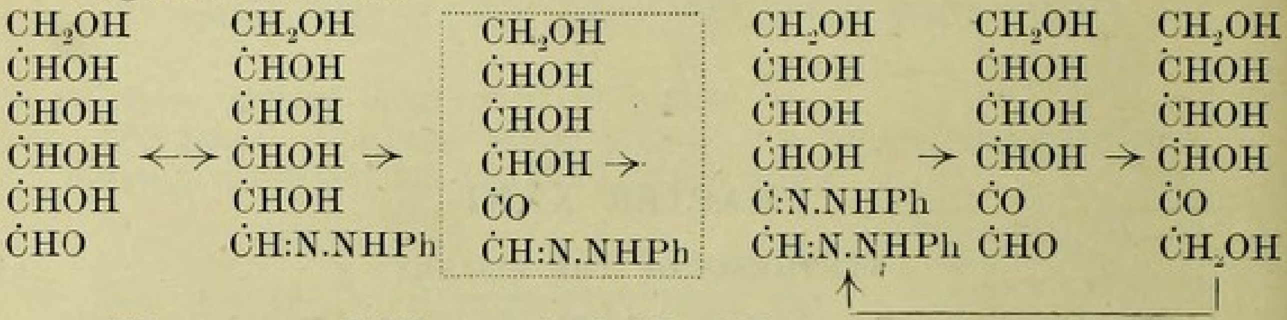
SYNTHESIS OF THE SUGARS

Glucosazone: Conversion of Glucose into Fructose.—As already stated, glucose under certain conditions (p. 190) forms a crystalline phenyl-hydrazone, a very soluble substance from which it can be easily recovered (Fischer, 1885). When heated on a water-bath for half an hour however with phenyl-hydrazine and excess of acetic acid, the whole of the sugar is precipitated in the more complex form of glucosazone. If the original solutions are clear, this only needs washing with water and drying, but otherwise it must be recrystallised from hot alcohol. Fructose yields precisely the same compound, and the osazone is best made in quantity from invert sugar, formed by heating cane-sugar solution on a water-bath for an hour with a little dilute sulphuric acid. The mineral acid must be neutralised before adding the hydrazine.

Phenyl - glucosazone, $CH_2OH.[CHOH]_3.C(:N.NHPh).CH:N.NHPh$ (Fischer, 1884), is a golden-yellow crystalline substance, melting at 204°. Its constitution follows from its composition, and from the manner of its formation and hydrolysis. When warmed with concentrated hydrochloric acid for a minute, it is completely hydrolysed, and in the course of half an hour at the ordinary temperature a quantity of phenyl-hydrazine hydrochloride crystallises out. On neutralising the ice-cold and diluted solution with lead carbonate, a lead compound is obtained from which a sweet fermentable substance, glucosone, is set free by dilute sulphuric acid.

Glucosone or oxyglucose, $CH_2OH.[CHOH]_3.CO.CHO$ (Fischer, 1888), is an exceedingly soluble substance, which has not been crystallised; but that it is both a ketone and an aldehyde is proved by its immediate conversion into glucosazone when mixed with phenyl-hydrazine acetate solution, and by its reduction to fructose by zinc dust and acetic acid, the aldehyde group alone being affected.

In this way, therefore, the aldehyde sugar or aldose may be converted into the ketonic sugar or ketose. The reverse transformation may also be effected, but only by a circuitous method (p. 191). The conversion of glucose and fructose into glucosazone is due to the oxidation of one of the alcohol groups by a third molecule of phenyl-hydrazine, which is reduced to ammonia and aniline (p. 246). All sugars which reduce metallic solutions, form such osazones, but the non-reducing sugars do not do so—



$$\begin{array}{lclclclclcl}
CH_2OH & & CH_2OH & & CH_2OH & & CH_2OH & & CH_2OH & & CH_2OH \\
\dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH \\
\dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH & & \dot{C}HOH \\
\dot{C}HOH & \longleftrightarrow & \dot{C}HOH & \rightarrow & \dot{C}HOH & \rightarrow & \dot{C}HOH & \rightarrow & \dot{C}HOH & \rightarrow & \dot{C}HOH \\
\dot{C}HOH & & \dot{C}HOH & & \dot{C}O & & \dot{C}:N.NHPh & & \dot{C}O & & \dot{C}O \\
\dot{C}HO & & \dot{C}H:N.NHPh & & \dot{C}H:N.NHPh & & \dot{C}H:N.NHPh & & \dot{C}HO & & \dot{C}H_2OH
\end{array}$$

Mannose and Mannonic Acid.—When mannitol is warmed with dilute nitric acid it is partly oxidised to fructose, but partly also to mannose, an aldehyde sugar stereoisomeric with glucose. The mannose is readily separated from the ketonic sugar by adding phenyl-hydrazine and acetic acid to the cold neutralised solution. A dense yellow precipitate of the phenylhydrazone separates, from which the sugar can be recovered by hydrolysis with dilute hydrochloric acid, in the same way as gluconic acid from its hydrazide. Fructose does not form a hydrazone. Mannose can also be obtained in quantity by hydrolysing vegetable ivory with dilute sulphuric acid (Fischer, 1889).

Mannose, $CH_2OH.[CHOH]_4.CHO$ (Gorup-Besanez, 1861), is a sweet substance which resembles glucose in almost every respect, except that it is more strongly dextrogyrate. On further oxidation with bromine, etc., it yields mannonic and mannosaccharic acids, compounds which closely resemble, and are stereoisomeric with gluconic and saccharic acids. Conversely, mannonic lactone is reduced by sodium amalgam to mannose and mannitol, in the same way as gluconic lactone to glucose and sorbitol—

$$\begin{tikzcd}
CH_2OH.[CHOH]_4.CH_2OH \arrow[r, leftrightarrow] & CH_2OH.[CHOH]_4.CHO \arrow[d, leftrightarrow] \\
 & CH_2OH.[CHOH]_4.COOH.
\end{tikzcd}$$

Mannose and mannonic acid are very intimately related to glucose and gluconic acid, for mannosazone is identical with glucosazone, and mannonic and gluconic acids are interconvertible. When the one acid is heated with excess of quinoline (p. 383) and a little water, for an hour, at 140°, it is partially converted into the other, and vice versâ.

The two acids are separated by fractionally crystallising their brucine salts. The product is made alkaline with baryta, the liberated quinoline distilled off with steam, and the barium exactly precipitated with dilute sulphuric acid. The hot solution of the mixed acids is then saturated with brucine (p. 400), and on allowing it to crystallise, brucine mannonate separates. The brucine is precipitated with baryta from the residual solution of brucine gluconate, and the metal eliminated as before. The gluconic acid is then isolated from the product in the form of its hydrazide, and from this the lactone can be made in the manner described above (p. 185).

As the lactone is reducible to glucose, it follows that this sugar can be made from mannonic acid, and thus from fructose. This is an important step in the synthesis of the sugars.

Synthesis of Glucose and Fructose.—It has been already stated that formaldehyde and metaformaldehyde polymerise to sugars when digested with baryta water, and the same action occurs under various conditions with glycollic and glyceric aldehydes, both of which, like formaldehyde, have a "carbohydrate" formula. Until the osazones were made, however, it was not possible to isolate and examine these synthetic sugars, and beyond the fact that they reduce metallic solutions, and in general behave like glucose (Butlerow, 1864), little was known about them.

The first synthetic sugar thoroughly examined was obtained from acroleïn dibromide, and subsequently also from formaldehyde and glyceraldehyde. The product obtained by digesting acroleïn dibromide with ice-cold baryta water yields with phenyl-hydrazine and acetic acid, not the osazone of glyceraldehyde, $CH_2OH.CHOH.CHO$, as might be expected, but that of a polymeric sugar, *a*-acrose, isomeric with glucose and fructose (Fischer, 1887). Other products are also formed—

$$CH_2Br.CHBr.CHO \rightarrow CH_2OH.CHOH.CHO \rightarrow C_6H_{12}O_6.$$

a-Acrosazone is extremely like glucosazone, but like all synthetic products is optically inactive. It melts at 205°, however, and is converted by hydrochloric acid into *a*-acrosone, a syrupy liquid resembling glucosone. This, when digested with zinc dust and acetic acid, is reconverted into *a*-acrose.

a-Acrose is therefore a ketonic sugar. The product thus purified is in fact very like fructose, but again optically inactive. By further reduction with sodium amalgam it is converted into *a*-acritol, an inactive isomeride of mannitol and sorbitol, and that this is actually a "racemic" compound is proved by fermenting it with yeast. The ordinary fructose, to which the yeast is accustomed, is destroyed, and the solution becomes dextrogyrate from the liberation of the oppositely active isomeride. *a*-Acrose thus appears to be inactive fructose, and *a*-acritol, inactive mannitol—

$$CH_2{:}CH.CHO \rightarrow CH_2OH.[CHOH]_3.CO.CH_2OH$$
$$\longrightarrow CH_2OH.[CHOH]_4.CH_2OH.$$

Now if this alcohol is really inactive mannitol, it should be oxîdisable to a "racemic" mannonic acid, and this is actually the case. The oxidation is effected in the same way as with mannitol, by the successive action of dilute nitric acid and bromine water. By concentrating the solution of the strychnine salt of the acid thus obtained, strychnine lævomannonate separates, whilst by converting the mother liquor into the morphine salt, and again concentrating, morphine dextromannonate is obtained.

The dextromannonate yields an acid, which is identical with the mannonic acid from mannose, whilst the lævomannonate yields the opposite isomeride, the rotatory powers of the two acids being numerically equal.

Conversely, the active acids can be reconverted into the inactive acid, in the same way as with the lactic and tartaric acids. Lævomannonic acid can be obtained in quantity from a five-carbon sugar, arabinose (p. 193), by the cyanhydrin synthesis, and on mixing a solution of its lactone with that of an equal weight of ordinary mannolactone, an inactive acid and lactone are obtained, which are identical with those formed by oxidation of *α*-acritol, and are reducible by sodium amalgam to an inactive mannose and mannitol. The latter is identical with *α*-acritol.

There is no doubt, therefore, that the synthetic mannonic acid is the racemic compound corresponding with the ordinary acid and can be resolved into the latter—

$$\begin{tikzcd}
CH_2OH.[CHOH]_3.CO.CH_2OH \arrow[r] & CH_2OH.[CHOH]_4.CH_2OH \arrow[d, leftrightarrow] & \\
& CH_2OH.[CHOH]_4.CHO \arrow[r, leftrightarrow] & CH_2OH.[CHOH]_4{\cdot}COOH.
\end{tikzcd}$$

Now, as mannonic acid is convertible into gluconic acid, glucose and fructose, it follows that the synthetic chain between glycerol and these natural sugars is complete.* The validity of the synthesis rests on the identity of the two acids and alcohols, for owing to secondary actions, the yield of *α*-acrose is so small, the acroleïn from a kilogram of glycerol, for example, yielding only 18 grams of *α*-acrosazone, that it would be impracticable to actually convert glycerol into glucose. As previously explained, however, in connection with the cyanide synthesis, this is immaterial.

Sugars derived from Paraffins other than Hexane.—All the lower paraffins are connected with polyalcohols, aldoses, etc., in the same way as hexane with glucose and mannitol. The prototype of the glucose-saccharic series is, in fact, the glycoloxalic series. Glycollic aldehyde behaves in every respect as a true sugar. It is a carbohydrate, and is sweet like sugar. It reduces metallic solutions and forms a osazone. It is itself reducible to an alcohol, glycol, and oxidisable to mono- and di-carboxylic acids, glycollic and oxalic acids. The parallel to glucose is thus very close—

$$\begin{array}{l}CH_2OH\\ \dot{C}H_2OH\end{array} \rightarrow \begin{array}{l}CH_2OH\\ \dot{C}HO\end{array} \rightarrow \begin{array}{l}CH_2OH\\ \dot{C}OOH\end{array} \rightarrow \begin{array}{l}COOH\\ \dot{C}OOH.\end{array}$$

Glyceric aldehyde, again, or glycerose, has just the same

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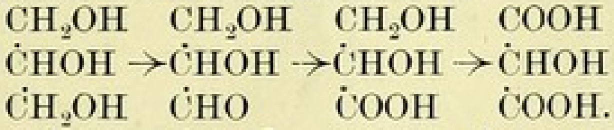
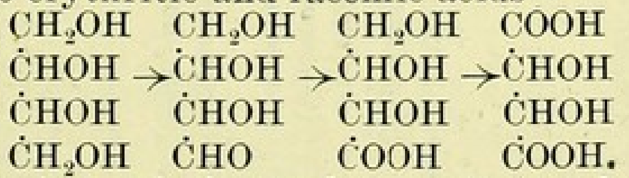
* See Chart at end of chapter.

properties, and undergoes the same transformations. It is reducible to glycerol, in the same way as glucose to sorbitol, and is oxisable to glyceric and tartronic acids, in the same way as glucose to gluconic and saccharic acids—



$$\begin{array}{llll} \mathrm{CH_2OH} & \mathrm{CH_2OH} & \mathrm{CH_2OH} & \mathrm{COOH} \\ \dot{\mathrm{C}}\mathrm{HOH} \rightarrow & \dot{\mathrm{C}}\mathrm{HOH} \rightarrow & \dot{\mathrm{C}}\mathrm{HOH} \rightarrow & \dot{\mathrm{C}}\mathrm{HOH} \\ \dot{\mathrm{C}}\mathrm{H_2OH} & \dot{\mathrm{C}}\mathrm{HO} & \dot{\mathrm{C}}\mathrm{OOH} & \dot{\mathrm{C}}\mathrm{OOH}. \end{array}$$

In the four-carbon series, the compounds are physically like the hexane sugars. Erythritol, $CH_2OH.CHOH.CHOH.CH_2OH$ (Stenhouse, 1848), is a crystalline substance resembling mannitol, and melting at 126°. It is found in combination in certain lichens. It is oxidised by dilute nitric acid to erythrose, $CH_2OH.CHOH.CHOH.CHO$, a four-carbon syrupy sugar resembling glucose, and this is convertible by bromine water and nitric acid into erythritic and racemic acids—



$$\begin{array}{llll} \mathrm{CH_2OH} & \mathrm{CH_2OH} & \mathrm{CH_2OH} & \mathrm{COOH} \\ \dot{\mathrm{C}}\mathrm{HOH} \rightarrow & \dot{\mathrm{C}}\mathrm{HOH} \rightarrow & \dot{\mathrm{C}}\mathrm{HOH} \rightarrow & \dot{\mathrm{C}}\mathrm{HOH} \\ \dot{\mathrm{C}}\mathrm{HOH} & \dot{\mathrm{C}}\mathrm{HOH} & \dot{\mathrm{C}}\mathrm{HOH} & \dot{\mathrm{C}}\mathrm{HOH} \\ \dot{\mathrm{C}}\mathrm{H_2OH} & \dot{\mathrm{C}}\mathrm{HO} & \dot{\mathrm{C}}\mathrm{OOH} & \dot{\mathrm{C}}\mathrm{OOH}. \end{array}$$

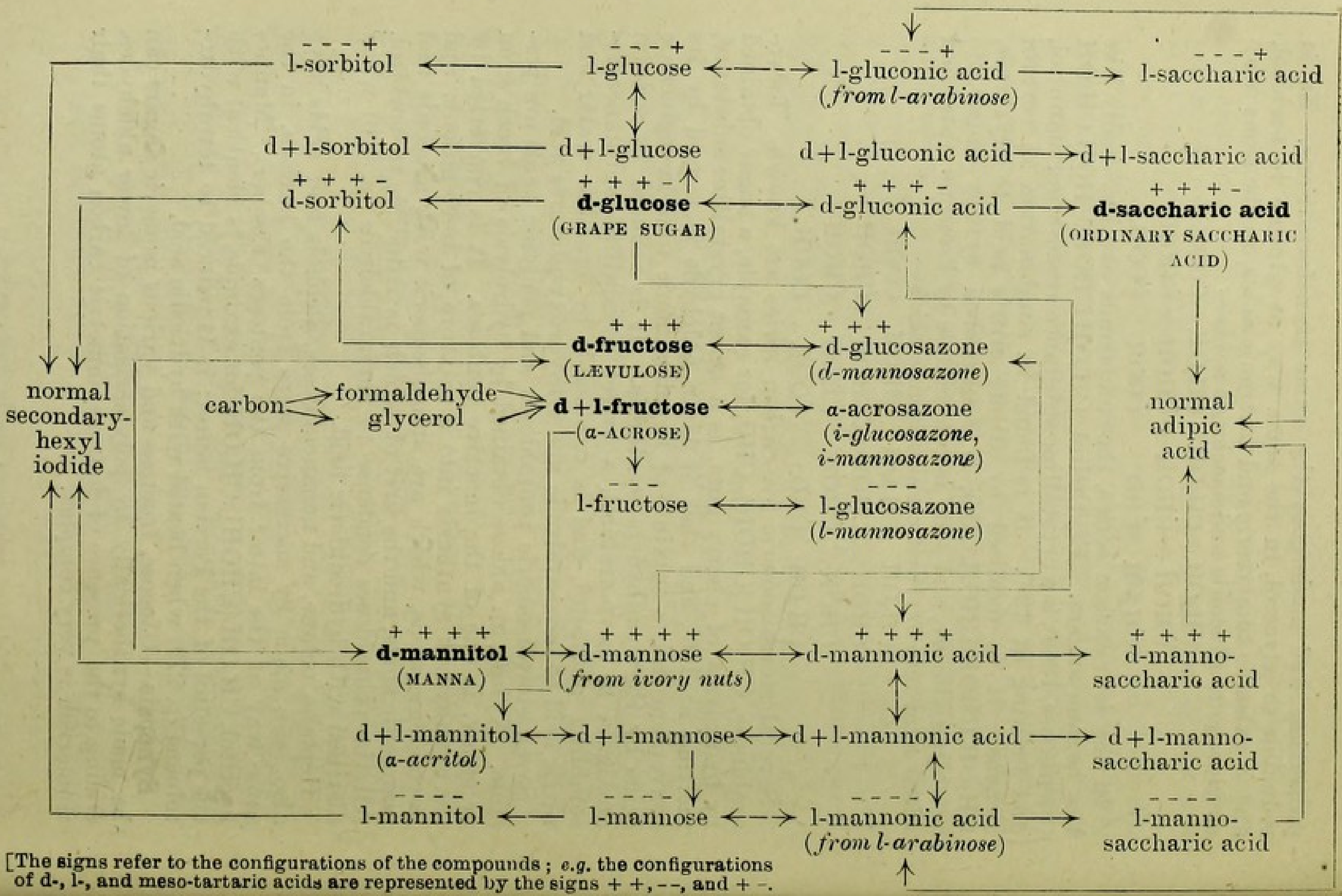
Several stereoisomeric five-carbon series are known. Lævo-arabinose, $CH_2OH.[CHOH]_3.CHO$, for example, a sugar obtained by hydrolysis of cherry gum, is a sweet crystalline substance, melting at 160°, and that it is an aldehyde is proved by its conversion into a mixture of lævomannonic and lævogluconic acids by the cyanhydrin synthesis. It is reduced by sodium amalgam to lævo-arabitol, a sweet crystalline substance resembling mannitol, and is oxidisable by bromine water and nitric acid to lævo-arabonic and trihydroxy-glutaric acid.

Seven stereoisomeric pentaldoses and pentonic acids are possible. Xylose, an aldose obtained by hydrolysis of beech gum or straw, is one of the inactive pentoses. It is converted by the cyanhydrin synthesis into a mixture of lævo-gulonic and lævo-idonic acids, which are stereoisomeric with gluconic and mannonic acids, and the first of which is reducible to sorbitol. All the pentaldoses condense to furfuraldehyde (p. 406) when distilled with hydrochloric acid.

Heptane, octane, and nonane aldoses, alcohols and acids have also been made by successive steps from the hexoses, in the same way as the latter from the pentoses (Fischer). Manno-heptitol, $CH_2OH.[CHOH]_5.CH_2OH$, for example, is identical with the perseïtol of the Persian laurel; it is reduced to tetrahydrotoluene (p. 279) when heated with hydriodic acid.

Synopsis.—Glucose, fructose and various isomeric sugars can be made synthetically by polymerisation of lower aldehydes. Owing to the presence of four asymmetric carbon atoms their isomerism is very complex.

SYNTHESIS OF THE NATURAL HEXOSES.



[The signs refer to the configurations of the compounds; *e.g.* the configurations of d-, l-, and meso-tartaric acids are represented by the signs + +, − −, and + −.

SECTION IX

ALIPHATIC DERIVATIVES OF NITROGEN, ETC

CHAPTER XXXII

CARBAMIDE

Urea or Carbamide.—The chief classes of oxygenated aliphatic compounds have now been dealt with, and the only group remaining to be considered, before passing on to derivatives of other hydrocarbons, is one comprising a number of compounds, in which nitrogen, or in some cases other elements, plays the predominant part. Some of these compounds, such as the simple amides and amines, and the nitriles, have been already incidentally dealt with, but there are others which are more complex.

The first of these are the complex amides of carbonic acid, which are substances of great physiological importance. The waste nitrogen of mammals is excreted in the urine, partly in the form of uric acid and allied compounds, but mainly in that of a basic substance, urea or carbamide. This base is readily separated from fresh urine.

The liquid is evaporated on a water-bath, and on adding an equal bulk of concentrated nitric acid to the cooled, thin syrup, it immediately becomes semi-solid from the separation of urea nitrate, which is insoluble in nitric acid. The nitrate is then purified by redissolving in water, and reprecipitating with nitric acid, and the base set free by adding barium carbonate to the aqueous solution as long as effervescence occurs. The urea carbonate, which might be expected, is too unstable to exist, and consequently on evaporating the product to dryness on a water-bath, a mixture of urea with barium nitrate and excess of carbonate is obtained. The urea is extracted from this with hot absolute alcohol, in which barium nitrate is insoluble, and readily crystallises on distilling off the solvent. It is most economically prepared synthetically from potassium cyanide (see below)—

$$2CO(NH_2)_2,HNO_3 + BaCO_3 = 2\ CO(NH_2)_2 + Ba(NO_3)_2 + CO_2 + H_2O.$$

Urea or carbamide, $CO(NH_2)_2$, (Rouelle, 1773), forms long, transparent prisms, resembling nitre in taste. It melts at 132°, and is freely soluble in water and alcohol. It is but a feeble base, and forms stable salts only with the stronger acids, such as nitric and oxalic acids. The oxalate, for example, is a sparingly soluble salt, which like the nitrate may be used in the preparation from urine. Urea also forms compounds with salts. Sodium chloride urea, $CON_2H_4,NaCl,H_2O$, for example, is a crystalline substance, and mercuric nitrate urea, $CON_2H_4,HgO,Hg(NO_3)_2$, an insoluble, basic substance, which is precipitated on adding mercuric nitrate to a solution of the base, and is sometimes used for its detection and estimation.

Urea thus resembles the amides in its chemical behaviour, and that it is the amide of carbonic acid is proved by boiling it with concentrated caustic soda, when it is hydrolysed to ammonia and sodium carbonate. A similar decomposition is effected naturally in the early stages of the putrefaction of urine, the urea being hydrated to ammonium carbonate by a microbe, micrococcus ureæ. Hence the ammoniacal odour—

$$CO(NH_2)_2+2NaOH=CO(ONa)_2+2NH_3.$$

The derivation of urea from ammonia is shown, moreover, by the action of nitrous acid, which converts it into carbon dioxide and nitrogen in the normal manner. The same decomposition is effected by sodium hypobromite, and the amount of urea in urine is readily estimated by measuring the nitrogen thus liberated from a known volume of the liquid. The hypobromite is made at the time by adding bromine to cooled caustic soda solution—

$$CO(NH_2)_2+3NaOBr+2NaOH=Na_2CO_3+N_2+3NaBr+3H_2O.$$

Synthesis of Urea.—The constitution of urea, as determined by these analytical methods, is confirmed by various syntheses from carbonic acid derivatives. Thus it is formed by heating ammonia with ethyl carbonate, a heavy liquid made by heating ethyl iodide with silver carbonate. The action is the same as that involved in the preparation of oxamide from ethyl oxalate—

$$C\rightarrow CO_2\rightarrow Na_2CO_3\rightarrow CO(OAg)_2\rightarrow CO(OEt)_2\rightarrow CO(NH_2)_2.$$

It is obtained also by the direct action of ammonia on carbonyl chloride or phosgene, an easily condensible gas, which is formed by oxidation of chloroform (p. 115), or by direct union of carbon monoxide with chlorine in sunlight. The action is here parallel to the formation of acetamide from acetyl chloride—

$$C\rightarrow CO\rightarrow COCl_2\rightarrow CO(NH_2)_2.$$

Urea is also obtained by the action of ammonia on ethyl chlorocarbonate or chloroformate, $Cl.COOEt$, a liquid which is formed, together with ethyl carbonate, by heating an alcoholic solution of phosgene gas. A crystalline substance, ethyl carbamate, $NH_2.COOEt$, analogous to ethyl oxamate, is produced in the first instance (Dumas)—

$$COCl_2\rightarrow Cl.COOEt\rightarrow NH_2.COOEt\rightarrow CO(NH_2)_2.$$

The corresponding ammonium carbamate or "sesquicarbonate," formed by the direct union of carbon dioxide and ammonia, is also convertible into urea, as it loses water when heated, in the same way as ammonium acetate, and a similar synthesis of carbamide from ammonium carbonate is believed to be effected in the liver—

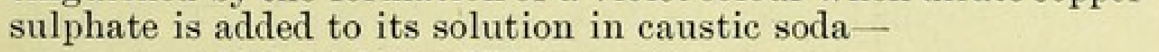
$$C \rightarrow CO_2 \rightarrow NH_2.COONH_4 \rightarrow CO(NH_2)_2.$$

These various syntheses render it clear that urea is the diamide of carbonic acid. They are not adapted for the preparation of the substance, however, and, as stated above, it is best made in quantity from potassium cyanide. The cyanide is fused with excess of litharge or red lead, and on evaporating the solution of the potassium cyanate thus formed with the equivalent amount of ammonium sulphate, a residue of potassium sulphate and urea is left, the ammonium cyanate initially formed undergoing molecular transformation. Much of the potassium sulphate crystallises out as the solution is concentrated, and the urea is separated from the remainder by extracting the dry product with hot absolute alcohol, in which the sulphate is insoluble. Traces of red and blue colouring matters are usually also formed—

$$C \rightarrow KCN \rightarrow KCNO \rightarrow NH_4.CNO \rightarrow CO(NH_2)_2.$$

The cyanide synthesis of urea is of peculiar interest, as it was the first synthesis of an Organic compound effected (Wöhler, 1828). Previously to this, and even long afterwards, it was maintained that the action of living organisms was essential to the formation of Organic compounds. This view has of course long been abandoned, but it is still held by many that "organised" or "living" matter is fundamentally different from that which is made in the laboratory.

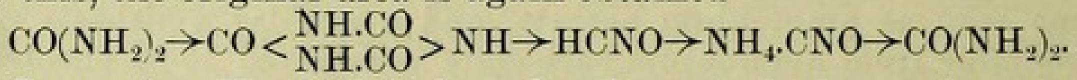
Condensation Products of Urea.—When urea is heated it loses ammonia, and passes through a characteristic cycle of changes. The first product, biuret or allophanamide, $NH_2.CO.NH.CO.NH_2$ (Liebig and Wöhler, 1834), a crystalline substance melting at 190°, is also formed by heating ammonia with ethyl allophanate, $NH_2.CO.NH.COOEt$, a substance formed synthetically by the action of carbamide on ethyl chlorocarbonate. Biuret is distinguished by the formation of a violet colour when dilute copper sulphate is added to its solution in caustic soda—



$$\begin{array}{l} \qquad\qquad 2NH_2.CO.NH_2 - NH_3 \searrow \\ NH_2.CO.NH_2 + Cl.COOEt \rightarrow NH_2.CO.NH.COOEt \nearrow \end{array} NH_2.CO.NH.CO.NH_2$$

By further heating carbamide or biuret, more ammonia is lost, and cyanuric acid, $C_3H_3N_3O_3$, is formed, a white crystalline substance. It is more readily prepared by dissolving urea in dilute hydrochloric acid, and heating the evaporated residue as long as heavy fumes of ammonium chloride are given off. The acid is converted into a characteristic insoluble crystalline barium salt, when barium chloride is added to its solution in dilute ammonia, and thus serves for the detection of urea.

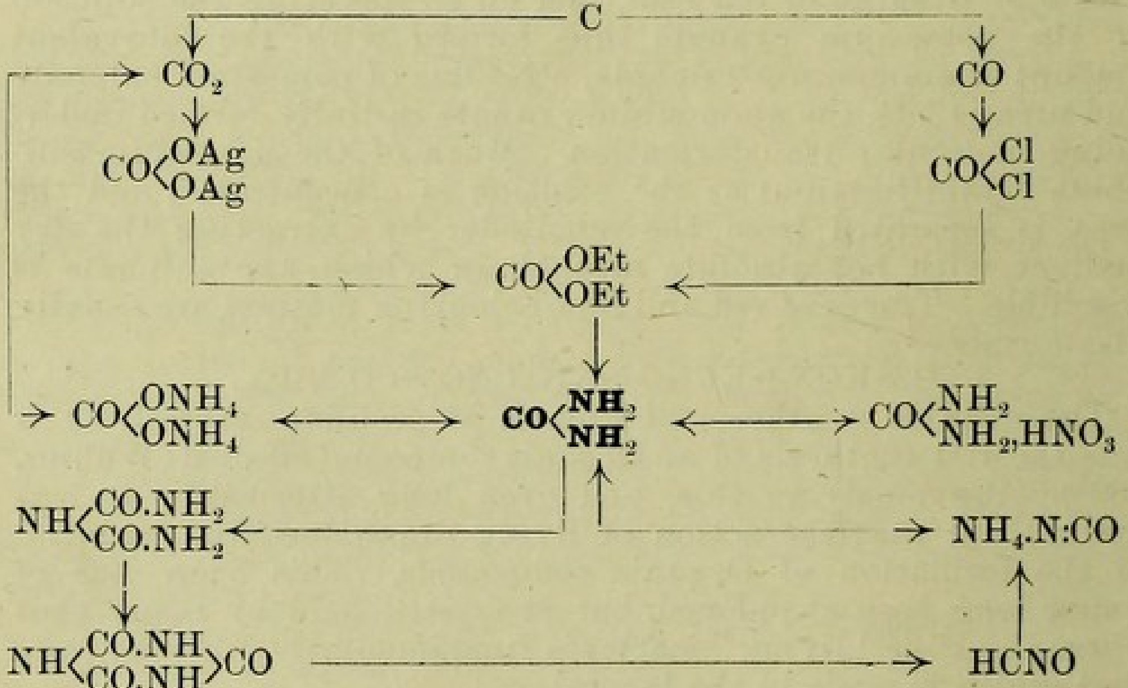
When cyanuric acid is heated to dull redness, it is converted into cyanic acid, HCNO (p. 209), and by the addition of ammonia to this, the original urea is again obtained—



$$CO(NH_2)_2 \rightarrow CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>NH \rightarrow HCNO \rightarrow NH_4.CNO \rightarrow CO(NH_2)_2.$$

Synopsis.—Urea or carbamide, the principal constituent of mammalian urine, is the diamide of carbonic acid.

UREA.



CHAPTER XXXIII

THE URIC ACID GROUP

Uric Acid.—Whilst urea is the principal constituent of mammalian urine, the urine of birds and reptiles contains a large proportion of uric acid. Snakes' excrement in fact consists of fairly pure ammonium urate, and affords a convenient source of the acid. The excrement is boiled with dilute caustic soda until ammonia ceases to be evolved, and the uric acid is precipitated from the clear hot sodium urate solution by pouring it into excess of cold dilute hydrochloric acid. The product is dissolved in warm concentrated sulphuric acid, and reprecipitated by water, and the uric acid thus purified washed with water and dried.

The acid can be precipitated from human urine by acidifying it with hydrochloric acid, or better, by saturating it with ammonium chloride, when ammonium hydrogen urate is thrown down quantitatively (Hopkins, 1892). The latter is then treated in the same way as the snakes' excrement.

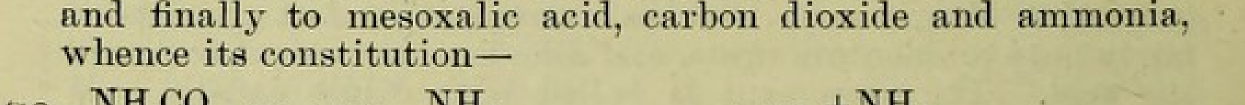
Uric acid, $C_5H_4N_4O_3$ (Scheele, 1776), is a white microcrystalline powder, which is very sparingly soluble in water. The solution is acid to litmus. The molecular weight of the acid is determined by the cryoscopic method, from the solution in monohydrated sulphuric acid.

Uric acid is a feeble dibasic acid, and forms salts such as potassium urate, $C_5H_3KN_4O_3$, and dipotassium urate, $C_5H_2K_2N_4O_3$, but the latter is decomposed even by carbon dioxide. By heating lead urate however with methyl iodide, it is converted into dimethyl-uric acid, $C_5H_2Me_2N_4O_3$, a crystalline substance which resembles uric acid and is also a dibasic acid. It thus follows that all four hydrogen atoms of the uric acid molecule are acid or replaceable by metals. The bearing of this on the constitution of the acid will be seen presently—

$$C_5H_4N_4O_3 \rightarrow C_5H_2PbN_4O_3 \rightarrow C_5H_2Me_2N_4O_3 \rightarrow C_5K_2Me_2N_4O_3.$$

The Ureïdes.—Uric acid is readily convertible into acidyl derivatives of urea, which are analogous to the amides, and hence termed the ureïdes. When, for example, the pure acid is added in small portions to moderately concentrated nitric acid, it dissolves with gentle effervescence, owing to the evolution of carbon dioxide and nitrogen. If the action is moderated, by cooling if necessary, and no nitrous fumes are evolved, crystals of a new substance, alloxan, begin to appear after a certain amount of the acid has been dissolved. The solution may now be warmed, but not above 50°, and more acid dissolved, and on finally cooling, the alloxan separates in quantity. It is drained on an asbestos filter, and after washing with a little ice-water, recrystallised from the minimum amount of warm water. Several further crops can be obtained by dissolving more acid in the mother liquor.

Alloxan or mesoxalyl urea, $CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>CO+4H_2O$ (Brugnatelli, 1817), is a crystalline, semi-acid substance, which stains the skin pink, and gives it a heavy, sickly odour. When boiled with caustic alkalies, it is hydrolysed, first to alloxanic acid, and finally to mesoxalic acid, carbon dioxide and ammonia, whence its constitution—



$$CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>CO\rightarrow CO<\begin{matrix}NH_2\\NH.CO.CO.COOH\end{matrix}\rightarrow CO_2\begin{matrix}+NH_3\\+NH_3\end{matrix}+COOH.CO.COOH$$

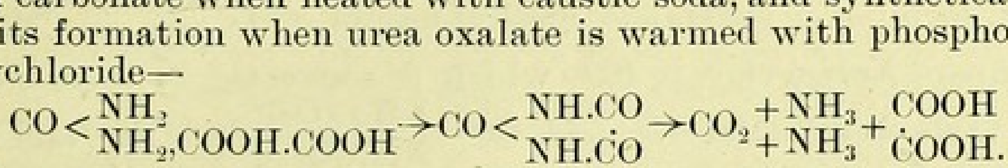
As a ketone, alloxan forms a crystalline bisulphite compound, and its relation to mesoxalic acid is further shown by the tenacity with which it retains the fourth molecule of its water of crystallisation. Three molecules separate at 100° in the ordinary manner, but the fourth is lost only at 150°. The carboxyl groups probably have the same influence as the chlorine in chloral hydrate.

Alloxan is reduced by sulphuretted hydrogen to alloxantin, a colourless substance, which is converted by ammonia into murexide, a fine purple dye, which was much used before the introduction of the synthetic coal-tar dyes. Some alloxantin is always formed in the preparation of alloxan, and if a little uric acid or urate is evaporated to dryness with a few drops of nitric acid in a porcelain dish, the purple murexide is at once formed on moistening the cold, dry residue with ammonia. This affords a very delicate test for compounds of the uric acid group.

When alloxan is heated with excess of concentrated nitric acid at 70°, carbon dioxide is evolved, and on concentrating and cooling the product, a further oxidation product crystallises out, and after drying on a water-bath may be recrystallised from water.

Parabanic acid or oxalyl urea, $CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}$ (Liebig and Wöhler, 1838), is a soluble crystalline substance, which is strongly acid to litmus. It is a dibasic acid, the hydrogen of the imido-groups being mobile as in succinimide, owing to the juxtaposition of the carbonyl. The silver salt, $CO<\begin{matrix}NAg.CO\\NAg.CO\end{matrix}$, for example, is thrown down as a crystalline precipitate, on adding silver nitrate to a solution of the acid.

That parabanic acid is the ureïde of oxalic acid is shown analytically by its hydrolysis to ammonia and sodium oxalate and carbonate when heated with caustic soda, and synthetically, by its formation when urea oxalate is warmed with phosphorus oxychloride—



$$CO{<}\begin{matrix}NH_2\\NH_2,COOH.COOH\end{matrix} \rightarrow CO{<}\begin{matrix}NH.CO\\NH.CO\end{matrix} \rightarrow CO_2\begin{matrix}+NH_3\\+NH_3\end{matrix}+\begin{matrix}COOH\\|\\COOH.\end{matrix}$$

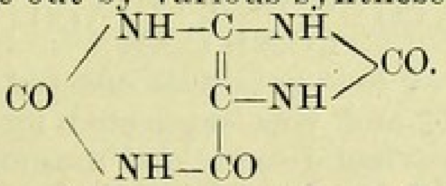
Parabanic acid is quite stable towards acids, but it is partially hydrolysed by bases. Thus on neutralising a warm solution of the acid with ammonia, ammonium oxalurate, $NH_2.CO.NH.CO.COONH_4$, crystallises out on cooling. Acids such as alloxanic and oxaluric acids are termed ureïde acids.

The carbon dioxide and nitrogen, liberated in the oxidation of uric acid to alloxan, are formed from urea by the action of the nitrous acid. Urea itself can be obtained by substituting lead peroxide for the nitric acid. On adding the peroxide in small portions to boiling water, in which uric acid is suspended, its colour disappears, and a heavy white precipitate of lead oxalate and carbonate remains, and on filtering the product as soon as decolorisation ceases, allantoïn, or glyoxylic diureïde, separates in small, brilliant crystals. More of these appear on concentrating the mother liquor, but, finally, the latter crystallises to a mass of the long, transparent crystals of urea—

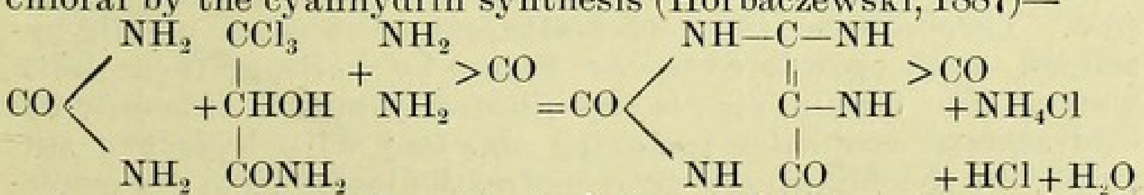
$$2C_5H_4N_4O_3+2O+5H_2O=C_4N_4H_6O_3+2CO(NH_2)_2+2COOH.COOH$$

Constitution and Synthesis of Uric Acid.—As uric acid is convertible into alloxan and urea, its molecule presumably contains the nuclei of both these substances. Now since all four hydrogen atoms are replaceable by metal, the probability is that the acid is a compound of the type of alloxan and parabanic acid, and that the hydrogen are linked to the nitrogen atoms; and that this is actually so, is proved by the elimination of the whole of the nitrogen as methylamine, when tetramethyluric acid is hydrolysed with concentrated hydrochloric acid at 70°, no ammonia appearing (Fischer, 1882).

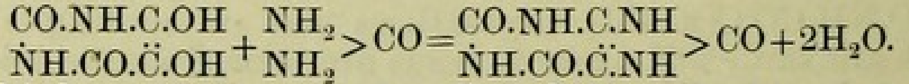
From these and other considerations it is held that uric acid is the diureïde of trihydroxy-acrylic acid (Medicus, 1875), and this view is borne out by various syntheses—



Small quantities of the acid are formed, for example, by heating urea with trichloro-lactamide, a substance made from chloral by the cyanhydrin synthesis (Horbaczewski, 1887)—



A more complicated synthesis, but one affording a better yield, is effected by means of ethyl acetoacetate. This combines with urea, forming a substance, methyl-uracyl, $\mathrm{CO}<\begin{matrix}\mathrm{NH.CMe}\\\mathrm{NH.CO}\end{matrix}>\mathrm{CH}$, (compare Antipyrine, p. 409) which is converted by a series of reactions into isodialuric acid, $\mathrm{CO}<\begin{matrix}\mathrm{NH.C(OH)}\\\mathrm{NH.CO}\end{matrix}>\mathrm{C(OH)}$, and the latter, when heated with urea in presence of concentrated sulphuric acid, condenses to uric acid (Behrend and Roosen, 1889)—



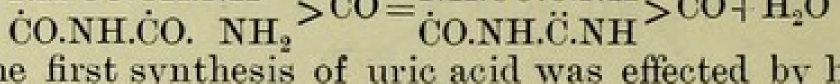
$$\begin{matrix}\mathrm{CO.NH.C.OH}\\\dot{\mathrm{N}}\mathrm{H.CO.}\dot{\mathrm{C}}\mathrm{.OH}\end{matrix}+\begin{matrix}\mathrm{NH_2}\\\mathrm{NH_2}\end{matrix}>\mathrm{CO}=\begin{matrix}\mathrm{CO.NH.C.NH}\\\dot{\mathrm{N}}\mathrm{H.CO.}\dot{\mathrm{C}}\mathrm{.NH}\end{matrix}>\mathrm{CO}+2\mathrm{H_2O}.$$

A third synthesis can be effected from barbituric acid or malonyl urea, $\mathrm{CO}<\begin{matrix}\mathrm{NH.CO}\\\mathrm{NH.CO}\end{matrix}>\mathrm{CH_2}$, a crystalline substance which was originally made from alloxantin, but can be synthesised by heating malonic acid with urea in presence of phosphorus oxychloride (Grimaux, 1879).

When barbituric acid is boiled with potassium nitrite solution, it is converted into isonitroso-barbituric or violuric acid, $\mathrm{CO}<\begin{matrix}\mathrm{NH.CO}\\\mathrm{NH.CO}\end{matrix}>\mathrm{C{:}N.OH}$, the oxime of alloxan, and this substance is reduced by hydriodic acid to amido-barbituric acid or uramil, $\mathrm{CO}<\begin{matrix}\mathrm{NH.CO}\\\mathrm{NH.CO}\end{matrix}>\mathrm{CH.NH_2}$, a basic, crystalline substance, which can also be made by boiling alloxantin with ammonium chloride solution.

On boiling uramil with aqueous potassium cyanate, the potassium salt of pseudo-uric acid is formed, $\mathrm{CO}<\begin{matrix}\mathrm{NH.CO}\\\mathrm{NH.CO}\end{matrix}>\mathrm{CH.NH.CO.NH_2}$, a crystalline substance isomeric with monohydrated uric acid (Baeyer, 1864). The conversion of the uramil into the pseudo-uric acid is parallel to that of ammonium cyanate into urea.

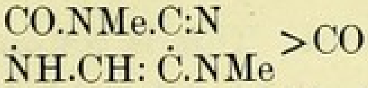
Finally, by heating pseudo-uric acid with anhydrous oxalic acid, it is dehydrated to uric acid (Fischer, 1895)—

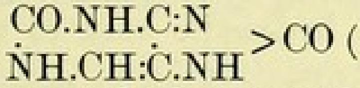
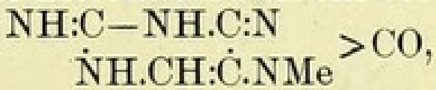


$$\begin{matrix}\mathrm{NH.CO.CH.NH}\\\dot{\mathrm{C}}\mathrm{O.NH.}\dot{\mathrm{C}}\mathrm{O.\ \ NH_2}\end{matrix}>\mathrm{CO}=\begin{matrix}\mathrm{NH.CO.C.NH}\\\dot{\mathrm{C}}\mathrm{O.NH.}\dot{\mathrm{C}}\mathrm{.NH}\end{matrix}>\mathrm{CO}+\mathrm{H_2O}$$

The first synthesis of uric acid was effected by heating urea with glycosine (p. 222), and was suggested by the reduction of the acid to glycosine, carbon dioxide and ammonia, when heated with hydriodic acid (Horbaczewski, 1883).

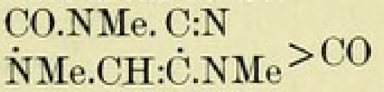
Theobromine and Caffeïne.—The active principles of tea, coffee and cocoa are two basic substances, closely related to uric acid. Theobromine, the active alkaloid of cocoa, is readily extracted from powdered cocoa beans by boiling them with water. The tannin, etc., is precipitated from the infusion with lead acetate, and after removing the lead with hydrogen sulphide, the theobromine is extracted with alcohol from the evaporated residue.

Theobromine,  $\genfrac{}{}{0pt}{}{\text{CO.NMe.C:N}}{\text{NH.CH: C.NMe}}>\text{CO}$ (Woskresensky, 1842), is a bitter, crystalline powder, which forms salts with acids, as well as with metals. Its molecular formula as a monacid base follows from the analysis of its platinochloride, and its relation to uric acid is established by its oxidation by chlorine water to methyl-alloxan and methyl-urea (Fischer, 1882). Its constitution is confirmed, moreover, by its synthetic relations to xanthine and caffeine.

Xanthine,  $\genfrac{}{}{0pt}{}{\text{CO.NH.C:N}}{\text{NH.CH:C.NH}}>\text{CO}$ (Marcet, 1819), is a white amorphous substance, which occurs in the animal organism and in tea, but is best prepared by the action of nitrous acid on the corresponding imido-compound, guanine,  $\genfrac{}{}{0pt}{}{\text{NH:C}-\text{NH.C:N}}{\text{NH.CH:C.NMe}}>\text{CO}$, a base which occurs in guano. Both guanine and xanthine are oxidised by chlorine water, in precisely the same way as theobromine, and therefore also contain the uric acid nucleus. Guanine yields guanidine (p. 226), together with parabanic acid and carbon dioxide—the oxidation products of alloxan—and xanthine yields urea and alloxan itself.

Now xanthine is a semi-acid substance, like uric acid, and when its lead salt is heated with methyl iodide, it is converted into dimethyl-xanthine. This is identical with theobromine (Fischer, 1882). Similarly, when silver theobromine is heated with methyl iodide, it is converted into methyl-theobromine or trimethyl-xanthine. This base is identical with caffeïne or theïne, the alkaloid of tea and coffee (Strecker, 1861).

Caffeïne is best extracted from tea, in the same way as theobromine from cocoa, and is physiologically and chemically identical with the product from coffee.

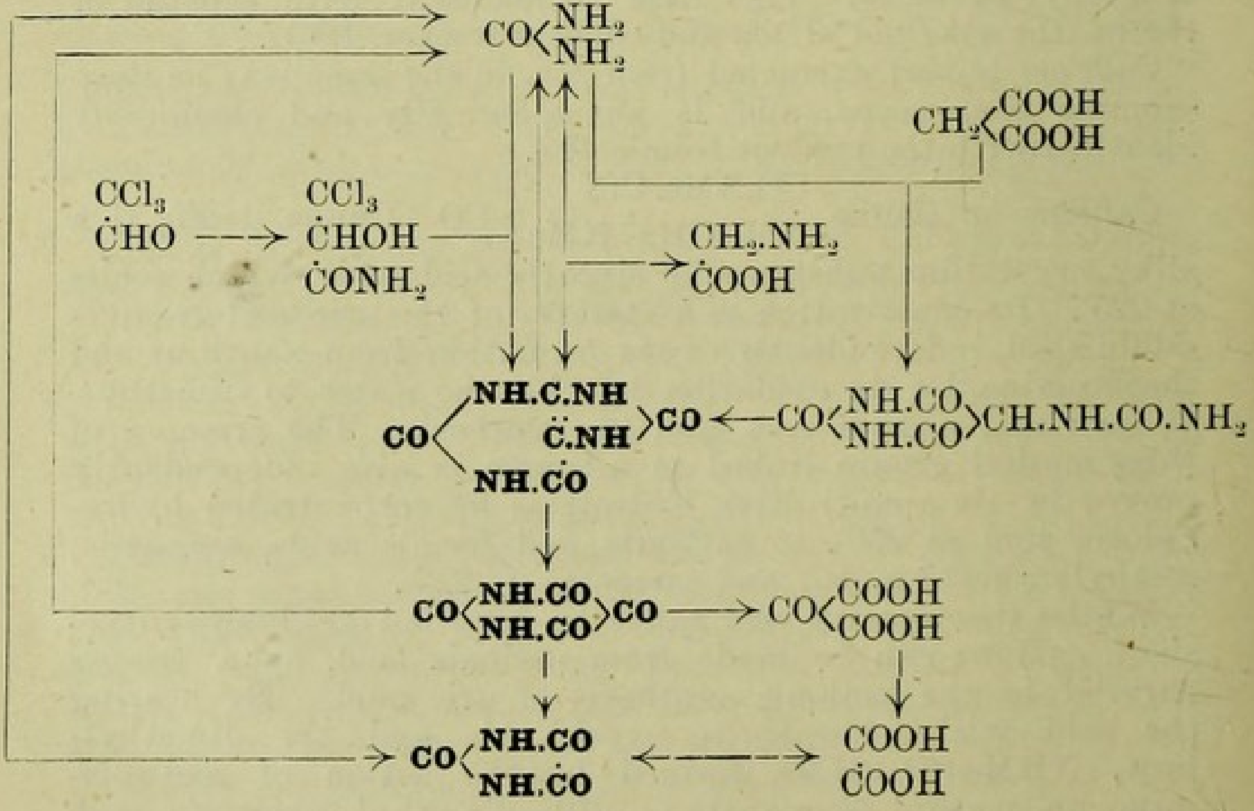
Caffeïne or theïne,  $\genfrac{}{}{0pt}{}{\text{CO.NMe. C:N}}{\text{NMe.CH:C.NMe}}>\text{CO}$ (Runge, 1820), is a silky, crystalline substance, of slightly acid taste, which melts at 225°. Its constitution as a member of the uric acid group is established, independently of its formation from xanthine and theobromine, by its oxidation by chlorine water to dimethyl-alloxan and methyl-urea, and by synthesis. The presence of three methyl groups linked to nitrogen is also independently proved by its quantitative hydrolysis by concentrated hydrochloric acid at 250°, to carbonic and formic acids, ammonia, methylamine (2 mols.), and sarcosine (p. 223).

Whilst theobromine and xanthine have not yet been synthesised, caffeïne can be made from malonic acid, by a process parallel to the malonic synthesis of uric acid. By heating the acid with phosphorus oxychloride and the dimethyl-urea, NHMe.CO.NHMe, formed by the action of methylamine on methyl isocyanate (p. 210), dimethyl-barbituric acid,

$CO<\begin{matrix}NMe.CO\\NMe.CO\end{matrix}>CH_2$ is formed. This is convertible by a series of operations, precisely parallel to those of the uric acid synthesis, into γ-dimethyl-uric acid, $\begin{matrix}CO.NMe.C.NH\\\dot{N}Me.CO.\ddot{C}.NH\end{matrix}>CO$. The dimethyl-uric acid is converted by phosphorus pentachloride into chloro-dimethyl-xanthine, $\begin{matrix}\dot{C}O.NMe.\ \dot{C}{:}N\\\dot{N}Me.CCl{:}\dot{C}.NH\end{matrix}>CO$, the dichloro-compound first formed losing hydrogen chloride, and this chloro-xanthine is reduced by hydriodic acid to theophylline, $\begin{matrix}\dot{C}O.NMe.\ \dot{C}{:}N\\\dot{N}Me.CH{:}\dot{C}.NH\end{matrix}>CO$, the dimethyl-xanthine isomeric with theobromine. Finally, when silver theophylline is heated with methyl iodide, it is converted into methyl-theophylline, $\begin{matrix}\dot{C}O.NMe.\dot{C}{:}N\\\dot{N}Me.CH{:}\dot{C}.NMe\end{matrix}>CO$, which is identical with methyl-theobromine and caffeïne (Fischer, 1895).

Synopsis.—Uric acid, an important constituent of mammalian urine, and the chief constituent of the urine of birds and snakes, is a complex ureïde, or urea amide. Theobromine and caffeine, the active constituents of tea, coffee, and cocoa, are intimately related to it.

URIC ACID.



CHAPTER XXXIV

THE CYANOGEN COMPOUNDS

The Double Cyanides.—Besides the alkyl cyanides or nitriles, which have been already incidentally considered, there are numerous other cyanogen compounds. Some of these are purely organic in character, whilst others approximate in their behaviour to the inorganic halogen salts. The utility of the alkyl cyanides in synthesis is due to this dual character. In their sensitiveness to change, they must be classed with the unsaturated organic compounds, whilst, in the mode of their formation, they are closely allied to the inorganic chlorides. Cyanogen is sometimes termed, therefore, the organic halogen.

The chief source of cyanogen is potassium ferrocyanide, which is manufactured by fusing potassium carbonate with scrap iron and nitrogenous organic matter, such as hoof-parings. The alkali cyanide which is initially formed, as in the cyanide test for nitrogen, acts on the ferrous hydroxide or carbonate, liberating alkali and generating the ferrocyanide. The latter may in fact be made by simply boiling ferrous sulphate with excess of potassium cyanide. The melt is extracted with water, and the ferrocyanide re-crystallised until pure—

$$Fe(OH)_2+6KCN=K_4Fe(CN)_6+2KOH.$$

Potassium ferrocyanide, $K_4Fe(CN)_6+H_2O$ (Macquer, 1750), forms large, transparent, lemon-yellow plates, which are tough and difficult to powder. It is not poisonous. The corresponding acid, hydroferrocyanic acid, $H_4Fe(CN)_6$, separates as a white precipitate on adding concentrated hydrochloric acid to a cold solution of the potassium salt.

The ferrocyanides of the heavy metals are insoluble in water, and are therefore precipitated by the addition of potassium ferrocyanide to metallic solutions. Prussian blue, or ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ (Diesbach, 1704), is a dark blue powder formed in this way from ferric salts. As already stated, it forms a convenient test for organic nitrogen. The cyanide formed by igniting a portion of the nitrogenous matter with metallic sodium is dissolved in water, a little ferrous sulphate and ferric chloride are added, and the solution made alkaline if necessary with caustic soda. The product is then warmed and acidified with dilute hydrochloric acid, and if nitrogen is present, a blue colour is developed.

Copper and potassium-ferrous ferrocyanides are the familiar reddish-brown and light-blue (white) precipitates used in testing for cupric and ferrous salts. The insoluble ferrocyanides are all hydrolysed by caustic alkalies. Prussian blue, for example, is converted into ferric hydroxide and the alkali ferrocyanide (Macquer).

When a solution of potassium ferrocyanide is saturated with chlorine, it darkens in colour, and on concentrating the product, an oxidation product, potassium ferricyanide separates—

$$2K_4Fe(CN)_6+Cl_2=2K_3Fe(CN)_6+2KCl.$$

Potassium ferricyanide, $K_3Fe(CN)_6$ (Gmelin, 1822), crystallises in dark red prisms, and dissolves to a brownish solution. Its ferrous salt, Turnbull's blue, is a dark blue precipitate, which is probably identical with Prussian blue. Ferric ferricyanide is soluble in water, however, and greenish brown in colour.

These double cyanides may be regarded as molecular compounds of the alkali cyanides with ferrous or ferric cyanide, $Fe(CN)_2+4KCN$, but it is more probable that the three cyanogen groups are combined in a ring, as in cyanuric acid.

The Simple Cyanides.—The synthesis of potassium cyanide from Inorganic materials has been already dealt with (p. 58). The salt is usually manufactured by heating the ferrocyanide, either alone, when ferrous carbide is formed, and some nitrogen liberated, or with potassium carbonate, when the iron separates in the metallic state, and the whole of the nitrogen is retained, partly as cyanate. This mixture of cyanide and cyanate constitutes the ordinary product of commerce. The pure salt may be prepared by neutralising hydrocyanic acid with potash, and precipitating the solution with alcohol—

$$5KCN+KCNO \leftarrow K_4Fe(CN)_6 \rightarrow 4KCN+FeC_2+N_2,$$

Potassium cyanide, KCN, is a deliquescent crystalline substance, which closely resembles the corresponding halogen compounds in its actions. It precipitates silver cyanide in white curds from solutions of silver salts, and this precipitate, like silver chloride, is soluble in ammonia, and reprecipitated by nitric acid. It differs from the chloride, however, in that it is redissolved by excess of the alkali cyanide, owing to the formation of a soluble double salt, AgCN,KCN.

Hydrocyanic acid, HCN, as already mentioned, is a volatile liquid, boiling at 26°. Although its salts are analogous to those of the halogen acids, its acid properties are very feeble. Its solution only faintly reddens litmus, and potassium cyanide is decomposed even by the carbon dioxide of the air. Hydrogen cyanide can be made from ammonium formate, as well as from the cyanides and formamide (p. 57), and, as already mentioned, it can be synthesised from chloroform and acetylene (pp. 115, 111).

When mercuric oxide is dissolved in warm dilute hydrocyanic acid, or mercuric sulphate is boiled with potassium ferrocyanide, mercuric cyanide is formed. In the latter case, on filtering the hot product from the potassium ferrous ferrocyanide, which is formed from the ferrous sulphate initially produced, the mercuric cyanide rapidly crystallises—

$$2K_4Fe(CN)_6+3HgSO_4=3Hg(CN)_2+3K_2SO_4+K_2Fe[Fe(CN)_6]$$

Mercuric cyanide, $Hg(CN)_2$, is a colourless crystalline substance, resembling mercuric chloride. It is not an electrolyte, however, and mercury is therefore not precipitated from its solution by the ordinary agents, with the exception of metallic zinc. The solution must therefore be boiled with this metal before the cyanogen radicle can be detected.

Cyanogen.—When dry mercuric cyanide is heated, it is resolved into mercury and cyanogen, C_2N_2, in the same way as mercuric oxide into the metal and oxygen. The gas may also be prepared by warming copper sulphate solution with potassium cyanide, cuprous cyanide being precipitated, and it can be synthesised from its elements by passing electric sparks between carbon terminals in an atmosphere of nitrogen—

$$\begin{tikzcd}
2CuSO_4+4KCN \arrow[r] & CN.CN & Hg(CN)_2 \arrow[l] \\
 & & 2C+N_2 \arrow[ul]
\end{tikzcd}$$

Cyanogen, CN.CN (Gay-Lussac, 1815—*κυανος*=blue) is a colourless, intensely poisonous gas, which condenses at 21° to a colourless liquid, freezing at 32°. Like most of its compounds, it burns with a coloured (pink-mantled) flame; but in the absence of oxygen, it is stable even at very high temperatures, and occurs in blast furnace gases.

The molecular formula of the gas follows from its density and chemical relations, and is confirmed by analysis. On exploding 5 c.c. with 10 c.c. of oxygen, for example, 10 c.c. of carbon dioxide and 5 c.c. of nitrogen are formed, so that

$$x+2O_2=2CO_2+N_2$$
$$\text{and } x=2CO_2+N_2-2O_2=C_2N_2.$$

Cyanogen is thus analogous to chlorine in constitution, the monovalent radicles uniting in the same way as the atoms of the halogen. The cyanogen radicle, in fact, was the first organic radicle isolated. The analogy extends to several other of its actions. Thus, on passing the gas into caustic potash, potassium cyanide and cyanate are formed in equal proportions, in the same way as the chloride and hypochlorite from chlorine, and similarly by heating potassium in cyanogen, potassium cyanide is formed—

$$KCN \leftarrow CN.CN \rightarrow KCN+KCNO.$$

In the latter case, however, part of the cyanogen is polymerised to a brown solid, paracyanogen $(C_2N_2)_x$. This is formed whenever the gas is heated, and thus occurs in its preparation from mercuric cyanide.

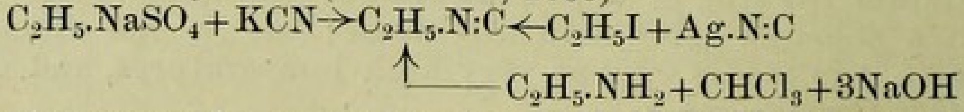
Like hydrocyanic acid, cyanogen has organic as well as inorganic relations, and thus, as already stated, it is the nitrile of oxalic acid.

It is accordingly formed by heating either oxamide or ammonium oxalate with phosphorus pentoxide, and conversely is convertible into the substances by hydration. Ammonium oxalate is formed, amongst other products, by simply heating an aqueous solution of cyanogen, whilst oxamide results, under the same conditions, if a trace of aldehyde be present—

$$COONH_4.COONH_4 \longleftrightarrow CONH_2.CONH_2 \longleftrightarrow CN.CN.$$

The Alkyl Cyanides.—Hydrocyanic acid forms two classes of alkyl derivatives. In addition to the ordinary cyanides or nitriles, in which the alkyl is linked to the cyanogen carbon (p. 57), there is a group of isomeric compounds termed the isocyanides or carbamines, in which the alkyl is linked to the nitrogen. These compounds are formed to some extent in the preparation of the normal cyanides from the alkyl sulphates, but they are more conveniently made in other ways.

Ethyl isocyanide, for example, constitutes the oily impurity in the preparation of ethyl cyanide from ethyl sodium sulphate (Gautier, 1868), and can be made in a similar manner by heating ethyl iodide with silver cyanide. It is best prepared, however, by warming an alcoholic solution of ethylamine and chloroform with caustic alkali. The reaction is the same as that involved in the conversion of chloroform and ammonia into potassium cyanide (Hofmann, 1868)—



$$\begin{tikzcd}[column sep=small] C_2H_5.NaSO_4+KCN \arrow[r] & C_2H_5.N{:}C & C_2H_5I+Ag.N{:}C \arrow[l] \\ & & C_2H_5.NH_2+CHCl_3+3NaOH \arrow[ul] \end{tikzcd}$$

Ethyl isocyanide or carbamine, $C_2H_5.N{:}C$ (Hofmann, 1867), is a colourless liquid, which boils at 77°, and is further distinguished from propionitrile by its rank and offensive odour, and by its insolubility in water and dilute acids.

The constitution of the isocyanide as a carbamine follows from its formation from ethylamine and chloroform, and from its converse hydrolysis by concentrated hydrochloric acid to ethylamine and formic acid—

$$C_2H_5.NH_2+CHCl_3 \rightarrow C_2H_5.N{:}C \rightarrow C_2H_5.NH_2+H.COOH.$$

In silver cyanide, and perhaps in potassium cyanide, the metal thus appears to be linked to nitrogen, and as both salts can be prepared from the acid, it would seem that the latter is represented by two constitutional formulæ, $H.C{\vdots}N$ and $H.N{:}C$. Either formula is consistent with its decompositions. As a normal cyanide, it yields a fatty acid, and ammonia, whilst as an isocyanide, it yields formic acid and an amine; in this case ammonia itself. But once the hydrogen is replaced by alkyl, these decompositions diverge. On the one hand, substituted fatty acids and ammonia are formed, and on the other hand substituted ammonias and formic acid.

The Cyanates and Cyanurates.—The conversion of potassium cyanide into the cyanate has been already described (p. 197). The corresponding acid cannot be prepared from this potassium salt, but, as already noted, is formed by dry-distilling cyanuric acid—

$$C_3H_3N_3O_3=3HCNO.$$

Cyanic acid, CN.OH (Wöhler, 1824), is a volatile acid liquid, resembling acetic acid in odour. It is very unstable, the pure liquid polymerising above 0°, with explosive violence, to a white substance, cyamelide, resembling porcelain, and its aqueous solution is hydrolysed to carbon dioxide and ammonia at the same temperature—

$$CN.OH+H_2O=CO_2+NH_3.$$

The chloride of the acid is formed by the action of chlorine on mercuric cyanide or aqueous hydrocyanic acid.

Cyanogen or cyanic chloride, CN.Cl, is an extremely pungent and poisonous gas, which condenses at $-15°$, and freezes at $-18°$. It is hydrolysed by alkalies in the normal manner to the alkali chloride and cyanate, and when its vapour is led into concentrated ammonia, it is converted, also normally, into the corresponding amide. The latter is best prepared, however, by the action of mercuric oxide on thiocarbamide (p. 211).

Cyanamide, $CN.NH_2$, is a crystalline substance, melting at 40°. As an ammonia derivative, it forms salts with the stronger acids, but owing to the influence of the electro-negative cyanogen, its acid properties are the more prominent. Thus, on adding ammoniacal silver nitrate to an aqueous solution of the amide, the white silver salt, CN_2Ag_2, is precipitated.

Cyanamide combines with water, forming carbamide, to which it is thus related in the same way as acetonitrile to acetamide. It has been used also in the synthesis of various physiological products such as creatine (p. 227)—

$$CS(NH_2)_2 \rightarrow CN.NH_2 \rightarrow CO(NH_2)_2.$$

Corresponding with the cyanides and isocyanides, there are two classes of alkyl cyanates. The normal salts are formed by the action of cyanogen chloride on the sodium alkyloxides.

Ethyl cyanate, $C_2H_5.O.CN$, is a colourless oil, which is formed when cyanogen chloride is passed into alcoholic sodium ethoxide. It is hydrolysed by aqueous caustic soda to alcohol, carbon dioxide and ammonia, and the alkyl is therefore linked to the cyanogen through oxygen, and not directly to carbon or nitrogen—

$$CN.Cl+NaOEt \rightarrow CN.O.Et \rightarrow CO_2+NH_3+EtOH.$$

The isocyanates are formed in the same way as the isocyanides, and are hydrolysed in an analogous manner by alkalies. Ethyl isocyanate, for example, is formed either by distilling a dry mixture of ethyl potassium sulphate and potassium cyanate, or by heating silver cyanate with ethyl iodide.

Ethyl isocyanate, $C_2H_5.N{:}CO$ (Wurtz, 1848), is a liquid which boils at 60°, and has a very pungent and unpleasant odour. It is hydrolysed by caustic soda to sodium carbonate and ethylamine—

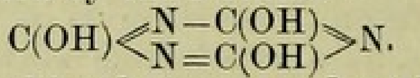
$$\mathrm{Et.KSO_4 + KNCO \rightarrow Et.N{:}CO \leftarrow EtI + Ag.N{:}CO}$$
$$\mathrm{\rightarrow Et.NH_2 + CO_2.}$$

When heated with water, however, in a sealed tube, the isocyanate is converted into a substituted urea, diethylcarbamide, the ethylamine combining with a second molecule in the same way as ammonia with cyanic acid—

$$\mathrm{CO{:}N.Et + NH_2.Et = CO(NHEt)_2.}$$

The cyanuric acid, which is formed by heating urea, and which is resolved into cyanic acid by dry distillation, is a tribasic acid, forming three classes of salts. The hydrogen is in the form of hydroxyl, for when the acid is heated with phosphorus pentachloride, the three hydroxyl groups are replaced by chlorine.

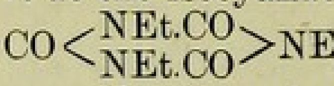
Cyanuric chloride, $C_3N_3Cl_3$, is a crystalline substance melting at 146°. It is also formed by polymerisation when cyanogen chloride is kept in a sealed tube, and is hydrolysed to the alkali cyanurate by alkalies. The constitution of cyanuric acid is probably represented by the formula—



$$\mathrm{C(OH)\lessgtr\begin{matrix}N-C(OH)\\N=C(OH)\end{matrix}\gtrless N.}$$

When cyanuric chloride is warmed with an alcoholic solution of sodium ethoxide, it is converted in the normal manner into the ethyl salt of the acid. Ethyl cyanurate, $C_3N_3(OEt)_3$, is a crystalline substance, which is also formed by spontaneous polymerisation of ethyl cyanate. It is hydrolysed by alkalies to alcohol and the sodium cyanurate, in the normal manner.

When, however, ethyl cyanurate is overheated, it is converted into an isomeric salt, which bears the same relation to it as the isocyanates to the normal salts. Ethyl isocyanurate,



$\mathrm{CO\lessgtr\begin{matrix}NEt.CO\\NEt.CO\end{matrix}\gtrless NEt}$, is a crystalline substance resembling the normal cyanurate, but it is resolved by caustic soda into sodium carbonate and ethylamine, so that the alkyl groups are attached to nitrogen.

The Thiocyanates.—Potassium cyanide combines with sulphur as readily as with oxygen, forming potassium thiocyanate or sulphocyanide. The salt is most economically prepared by fusing potassium ferrocyanide with potassium carbonate and sulphur, and is extracted from the cooled melt with hot alcohol. The corresponding ammonium salt is made by the action of alcoholic ammonia on carbon bisulphide. The mixture is kept for a day or two in the cold, and, on distilling the product, ammonium sulphide passes over, whilst an impure alcoholic solution of the thiocyanate remains. Ammonium thiocyanate is also formed when hydrocyanic acid is evaporated to dryness with yellow ammonium sulphide—

$$\mathrm{CS_2 + 4NH_3 \rightarrow NH_4.CNS \leftarrow HCN + (NH_4)_2S_2.}$$

Potassium thiocyanate, KCNS (Porret, 1814), is a deliquescent salt, which is extremely soluble in water, and the ammonium salt is very similar. The free acid, thiocyanic acid, HCNS, obtained by distilling either salt with dilute sulphuric acid, is a pungent liquid. It is hydrolysed to ammonia and carbon oxysulphide by more concentrated acid. Other thiocyanates of interest are the ferric salt, which dissolves to an intensely red solution in water, and hence serves as a delicate test both for ferric iron and for hydrocyanic acid; and the mercuric salt, an amorphous, grey precipitate, which swells up curiously when burned.

When ammonium thiocyanate is heated for some time at 170°, it is transformed into thiocarbamide, in precisely the same way as ammonium cyanate into carbamide itself. Thiocarbamide or thiourea, $CS(NH_2)_2$ (Reynolds, 1869), is a silky, crystalline substance, which melts at 169°, and resembles urea in its actions.

As in the previous cases, there are two classes of alkylic thiocyanates. The normal salts are formed by the interaction of the alkyl iodides with the alkali thiocyanates. Ethyl thiocyanate, $C_2H_5.S.CN$, is a liquid boiling at 141°. It is hydrolysed by caustic soda to sodium cyanide and cyanate, and an alkylic sulphur derivative, ethyl disulphide, so that the ethyl is attached to the sulphur, and not to the cyanogen—

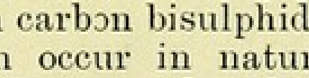
$$K.S.CN + EtI \rightarrow Et.S.CN \rightarrow NaCN + NaCNO + Et_2S_2.$$

The isothiocyanates are made from carbon bisulphide and the primary amines, and some of them occur in nature as the mustard oils. As already stated, black mustard seed contains a glucoside, potassium myronate, $C_{10}H_{18}KO_{10}NS_2$, which is hydrolysed by an accompanying enzyme, myrosin, to glucose, potassium hydrogen sulphate, and allyl isothiocyanate, $C_3H_5.N{:}CS$, or oil of mustard. The oil can be distilled with steam from the product obtained by digesting the ground seed with water.

In synthesising the mustard oils, the amine, ethylamine for example, and carbon bisulphide are dissolved in alcohol. The mixture becomes hot, and at the same time loses its alkaline reaction, and on cooling crystallises to the alkylic dithiocarbamate. On boiling the dithiocarbamate with mercuric chloride solution, the mercuric salt at first precipitated is decomposed into mercuric and hydrogen sulphides, and the isothiocyanate. The latter is distilled off with steam, and the oily layer which collects beneath the water in the receiver dried in the usual manner—

$$NHEt.CS.S.NH_3Et \rightarrow (NHEt.CS.S)_2Hg \rightarrow 2NEt.CS + HgS + H_2S.$$

Ethylamine ethyl-dithiocarbamate,



$CS{<}\begin{matrix}NHEt\\ S.NH_3Et\end{matrix}$, is a crystalline substance analogous to ammonium carbamate. The mode of its formation is precisely parallel in fact to that of the inorganic salt from ammonia and carbon dioxide—

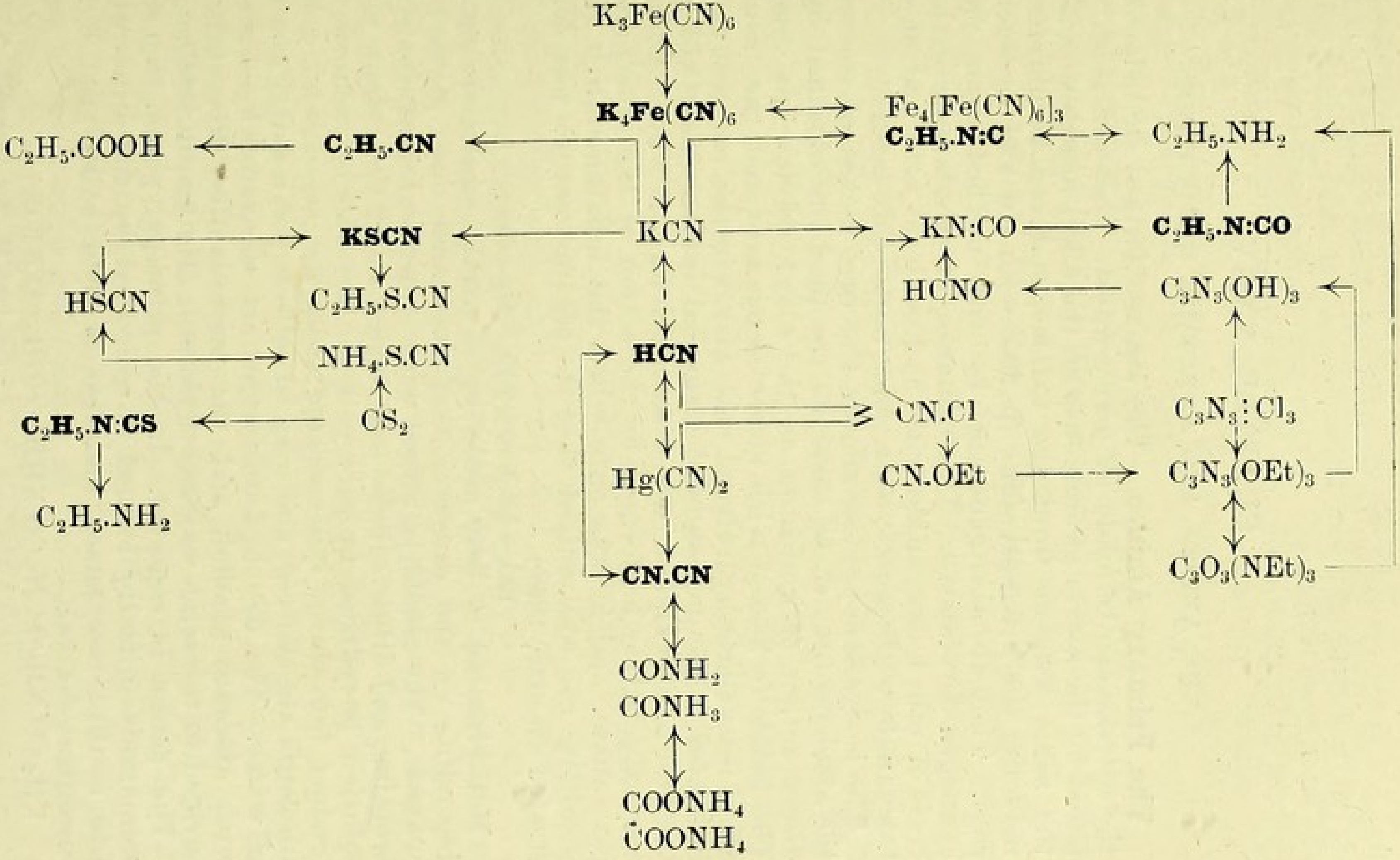
$$CS_2 + 2NH_2.Et = NHEt.CS.S.NH_3Et.$$

Ethyl isothiocyanate or mustard oil, $C_2H_5.N{:}CS$ (Hofmann, 1868), is a liquid which boils at 131°, and has the intensely pungent and characteristic odour of mustard. It is hydrolysed by acids to ethylamine and carbon oxysulphide, or the products of hydrolysis of the latter, and the ethyl group is therefore linked to nitrogen—

$$C_2H_5.N:CS \rightarrow C_2H_5.NH_2 + CO_2 + H_2S.$$

Synopsis.—The cyanogen radicle resembles the halogens in forming metallic salts akin to the haloid salts in stability. On the other hand, the corresponding alkyl salts show the characteristic mobility of organic compounds. All the alkyl cyanogen compounds exist in two isomeric forms, in one of which, the iso-form, the alkyl is linked directly to nitrogen.

THE CYANOGEN COMPOUNDS.



CHAPTER XXXV

THE AMINES AND AMMONIUM DERIVATIVES

The Primary Amines.—The amines formed by reduction of the nitriles can be made in many ways. They are readily prepared by the action of ammonia on the alkyl nitrates (p. 229), in the same way as from the iodides, and can be obtained by reducing the nitro-paraffins (p. 230) with tin and hydrochloric acid. They are also generated by other methods from various cyanogen derivatives. The formation of ethylamine by hydrolysis of ethyl isocyanide with hydrochloric acid, and of ethyl isocyanate with caustic soda, come under this category.

The isocyanate process affords the best means of converting the alcohols into these bases, as the products obtained by the direct action of ammonia on the alkyl iodides are complex. The iodide is heated with silver isocyanate, and the resulting alkyl isocyanate hydrolysed with alkali in the manner already indicated. The process is of historical interest, as ethylamine, the first amine known, was discovered in this way. Ammonia was expected to be formed by the action of the alkali on the isocyanate, and it was only when the inflammability of the resulting gas was noticed that its organic nature was demonstrated (Wurtz, 1848)—

$$\mathrm{EtI} \rightarrow \mathrm{Et.N{:}CO} \rightarrow \mathrm{Et.NH_2} + \mathrm{CO_2}.$$

Methylamine is best made by a partly analogous process, depending on the conversion of acetamide into methyl isocyanate. The amide is mixed with a molecular equivalent of bromine, and dilute caustic soda added until the colour of the solution is reduced to pale yellow. On slowly running this product into warm concentrated soda, the amine and a little ammonia are evolved, and may be collected in a small quantity of water. The dry hydrochlorides are separated by digestion with absolute alcohol, and the methylamine liberated and purified in the same way as ethylamine (Hofmann, 1882).

The action is complex. In the principal phase, the acetobromamide initially formed is converted by the dilute alkali into methyl isocyanate, and this is then hydrolysed by the concentrated alkali—

$$\begin{aligned}&\mathrm{CH_3.CO.NH_2} \rightarrow \mathrm{CH_3.CO.NHBr} \rightarrow [\mathrm{CH_3.CO.NKBr}]\\ &\qquad\qquad\qquad\qquad \hookrightarrow \mathrm{CH_3.N{:}CO} \rightarrow \mathrm{CH_3.NH_2}.\end{aligned}$$

But the change may proceed in two other directions. In the first place, the isocyanate may combine with unchanged acetamide, forming a substituted urea, methyl-acetyl-carbamide, which is slowly hydrolysed to methylamine, ammonia, and the alkali acetate and carbonate—

$$NMe{:}CO + NH_2Ac \rightarrow NHMe.CO.NHAc \rightarrow NH_2.Me + CO_2 + NH_3 + Ac.OH$$

In the second place, the amine itself may be attacked by the bromine and oxidised to the nitrile, probably owing to the formation and debromination of a dibromo-substitution product. With the higher amines this secondary action becomes the principal, and affords a means of descending homologous series of acids. Valeramide, for example, is thus converted almost quantitatively into butyronitrile—

$$C_4H_9.CH_2.CO.NH_2 \rightarrow C_4H_9.CH_2.NH_2 \rightarrow [C_4H_9.CH_2.NBr_2] \rightarrow C_4H_9.NH_2.$$

Methylamine, $CH_3.NH_2$ (Wurtz, 1849), is a gas resembling ammonia, but like ethylamine is inflammable, and easily condensible, at -6°, to a very light, fuming liquid. It is made on a large scale from beet residues (p. 216), and is one of the most soluble gases known, no less than 1,150 c.c. dissolving in 1 c.c. of water at 12°.

From a chemical point of view methylamine and the higher amines resemble their prototype. They are all more basic than ammonia, and form salts which resemble the ammonium salts, except in their solubility in alcohol. The platinochlorides are also characteristic. Like ethylamine, they are not hydrolysed by acids or alkalies, and are converted by nitrous acids into alcohols, which, as previously stated, are mostly secondary. This anomaly is probably due to the transient formation of olefines—

$$CH_3.CH_2.CH_2.NH_2 \rightarrow [CH_3.CH{:}CH_2] \rightarrow CH_3.CHOH.CH_3.$$

The amines resemble ethylamine also in forming evil-smelling isocyanides with chloroform and alcoholic alkali, and pungent mustard oils with carbon bisulphide and mercuric or ferric chloride, and these three reactions afford convenient tests for compounds of this class.

The gradation of physical properties in the amine series is very similar to that observed in the other homologous series. Ethylamine, as already stated, is a liquid boiling at 18°. Propylamine is a similar liquid boiling at 49°. As the series is ascended, the boiling points rise, and the mobility and solubility decrease. Hexylamine, for example, is an oily, insoluble liquid boiling at 128°. The amines are all lighter than water.

The Secondary and Tertiary Amines.—It has been already stated that in preparing ethylamine from ethyl iodide and ammonia, several other compounds are formed. In fact, since ethylamine resembles ammonia in all essentials, it might be expected to act with ethyl iodide in the same way, and this is actually the case—

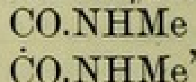
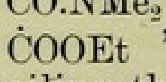
$$C_2H_5I + NH_2.Et = C_2H_5.NHEt.HI.$$

The product thus formed, diethylamine, $NHEt_2$, acts in turn in a precisely similar manner, forming triethylamine hydriodide; and finally, the triethylamine unites with the alkyl haloid, forming an ammonium derivative, triethylamine ethiodide or tetrethylammonium iodide—

$$NHEt_2 \rightarrow NEt_3 \rightarrow NEt_4.I.$$

The actual product obtained by heating ethyl iodide with alcoholic ammonia, is therefore a mixture of all four salts with ammonium iodide. On a large scale, the alkyl bromides give better yields than the iodides.

The separation of these amines is a matter of some difficulty, as the results of fractionation are unsatisfactory. It has been effected in the case of the lower amines by means of ethyl oxalate. The crude mixed methylamine product, for example, is first of all distilled with caustic potash solution, by which the amine and ammonia salts are decomposed, whilst the tetramethylammonium iodide is unaffected.

The aqueous solution of the amines is then shaken with ethyl oxalate, with which the methylamine and dimethylamine interact, forming respectively dimethyloxamide,  $\begin{array}{l}CO.NHMe\\ \dot{C}O.NHMe\end{array}$, and ethylic dimethyloxamate,  $\begin{array}{l}CO.NMe_2\\ \dot{C}OOEt\end{array}$, whilst the trimethylamine remains unchanged. On boiling the product the latter accordingly passes over, and after drying with solid potash, is pure.

The dimethyloxamide, which is a semi-crystalline substance resembling oxamide, dissolves in the water, whilst the ethylic dimethyloxamate, an oily liquid, remains undissolved beneath the solution, and can therefore be separated mechanically.

Finally, on distilling the two portions separately with potash, the dimethyloxamide is hydrolysed to the alkali oxalate and methylamine—

$$NHMe.CO.CO.NHMe + 2KOH = COOK.COOK + 2NH_2.Me,$$

whilst the dimethyloxamate yields dimethylamine, alkali oxalate, and alcohol—

$$NMe_2.CO.COOEt + 2KOH = NHMe_2 + COOK.COOK + Et.OH.$$

The two amines are then dried with solid potash and redistilled (Hofmann, 1862).

Dimethylamine is more conveniently prepared, however, from nitroso-dimethylaniline (p. 284), and trimethylamine is obtained on a large scale from "vinasses," the residual liquor from the distillation of beet alcohol. The solids left on evaporating this liquid are dry-distilled, and the distillate, which contains ammonia, trimethylamine, acetonitrile, and methyl alcohol, is neutralised with hydrochloric acid. The acetonitrile and alcohol are then distilled off (and separated by boiling with lime), and the residual impure chlorides heated at 260°. Methyl chloride and trimethylamine pass over, and methylamine hydrochloride and ammonium chloride remain behind. The two gases are separated by means of acid, and the amine finally regenerated (Vincent, 1874)—

$$3NMe_3,HCl = MeCl + 2NMe_3 + NH_2Me.HCl.$$

Dimethylamine, $NH(CH_3)_2$ (Hofmann, 1851), is a soluble alkaline liquid, which boils at 7°, and resembles ammonia and stale fish in odour. Trimethylamine, $N(CH_3)_3$ (Hofmann), is a similar liquid, which boils at 3°, and has a still more pronounced odour of fish. The odour of herring-brine and hawthorn blossom are, in fact, largely due to this substance. Trimethylamine is used instead of ammonia in making potassium carbonate by the Solvay process, its hydrochloride being much much more soluble than ammonium chloride. The corresponding ethyl compounds boil at comparatively high temperatures.

Whilst di- and trimethylamine resemble the mon-alkyl-compound in forming salts, they differ from it in that they do not form isocyanides with chloroform, or mustard oils with carbon bisulphide. Nitrous acid, too, has no action on the trialkyl-compound, whilst it converts dimethylamine into an oily nitroso derivative without evolution of nitrogen. Dimethylnitrosamine, $NMe_2.NO$, is a yellow oil, boiling at 153°—

$$NH.Me_2 + NO.OH = NMe_2.NO + H_2O.$$

The three amines are also distinguished by their behaviour when heated with excess of methyl iodide. All are converted into the corresponding ammonium iodide, but whilst the trialkyl-amine takes up only one methyl group, the dialkyl-compound takes up two, and the mon-alkyl three, so that the class can be determined by analysing initial and final products—

$$NH_2Me \rightarrow NMe_4.I.$$

The simple and complex amines are termed primary, secondary, or tertiary, accordingly as one, two or three of the ammonia hydrogen atoms are replaced by alkyl. Their isomerism is analogous to that of the ethers and alcohols. Thus there are four compounds of the formula C_3H_9N: two primary amines, propylamine and isopropylamine, $C_3H_7.NH_2$; one secondary, methyl-ethyl-amine, $CH_3.NH.C_2H_5$; and one tertiary, trimethylamine, $N(CH_3)_3$. Trimethylamine was originally thought to be propylamine, and the recognition of this and similar cases of isomerism formed a strong confirmation of the theory of structure. The mixed amines are formed by the interaction of the simple amines with alkyl iodides, methyl-ethyl-amine, for example, from methylamine and ethyl iodide or ethylamine and methyl iodide—

$$NH_2Me + EtI \rightarrow NHMeEt,HI \leftarrow NH_2Et + MeI.$$

The Ammonium Compounds.—The residue left on distilling the interaction product of ethyl iodide and ammonia with potash contains, as indicated above, a substituted ammonium iodide, which may be crystallised from the solution.

Tetrethyl-ammonium iodide, $NEt_4.I$ (Hofmann, 1851) is a crystalline substance, which resembles ammonium chloride in appearance. It is difficultly soluble in cold water, however, and, unlike the amine hydrochloride, practically insoluble in alcohol. At a temperature a little above its melting point it is resolved into triethylamine and ethyl iodide, but is formed again when these substances are heated together in a sealed tube—

$$NEt_3 + EtI \longleftrightarrow NEt_4.I.$$

As stated above, it is not affected by caustic alkalies, but it is converted by digestion with moist silver oxide into a substitution product of ammonium hydroxide, $NH_4.OH$, and this is strikingly similar to the caustic alkalies in appearance and actions.

Tetrethyl-ammonium hydroxide, $NEt_4.OH$ (Hofmann, 1862), is a crystalline, deliquescent substance, which, like caustic potash, is highly alkaline and greasy to the touch. It forms salts with even greater energy than the inorganic alkali, and rapidly absorbs carbon dioxide, forming a stable carbonate. It precipitates metallic hydroxides from their solutions, and even saponifies fats, and that it is a stronger base even than caustic potash is shown by the inability of the latter to liberate it from its salts.

When the hydroxide is distilled, it is resolved into triethylamine and alcohol, but that it is not a molecular compound of these substances is shown in the first place by its forming salts with acids in the same way as the caustic alkalies, with elimination of water, and in the second place by the non-existence of isomerism in the mixed ammonium salts. Dimethyl-diethyl-ammonium iodide is formed equally well from dimethyl-ethyl-amine and ethyl iodide, as from methyl-diethyl-amine and methyl-iodide, whereas if the ammonium iodide and hydroxide were molecular compounds, two different substances, of the formulæ NMe_2Et,EtI and $NMeEt_2,MeI$, would be formed. The ammonium theory of Inorganic Chemistry thus receives striking confirmation—

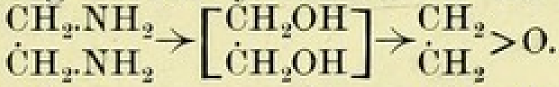
$$\begin{tikzcd}
NMe_2Et. + EtI \arrow[r] & NMe_2Et_2.I \arrow[d, leftrightarrow] & NMeEt_2 + MeI \arrow[l] \\
 & NMe_2Et_2.OH &
\end{tikzcd}$$

The Diamines.—Although the amines are best regarded as derivatives of ammonia, they may also be considered as substitution products of the hydrocarbons, methylamine for example as amido- or amino-methane. From this point of view there may be expected poly-amido-derivatives analogous to the glycols. Several such classes are known, of which the chief are the diamines. Ethylene diamine, for example, the analogue of glycol, is obtained by the action of alcoholic ammonia on ethylene bromide at 100°, and by the reduction of cyanogen with sodium in alcoholic solution, in the same way as methylamine from hydrogen cyanide—

$$CH_2Br.CH_2Br \rightarrow NH_2.CH_2.CH_2.NH_2 \leftarrow CN.CN.$$

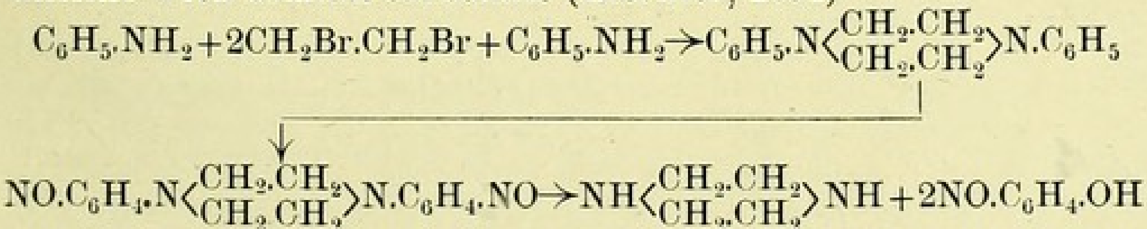
Ethylene diamine or 1-2-diamino-ethane, $\begin{array}{l}CH_2.NH_2\\ \dot{C}H_2.NH_2\end{array}$, (Cloëz, 1853), is an alkaline liquid of ammoniacal odour, boiling at 123°. It forms additive salts with acids in the same way as the monamines, but as the molecule contains two basic nitrogen atoms, twice as much acid is neutralised as by a molecular proportion of a monamine. Similarly, the salts thus formed, such as the dihydrochloride, $C_2H_4(NH_2)_2,2HCl$, are convertible into diplatinochlorides, $C_2H_4(NH_2)_2,2HCl,PtCl_4$, which contain only one molecule of the base per atom of platinum, instead of two, as with the monamines (p. 54). The number of basic nitrogen atoms is thus readily determined.

Ethylene diamine, like all amines, is not decomposed by alkalies or acids, and is converted by nitrous acid into ethylene oxide, glycol being obviously formed in the first instance—



$$\begin{array}{l}CH_2.NH_2\\ \dot{C}H_2.NH_2\end{array} \rightarrow \left[\begin{array}{l}CH_2OH\\ \dot{C}H_2OH\end{array}\right] \rightarrow \begin{array}{l}CH_2\\ \dot{C}H_2\end{array}\!\!>O.$$

There are diamines corresponding with the secondary and tertiary amines, and formed in an analogous manner. The secondary compound diethylene-diamine, for example, is formed by the interaction of ethylene diamine with ethylene bromide, and therefore by the action of alcoholic ammonia on ethylene chloride. It is best prepared, however, by the hydrolysis with alcoholic potash of the dinitroso-compound of diphenyl-piperazine (compare Nitroso-dimethyl-aniline, p. 284), a crystalline substance formed by heating a mixture of ethylene bromide and aniline with sodium carbonate (Bischler, 1891)—

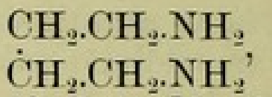
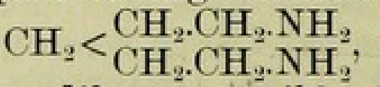


$$C_6H_5.NH_2+2CH_2Br.CH_2Br+C_6H_5.NH_2 \rightarrow C_6H_5.N\langle\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}\rangle N.C_6H_5$$

$$NO.C_6H_4.N\langle\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}\rangle N.C_6H_4.NO \rightarrow NH\langle\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}\rangle NH+2NO.C_6H_4.OH$$

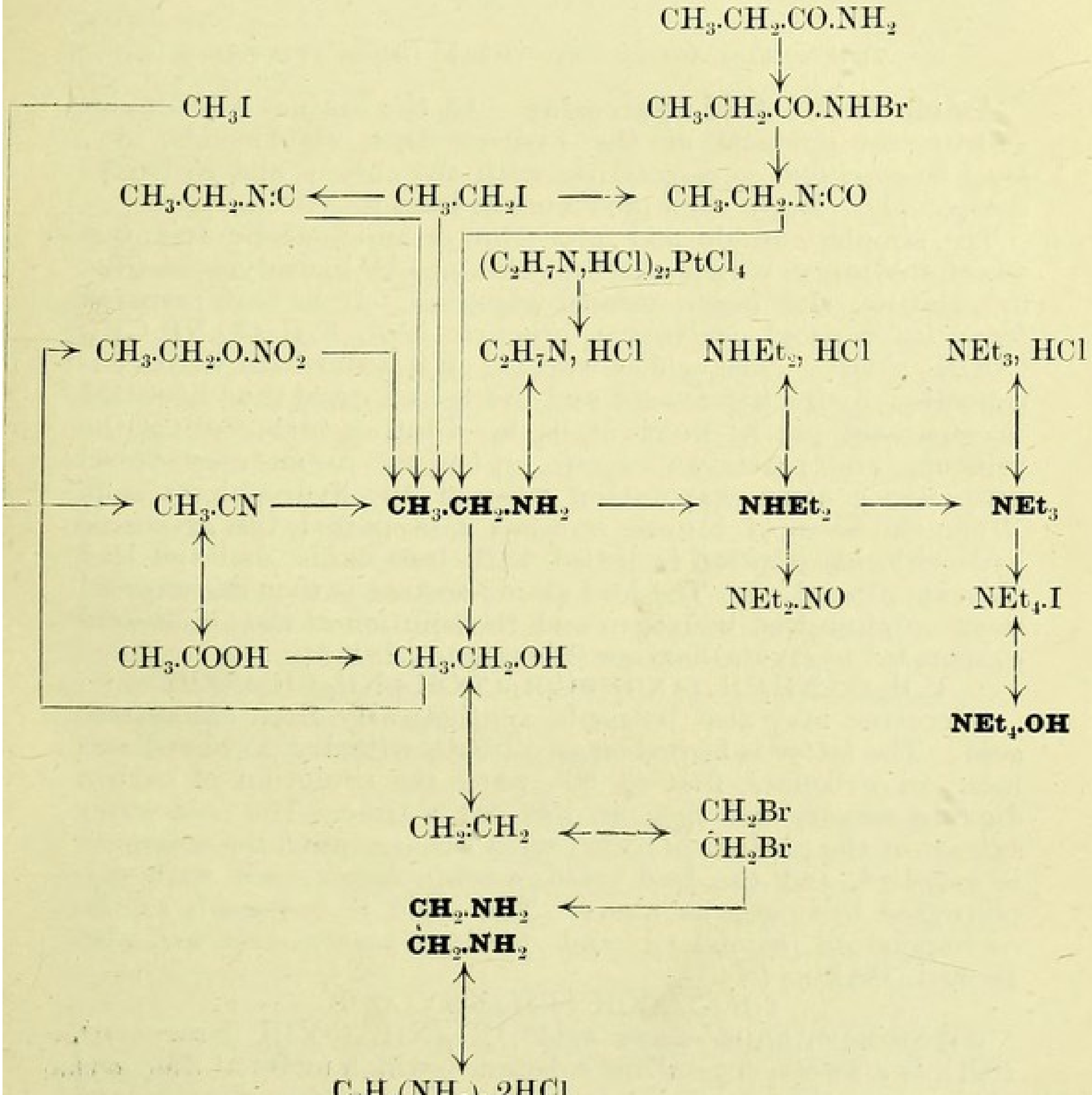
Diethylene-diamine or piperazine, $NH<\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}>NH$ (Cloëz, 1853), is a crystalline basic substance, melting at 104°, which is closely akin to the natural alkaloids (p. 392). On account of the ready solubility of its urate, it has been stated to be of utility in diseases such as gout, in which uric acid is deposited in the system.

The higher homologues of ethylene diamine are of importance on account of the identity of some of them with the ptomaïnes or animal alkaloids, formed by the putrefactive action of pathological bacteria on albumen and related animal products. The tetramethylene compound, for example, is formed by the reduction of ethylene cyanide with sodium amalgam in alcoholic solution, and the pentamethylene compound is made from trimethylene cyanide in a similar manner. The latter cyanide is made synthetically from the corresponding bromide, which is formed by the addition of hydrobromic acid to allyl bromide.

Tetramethylene-diamine or putrescine,  $\begin{array}{l}CH_2.CH_2.NH_2\\ \vdots \\ CH_2.CH_2.NH_2\end{array}$, is an alkaline liquid boiling at 158°. Pentamethylene diamine, or cadaverine,  $CH_2<\begin{array}{l}CH_2.CH_2.NH_2\\ CH_2.CH_2.NH_2\end{array}$, is a similar liquid, boiling at 178°; it is readily convertible into piperidine (p. 385), an alkaloid obtained from pepper.

Synopsis.—The amines may be regarded as derived either from ammonia by replacing hydrogen by one or more alkyl groups, or from the hydrocarbons by thus replacing one or more amido-groups. They are all highly basic substances, which form ammonium salts with acids and alkyl iodides, and are not hydrolysed by alkalies.

THE AMINES AND AMMONIUM DERIVATIVES.



CHAPTER XXXVI

THE AMIDO-ACIDS AND THEIR DERIVATIVES

Amido-Acetic Acid: Sarcosine.—As the amines are amido-substitution-products of the hydrocarbons, amido-acids, etc., may be expected, corresponding with the chloro- and hydroxy-compounds. Many such products are known.

The simplest amido-acid, glycosine or amido-acetic acid, is a sweet substance, which was first obtained by hydrolysis of glue or gelatine, and hence termed glycocoll. It is best prepared from its benzoyl derivative, hippuric acid, $C_6H_5.CO.NH.CH_2.COOH$ (p. 263). The acid is warmed on a water-bath with concentrated hydrochloric acid, and the benzoic acid thus liberated is separated partly in crystals, by diluting and cooling the solution, and partly as vapour, by boiling in an open vessel with water after evaporating most of the hydrochloric acid. When the odour of benzoic acid has disappeared, the glycosine hydrochloride solution is boiled with lead oxide, and the lead chloride filtered off. The lead amido-acetate is then decomposed with sulphuretted hydrogen and the solution of the amido-acid evaporated to crystallisation (Dessaignes, 1846)—

$$C_6H_5.CO.NH.CH_2.COOH \rightarrow C_6H_5.COOH + NH_2.CH_2.COOH.$$

Glycosine may also be made synthetically from chloracetic acid. The latter is heated on an oil-bath with dry powdered ammonium carbonate, first at 90°, until the evolution of carbon dioxide ceases, and then at 130° for a time. The cold-water extract of the product is boiled with litharge until the ammonia is expelled, and the lead amido-acetate decomposed with sulphuretted hydrogen as above. The yield is not good, as the corresponding secondary and tertiary amido-acids are also formed (Perkin, 1859)—

$$CH_2Cl.COOH \rightarrow CH_2(NH)_2.COOH.$$

Glycosine or amido-acetic acid*, $CH_2(NH_2).COOH$ (Braconnot, 1821), is a sweet, crystalline substance, which melts at 232°, and at the same time partially decomposes into carbon dioxide and methylamine. The decomposition becomes quantitative when the substance is heated with solid baryta, and is parallel to that of acetic acid into methane and carbon dioxide—

$$CH_2(NH_2).COOH \rightarrow CH_3.NH_2 + NH_3.$$

Owing to the opposite actions of the amido-group and the

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* Better amino-acetic acid.

carboxyl, glycosine is practically a neutral substance, and is not appreciably decomposed by aqueous alkalies or acids. Like acetamide, however, it forms unstable salts, such as glycosine nitrate, $C_2H_5NO_2,HNO_3$, and the deep blue copper amido-acetate, $Cu(C_2H_4NO_2)_2 + H_2O$; and double salts, such as the molecular compound of copper nitrate and copper amido-acetate.

Glycosine differs from acetamide, however, in that it is an amine, and is not hydrolysed by acids or alkalies. That it is a primary amine is proved by its conversion by nitrous acid into the corresponding hydroxy-compound, glycollic acid, which, as already stated, was first made in this way—

$$CH_2(NH_2).COOH \rightarrow CH_2OH.COOH.$$

By the interaction of chloracetic acid with methylamine, a secondary amido-acid is formed, which bears the same relation to glycosine as dimethylamine to methylamine.

Sarcosine or methyl-glycosine, $NHMe.CH_2.COOH$ (Liebig, 1847), is a crystalline substance melting and decomposing at 220°. It occurs naturally in muscle juice, and is formed by the hydrolysis of creatine (p. 227) and caffeïne. Like glycosine it is neutral, and unaffected by acids and alkalies. It is decomposed by heat into carbon dioxide and dimethylamine, and its constitution as a secondary amine is further confirmed by the action of nitrous acid, which converts it into nitroso-sarcosine, $COOH.CH_2.NMe.NO$—

$$NH_2Me + CH_2Cl.COOH \rightarrow NHMe.CH_2.COOH \rightarrow NHMe_2 + CO_2.$$

The Primary Amido-Acids.—The chief of the fatty acid derivatives analogous to glycosine are alanine and leucine. The first can be made synthetically from ammonia and α-chloropropionic acid, and by the hydrolysis of aldehyde-ammonia cyanide with hydrochloric acid—

$$\begin{tikzcd} CH_3.CHCl.COOH \arrow[r] & CH_3.CH(NH_2).COOH & & \\ & & CH_3.CH(NH_2).CN \arrow[ul] & CH_3.CHOH.NH_2. \arrow[l] \end{tikzcd}$$

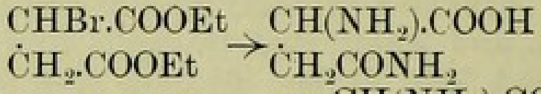
Alanine or α-amido-propionic acid, $CH_3.CH(NH_2).COOH$ (Strecker, 1850), is a crystalline solid, which melts at 255°, and resembles glycosine It is decomposed when heated, quantitatively when heated with lime, into ethylamine and carbon dioxide. It is indifferent to acids, and as a primary amine is converted by nitrous acid into the corresponding hydroxy-compound, lactic acid, which, as already noted, was first synthesised in this manner.

Leucine or α-amido-isocaproic acid, $CHMe_2.CH_2.CH(NH_2).COOH$ (Proust, 1818), a similar crystalline substance, melting at 170°, is present in saliva, and is formed by the alkaline hydrolysis of albumen, and by boiling horn shavings with dilute sulphuric acid. It resembles its lower homologues in every respect, and can be made synthetically from α-brom-isovaleric acid and from isovaleraldehyde.

Besides the monobasic amido-acids there are amido-derivatives of the dibasic acids. The most important of these is amido-succinic acid, a substance which occurs in beet-root, and can be extracted from beet molasses. The corresponding monamide is found in young beans and vetches, and especially in asparagus juice, from which it may be obtained by simple evaporation.

Asparagine or amido-succinamide, $\begin{array}{l}CH_2(NH_2).COOH\\ \dot{C}H_2.CONH_2\end{array}$ (Vauquelin and Robiquet, 1805), is a sweet crystalline substance, which is soluble in water, but insoluble in alcohol. As an amide, it forms salts both with bases and acids, and is hydrolysed by alkalies to the corresponding acid, amido-succinic acid.

The asparagine molecule contains asymmetric carbon, and the compound can therefore be optically active. Both active modifications occur in nature, and as with the tartaric acids, the dextrogyrate variety forms dextro-hemihedral crystals, and the lævogyrate, lævohemihedral. The inactive form is made synthetically by heating ethyl bromosuccinate with strong ammonia at 100°—

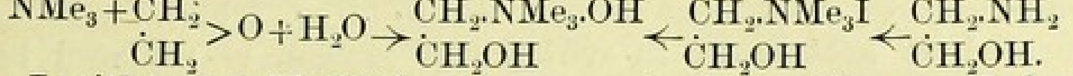


$$\begin{array}{l}CHBr.COOEt\\ \dot{C}H_2.COOEt\end{array} \rightarrow \begin{array}{l}CH(NH_2).COOH\\ \dot{C}H_2CONH_2\end{array}$$

Amido-succinic or aspartic acid, $\begin{array}{l}CH(NH_2).COOH\\ \dot{C}H_2.COOH\end{array}$, is a crystalline substance resembling the other amido-acids. The acid of beet is dextrogyrate, and is also formed amongst other products, by hydrolysis of albumen with alkali. It is produced, as stated above, by the hydrolysis of dextro-asparagine, and as an amine is converted by nitrous acid into the corresponding hydroxy-compound, dextro-malic acid. The inactive aspartic acid, which is more soluble than the active varieties, is made synthetically by the action of alcoholic ammonia on ethyl maleate. It is converted by nitrous acid into inactive malic acid.

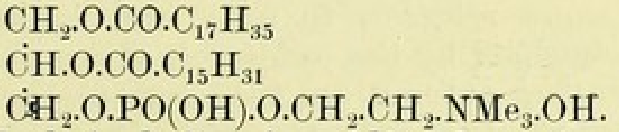
The Quaternary Amido-Compounds.—Several quaternary ammonium derivatives are known, which are closely related to glycosine, the most important being the natural bases, choline, neurine and betaïne. Choline is found in combination in bile, and in the brain and spinal cord. It occurs also in hops, and can be made synthetically.

Choline or hydroxy-ethyl-trimethylammonium hydroxide, $CH_2OH.CH_2.NMe_3.OH$ (Strecker, 1862), is a deliquescent substance, which is difficult to crystallise. It is a powerful base, resembling the ammonium hydroxides in character, and absorbing carbon dioxide with avidity. Its constitution is proved by two syntheses. The first, which proves its relation to glycol, consists in the union of trimethylamine with ethylene oxide and water, and the second, which confirms its constitution as a quaternary ammonium compound, is effected by the successive action of methyl iodide and moist silver oxide on hydroxyethylamine, a base formed by hydration of vinylamine (Baeyer, Wurtz, 1866)—



$$\left.\begin{array}{l}\mathrm{NMe_3+CH_2}\\ \quad\mathrm{\dot{C}H_2}\end{array}\right>\mathrm{O+H_2O}\rightarrow\begin{array}{l}\mathrm{CH_2.NMe_3.OH}\\ \mathrm{\dot{C}H_2OH}\end{array}\leftarrow\begin{array}{l}\mathrm{CH_2.NMe_3I}\\ \mathrm{\dot{C}H_2OH}\end{array}\leftarrow\begin{array}{l}\mathrm{CH_2.NH_2}\\ \mathrm{\dot{C}H_2OH.}\end{array}$$

Lecithin, $C_{42}H_{84}NPO_8$, an important constituent of brain matter, yolk of egg, etc., is a complicated fat or glyceride containing choline. It is a crystalline, wax-like substance, which dissolves only imperfectly in water. As it is hydrolysed by acids and alkalies to choline and glycero-phosphoric, stearic and palmitic acids, its constitution is probably represented by the formula

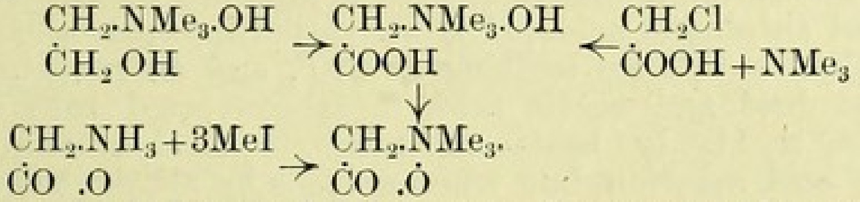


$$\begin{array}{l}\mathrm{CH_2.O.CO.C_{17}H_{35}}\\ \mathrm{\dot{C}H.O.CO.C_{15}H_{31}}\\ \mathrm{\dot{C}H_2.O.PO(OH).O.CH_2.CH_2.NMe_3.OH.}\end{array}$$

As a primary alcohol, choline is oxidisable to the corresponding acid, hydroxy-trimethyl-amidoacetic acid (or more correctly, to its anhydride), the ammonium hydroxide, corresponding with glycosine and sarcosine. The anhydride is identical with betaïne, the alkaloid of beet-root.

Betaïne or trimethyl-glycosine, $\begin{array}{l}\mathrm{CH_2.NMe_3}\\ \mathrm{\dot{C}O.\ \dot{O}}\end{array}$ (Liebreich, 1869), is a sweet, deliquescent substance, which was first formed in the above manner. Unlike choline, it is neutral, the carboxyl forming a kind of internal ammonium salt with the ammonium group. It is broken up when heated with caustic alkali, the nitrogen being eliminated as trimethylamine.

The constitution of betaïne is confirmed by synthesis from chloracetic acid and trimethylamine, and from glycosine and methyl iodide in presence of methyl alcohol; and it is possible that glycosine and sarcosine are also internal anhydrides of this type—



$$\begin{array}{ccccc}\begin{array}{l}\mathrm{CH_2.NMe_3.OH}\\ \mathrm{\dot{C}H_2\,OH}\end{array} & \rightarrow & \begin{array}{l}\mathrm{CH_2.NMe_3.OH}\\ \mathrm{\dot{C}OOH}\end{array} & \leftarrow & \begin{array}{l}\mathrm{CH_2Cl}\\ \mathrm{\dot{C}OOH+NMe_3}\end{array}\\ & & \downarrow & & \\ \begin{array}{l}\mathrm{CH_2.NH_3+3MeI}\\ \mathrm{\dot{C}O\ \ .O}\end{array} & \rightarrow & \begin{array}{l}\mathrm{CH_2.NMe_3.}\\ \mathrm{\dot{C}O\ .\dot{O}}\end{array} & & \end{array}$$

Although choline and betaïne are innocuous, the corresponding ethylene derivative, neurine, is extremely poisonous. Neurine occurs in the brain, and is one of the ptomaines formed in the putrefaction of albumen. It can also be made synthetically.

Neurine or trimethyl-vinyl-ammonium hydroxide, $CH_2{:}CH.NMe_3.OH$, is a crystalline, and powerfully basic substance. It is made from choline by the successive action of hydriodic acid and moist silver oxide, and in a similar manner from ethylene bromide and trimethylamine—

$$\left.\begin{array}{l}\mathrm{CH_2OH.CH_2.NMe_3.OH\rightarrow CH_2I.CH_2.NMe_3I}\\ \mathrm{CH_2Br.CH_2Br+NMe_3\rightarrow CH_2.Br.CH_2.NMe_3Br.}\end{array}\right\rangle\mathrm{CH_2{:}CH.NMe_3.OH.}$$

Guanidine.—When acetamide is digested with hydrochloric acid under certain conditions, it is partially converted into the hydrochloride of a base termed acetamidine, which may be regarded as acetamide, in which the oxygen is replaced by amidogen.

Acetamidine, $CH_3.C(:NH).NH_2$, is a highly alkaline liquid, which is easily hydrolysed to ammonia and acetic acid. It may also be formed directly by heating acetonitrile with ammonium chloride—

$$2CH_3.CONH_2 + HCl \rightarrow CH_3.C(:NH).NH_2.HCl \leftarrow CH_3.CN + NH_3.HCl.$$

The corresponding carbonic acid derivative, carbamidine, bears the same relation to urea, and is identical with the guanidine obtained by the oxidation of guanine. It is best prepared by heating ammonium thiocyanate, the thiourea at first formed being resolved into guanidine thiocyanate and hydrogen sulphide—

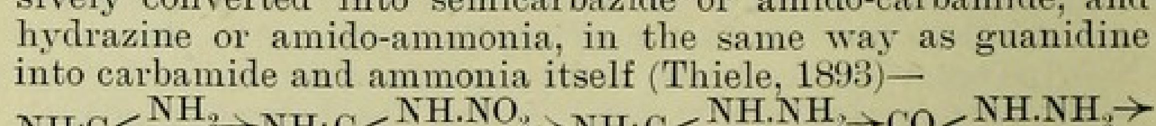
$$2NH_4.SCN \rightarrow 2CS(NH_2)_2 \rightarrow NH:C(NH_2).HCNS + H_2S.$$

Guanidine or carbamidine, $NH:C(NH_2)_2$ (Strecker, 1861), is a very soluble, deliquescent crystalline substance, which absorbs carbon dioxide freely, forming a crystalline carbonate. It is thus a powerful base. Like carbamide, it forms salts with one equivalent of acid only.

Guanidine is hydrolysed by baryta to ammonia and carbamide, and its constitution is confirmed by synthesis. Thus it is formed by the action of ammonia on chloropicrin (p. 231), and ethyl orthocarbonate, $C(OEt)_4$, the tetramido-derivative that might be expected breaking up into ammonia and the amidine. It is also produced by the direct union of cyanamide with ammonium chloride at 100°, in the same way as acetamidine from acetonitrile—

$$C(OEt)_4 \rightarrow [C(NH_2)_4] \rightarrow NH:C(NH_2)_2 \leftarrow CN.NH_2 + NH_3.HCl.$$

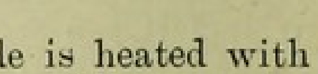
When guanidine is digested with a mixture of concentrated nitric and sulphuric acids, it is converted into nitroguanidine, a crystalline substance melting at 230°, and on reducing this with zinc dust and acetic acid, it is converted into amidoguanidine, a highly basic substance. Amido-guanidine is stable in acid solution, but when set free by alkali it is successively converted into semicarbazide or amido-carbamide, and hydrazine or amido-ammonia, in the same way as guanidine into carbamide and ammonia itself (Thiele, 1893)—



$$NH{:}C<\begin{matrix}NH_2\\NH_2\end{matrix} \rightarrow NH{:}C<\begin{matrix}NH.NO_2\\NH_2\end{matrix} \rightarrow NH{:}C<\begin{matrix}NH.NH_2\\NH_2\end{matrix} \rightarrow CO<\begin{matrix}NH.NH_2\\NH_2\end{matrix} \rightarrow CO_2\begin{matrix}+NH_2.NH_2\\+NH_3\end{matrix}$$

Creatine and Creatinine.—When cyanamide is heated with glycosine it unites with it in the same way as with ammonia, forming a guanidine derivative.

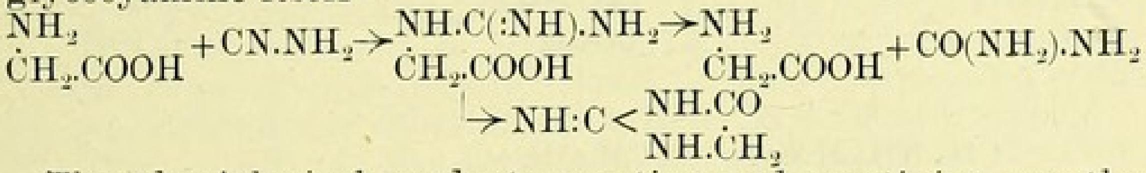
Glycocyamine or guanidine-acetic acid,



$$\begin{matrix}NH.C(:NH).NH_2,\\ \dot{C}H_2.COOH\end{matrix}$$

is a neutral, crystalline substance, which forms salts with both acids and bases. It is readily oxidised to guanidine and oxalic acid, and is hydrolysed by baryta to urea and glycosine. On heating glycocyamine hydrochloride in a stream of hydrogen chloride at 100°, it is dehydrated to an internal amide, glycocyamidine.

Glycocyamidine, $\mathrm{NH{:}C}<\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CH_2}\end{matrix}$, is a highly alkaline, deliquescent substance, which is much less easily hydrolysed than glycocyamine itself—

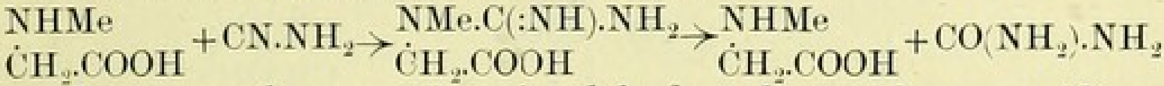


$$\begin{matrix}\mathrm{NH_2}\\ \mathrm{CH_2.COOH}\end{matrix}+\mathrm{CN.NH_2}\rightarrow\begin{matrix}\mathrm{NH.C(:NH).NH_2}\\ \mathrm{CH_2.COOH}\end{matrix}\rightarrow\begin{matrix}\mathrm{NH_2}\\ \mathrm{CH_2.COOH}\end{matrix}+\mathrm{CO(NH_2).NH_2}$$
$$\rightarrow\mathrm{NH{:}C}<\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CH_2}\end{matrix}$$

The physiological products creatine and creatinine are the methyl derivatives of these compounds, and the former thus bears the same relation to guanidine as sarcosine to ammonia. Creatine exists in large quantities in the muscle fluid of animals, and may be extracted from minced raw meat with cold water. The solution is boiled to coagulate albumen, and the phosphates precipitated with baryta, and on evaporating the filtrate the creatine crystallises out.

Creatine, $\begin{matrix}\mathrm{NMe.C(:NH).NH_2}\\ \mathrm{CH_2.COOH}\end{matrix}$ (Chevreul, 1834), is a neutral substance, having a somewhat bitter taste, and is freely soluble in warm water.

It forms salts with acids, but is hydrolysed by alkalies to urea and sarcosine. Part of the urea excreted by the kidneys is probably formed in this way. Conversely, creatine can be synthesised, in a parallel manner to guanidine and glycocyamine, by heating cyanamide with sarcosine—



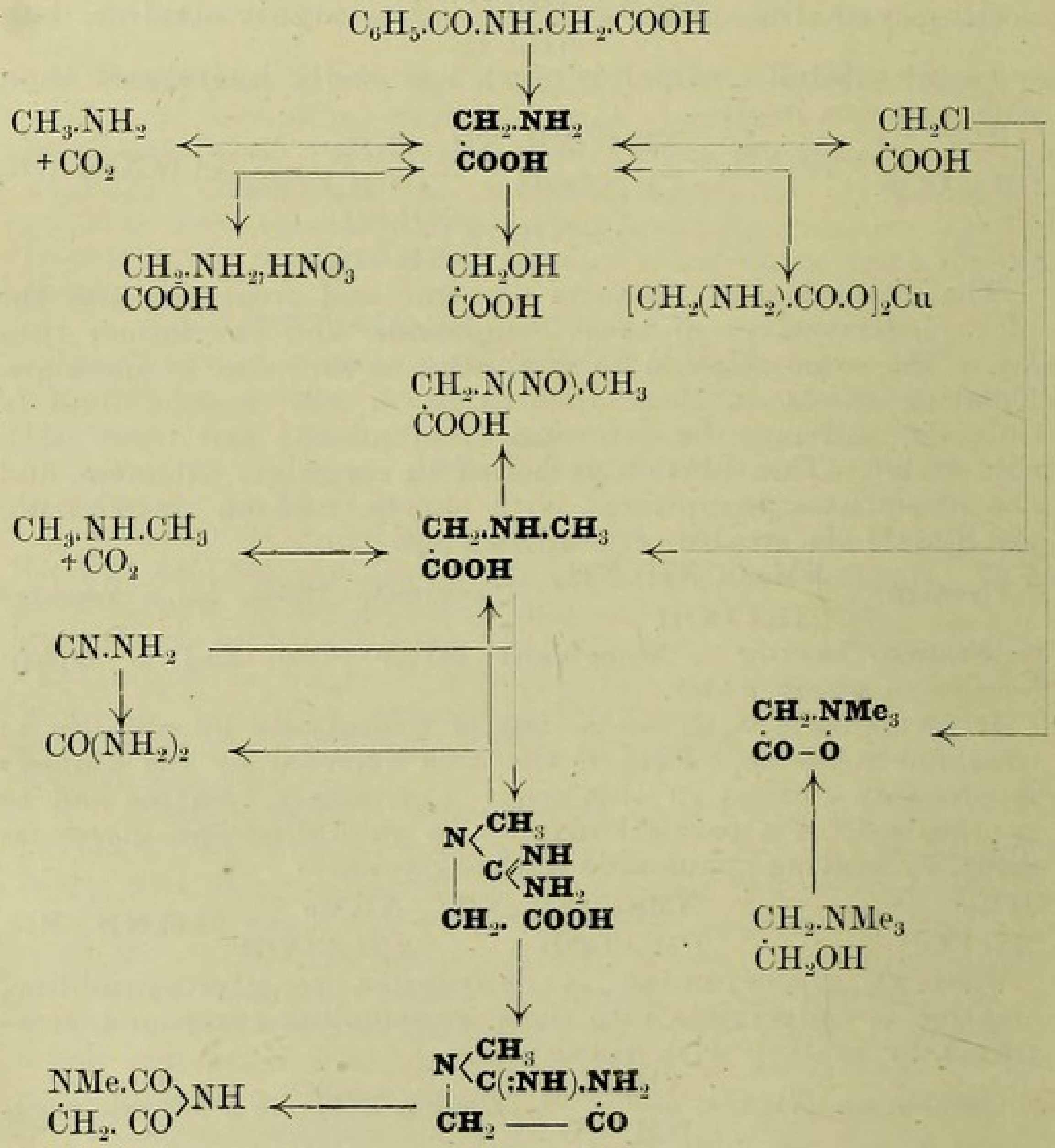
$$\begin{matrix}\mathrm{NHMe}\\ \mathrm{CH_2.COOH}\end{matrix}+\mathrm{CN.NH_2}\rightarrow\begin{matrix}\mathrm{NMe.C(:NH).NH_2}\\ \mathrm{CH_2.COOH}\end{matrix}\rightarrow\begin{matrix}\mathrm{NHMe}\\ \mathrm{CH_2.COOH}\end{matrix}+\mathrm{CO(NH_2).NH_2}$$

Just as glycocyamine is dehydrated to glycocyamidine, creatine is convertible into the corresponding compound, creatinine, by heating with dilute acids.

Creatinine, $\mathrm{NH{:}C}<\begin{matrix}\mathrm{NMe.CH_2}\\ \mathrm{NH.\ CO}\end{matrix}$ (Liebig, 1847), is a soluble crystalline base which forms well defined salts with acids, and liberates ammonia from ammonium salts. It is hydrolysed by baryta, not to sarcosine, but to methyl-hydantoïn, $\mathrm{CO}<\begin{matrix}\mathrm{NMe.CH_2}\\ \mathrm{NH.\ CO}\end{matrix}$, the methyl derivative of hydantoïn or glycollyl urea, so that these complex amidines are closely related to the natural ureïdes.

Synopsis.—The amido-acids are amido- or amino-substitution-products of the carboxylic acids. They resemble the acid amides in their neutrality, but as amines, they are not hydrolysable, but convertible into hydroxy-acids or nitroso-compounds. The quaternary amido-acids form internal anhydrides related to the ureïdes.

THE AMIDO-ACIDS.



CHAPTER XXXVII

THE OXY-NITROGEN COMPOUNDS

The Alkyl Nitrates and Nitrites.—The last class of aliphatic nitrogen derivatives to be considered comprises several types, in which the nitrogen is more or less intimately associated with oxygen. Particular cases of these have been already incidentally dealt with. It has been seen for example, that glycerol and other poly-hydroxy-compounds form ethereal nitrates, which are hydrolysable to alcohol and acid in the normal manner, and that aldehydes and ketones condense with hydroxylamine to products in which hydroxyl is linked to nitrogen.

Practically all alcohols form nitrates of the type of the glycerol and cellulose compounds. Ethyl nitrate, for example, is formed by heating alcohol with nitric acid, provided a little urea is present to decompose any nitrous acid that is formed. The product is purified by washing with water, and dried in the usual way.

Ethyl nitrate, $C_2H_5.O.NO_2$ (Millon, 1843), is a heavy, insoluble liquid, which boils at 87°, and has a pleasant odour. Like glycerol trinitrate, it is stable at ordinary temperatures, but when suddenly heated it explodes very violently. Its constitution as an ethereal salt is proved by its hydrolysis by caustic soda to alcohol and sodium nitrate—

$$C_2H_5.OH+NO_2.OH \longleftrightarrow C_2H_5.O.NO_2+H_2O.$$

As already stated, the nitrate is readily converted into ethylamine by ammonia, but the method is little used, on account of the risk. It is reduced by tin and hydrochloric acid to alcohol and hydroxylamine—

$$C_2H_5.OH+NH_2.OH \leftarrow C_2H_5.O.NO_2 \rightarrow C_2H_5.NH_2,HNO_3.$$

The corresponding nitrite, ethyl nitrite, is formed in a similar manner by warming an alcoholic solution of nitrogen trioxide, or more simply, by distilling alcohol with copper, nitre and sulphuric acid. The higher nitrites are also produced by the interaction of the iodides with silver nitrite at a moderately high temperature.

Ethyl nitrite, $C_2H_5.O.NO$ (Kunkel, 1681), is an insoluble explosive liquid, which boils at 17°, and resembles apples in odour. The crude product obtained by the copper method is termed sweet spirit of nitre, and used in medicine. Amyl nitrite, $C_5H_{11}.OH$, a similar liquid, having a very oppressive odour, is made from fusel oil by the trioxide method, and is also used medicinally.

The constitution of ethyl nitrite as an ethereal salt is proved by its hydrolysis to alcohol and sodium nitrite by caustic soda—

$$C_2H_5.O.H + NO.OH \longleftrightarrow C_2H_5.O.NO + H_2O.$$

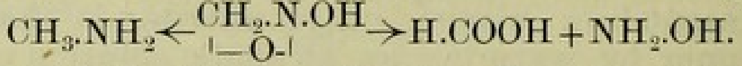
The Nitro-Paraffins.—As stated above, the higher alkyl iodides are converted into nitrites when heated with silver nitrite. With the lower compounds however, isomeric compounds are formed, the nitro-paraffins, and with methyl iodide, this nitro-methane is the exclusive product. The iodide is simply poured on the dry nitrite. After the violent action has ceased the excess of iodide is distilled from a water-bath, and the product repeatedly distilled from silver nitrite on an oil bath.

Nitro-methane is more conveniently obtained however, by boiling potassium chloracetate with potassium nitrite solution, the transiently formed nitro-acetate decomposing into the nitro-paraffin and potassium carbonate, in much the same way as amido-acetic acid into methylamine and carbon dioxide—

$$CH_2Cl.COOK + K.NO_2 \rightarrow CH_2(NO_2).COOK \rightarrow CH_3.NO_2 \leftarrow CH_3I + Ag.NO_2$$

Nitromethane, $CH_3.NO_2$ (V. Meyer, 1872), is a heavy, insoluble, explosive liquid, which boils at 101°, and has a pleasant odour. Its behaviour with alkalies is radically different from that of the isomeric nitrite. Instead of undergoing hydrolysis, it acts as a weak acid, and forms with alcoholic potash a crystalline salt, potassium nitromethane, $CH_2K.NO_2$, one of the hydrogen atoms becoming mobile under the influence of the nitro-group. Similarly, an explosive silver salt, $CH_2Ag.NO_2$, is precipitated, when the nitro-compound is shaken with silver-nitrate solution.

As already indicated, nitromethane is reduced to methylamine by nascent hydrogen, so that the nitrogen is linked directly to carbon, and not through oxygen, as in the nitrite; but it is doubtful whether its constitution is as simple as represented by the above formula, for it is hydrolysed by hydrochloric acid to hydroxylamine and a fatty acid, formic acid. Possibly one of the oxygen atoms is linked both to carbon and nitrogen—



$$CH_3.NH_2 \leftarrow \underset{|\!-\!O\!-\!|}{CH_2.N.OH} \rightarrow H.COOH + NH_2.OH.$$

One or two of the higher nitro-paraffins, however, have been made by the direct action of dilute nitric acid on the hydrocarbons at a high temperature, in much the same way as nitrobenzene (p. 242) from benzene.

In addition to the simple nitro-paraffins, poly-nitro-compounds, such as tetranitromethane, and mixed compounds, such as nitrotrichloromethane are known. The latter compound is formed, together with trichloracetic acid, by the action of nitric acid on chloral, and is also produced by direct chlorination of nitromethane. It is best made, however, by distilling a thin cream of bleaching powder and saturated solution of picric acid (p. 283) with steam.

Nitrochloroform or chlorpicrin, $CCl_3.NO_2$ (Stenhouse, 1848), is a heavy liquid, boiling at 113°. Its odour is exceedingly penetrating and pungent. It is reduced to methylamine when digested with reduced iron and acetic acid, and, as already stated, is converted by ammonia into guanidine—

$$CH_3.NH_2 \leftarrow CCl_3.NO_2 \rightarrow NH:C(NH_2)_2.$$

The Oximes and Allied Compounds.—The formation of aldoxime and acetoxime by condensation of aldehyde and acetone with hydroxylamine, and the conversion of aldoxime into the corresponding nitrile have been already dealt with (pp. 71, 76)—

$$CH_3.CHO + NH_2.OH \rightarrow CH_3.CH:N.OH \rightarrow CH_3.CN.$$

Aldoximes are also formed by the action of nitrous acid on the methyl ketones. Acetone, for example, yields isonitroso-acetone. Isonitroso-acetone or pyroracemic aldoxime, $CH_3.CO.CH:N.OH$, is a crystalline substance, melting at 65°, which is hydrolysed by hydrochloric acid in the normal manner to hydroxylamine and pyroracemic aldehyde—

$$CH_3.CO.CH_3 + NO.OH \rightarrow CH_3.CO.CH:N.OH \rightarrow CH_3.CO.CHO + NH_2.OH.$$

Substances which are both oximes and nitro-compounds are similarly formed by the action of nitrous acid on the nitro-paraffins. Isonitroso-nitro-ethane or ethyl-nitrolic acid, $CH_3.C(NO_2):N.OH$ (V. Meyer, 1875), is a crystalline substance, which from the influence of the nitro-group on the hydroxyl is strongly acid. The acid itself is colourless, but its alkali salts are deep crimson in colour—

$$CH_3.CH_2.NO_2 + NO.OH \rightarrow CH_3.C(NO_2):N.OH \rightarrow CH_3.C(NO_2):N.ONa.$$

By the action of nitrous acid on the secondary-alkyl nitro-compounds, however, isomeric nitroso-nitro-compounds are formed. Secondary propyl alcohol, for example, yields nitroso-nitro-propane. Propyl pseudo-nitrole or nitroso-nitro-propane, $NO.CMe_2.NO_2$ (V. Meyer, 1875), is a neutral crystalline substance, the acidifying influence of the nitro-group not extending to the methyl hydrogen. It is colourless when solid, but assumes a deep blue colour when melted or dissolved in water—

$$CH_3.CH(NO_2).CH_3 + NO.OH \rightarrow CH_3.C(NO)(NO_2).CH_3.$$

The nitro-compounds of tertiary alkyl radicles are not affected by nitrous acid, so that the class of an alcohol is readily determined by means of these reactions. The alcohol is converted into the iodide, the latter into the nitro-compound by boiling with silver nitrite, and the nitro-compound is mixed, first with potash solution and potassium nitrite, and then with a little dilute sulphuric acid. If the alcohol is primary, a red colour is developed, if it is secondary, a blue colour appears, whilst if it is tertiary, the product remains colourless (V. Meyer).

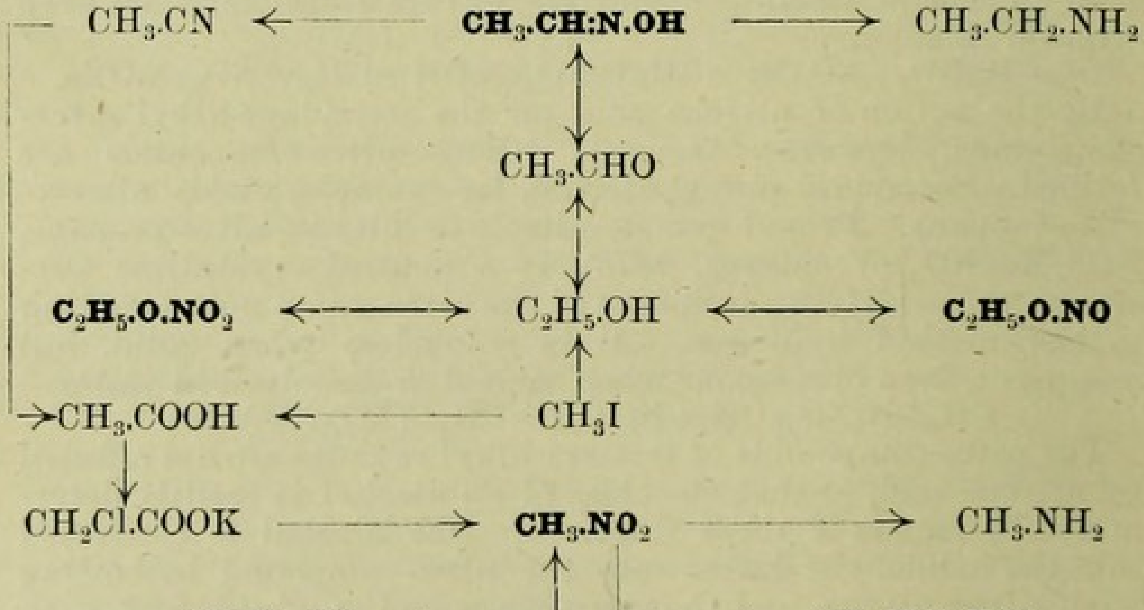
By the action of metallic mercury or silver on a mixture of alcohol and nitric acid, explosive metallic compounds are formed, termed fulminates, which are probably related to these isonitroso-compounds. The alcohol is cautiously poured into a large flask containing the mercury and moderately concentrated nitric acid, and the violent action which soon sets in is moderated by adding more spirit. On cooling the product, after the action has ended, the metallic fulminate crystallises out.

Mercuric fulminate, $HgC_2N_2O_2$ (Howard, 1800), is a crystalline highly explosive substance, which detonates when struck, and is used in percussion caps and dynamite fuses. It is hydrolysed by hydrochloric acid to mercuric chloride, formic acid, carbon dioxide, and hydroxylamine, and affords the most convenient source of the latter base. From this it would appear to be an oxime or isonitroso-compound. With other agents however it yields cyanogen derivaties. The free acid is unknown, but the constitution of the mercury salt is possibly represented by the formula—

$$Hg<\begin{matrix} C:N.O \\ \dot{C}:N.\dot{O} \end{matrix}$$

Synopsis.—In addition to the alkyl nitrates and nitrites, in which the alkyl is linked to oxygen, there are various oxy-nitrogen compounds, such as the nitro- and nitroso-compounds, and the oximes, in which the alkyl is directly linked to nitrogen.

THE OXY-NITROGEN COMPOUNDS.



CHAPTER XXXVIII

COMPOUNDS OF PHOSPHORUS, SULPHUR, METALS, ETC.

The Phosphines.—The remaining elements of the nitrogen group form alkyl compounds, which are analogous to the amines, and bear much the same relation to them as the elements themselves to nitrogen. The tertiary phosphines, for example, are made by the interaction of the alkyl iodides with hydrogen phosphide or phosphonium iodide, in the same way as the amines; and by the interaction of the zinc alkyls and phosphorus trichloride—

$$PH_3+3MeI=PMe_3,HI+2HI.$$

Trimethyl-phosphine, PMe_3 (Hofmann, 1857), is an insoluble and highly refractive liquid, which boils at 42°, and has an extremely repulsive odour. Like trimethylamine, it readily combines with methyl iodide, forming an "ammonium" iodide. Tetramethyl-phosphonium iodide, $PMe_4.I$, is a crystalline substance which resembles the corresponding nitrogen compound, and is similarly converted into a caustic hydroxide by moist silver oxide.

Tetramethyl-phosphonium hydroxide, $PMe_4.OH$, is a deliquescent, crystalline, and highly alkaline solid, which, like the ammonium compound, forms well defined salts with acids, precipitates metallic hydroxides, and expels ammonia from its salts. The tetramethyl-phosphonium radicle, like the corresponding nitrogen derivative, thus simulates the alkali metals.

The primary and secondary phosphines are formed by a special method, by the action of the alkyl iodides on phosphonium iodide in presence of zinc oxide, but resemble the tertiary compounds in character.

Methyl phosphine, $Me.PH_2$ (Hofmann, 1871), is a spontaneously inflammable gas, condensing at −14°, and di-ethyl phosphine, $PHMe_2$, is a similar liquid, boiling at 25°. Both, like the tertiary base, form phosphonium salts with acids, but their basicity is not so pronounced as that of the amines. They are insoluble in water also, and on account of the greater readiness of phosphorus to assume the pentavalent condition are easily oxidised. The tertiary compounds behave in fact like divalent metals, forming additive oxides, chlorides, sulphides, etc.

The Arsines, Stibines, and Bismuthines.—The primary and secondary alkyl derivatives of the higher members of the nitrogen group are scarcely known, but the tertiary and quaternary compounds resemble those of nitrogen and phosphorus. The tertiary arsenic compound, for example, is formed by the interaction of zinc methyl and arsenious chloride.

Trimethyl-arsine, $AsMe_3$ (Hofmann, 1855), is a colourless insoluble liquid, which boils at 200°, and is very repulsive in odour. It combines with methyl iodide in the same way as the amine and phosphine, forming a crystalline tetramethyl-arsonium iodide, $AsMe_4.I$, which is similarly convertible into a caustic tetramethyl-arsonium hydroxide, $AsMe_4.OH$. On the other hand, it does not form salts with acids, and its tendency to behave as a divalent metallic radicle, and form additive compounds with chlorine, etc., is much more marked than with the phosphine.

The dimethyl-arsine radicle, cacodyl, plays the part of an alkali metal, and may be considered as an Organic analogue of the electro-positive elements (Bunsen, 1843). Its oxide is formed by dry-distilling white arsenic with sodium acetate—

$$4CH_3.COONa + As_2O_3 = (AsMe_2)_2O + 2K_2CO_3 + 2CO_2.$$

Cacodyl oxide, $(AsMe_2)_2O$ (Cadet, 1760), is a colourless liquid, boiling at 160°, and having a most objectionable odour (*κακοδης*). In its chemical actions it is intermediate to the alkali and alkyl oxides. On the one hand it is converted by hydrochloric acid into cacodyl chloride, $AsMe_2.Cl$, a liquid which boils at 100°, but resembles the alkali chlorides in forming a sparingly soluble platinochloride, whilst on the other hand by heating with zinc dust it is converted into (di) cacodyl, $AsMe_2.AsMe_2$, in the same way as methyl iodide into dimethyl.

Cacodyl, $As_2(CH_3)_4$ (Bunsen, 1842), is a colourless, insoluble, and spontaneously inflammable liquid, which boils at 170°, and freezes at -6°. Like the oxide and other compounds its odour is very repulsive.

In the antimony and bismuth compounds, which are formed in the same way as those of arsenic, the pseudo-divalent character of the radicles is more pronounced, and there is a still greater tendency to form additive compounds with the negative elements rather than with acids.

Trimethylstibine, $SbMe_3$, is a liquid, which on the one hand is convertible into tetramethyl-stibonium iodide, $SbMe_4.I$, and a caustic tetramethyl-stibonium hydroxide, $SbMe_4.OH$, whilst on the other hand, its metallic character is so marked, that it expels hydrogen from hydrochloric acid, in the same way as a divalent metal—

$$SbMe_3 + 2HCl = SbMe_3.Cl_2 + H_2.$$

Trimethyl-bismuthine, $BiMe_3$, the highest member of the nitrogen-alkyl series, corresponding with the unknown bismuth trihydride, is a very unstable liquid. It does not appear to combine directly with oxygen or chlorine, and in its behaviour with acids resembles the metallic alkyl compounds, being resolved into a bismuth salt and methane.

The Metallic and other Alkyl Compounds.—Most of the elements form alkyl compounds. The silicon derivatives are of especial interest, as they closely resemble the paraffins, silicon being the element most closely allied to carbon. Silicon tetrethyl is made by heating silicon chloride with zinc ethyl in an inert atmosphere, and fractionating the product.

Silicon tetrethyl or silico-nonane, $Si(C_2H_5)_4$ (Friedel, 1865), is a light, spontaneously inflammable liquid, boiling at 160°, which, apart from its ready oxidability, closely resembles nonane in its chemical actions. It is stable towards nitric acid, and is converted by chlorine into a substitution product, silico-nonyl chloride, $SiEt_3.C_2H_4Cl$, a liquid boiling at 185°, and resembling the alkyl chlorides. This, when boiled with potassium acetate solution, is converted into the corresponding acetate, $SiEt_3.C_2H_4.OAc$, a liquid boiling at 214°, which is resolved by alkalies in the normal manner, into acetic acid and the corresponding alcohol. Silico-nonyl alcohol, $SiEt_3.C_2H_4.OH$, is a liquid of camphor odour, which boils at 190°, and like the purely carbon alcohols is converted by sodium into a solid sodium alkyl-oxide—

$$SiCl_4 + 2ZnEt_2 \rightarrow SiEt_4 \rightarrow SiEt_3.C_2H_4.Cl \rightarrow SiEt_3.C_2H_4.OH.$$

Silicon thus resembles carbon in its power of binding carbon atoms to stable aggregates. The less basic metals, such as tin and lead, share this power to a certain extent, and also distantly resemble the nitrogen elements in their combinations, but as the more positive metals are approached, and the oxidability of the alkyl compounds becomes more marked, their power of forming "ammonium" hydroxides decreases.

Tin tetrethyl, $SnEt_4$ (Ladenburg, 1872), is a liquid of pleasant odour, which boils at 181°, and is not spontaneously inflammable. It is converted by hydrochloric acid into ethane and triethylstannic chloride, $SnEt_3.Cl$, and this by caustic alkalies into the corresponding hydroxide. Triethylstannic hydroxide, $SnEt_3.OH$, is an alkali resembling the ammonium hydroxides, but is less soluble and energetic. Lead and mercury form similar derivatives. Ethylmercuric hydroxide, $HgEt.OH$, is a viscid alkaline liquid, which forms stable salts with acids.

The alkyl compounds of the highly positive metals do not form such hydroxides. Zinc ethyl, as already indicated, is hydrolysed to ethane and zinc oxide even by water, and the corresponding aluminium trimethyl, $AlMe_3$, and magnesium diethyl, $MgEt_2$, which are also spontaneously inflammable liquids, behave in a similar manner.

The alkyl compounds of the alkyl metals are not known in a pure state. Sodium methyl, NaMe, appears to be formed when sodium is digested with zinc methyl, for metallic zinc is precipitated, and the resulting liquid absorbs carbon dioxide, forming sodium acetate (Wanklyn, 1858)—

$$CH_3.Na + CO_2 = CH_3.CO_2Na.$$

The valencies of the various metals follow at once from the vapour densities of these volatile alkyl derivatives, and it was the discovery of these compounds that gave rise to the theory of valency.

The Sulphides and Sulphonium Compounds.—When ethyl bromide is boiled with potassium hydrosulphide solution, it is converted into ethyl hydrosulphide, the action being precisely parallel to the hydrolysis of the bromide by caustic soda. The sulphide is best prepared, however, by distilling ethyl sodium sulphate with a solution of caustic soda which has been saturated with sulphuretted hydrogen. The product passes over with the steam and forms an oily layer on the water. It is purified by shaking with mercury, with which it forms a crystalline compound, and decomposing the washed and dried crystals with hydrogen sulphide.

Ethyl hydrosulphide or mercaptan (*mercurium captans*), $C_2H_5.SH$ (Zeise, 1834), is a light, insoluble liquid, boiling at 36°. Its odour resembles that of garlic, but is more offensive. The hydrogen of the hydrosulphyl group is replaceable by metals, like that of hydroxyl, but the compounds thus formed, such as mercury mercaptan, $Hg(SEt)_2$, are much more stable than the metallic alkyl oxides. The constitution of mercaptan follows from the mode of its preparation, and is confirmed by its formation from alcohol by the action of phosphorus pentasulphide. The homologous alkyl compounds are similar liquids—

$$C_2H_5.NaSO_4 + NaSH \rightarrow C_2H_5.SH \leftarrow C_2H_5.OH.$$

The sulphide corresponding with mercaptan is formed by heating ether with phosphorus pentasulphide, or ethyl bromide with alcoholic potassium sulphide. Ethyl sulphide, Et_2S, is a liquid physically resembling mercaptan, but boiling at 91°. The corresponding allyl sulphide, $(C_3H_5)_2S$, made in a similar manner from allyl iodide, is, as already mentioned, identical with oil of garlic.

More complex sulphides are also known. Thus by the oxidation of the mercaptan with iodine, ethyl disulphide, Et_2S_2, is formed, and by the interaction of mercaptan with the aldehydes and ketones, liquids termed mercaptals and mercaptols are obtained, the sulphur analogues of the acetals. Ethylidene mercaptal, $CH_3.CH(SEt)_2$, is an oily liquid, boiling at 186°.

Divalent sulphur thus resembles oxygen in its combinations. Tetravalent sulphur on the other hand behaves in the same way as the elements of the nitrogen series, and forms compounds akin to those of the phosphonium group. Ethyl sulphide for example combines with ethyl iodide, forming an "ammonium" iodide, which is converted by caustic alkalies into an alkaline hydroxide—

$$SEt_2 + EtI \rightarrow SEt_3.I \rightarrow SEt_3.OH.$$

Triethyl-sulphonium iodide, $SEt_3.I$, is a crystalline substance resembling the corresponding compounds of the phosphorus group. Triethyl-sulphonium hydroxide, $SEt_3.OH$, is a deliquescent crystalline substance, which forms salts with acids, expels ammonia from its salts, absorbs carbon dioxide, and behaves in every respect as an alkali. Thus even sulphur is converted into a positive radicle by alkyl.

The Sulphonic Acids and Sulphones.—Mercaptan is readily oxidised by nitric acid to a derivative of sulphurous acid.

Ethyl-sulphonic acid, $C_2H_5.SO_2OH$ (Löwig, 1840), is a viscid, difficultly crystallisable, and acid liquid. It is is converted by phosphorus pentachloride into an acid chloride, $C_2H_5.SO_2Cl$, so that its molecule contains hydroxyl, but it is reduced to mercaptan by zinc and hydrochloric acid, so that the sulphur is linked to ethyl. By the action of sodium ethoxide, the chloride is converted into the corresponding ethyl salt, ethylic ethyl-sulphonate—

$$\begin{tikzcd} C_2H_5.SH \arrow[r] & C_2H_5.SO_2OH \arrow[r, leftrightarrow] & C_2H_5SO_2Cl \arrow[r] \arrow[ll, bend left] & C_2H_5.SO_2OEt. \end{tikzcd}$$

Ethylic ethyl-sulphonate, $C_2H_5.SO_2.OEt$, a liquid boiling at 213°, is also made by digesting silver sulphite with ethyl iodide. That only one of the ethyl radicles is in ethereal salt combination is confirmed by the hydrolysis of the salt to alcohol and the ethyl-sulphonate by alkalies. It follows therefore that the metallic sulphites are unsymmetrical compounds, and that one of the metallic atoms is directly linked to sulphur—

$$Ag.SO_2.OAg \rightarrow Et.SO_2.OEt \rightarrow Et.SO_2.OH + Et.OH.$$

The corresponding symmetrical sulphites are formed by the action of sulphuryl chloride on the alcohols. Ethyl sulphite, $SO(OEt)_2$, is a liquid of peppermint odour, which boils at 161°, and is hydrolysed by caustic soda to alcohol and sodium sulphite—

$$SOCl_2 + 2Et.OH \rightarrow SO(OEt)_2 \rightarrow Na_2SO_3 + 2Et.OH.$$

When ethyl sulphide is oxidised with nitric acid, it is converted into crystalline oxidation products, ethyl sulphoxide, Et_2SO, and ethyl sulphone, Et_2SO_2. Similar compounds are formed by the oxidation of the mercaptals and mercaptols, and the product sulphonal, thus obtained from acetone mercaptol, is of technical importance. The mercaptol is simply heated with permanganate solution—

$$CH_3.CO.CH_3 \rightarrow CH_3.C(SEt)_2.CH_3 \rightarrow CH_3.C(SO_2.Et)_2.CH_3.$$

Sulphonal, $CMe_2(SO_2.Et)_2$ (Baumann, 1886), is a sparingly soluble crystalline substance, which melts at 126°, and is used instead of chloral as a hypnotic.

Although many of the proteids are sulphur compounds, comparatively few natural organic sulphur derivatives have been isolated. One of the chief of these is taurine, a neutral aminoid substance, which is obtained by hydrolysis of the taurocholic acid of ox-bile.

Taurine or amido-isethionic acid, $CH_2(NH_2).CH_2.SO_2OH$ (Gmelin, 1848), is a crystalline substance, melting at 240°.

Like glycosine, it is indifferent to alkalies and acids, and that it is a primary amine is proved by its conversion by nitrous acid into the corresponding hydroxy-compound, isethionic acid, with elimination of nitrogen. Isethionic acid, $CH_2OH.CH_2.SO_2OH$, is a viscid liquid which crystallises only with difficulty. It can be made synthetically by dissolving sulphuric anhydride in well cooled alcohol, and also from synthetic taurine—

$$C_2H_5.OH + SO_3 = CH_2OH.CH_2SO_2.OH.$$

Taurine can be synthesised from ethylene. By the interaction of glycol chlorhydrin with potassium sulphite, potassium ethionate is formed, and this is converted by phosphorus pentachloride into chlorethyl-sulphonic chloride. This substance, like chloracetyl chloride, is only partially hydrolysed by cold water, the alkylic chlorine remaining untouched, and the chlorsulphonic acid thus obtained is converted by ammonia into the amido-acid, taurine, the constitution of which is thus fully demonstrated (Kolbe, 1862)—

$$\begin{tikzcd}
CH_2OH.CH_2Cl \arrow[r] & CH_2OH.CH_2.SO_2OK \arrow[r] & CH_2Cl.CH_2.SO_2Cl \arrow[dl] \\
 & CH_2Cl.CH_2.SO_2OH \arrow[r] & CH_2(NH_2).SO_2OH.
\end{tikzcd}$$

Synopsis.—Phosphorus and the other elements of the nitrogen group form alkyl derivatives resembling the amines and ammonium compounds, but progressively less stable. Most of the elements form such compounds. The sulphur alkyl derivatives are oxidisable to stable sulphones and sulphonic acids, derivatives of sulphurous acid in which the alkyl is linked directly to sulphur.

PART III

Aromatic or Ring Compounds

SECTION X

BENZENE AND THE PHENYL RADICLE

CHAPTER XXXIX

BENZENE AND ITS SUBSTITUTION PRODUCTS

Separation of Benzene from Coal Tar.—Although the compounds considered in the preceding sections are derived from the paraffins and related hydrocarbons, and can in many cases be made from them, the processes are rarely economical, and as a rule both wasteful and tedious. A very large and important group has now to be dealt with, the members of which are not only derived from the corresponding hydrocarbons, in the same way as the aliphatic compounds from the paraffins, etc., but in the majority of cases are most conveniently and economically made in this way. Most of the drugs and dye-stuffs are members of this group, which, owing to its technical importance and ease of manipulation, has been more studied than any other.

The central member of the aromatic group, as it is termed, from the pleasant odour of some of the earlier discovered members, is the hydrocarbon benzene. Benzene occurs with butylene in the liquid which condenses on compressing oil-gas (Faraday, 1825), and its name is derived from that of a compound, benzoic acid (p. 260), from which it is readily prepared (Mitscherlich, 1834). The hydrocarbon can also be made synthetically by passing a slow current of acetylene through a combustion tube heated to dull redness (Berthelot, 1870), but its chief source is coal-tar, the black, viscid liquid which collects beneath the ammoniacal "gas-liquor" in the dry distillation of coal (Mansfield, 1848). Coal gas, as is well known, contains methane and ethylene, and it is probable that the benzene is formed synthetically by the action of the red-hot retort walls on these simple hydrocarbons.

Coal tar is a complex mixture containing many valuable products—benzene and homologous hydrocarbons; phenols (p.

251); and solid hydrocarbons, such as naphthalene (p. 363) and anthracene (p. 370)—and these are roughly separated on a manufacturing scale by a single fractional distillation from large iron stills. The head fraction, distilling below 150°, consists principally of benzene and its near homologues. It constitutes about 5 per cent. of the tar, and is termed light oil, as it floats on water.

To isolate the benzene the crude oil is shaken with concentrated sulphuric acid to remove olefines and thiophene (p. 405), and such basic impurities as pyridine (p. 384). Phenols are dissolved out by shaking with caustic soda, and the dried liquid fractionated in a column apparatus. The fraction 80–110° contains 65 to 75 per cent. of benzene, whilst the higher fractions consist principally of homologous hydrocarbons—toluene, the xylenes, etc. The benzene is finally purified from toluene and paraffins by freezing, the crystals being repeatedly drained, melted, and re-frozen in the same way as with acetic acid.

Benzene, C_6H_6 (Faraday, 1825), is a mobile liquid, having a pleasant, characteristic odour. It freezes at 5°, and boils at 80°, and its specific gravity is 0·880 at 20°. It is insoluble in water, but miscible with alcohol and ether in all proportions, and, like the latter, dissolves fats, resins, phosphorus, etc. The liquid is very inflammable also, and burns with a luminous, smoky flame, its vapour being sometimes used for enriching coal-gas.

Bromobenzene and Dibromobenzene.—Benzene is a very stable substance. It can be boiled with oxidising mixtures, such as chromic acid or acid permanganate, without being appreciably decomposed, and in this respect, in fact, is practically as stable as the paraffins. But on the other hand it is much more readily chlorinated and brominated than these saturated hydrocarbons, and is attacked by nitric and sulphuric acids.

When the hydrocarbon is boiled in a reflux apparatus with a molecular equivalent of bromine, hydrogen bromide is evolved in large quantities, and a bromo-substitution product formed. The action proceeds more quickly with a carrier (Müller, 1862)—iodine, aluminium chloride, or preferably, ferric bromide, made by dissolving some iron filings in the mixture. As soon as bromine vapours cease to appear, the product is washed with water and dilute caustic soda, and then distilled with steam, in the same way as in the isolation of glycerol (Fig. 10). Some unchanged benzene first passes over, but as soon as the oily drops sink to the bottom of the water the distillate is collected apart. Towards the end of the distillation crystals of dibromobenzene appear in the condenser. The heavy bromobenzene is then dried with calcium chloride and fractionated.

The dibromo-compound is readily purified by recrystallisation from alcohol. The product is dissolved in hot alcohol, and the solution cautiously diluted with hot water until slightly but permanently turbid. It is then filtered through a hot funnel, the dibromo-derivative quickly crystallising out as the filtrate cools.

Bromobenzene, C_6H_5Br (Couper, 1857), is a heavy, colourless, insoluble liquid, which boils at 157°, and has a specific gravity of 1·52 at 0°. Its odour is aromatic and pleasant (see also p. 272).

Paradibromobenzene, $C_6H_4Br_2$, is a colourless, crystalline substance, which melts at 89°, and boils at 219°.

Although formed from benzene in the same way as ethyl chloride from ethane, bromobenzene differs markedly from the paraffinoid compounds. Boiling alkalies do not affect it, and it remains unchanged when heated with alcoholic ammonia. Potassium cyanide does not displace the halogen, nor is the latter withdrawn by boiling with silver acetate.

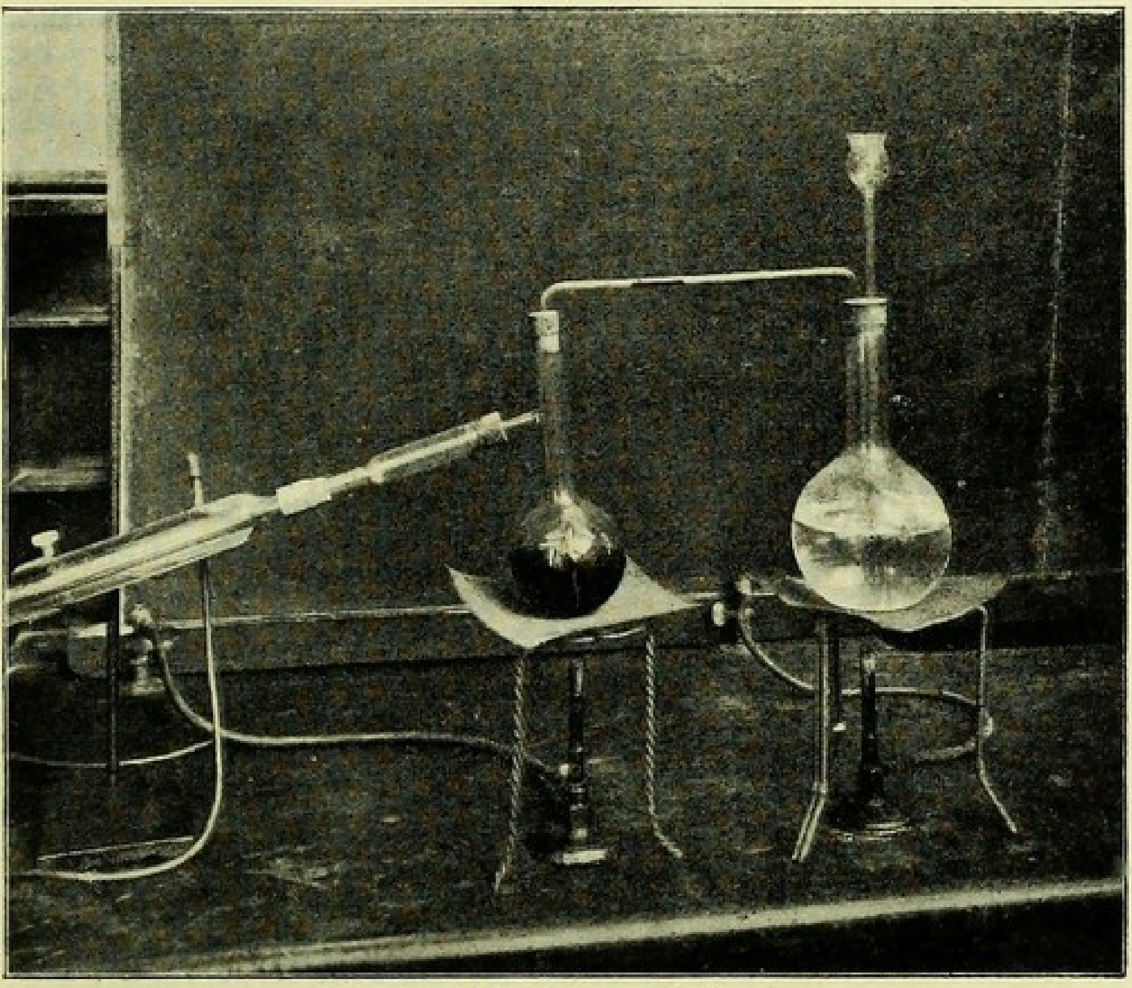


Fig. 10.—Distillation with Steam.

But, on the other hand, the aromatic compound is slowly reduced to the hydrocarbon when its alcoholic solution is digested with sodium amalgam, and the halogen is removed by boiling with sodium, a complex hydrocarbon, diphenyl, $C_6H_5.C_6H_5$ (p. 348), being formed, in the same way as butane from ethyl iodide—

$$C_6H_6 \longleftrightarrow C_6H_5.Br \rightarrow C_6H_5.C_6H_5.$$

Chlorobenzene and Benzene Hexachloride.—The corresponding chloro-derivative is formed in a similar manner, and the iodo-compound can also be made by direct action, provided iodic acid is present to oxidise the hydrogen iodide. All three, however, are more conveniently made through aniline (p. 256). Chlorobenzene, C_6H_5Cl, boils at 132°, and iodo-benzene, C_6H_5I, at 188°.

Benzene thus behaves with the halogens in the same way as the paraffins, except that the substitution is more easily effected, and the products more stable. By the prolonged action of chlorine or bromine the whole of the hydrogen can be displaced in this way, so that here, again, benzene resembles the paraffins. But it can also behave in a different manner, for, when chlorine is saturated with benzene vapour and exposed to direct sunlight, the walls of the vessel become coated with a crystalline additive hexachloride; the compound is more readily prepared by passing chlorine into 1 per cent. caustic soda, on which the benzene is floating, and is purified by distillation with steam. In this respect, therefore, benzene resembles the unsaturated hydrocarbons.

Benzene hexachloride, $C_6H_6Cl_6$ (Faraday, 1825), is a crystalline substance, melting at 157°. Although formed in the same way as the additive olefine and acetylene chlorides, however, it is much less stable, and is readily resolved by heat into hydrogen chloride and trichlorbenzene. On the whole, therefore, benzene behaves as a saturated compound, and only exceptionally and with difficulty as an unsaturated compound—

$$C_6H_6Cl_6 \leftarrow C_6H_6 \rightarrow C_6H_3Cl_3.$$

Nitrobenzene.—The action of nitric acid on benzene is similar to that of the halogens, substitution products being formed. The mono-derivative is easily made by slowly pouring a cold mixture of concentrated nitric and sulphuric acids, with constant agitation, into cold benzene. Heat is evolved, but the temperature must not rise above 45°. The brown, oily product is heated with the acid mixture for half an hour on a water-bath, and after well washing with water and sodium carbonate solution is distilled with steam, any unchanged benzene being collected apart in the same way as with the bromobenzene. The heavy yellow insoluble liquid is separated from the water, and fractionated without drying, and without water, in the condenser, the boiling point being high—

$$C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O.$$

Nitrobenzene, $C_6H_5.NO_2$ (Mitscherlich, 1834), is a yellowish liquid, which has a strong aromatic odour, resembling that of almond essence, but ranker. It is poisonous, and its vapour should not be inhaled. The liquid boils at 209°, and freezes to a crystalline solid, melting at 5°, and its specific gravity is 1·21 at 20°. It is scarcely soluble in water, but freely in organic solvents.

Nitrobenzene is thus formed in the same way as the bromo-compound, by the direct displacement of hydrogen. The action is not without analogy amongst the aliphatic compounds, for, as previously noted, normal decane is nitrated in a similar manner—by dilute nitric acid, however, and only at a high temperature. But the aromatic compound does not resemble the nitro-paraffins in its behaviour. Whilst the latter are acid, and highly unstable, nitrobenzene is a perfectly stable substance, and its hydrogen is not displaceable even by sodium. The nitrogen is directly linked to carbon, for the compound is not hydrolysed by alkalies, and, as will be seen presently (p. 246), the nitro-group is readily reduced to amidogen, NH_2. Nitrobenzene can be reconverted into benzene, but in an indirect manner (p. 256)—

$$C_6H_6 \rightarrow C_6H_5.NO_2 \rightarrow C_6H_5.NH_2.$$

Benzene-Sulphonic Acid.—As stated above, benzene interacts with sulphuric acid, as well as with nitric acid and the halogens. When the hydrocarbon is gently boiled in a reflux apparatus with concentrated sulphuric acid, or better, when it is shaken with warm fuming sulphuric acid, it is gradually dissolved. The product is separated from the excess of sulphuric acid by conversion into the calcium salt, in the same way as ethyl hydrogen sulphate (p. 20), but both the acid and its sodium salt can be boiled down without risk of hydrolysis, as they are quite stable.

The sodium salt may also be separated in a single operation. The crude solution of the hydrocarbon in the acid is cooled with ice, and slowly poured into an excess of ice-cold brine, which is again cooled to 0°. On stirring the liquid mixture it soon begins to crystallise, and eventually becomes almost solid with sodium benzene-sulphonate. This is drained and washed with ice-cold brine until free from acid, and then dried and recrystallised from absolute alcohol until free from chloride (Gattermann, 1891)—

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5.SO_2.OH + H_2O \rightarrow C_6H_5SO_2.ONa + HCl.$$

Benzene-sulphonic acid, $C_6H_5.SO_2.OH$ (Mitscherlich, 1834), is a crystalline substance, which melts at 100° when anhydrous. The sodium salt is similar. The acid differs from the product of the action of sulphuric acid on olefines, in that it is a substitution product, and not an additive compound. It is not affected, moreover, by boiling with caustic alkali, so that it is not an ethereal salt, and the sulphur must therefore be linked to carbon.

Acid hydroxyl is present, however, for by the action of phosphorus pentachloride an acid chloride is formed. A rough mixture of the sodium benzene-sulphonate and solid pentachloride is heated on a water-bath for half an hour. The product is poured into cold water, and kept for a few hours to ensure the complete decomposition of the phosphorus oxychloride and any unchanged pentachloride, and the benzene-sulphonic chloride is extracted with ether (p. 71) and fractionated—

$$C_6H_5.SO_2.ONa + PCl_5 = C_6H_5.SO_2Cl + NaCl + POCl_3.$$

Benzene-sulphonic chloride, $C_6H_5.SO_2Cl$ (Gerhardt, 1852), is an oily liquid which boils at 116°, and freezes to a crystalline solid, melting at 14°. Its odour is pungent and unpleasant. When boiled with water, it is slowly hydrolysed to the acid, and it is readily converted into the corresponding amide by ammonium carbonate. The chloride is simply rubbed in a mortar with excess of the powdered carbonate, and after the violent action has subsided the cooled product is washed with cold water and recrystallised from hot alcohol in the same way as dibromo-benzene.

Benzene-sulphonamide, $C_6H_5.SO_2.NH_2$ (Gerhardt, 1852), is a well defined, easily crystallisable substance, melting at 150°. As a true amide, it is hydrolysed to ammonia and the sodium salt of the acid when boiled with caustic soda solution—

$$C_6H_5.SO_2Cl \rightarrow C_6H_5.SO_2.NH_2 \rightarrow C_6H_5.SO_2.ONa + NH_3.$$

That the sulphur in these sulphonic derivatives is directly linked to carbon, is confirmed by the reduction of the chloride by sodium amalgam to phenyl mercaptan, $C_6H_5.SH$ (p. 254), and by the re-oxidation of this substance to the sulphonic acid by nitric acid—

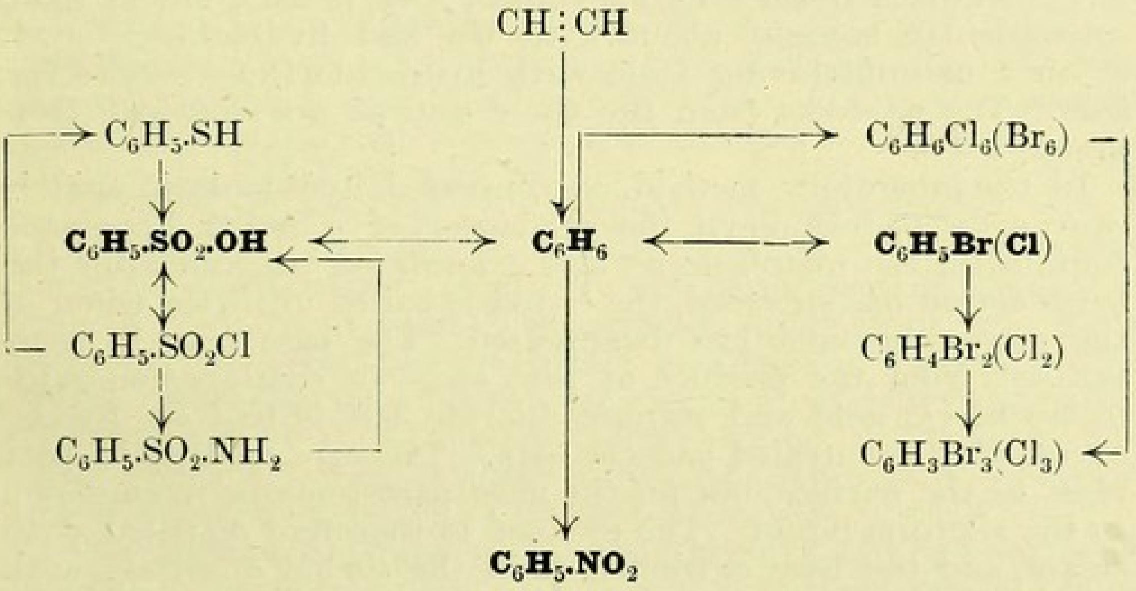
$$\begin{tikzcd}
C_6H_5.SO_2OH \arrow[r] & C_6H_5.SO_2Cl \arrow[r] & C_6H_5.SH \arrow[ll, bend left]
\end{tikzcd}$$

Although benzene-sulphonic acid is stable towards aqueous alkalies it is readily hydrolysed to the hydrocarbon when heated at 170° with sulphuric acid, while steam is led into the solution (Armstrong, 1884). In this way therefore, benzene may be separated both from olefines and from paraffins. As will be seen presently also, when sodium benzene-sulphonate is actually fused with caustic soda, it is hydrolysed, in a different manner, to a hydroxy-derivative of benzene—

$$C_6H_5.OH + K_2SO_3 \leftarrow C_6H_5.SO_2.OH \rightarrow C_6H_6 + H_2SO_4.$$

Synopsis.—The hydrocarbon benzene is formed by the action of heat on gaseous hydrocarbons, and thus in the distillation of coal. It resembles the paraffins in stability and in its action with halogens, but differs from them in readily forming substitution products with nitric and sulphuric acid at ordinary temperatures. It also resembles the olefines in forming additive products with halogens, but these, unlike the olefine additive compounds, are unstable.

BENZENE AND ITS DIRECT SUBSTITUTION PRODUCTS.



CHAPTER XL

ANILINE

Aniline.—When indigo is distilled alone, or with caustic potash, an oily basic liquid passes over, which is termed aniline, from the Portuguese name of the dye—anil (Unverdorben, 1826; Fritzsche, 1840), and the same base can be extracted by shaking coal tar with dilute acids, with which it forms well defined, crystalline salts (Runge, 1834). It is best prepared, however, by reducing nitrobenzene. The reduction was first effected by means of ammonium sulphide (Zinin, 1842, p. 281), but is more conveniently brought about with tin and hydrochloric acid, or on a manufacturing scale with hydrochloric acid and scrap iron. The products from the three sources are identical (Hofmann, 1844).

In the laboratory method, concentrated hydrochloric acid is cautiously poured down the condenser of a reflux apparatus containing the nitrobenzene and granulated tin, and after the brisk action has subsided, the liquid is boiled until the odour of the nitro-compound has disappeared. The base may be crystallised from the product at this stage in combination with hydrochloric acid and stannic chloride, but is best set free by excess of concentrated caustic soda. The oily aniline in part rises to the surface, but for the most part remains in emulsion in the alkaline liquid. The product is therefore distilled with steam, and the base extracted from the turbid distillate with ether. The ethereal solution, dried with solid caustic soda, is then fractionated, first from a water-bath, finally over a flame. On a manufacturing scale, the aniline, which is used in large quantities in the preparation of dyes, drugs, etc., is set free with milk of lime—

$$2C_6H_5.NO_2+3Sn+14HCl=$$
$$(C_6H_5.NH_2,HCl)_2,SnCl_4,2H_2O+2SnCl_4+2H_2O.$$

Aniline or amido-benzene, $C_6H_5.NH_2$ (Unverdorben, 1826), is a colourless, highly refractive liquid, which soon darkens in air, from oxidation. It boils at 184°, and freezes to a crystalline solid, melting at 8°, and its specific gravity is 1·026 at 16°. The liquid, which is somewhat poisonous, is sparingly soluble in water, but freely in organic solvents and in acids, and its odour is faint, but characteristic, resembling that of gas lime.

In its chemical actions, aniline behaves only as a feeble base. It precipitates ferric hydroxide, but does not blue reddened litmus, and although it expels ammonia from ammonium salts this is because of its inferior volatility, the action being parallel to that of silica on fused carbonates. As stated above, its salts are very well defined. The hydrochloride, $C_6H_5.NH_2,HCl$, for example, is precipitated in crystalline flocks on adding hydrochloric acid to the base, and the nitrate, $C_6H_5.NH_2,HNO_3$, is formed in a similar manner with dilute nitric acid. Both can be crystallised from water. Aniline thus resembles the amines in the additive character of its salts, as well as in the manner of its formation, and its aminoid character is confirmed by the ready formation of double salts, such as the yellow platinochloride $(C_6H_5.NH_2,HCl)_2,PtCl_4$, and the stannichloride mentioned above.

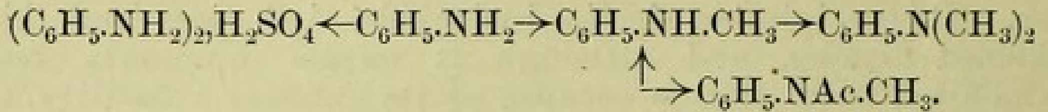
That aniline is a primary amine is proved by the usual reactions. When heated with chloroform and alcoholic soda it is converted, as already noted, into phenyl isocyanide, $C_6H_5.N{:}C$ (p. 253). With carbon bisulphide and mercuric chloride it yields a pungent mustard oil, $C_6H_5.N{:}CS$ (p. 253), in precisely the same way as ethylamine. Finally, it is converted by nitrous acid into the corresponding hydroxy-compound, phenol, $C_6H_5.OH$, with liberation of nitrogen (p. 252)—

$$\begin{array}{c} C_6H_5.N{:}C \leftarrow C_6H_5.NH_2 \\ C_6H_5.OH + N_2 \longleftarrow \quad \longrightarrow CS(NH.C_6H_5)_2 \rightarrow CS{:}N.C_6H_5. \end{array}$$

Aniline is much less stable than benzene and nitrobenzene, and, as noted above, is slowly oxidised even by air. It is reconverted by alkaline permanganate ultimately into nitrobenzene, but several intermediate products are known (p. 376). With bleaching solution the base forms a characteristic violet coloration, and it is also distinguished by the intense blue colour which is formed when a drop of bichromate is added to its solution in excess of concentrated sulphuric acid.

The Methyl-Anilines and Phenylamines.—When aniline is heated with methyl iodide, it takes up three methyl groups, in the same way as any other primary amine, forming an ammonium salt. Phenyl-trimethyl-ammonium iodide, $C_6H_5.NMe_3I$, is a crystalline substance, which resembles the alkyl-ammonium salts, and is similarly convertible into a crystalline caustic hydroxide, $C_6H_5.NMe_3.OH$.

Intermediate compounds are also formed, just as with ethylamine. On acidifying the product of the action with dilute sulphuric acid, unchanged aniline sulphate crystallises out, and on steam-distilling the mother liquor with caustic soda, a mixture of methyl-aniline and dimethyl-aniline passes over. As methyl-aniline forms a solid acetyl derivative, which separates on adding acetic chloride to the mixture, whilst dimethyl-aniline, as a tertiary amine is unaffected by this agent, the two amines are readily separated, and can be recovered by distilling the amine and mother liquor with caustic soda—



$$(C_6H_5.NH_2)_2,H_2SO_4 \leftarrow C_6H_5.NH_2 \rightarrow C_6H_5.NH.CH_3 \rightarrow C_6H_5.N(CH_3)_2$$
$$\uparrow\!\!\rightarrow C_6H_5.NAc.CH_3.$$

As in the case of the aliphatic compounds, however, the derived amines are best made by special methods, the secondary compound from acetanilide (below), and the tertiary compound, which is used in large quantities in the dye industry, by passing methyl chloride under pressure into an agitated mixture of aniline and milk of lime at 100°—

$$C_6H_5.NH_2+2CH_3Cl+Ca(OH)_2=C_6H_5.N(CH_3)_2+CaCl_2+2H_2O$$

Methyl-aniline, $C_6H_5.NH.CH_3$ (Hofmann, 1850), is an oily liquid resembling aniline, and boiling at 193°. As an amine, it forms the usual additive salts, and as a secondary amine, an oily nitroso-compound, $C_6H_5.N(NO).CH_3$.

Dimethyl-aniline, $C_6H_5.N(CH_3)_2$ (Hofmann), is a similar liquid, boiling at 192°. It is distinguished from the aliphatic tertiary amines by forming with nitrous acid a crystalline nitroso-compound, nitroso-dimethylaniline, $NO.C_6H_4.N(CH_3)_2$ (p. 284), in which the nitroso-group is linked to the hydrocarbon nucleus.

Although aniline is thus on the whole analogous to the alkyl-amines, it differs from them in certain respects. Thus sodium dissolves in it, just as in alcohol, displacing hydrogen, and the disodium aniline, $C_6H_5.NNa_2$, thus formed, an amorphous and easily soluble powder, interacts with bromobenzene in much the same way as sodium ethoxide with ethyl bromide, forming diphenyl-aniline or triphenylamine.

Triphenylamine, $N(C_6H_5)_3$, is a neutral crystalline substance, which melts at 127°, and does not form salts with acids. The intermediate phenyl-aniline or diphenylamine is made in quantity for the dye industry by heating aniline hydrochloride with aniline, at 240°.

Diphenylamine, $NH(C_6H_5)_2$ (Hofmann, 1864), is a crystalline substance, which melts at 54°, and boils at 302°. Its properties are intermediate to those of the primary and tertiary amine, and it is a feeble base, although its salts are decomposed by water. Like aniline it forms a sodium derivative, which is converted into triphenylamine when heated with bromobenzene, and its solution in concentrated sulphuric acid gives an intense blue colour with nitrites.

Acetanilide.—As noted above, methyl-aniline readily interacts with acetyl chloride. All primary and secondary amines in fact behave in this way, and as the aromatic compounds of this class are well defined, stable, crystalline substances, they are useful in isolating the amines, and as will be seen later, in other respects also.

The aniline compound, acetanilide, is formed when aniline is mixed with acetic chloride or oxide, a violent action occurring, and the product becoming solid. It is more economically made by boiling the base with glacial acetic acid in a reflux apparatus. The aniline acetate at first formed is gradually dehydrated, and on fractionating the product after some hours boiling, the new product passes over, preceded by water and a little unchanged acetic acid. It is collected in the same way as acetamide, and recrystallised several times from boiling water—

$$C_6H_5.NH_2 + CH_3.COOH \rightarrow C_6H_5.NH_3.O.CO.CH_3 \rightarrow C_6H_5.NH.CO.CH_3 + H_2O.$$

Acetanilide or phenyl-acetamide, $C_6H_5.NH.CO.CH_3$ or $CH_3.CO.NH.C_6H_5$ (Gerhardt, 1853), is a white crystalline substance, which melts at 112° and boils at 304°, but unlike acetamide is only sparingly soluble in cold water. It is used as an antipyretic, under the name of antifebrin.

As an amide, acetanilide is readily hydrolysed by caustic alkalies to acetic acid and the ammonia, aniline. The imido-hydrogen is easily replaced by sodium, in the same way as that of aniline, and when the crystalline sodium derivative is boiled with methyl iodide in toluene solution, methyl-acetanilide is formed, identical with the acetyl derivative of methyl-aniline, and resolvable into this base by hydrolysis—

$$\begin{aligned}
&C_6H_5.NH_2 + CH_3.COOH \rightarrow C_6H_5.NH.CO.CH_3 \\
&\qquad\qquad \rightarrow C_6H_5.NNa.CO.CH_3 \, C_6H_5.NMe.CO.CH_3 \rightarrow \\
&\qquad\qquad\qquad\qquad \uparrow \\
&\qquad\qquad\qquad\qquad \rightarrow C_6H_5.NH.CH_3.
\end{aligned}$$

Many other anilides or aniline-amides have been made—oxanilide, for example, $[CO.NH.C_6H_5]_2$. They are similar to acetanilide, and are prepared in a similar manner. Thiocarbanilide, the anilide of thiocarbonic acid, is readily made from aniline and carbon bisulphide. The two liquids are heated with alcoholic potash on a water bath for an hour or two, and after distilling off the excess of bisulphide, the anilide is precipitated by pouring the product into cold water. The precipitate is washed with dilute hydrochloric acid and water, and recrystallised from alcohol.

Thiocarbanilide, $CS(NH.C_6H_5)_2$, is a crystalline substance, melting at 154°. It is converted into phenyl mustard oil (p. 253) when boiled with concentrated hydrochloric acid.

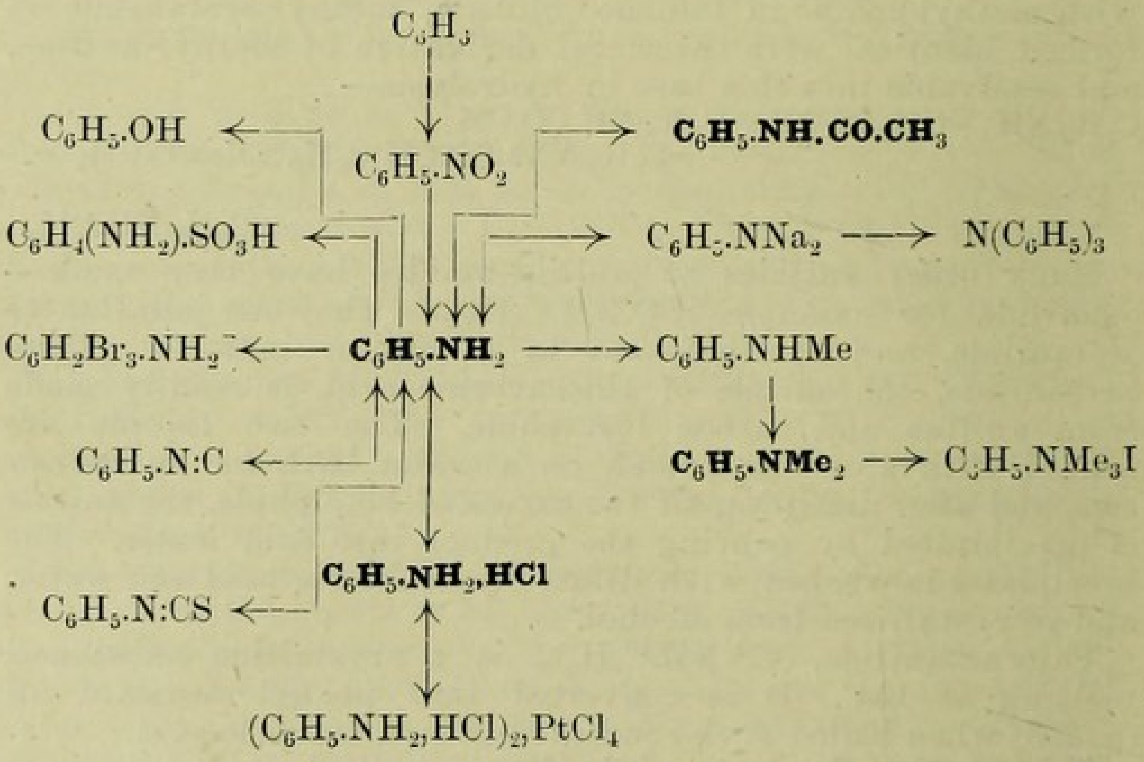
Substitution Products of Aniline.—Aniline is not only more unstable than benzene, but more readily affected by substituting agents. Thus on adding bromine water to aniline hydrochloride solution, tribromaniline is precipitated. Tribromaniline, $C_6H_2Br_3.NH_2$ (Fritzsche, 1842), is a crystalline solid melting at 119°. It is a neutral substance, the bromine counteracting the basic effect of the amido-group. The mono- and di-bromo-compounds, which are obtained by distilling mono- and dibrom-indigo with potash (Hofmann, 1845), and in other ways, are intermediate in properties, the basicity of the molecule diminishing as the number of bromine atoms increases.

With sulphuric acid aniline not only forms a sulphate, but an amido-acid akin to the aliphatic amido-acids. The aniline is dissolved in the concentrated acid, and the solution heated in an oil bath at 200° until the base is no longer liberated by the addition of caustic soda to a sample of the product. The mass is then poured into cold water, and recrystallised, with the addition of animal charcoal to remove colouring matter.

Sulphanilic acid, $C_6H_4(NH_2).SO_2.OH$ (Gerhardt, 1846), is a crystalline, neutral substance, which chars when heated. Its basic and acid properties, like those of the aliphatic amido-acids, are very feeble. It is used in the dye industry (p. 379).

Synopsis.—Aniline is the amido-compound corresponding with nitro-benzene. In many respects it resembles the aliphatic primary amines, but it is much less basic, and as a benzene derivative readily forms substitution products.

ANILINE.



CHAPTER XLI

PHENOL: THE PHENYL RADICLE

Phenol.—The second fraction obtained in the distillation of coal tar, passing over below 210°, and termed the middle oil, consists chiefly of a semi-acid substance, phenol, and a solid hydrocarbon, naphthalene. It constitutes about 10 per cent. of the tar, and is approximately equal in specific gravity to water.

After the oil has been cooled, and separated from the naphthalene which crystallises out, it is agitated with warm caustic soda, which dissolves the phenol. The solution is then fractionally neutralised with dilute sulphuric acid, tarry matter, and compounds homologous with phenol being first precipitated, and finally the oily phenol itself. This is purified by redistillation and fractional crystallisation, in much the same way as acetamide, the oily mother liquors constituting the inferior forms of commercial carbolic acid.

Phenol, or carbolic acid, $C_6H_5.OH$ (Runge, 1834), is a colourless, crystalline substance, which melts at 43°, and boils at 181°. On exposure to air and daylight, especially when not quite pure, it slowly reddens and deliquesces. Phenol is very corrosive and poisonous, and it is a powerful antiseptic. The odour of the pure substance is aromatic and pleasant, and its taste sweet, but burning. Phenol is soluble in water and organic solvents, and is volatile with steam.

Phenol is slightly acid, and was hence originally termed carbolic or phenic acid, but its acid properties are very feeble, for it does not interact with alkali carbonates. It is dissolved by caustic alkalies, however, as noted above, and the solutions yield on evaporation crystalline compounds, the carbolates or phenates, in which an atom of hydrogen is replaced by metal. Similarly, a violet coloration, destroyed even by acetic acid, is produced when ferric chloride is added to a solution of phenol.

On the other hand, phenol shows many of the properties of an alcohol, and has on this account been termed phenyl hydrate, or phenyl alcohol (Laurent, 1841; *φαινειν*, to give light).* Thus, when heated with acetic anhydride, it is converted into phenyl acetate, $C_6H_5.OAc$, a liquid boiling at 195°, and hydrolysable in the normal manner to phenol and acetic

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* From its occurrence in coal-gas bye-products.

acid. Phenol potassium sulphate, $C_6H_5.KSO_4$, also, is formed by boiling a solution of potassium phenate and pyrosulphate, and is excreted in the urine after the administration of phenol. It is a crystalline solid.

On heating sodium phenate with methyl iodide, phenyl methyl ether is formed, in the same way as methyl ethyl ether from methyl iodide and sodium ethoxide, but the action proceeds much more readily, and even in presence of water. Phenyl methyl ether, or anisole, $C_6H_5.O.CH_3$, is a light, insoluble liquid, which boils at 154°, and has a very fragrant odour. It is quite stable towards caustic alkalies, and is, therefore, not an ethereal salt, but, unlike the aliphatic ethers, it is hydrolysable by hydriodic acid at the ordinary boiling temperature (see also p. 398). Phenyl oxide or ether, $(C_6H_5)_2O$, a crystalline compound formed by fusing phenol with zinc chloride, is also quite stable.

The presence of hydroxyl, suggested by these acid and alcoholic properties, can be proved in the usual manner by the action of the phosphorus halogen compounds. When phenol is heated with phosphorus pentabromide, for example, the hydroxyl is replaced by bromine, and as the phenyl bromide thus formed is identical with bromobenzene (Riche, 1862), phenol itself is hydroxy-benzene. This is confirmed, moreover, by various syntheses, and by the direct conversion of phenol into benzene when its vapour is passed over red-hot zinc, best in the form of dust spread over pumice (Baeyer, 1866)—

$$\begin{tikzcd}C_6H_6 & C_6H_5.OH \arrow[l] \arrow[r] & C_6H_5.Br \arrow[ll, <->, bend left]\end{tikzcd}$$

Considered as an alcohol, phenol resembles the tertiary alcohols, for, when strongly oxidised, it does not yield an acid or a ketone containing the same number of carbon atoms, but simply breaks up. Carbon dioxide is the principal product with concentrated permanganate at a high temperature. With nitric acid and bromine, however, substitution products are formed.

Thus, when bromine water is added to phenol solution, tribromophenol is precipitated in light, white flocks. Tribromophenol, $C_6H_2Br_3.OH$ (Laurent, 1842), is a crystalline substance having a very characteristic odour. It is reconverted into phenol by reduction with sodium amalgam in aqueous solution, and thus serves for the identification of the hydroxy-compound.

Phenol also gives two characteristic colour reactions: a bluish colour when mixed with bleaching solution, and a change from brown through green to intense blue when added to a solution of sodium nitrite in a large excess of concentrated sulphuric acid (Liebermann).

Conversion of Benzene into Phenol.—As stated above, aniline is readily converted into phenol. The operation is conducted in the same way as with acetamide and ethylamine, cold sodium nitrite solution being added to an ice-cold solution of the base in dilute sulphuric acid, until excess is shown by the nitrous acid blueing a paper soaked in potassium-iodide-starch solution. The product is heated for half an hour on a water-bath, and after the evolution of nitrogen has ceased the phenol is extracted with ether and fractionated (Hunt, 1859)—

$$C_6H_5.NH_2+NO.OH=C_6H_5.OH+N_2+2H_2O.$$

A second important synthesis consists in fusing potassium benzene-sulphonate with caustic potash. The alkali is melted in an iron or nickel dish with a little water, and the powdered sulphonate slowly stirred in. The mass is kept fused for half an hour at a temperature not exceeding 200°, and is then cooled and dissolved in water. On acidifying the filtered solution with dilute sulphuric acid, sulphur dioxide is given off in abundance, and, after this has been expelled by boiling, the phenol can be extracted with ether (Kekulé, Wurtz, 1867). The yield with caustic soda is not as good—

$$C_6H_5.SO_2.OK+2KOH=C_6H_5.OK+K_2SO_3+H_2O.$$

Conversely, phenol can be converted into aniline by heating with solid ammonio-zinc chloride, $ZnCl_2,NH_3$, at a high temperature. This double salt, which is formed by passing dry ammonia over zinc chloride, is dissociated by heat, and the zinc chloride thus set free assists the action of the ammonia in withdrawing water. The yield is very small, however—

$$C_6H_5.OH+NH_3=C_6H_5.NH_2+H_2O.$$

The Phenyl Radicle.—The mono-substitution products of benzene are thus intermediate to the derivatives of the aliphatic acids and alcohols, the phenyl radicle, C_6H_5 or Ph, which passes through the various reactions, resembling on the one hand the tertiary alkyl radicles, and on the other hand, to a certain extent, those of the feebler acids. Phenol, or phenyl hydroxide, is thus intermediate to the alcohols and acids, just as aniline or phenylamine falls between the amines and the amides.

The phenyl radicle enters into combination with metals and other elements in the same way as the alkyl radicles. Thus by the action of sodium amalgam on a boiling solution of bromobenzene in benzene, mercury diphenyl, $Hg(C_6H_5)_2$, is formed, a crystalline substance melting at 120°.

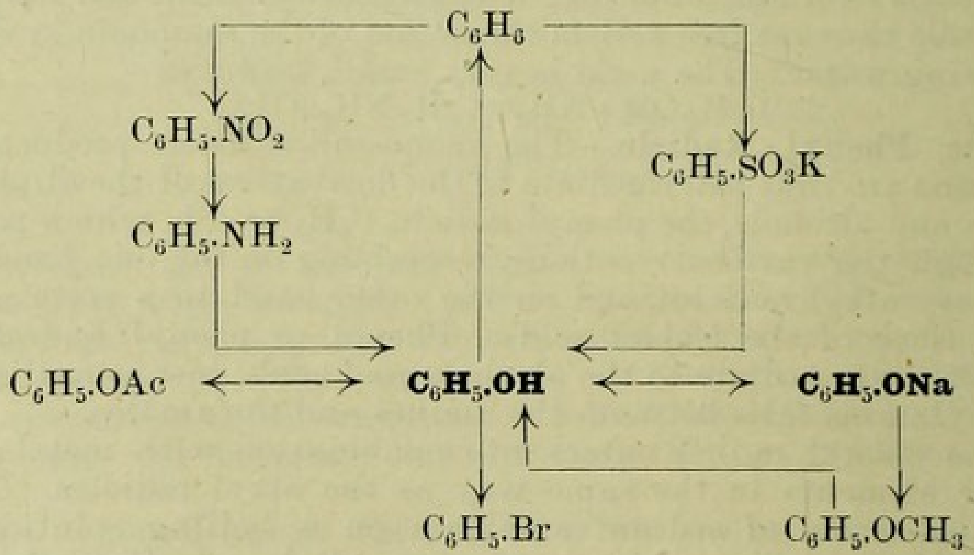
The nitrogen compounds have been already mentioned. Phenyl isocyanide, $C_6H_5.N{:}C$ (p. 115), is a liquid which boils at 165°, and resembles the alkyl isocyanides in odour. Phenyl mustard oil, or isothiocyanate, is formed, as already noted, by the action of carbon bisulphide and mercuric chloride on aniline, and by boiling thiocarbanilide with excess of concentrated hydrochloric acid in a reflux apparatus. It separates as an oil, which can be distilled off with steam. Phenyl isothiocyanate, $C_6H_5.N{:}CS$, is a colourless liquid, which boils at 222°, and has the pungent and characteristic odour of the mustard oils.

Phosphorus and sulphur compounds analogous to aniline and phenol are also known. The phenyl mercaptan, for example, formed by reducing benzene-sulphonic chloride (p. 244), is also formed by fusing potassium benzene-sulphonate with potassium hydrosulphide, and from phenol itself by the action of phosphorous pentasulphide. Phenyl mercaptan, $C_6H_5.SH$, is a mobile liquid, which boils at 168°. Its vapour is very irritating to the eyes.

Owing to the unique character of the radicle, and in particular the fixity of the halogen in the halogen compounds, the phenyl compounds are regarded simply as substitution products of benzene; aniline, for example, as amido-benzene (Griess), and not as phenylamine. As will be seen later, there are other aromatic ammonia and hydroxy-derivatives which much more closely resemble the aliphatic amines and alcohols.

Synopsis.—Phenol is the hydroxy-compound corresponding with bromobenzene, and, owing to the somewhat acid character of the phenyl radicle, is intermediate in character to the aliphatic tertiary alcohols and acids.

PHENOL AND THE PHENYL RADICLE.



CHAPTER XLII

DIAZOBENZENE AND PHENYLHYDRAZINE

Diazobenzene and its Salts.—In the conversion of aniline into phenol, it is noteworthy that until the temperature is allowed to rise no phenol is formed, nor nitrogen evolved, and that beyond the disappearance of the nitrous acid no change appears to take place. The action, in fact, occurs in two stages, in the first of which the nitrogen remains in combination with the aniline as a condensation product; and if the temperature be kept low throughout, and the presence of excess of water avoided by using nitrous anhydride instead of the acid, this intermediate product can be isolated.

The aniline is dissolved in the requisite amount of dilute nitric acid, and nitrogen trioxide passed into the ice-cooled crystalline paste of the nitrate until a brown liquid is obtained, and on adding ice-cold alcohol-ether to this liquid product, the intermediate diazobenzene nitrate is thrown down as a copious crystalline precipitate. The felted mass is collected in a funnel stopped with a perforated platinum cone, and washed with ice-cold alcohol-ether until white; it must not be allowed to become dry, as it is then dangerously explosive—

$$C_6H_5.NH_2,HNO_3+NO.OH \rightarrow C_6H_5.N{:}N.NO_3+2H_2O.$$

Diazobenzene nitrate, $C_6H_5.N{:}N.NO_3$ (Griess, 1864), is a colourless substance crystallising in long silky needles. It is a salt of a half basic, half acid hydroxide, diazobenzene, $C_6H_5.N{:}N.OH$, an oily liquid which can be precipitated from the solution of its potassium salt with acetic acid. The chloride and sulphate can be obtained in the same way, in the latter case substituting amyl nitrite for the nitrous anhydride, and the crystalline potassium salt, $C_6H_5.N{:}N.OK$, is formed by pouring an ice-cold solution of the chloride into a saturated solution of caustic potash. Diazobenzene and its salts are exceedingly unstable, the dry crystals of the nitrate detonating with great violence when struck with a hammer, or even when pressed or slightly heated.

The constitution of the diazobenzene salts as monosubstitution products of benzene follows from their conversion into phenol when warmed with water (p. 256), and that the second nitrogen atom is directly linked to the first is proved by the reduction of the chloride to the corresponding salt of phenylhydrazine (p. 257)—

$$C_6H_5.OH \leftarrow C_6H_5.N{:}N.Cl \rightarrow C_6H_5.NH.NH_2.$$

Diazobenzene itself may be regarded as the phenyl derivative of an unknown nitrogen compound of the formula NH:N.OH, or $NH_2.NO$, which may be imagined to exist transiently in the conversion of ammonium nitrite into nitrogen and water—

$$NH_2+NO.OH \rightarrow NH_4.O.NO[\rightarrow NH_2.NO+H_2O] \rightarrow N_2+2H_2O.$$

The aliphatic amines do not form diazo-compounds, but derivatives of this kind can be made from glycosine and guanidine (p. 259).

The Diazo-Reactions.—The diazo-compounds are useful by reason of their very instability. The conversion of aniline into phenol is due, as already indicated, to the formation and decomposition of the diazo-sulphate, for on warming the solution of the latter, nitrogen is at once evolved, as in the nitrous acid reaction, and phenol set free. The sulphuric acid radicle unites with the hydrogen of the water, and the phenyl with the hydroxyl—

$$C_6H_5.N:N.HSO_4+H.OH \rightarrow C_6H_5.OH+N_2+H_2SO_4.$$

But besides this simple hydrolysis, various other decompositions can be effected, and the phenyl brought into combination with halogen and other radicles. On warming a solution of a diazo-salt to which excess of concentrated hydrochloric acid, for example, has been added, nitrogen is evolved and acid set free as before, but the phenyl radicle now unites with the chlorine, and chlorobenzene is thrown down as a heavy oil. Similarly with hydrobromic and hydriodic acids or their alkali salts, bromobenzene and iodobenzene are produced—

$$C_6H_5.N:N.Cl+=C_6H_5Cl+N_2.$$

The diazo-reaction in fact affords the best and quickest method of making the halogen benzenes, for it is unnecessary to actually isolate the diazo-salt. The aniline is dissolved in exactly double the amount of acid required to combine with it, the alkali nitrite slowly added to the cold solution in the manner previously described, and the aniline thus "diazotised" is mixed with a solution of the requisite acid or salt. On heating the product, nitrogen is evolved, and the dark oily halogen benzene—iodobenzene, for example—separates. After distilling it with steam, and shaking the ethereal extract of the distillate with strong caustic soda solution to remove phenol, the halogen-benzene is dried and rectified in the usual manner—

$$C_6H_5.N:N.Cl+KI \rightarrow C_6H_5.I+N_2+KCl.$$

The action proceeds particularly smoothly with the cuprous salts of the acids, or more conveniently with the halogen acids and precipitated copper, owing to the formation of unstable additive compounds (Sandmeyer, 1884), and in this way also, by means of cuprous cyanide, the diazo-group may be replaced by cyanogen, an action of great synthetic importance (p. 260)—

$$C_6H_5.N:N.Cl,2CuCl=C_6H_5.Cl+N_2+2CuCl.$$

The diazo-group may even be replaced by hydrogen, for when the sulphate is boiled with alcohol, or better with a solution of stannous hydroxide in caustic soda, nitrogen and sulphuric acid are eliminated, and benzene itself is formed, and may be distilled off with steam in practically theoretical amount. The same transformation is effected by adding powdered sodium nitrite, with the usual precautions, to an alcoholic solution of aniline saturated with hydrogen chloride gas. In either case the phenyl radicle combines with the nascent hydrogen, which thus replaces the amido-group of the aniline. The amido-group is said to be eliminated from the compound—

$$C_6H_5.N{:}N{:}Cl + 2H = C_6H_5.H + N_2 + HCl.$$

Diazobenzene forms an additive compound with bromine, diazobenzene perbromide, $C_6H_5.NBr.NBr_2$, which is precipitated as a crystallisable oil on adding a solution of bromine in potassium bromide to a diazotised solution of the amine. The perbromide is converted into bromobenzene by boiling with alcohol, the latter being oxidised to aldehyde. In these diazo-transformations, as in the ease with which it forms substitution products, aniline is thus markedly different from the aliphatic amines.

Phenylhydrazine.—The reagent phenyl-hydrazine is formed by addition of hydrogen to diazobenzene chloride. The reduction is effected by means of stannous chloride in acid solution, and as in the previous cases the diazo-compound need not be isolated. The chloride having been formed by adding an ice-cold solution of sodium nitrite to a paste of aniline hydrochloride, a solution of stannous chloride in concentrated hydrochloric acid is slowly added with constant stirring, care of course being taken to avoid rise of temperature. The phenyl-hydrazine hydrochloride, thus rapidly precipitated, is collected and dissolved in a little water, and the base set free with excess of caustic soda solution and extracted with ether. The ethereal solution is then dried with solid potassium carbonate, and fractionated, best under somewhat reduced pressure—

$$C_6H_5.N{:}N.Cl + 2SnCl_2 + 5HCl = C_6H_5.NH.NH_2,HCl + 2SnCl_4.$$

On a large scale the reduction is effected with sodium sulphite. The diazotised solution is added to a concentrated ice-cold solution of sodium sulphite, the product becoming almost solid from the separation of a yellow crystalline compound, sodium diazobenzene-sulphite, $C_6H_5.N{:}N.SO_3K$. This is Na then warmed with excess of the sulphite, and thus reduced to the corresponding phenyl-hydrazine-sulphite, a colourless salt which is hydrolysed to sulphuric acid and phenyl-hydrazine hydrochloride by boiling with concentrated hydrochloric acid. The base is then separated as before—

$$\begin{aligned} C_6H_5.N{:}N.Cl + Na.SO_3Na &\rightarrow C_6H_5.N{:}N.SO_3Na + NaCl \\ &\rightarrow C_6H_5.NH.NH.SO_3Na \rightarrow C_6H_5.NH.NH_2 \\ &\qquad + NaCl + H_2SO_4. \end{aligned}$$

Phenyl-hydrazine, $C_6H_5.NH.NH_2$ (Fischer, 1878), is a colourless crystalline solid, having a pleasant and slightly acid aromatic odour. It melts at 23°, and boils at 242°, decomposing slightly at the latter temperature. Like aniline it is slowly oxidised by the air, turning brown and syrupy. The hydrochloride is a stable crystalline salt, and the acetate, which is unstable, may be made by simply adding excess of sodium acetate and a little acetic acid to its aqueous solution. It is also readily prepared by dissolving the base in dilute acetic acid, filtering from impurity if necessary.

Phenyl-hydrazine is a moderately powerful reducing agent. When it is boiled with alkaline copper tartrate, for example, cuprous oxide is precipitated, whilst with acetic acid and copper sulphate solution, nitrogen is eliminated, and benzene set free. The reaction is quantitative, and the hydrochloride under the same conditions is converted into chlorobenzene. When however the hydrochloride is distilled with zinc dust it is reduced to aniline and ammonia—

$$C_6H_5.NH_2+NH_3 \leftarrow C_6H_5.NH.NH_2 \rightarrow C_6H_5.H+N_2+H_2O.$$

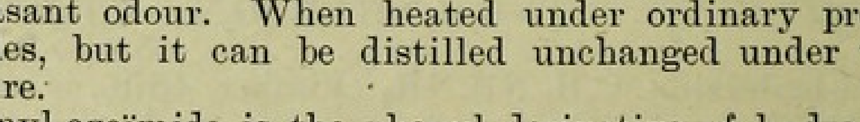
As an aminoid compound the hydrazine forms additive salts with acids. With alkyl iodides and nitrous acid it behaves as a secondary amine, phenyl-nitroso-hydrazine, $C_6H_5.N(NO).NH_2$, being formed in the latter case, an unstable substance which is quickly dehydrated to phenyl-azoïmide (below).

As previously stated, phenyl-hydrazine is a valuable reagent for aldehydes and ketones, with which, in acetic acid solution, it forms condensation products, the hydrazones (Fischer, 1884, pp. 72, 76) which are readily hydrolysed by mineral acids. The osazones, or double hydrazones (p. 189); and the hydrazides, or hydrazine amides (p. 185) have also been already dealt with.

The constitution of phenyl-hydrazine follows in part from its interconvertibility with aniline, and in part from its relation to ethylaniline. By reducing the nitroso-compound of this secondary amine (p. 217), ethyl-phenyl-hydrazine is formed, and this base combines with ethyl bromide to form an additive compound identical with that resulting from the action of ethyl bromide on phenyl-hydrazine itself—

$$C_6H_5.NEt.NO \rightarrow C_6H_5.NEt.NH_2 \rightarrow C_6H_5.NEt.NH_2,EtBr \leftarrow C_6H_5.NH.NH_2$$

Phenyl-azoïmide: Hydrazine and Azoïmide.—The dehydration product formed by warming phenyl-nitroso-hydrazine with water is also produced by the action of ammonia on diazobenzene perbromide—



$$C_6H_5.N{<}\begin{matrix}NO\\NH_2\end{matrix} \rightarrow C_6H_5N{<}\begin{matrix}N\\ \cdot\cdot\\ N\end{matrix} \leftarrow C_6H_5.NBr.NBr_2+NH_3.$$

Phenyl-azoïmide or diazobenzene-imide, $C_6H_5.N_3$ (Griess, 1867), the constitution of which follows from these methods of formation, is a yellow insoluble oil of very penetrating and unpleasant odour. When heated under ordinary pressure it explodes, but it can be distilled unchanged under very low pressure.

Phenyl-azoïmide is the phenyl derivative of hydrazoic acid or azoïmide, N_3H. Like the halogen benzenes it cannot itself be hydrolysed, but its nitro-derivative, prepared from nitraniline (p. 282), is readily resolved by boiling potash into nitrophenol and potassium azoïmide, $N_3.K$—

$$C_6H_4(NO_2).N_3 + 2KOH = C_6H_4(NO_2).OK + N_3.K + H_2O.$$

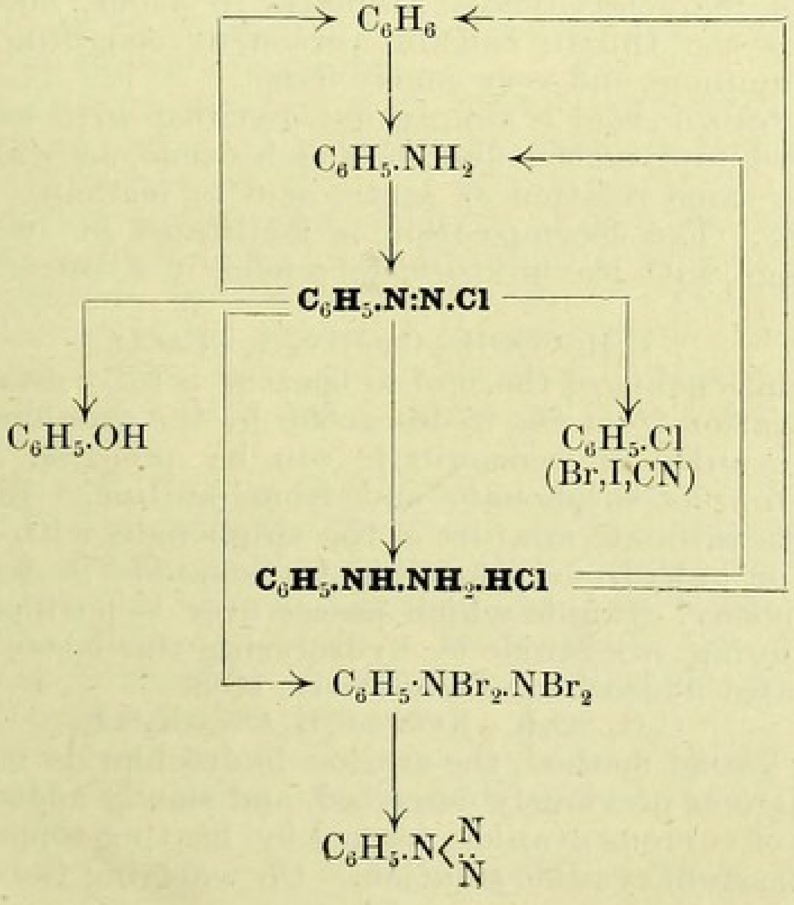
Azoïmide can itself be made in this way from guanidine. Amido-guanidine hydrochloride (p. 226) is diazotised in the same way as aniline, and the diazo-guanidine chloride thus formed is resolved by caustic soda into cyanamide and sodium azoïmide, from which the azoïmide gas is set free by acids—

$$NH{:}C\left<\begin{matrix}NH_2\\NH.NH_2\,HCl\end{matrix}\right. \rightarrow NH{:}C\left<\begin{matrix}NH_2\\NH.N{:}NCl\end{matrix}\right. \rightarrow NH_2.CN + N_3.H + HCl.$$

Free hydrazine can also be made from amido-acetic acid by the diazo-reaction. Ethyl amido-acetate is converted in the usual manner into the corresponding diazo-acetate, and the latter reduced and hydrolysed (Curtius, 1887).

Synopsis.—Aniline differs from the aliphatic amines in that it forms with nitrous acid a condensation product, diazobenzene, by means of which it is convertible not only into the corresponding hydroxy-compound, phenol, but also into the hydrocarbon and its halogen and cyano-derivatives, and into a derivative of hydrazine.

DIAZOBENZENE AND PHENYLHYDRAZINE.



SECTION XI

THE BENZYL-BENZOIC GROUP

CHAPTER XLIII

BENZOIC ACID: THE BENZOYL RADICLE

Benzoic Acid.—The benzoic acid from which, as already stated, benzene derives its name, is a volatile substance which occurs free in gum benzoïn, and sublimes on gently heating this natural product (16th century). It is more economically extracted by boiling the gum with milk of lime, and precipitating the acid from the resulting calcium benzoate with hydrochloric acid (Scheele), but is now manufactured by heating calcium phthalate (p. 318) with slaked lime at a moderate temperature.

Benzoic acid, $C_6H_5.COOH$, is a feathery crystalline substance, which melts at 121°, and boils at 249°, but sublimes readily far below its boiling point. It is also volatile with steam. The vapour is characteristically aromatic in odour, but very irritating to the throat, causing persistent coughing; it burns with a luminous and very smoky flame.

When benzoic acid is simply dry-distilled with soda-lime, it is resolved into carbon dioxide and benzene, to which it thus bears the same relation as acetic acid to methane (Mitscherlich, 1834). The decomposition is facilitated by incorporating iron filings with the mixture, to render it a better conductor of heat—

$$C_6H_5.COOH + CaO = C_6H_6 + CaCO_3.$$

The relationship of the acid to benzene is fully established by its preparation from the hydrocarbon by the cyanide synthesis. Phenyl cyanide or benzonitrile can be prepared both from sodium benzene-sulphonate and from aniline. In the first method an intimate mixture of the sulphonate with potassium cyanide or anhydrous potassium ferrocyanide is dry-distilled, and the phenyl cyanide which passes over is purified from the accompanying isocyanide by hydrolysing the latter with cold concentrated hydrochloric acid (Merz, 1868)—

$$C_6H_5.SO_3K + KCN = C_6H_5.CN + K_2SO_3.$$

In the second method, the aniline hydrochloride is diazotised in the manner previously described, and slowly added to a cold solution of cuprous cyanide, formed by heating copper sulphate with potassium cyanide solution. On warming the product on a water-bath nitrogen is evolved in the usual manner, and the cyano-benzene set free as a yellow oil, which is purified by distillation with steam, and extraction with ether (Sandmeyer, 1884)—

$$C_3H_5.NH_2,HCl \rightarrow C_3H_5.N{:}N.Cl \rightarrow C_6H_5.N{:}N.Cl,CuCN \longrightarrow C_6H_5.CN + N_2 + CuCl.$$

Benzonitrile or phenyl cyanide, $C_6H_5.CN$, is a colourless liquid, which has a strong odour of bitter almonds, and boils at 191°. It can also be prepared from benzoic acid by dry-distillation with lead thiocyanate. On boiling the nitrile from any of these sources with caustic soda solution, ammonia is evolved in the normal manner, and on acidifying the cooled product after the evolution of ammonia has ceased, benzoic acid is precipitated. After purification by repeated precipitation from caustic soda solution, it is dried and sublimed through filter paper between watch glasses—

$$C_6H_5.CN + NaOH + H_2O = C_6H_5.COONa + NH_3.$$

The synthetic benzoic acid is in every respect identical with the natural product. It can also be prepared from benzaldehyde, and from toluene (p. 271) and hippuric acid (p. 263).

Acid Derivatives of Benzoic Acid: the Benzoyl Radicle.—Benzoic acid resembles acetic acid in most of its actions. Thus its alkali salts, such as potassium benzoate, $C_6H_5.COOK$, are crystalline, and the silver salt, $C_6H_5.COOAg$, crystallises well and is anhydrous. The ferric salt, $Fe(O.CO.C_6H_5)_3$, however, is a buff, pulverulent precipitate, but like ferric acetate is at once hydrolysed by hydrochloric acid, benzoic acid crystallising out on cooling the yellow solution.

The acid also forms alkyl salts resembling those of acetic acid. Ethyl benzoate, $C_6H_5.COOEt$, for example, is a fragrant, mobile liquid boiling at 213°. It is formed by the action of benzoyl chloride and caustic soda on alcohol, but more conveniently by saturating an alcoholic solution of the acid with hydrogen chloride in the ordinary manner. The product is simply boiled until the excess of the acid gas is expelled, and is then poured into water, the ethereal salt separating as a heavy layer, which is washed, dried and fractionated in the usual way.

Like acetic acid, benzoic acid forms a chloride and oxide, and the former in fact was the first acid chloride prepared. It is made by the action of phosphorus pentachloride on the acid. The two solids are shaken together until the mass is liquid, and hydrogen chloride ceases to be evolved, and the high-boiling benzoyl chloride is separated from the phosphorus oxychloride by simple fractionation.

The chloride was originally made by direct chlorination of benzaldehyde, $C_6H_5.CHO$, and is still prepared on the large scale in this way—

$$C_6H_5.COOH + PCl_5 = C_6H_5.COCl + HCl + POCl_3.$$

Benzoic or benzoyl chloride, $C_6H_5.COCl$ (Liebig and Wöhler, 1832), is a heavy, colourless liquid, having a pungent and unpleasant odour. It boils at 198° and freezes at $-1°$, and its specific gravity is 1·21 at 20°. Like acetyl chloride it is hydrolysed by water, although much more slowly. It is unaffected by cold water, and only slowly affected by boiling water, but it is at once dissolved by caustic soda.

On account of its comparative stability, and by reason also of the better definition and higher melting points of its derivatives, benzoic chloride is often used instead of acetic chloride as a test for alkylic and phenolic hydroxyl. Hexabenzoylmannitol, $C_6H_8(O.CO.C_6H_5)_6$, for example, a well defined crystalline substance, melting at 132°, is readily formed by alternately adding small quantities of benzoyl chloride and caustic soda solution to a cooled solution of the mannitol, the alkali serving to neutralise the hydrochloric acid. All alcoholic and phenolic compounds can be benzoated in this way.

The corresponding oxide, benzoic anhydride, is formed in the same way as acetic anhydride, by boiling benzoyl chloride with sodium benzoate, and then distilling the chlorine-free product. Benzoic anhydride, $(C_6H_5.CO)_2O$, is a crystalline substance melting at 42°. It is used in the same way as benzoic chloride and the acetyl derivatives, as a test for alkylic and phenolic hydroxyl.

Whilst benzoic chloride is less easily hydrolysed than acetic chloride, its oxygen is readily replaced by chlorine by the action of phosphorus pentachloride, and the benzotrichloride thus formed, $C_6H_5.CCl_3$, a liquid boiling at 213°, is hydrolysed by boiling water to benzoic and hydrochloric acids, in the same way as trichlorethane to acetic acid—

$$C_6H_5.CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl.$$

Similarly, when boiled with alcoholic sodium ethoxide, the trichloride is converted into ethyl orthobenzoate, $C_6H_5.C(OEt)_3$, a liquid resembling ethyl orthoacetate and boiling at 220°.

As regards those actions into which it enters as a carboxylic acid benzoic acid is thus very similar to acetic acid, and may be considered as the hydroxide of an acid or oxylic radicle benzoyl, $C_6H_5.CO$ or Bz (benzoic and ὕλη, Liebig and Wöhler). This was the first acid radicle recognised.

Benzamide and Hippuric Acid.—Benzoyl chloride acts with ammonium carbonate or ammonia in the same way as, but much more vigorously than, acetyl chloride, forming the corresponding amide, benzamide. Benzamide, $C_6H_5.CONH_2$, is a crystalline substance which melts at 130°, and is soluble only in boiling water.

As an amide it is hydrolysed by boiling caustic soda solution to ammonia and sodium benzoate, and is dehydrated to benzonitrile by distillation with phosphorus pentoxide. It forms the usual unstable compounds with acids and bases.

The corresponding benzoyl derivative of glycosine occurs in the urine of herbivorous animals, and is known as hippuric acid. It is readily obtained by evaporating horses' or cows' urine to one-sixth, and purifying the crude acid which crystallises out by boiling with water and animal charcoal and recrystallising.

Hippuric acid or benzoyl-amidoacetic acid, $C_6H_5.CO.NH.CH_2.COOH$ (Rouelle, 1773), is a colourless, crystalline substance, melting at 187°. It is readily soluble in hot, but only sparingly in cold, water. As an amide it is hydrolysed by boiling concentrated hydrochloric acid to benzoic acid and the compound ammonia, glycosine, the benzoic acid crystallising out on cooling (Dessaignes, 1846),—

$$C_6H_5.CO.NH.CH_2.COOH + H_2O = C_6H_5.COOH + NH_2.CH_2.COOH$$

Hippuric acid may be synthesised from glycosine by adding benzoyl chloride and caustic soda alternately to its solution in the manner already indicated—

$$C_6H_5.COCl + NH_2.CH_2.COOH + NaOH = C_6H_5.CO.NH.CH_2.COOH + NaCl + H_2O.$$

and it may be synthesised also by heating benzamide with chloracetic acid—

$$C_6H_5.CO.NH_2 + Cl.CH_2.COOH = C_6H_5.CO.NH.CH_2.COOH + HCl.$$

As a monobasic acid, hippuric acid forms metallic and alkylic salts. The ferric salt, for instance, precipitated by ferric chloride from a neutral solution of a hippurate, is a brown flocculent precipitate, which is readily distinguished from the corresponding benzoate by yielding ammonia when heated with soda-lime.

Benzophenone and Acetophenone.—Benzoic acid further resembles acetic acid in that it is converted into a ketone when its calcium salt is dry-distilled—

$$Ca<\begin{matrix}O.CO.C_6H_5\\O.CO.C_6H_5\end{matrix} = CaCO_3 + CO<\begin{matrix}C_6H_5\\C_6H_5\end{matrix}$$

Benzophenone, $C_6H_5.CO.C_6H_5$, is a crystalline substance of very pronounced aromatic odour, which melts at 48° and boils at 307°. It is also formed by boiling benzene with benzoyl chloride in presence of aluminium chloride (see p. 271)—

$$C_6H_5.COCl + C_6H_6 = C_6H_5.CO.C_6H_5 + HCl.$$

Like the aliphatic ketones it is reduced to a secondary alcohol by sodium amalgam. Benzhydrol, $C_6H_5.CHOH.C_6H_5$, is a crystalline substance, melting at 68°, and is reconverted into benzophenone by oxidation. Benzophenone is hydrolysed to benzoic acid and benzene when fused with caustic potash—

$$C_6H_5.CO.C_6H_5 + KOH = C_6H_5.COOK + C_6H_6.$$

A similar mixed ketone, acetophenone, $CH_3.CO.C_6H_5$, is formed by distilling a mixture of calcium benzoate and acetate, and by the action of acetyl chloride on benzene in presence of aluminium chloride, as well as by all the methods used in the formation of acetone.

Acetophenone is a crystalline substance, melting at 20°, and boiling at 202°. It is oxidised by chromic acid in the usual manner to benzoic acid and carbon dioxide—

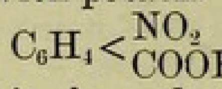
$$C_6H_5.CO.CH_3.+3O=C_6H_5.COOH+CO_2.$$

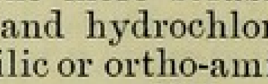
and is reduced by sodium amalgam to a crystalline secondary alcohol, phenyl methyl carbinol, $C_6H_5.CHOH.CH_3$. Many similar ketones have been prepared with other alkyl radicles. Both benzophenone and acetophenone form crystalline phenylhydrazones and oximes, but neither forms a bisulphite compound.

Substitution Products of Benzoic Acid.—Whilst benzoic acid is closely parallel to the acetic acid in its actions as an acid, as a benzene derivative it resembles the aromatic hydrocarbon in readily forming substitution products.

As will be seen later, there are three classes of di-substitution products of benzene, the ortho-, meta-, and para-compounds, and the direct substitution products of benzoic acid belong mainly to the second class.

Meta-chloro- and meta-bromo-benzoic acids are readily formed by direct action of the halogen, whilst the ortho- and para-compounds are prepared indirectly, from the amido-benzoic acids (see below) by the diazo-reaction. The halogen benzoic acids are colourless crystalline substances of high melting point. All the benzene hydrogen atoms can be thus substituted, pentachlorobenzoic acid being known. Owing to the presence of the carboxyl group, the halogen is more easily displaced than in the substituted benzenes, hydroxy-benzoic acids $C_6H_4(OH).COOH$ (p. 302) being formed, for example, when the chloro-compounds are fused with potash.

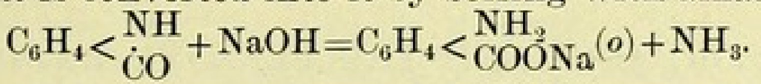
Ortho-nitro-benzoic acid,  $C_6H_4{<}^{NO_2}_{COOH}$ (*o*), a crystalline substance melting at 147°, is formed, together with a large amount of the meta-compound, by direct nitration of benzoic acid with nitre and concentrated sulphuric acid. The two acids are separated by means of their barium salts, the ortho-salt being much the more soluble. Ortho-nitro-benzoic acid is reduced by tin and hydrochloric acid, in the same way as aniline, to anthranilic or ortho-amido-benzoic acid.

Anthranilic acid,  $C_6H_4{<}^{NH_2}_{COOH}$ (*o*) (Fritzsche, 1841), is a crystalline substance melting at 145° It is akin to glycosine in its actions—forms unstable salts with both acids and bases, is neutral to litmus, and is resolved by heat into aniline and carbon dioxide. It differs from the aliphatic compound, however, in that it is converted not only into the corresponding hydroxy-acid, salicylic acid (p. 302), but also by the diazo reaction into chlorobenzoic acid, etc., and into benzoic acid itself—

$$C_6H_4(OH).COOH \leftarrow C_6H_4(NH_2).COOH(o) \rightarrow C_6H_5.NH_2+CO_2.$$

Anthranilic acid is of interest from its genetic connection with indigo (p. 332), from which it was first prepared by distillation with potash, aniline being of course also formed by its further decomposition.

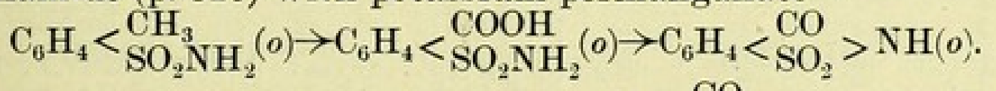
By reducing ortho-nitro-benzaldehyde (p. 269) with tin and hydrochloric acid, anthranil, an internal anhydride or lactame of anthranilic acid is formed. Anthranil, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}$, is a liquid which boils and decomposes at about 210°, and has a characteristic odour. It cannot be formed by dehydration of the acid, but is converted into it by boiling with alkalies—



$$C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}+NaOH=C_6H_4<\genfrac{}{}{0pt}{}{NH_2}{COONa}(o)+NH_3.$$

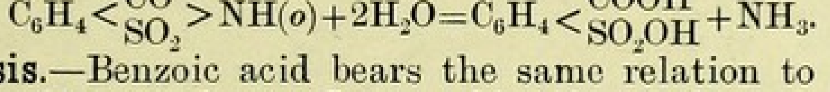
Benzoic acid is not sulphonated by ordinary sulphuric acid, but substitution can be effected by passing sulphuric anhydride vapour into the melted acid. Meta-sulpho-benzoic acid, $C_6H_4<\genfrac{}{}{0pt}{}{SO_3H}{COOH}$ (m), thus formed, is a deliquescent crystalline substance. The ortho- and para-acids are best made indirectly, by oxidising the toluene-sulphonic acids (p. 310).

The imide of ortho-sulpho-benzoic acid, the well-known sweet substance, saccharin, is made by oxidising ortho-toluene-sulphonamide (p. 310) with potassium permanganate—



$$C_6H_4<\genfrac{}{}{0pt}{}{CH_3}{SO_2NH_2}(o)\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{COOH}{SO_2NH_2}(o)\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO_2}>NH(o).$$

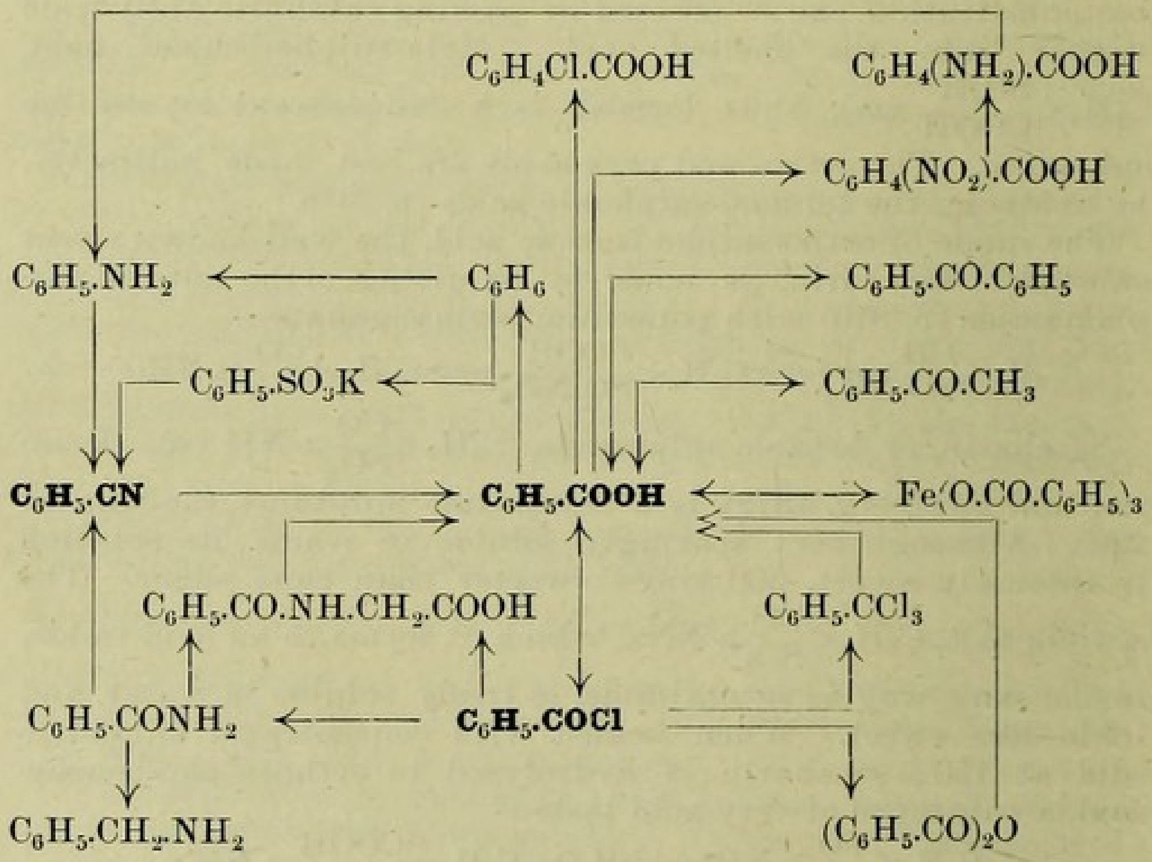
Saccharin, or benzoic sulphinide, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO_2}>NH$ (o), (Remsen and Fahlberg, 1879), is a crystalline substance, melting at 220°. Although very sparingly soluble in water, its solution is intensely sweet, 500 times sweeter than cane sugar. The sodium salt, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO_2}>NNa$, which it forms as an acid imide, in the same way as succinimide, is freely soluble in water, and little less sweet. When heated with concentrated sulphuric acid at 150°, saccharin is hydrolysed to orthosulpho-benzoic acid, a substance of very acid taste—



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO_2}>NH(o)+2H_2O=C_6H_4<\genfrac{}{}{0pt}{}{COOH}{SO_2OH}+NH_3.$$

Synopsis.—Benzoic acid bears the same relation to benzene as acetic acid to methane. It resembles the aliphatic compound in most of its actions, but as a benzene derivative readily forms substitution products.

BENZOIC ACID AND THE BENZOYL RADICLE.



CHAPTER XLIV

BENZALDEHYDE

Benzaldehyde and the Benzal Radicle. — The aldehyde of benzoic acid is the well-known flavouring matter, oil of bitter almonds. When almonds are subjected to pressure, a quantity of almond oil or glycerol trioleate (p. 138) is expressed, but on distilling the residue with steam, benzaldehyde and hydrocyanic acid pass over. These products result from the hydrolysis of the glucoside amygdalin (p. 176) by the accompanying enzyme emulsin.

Benzaldehyde is manufactured on a large scale for the colour industry, etc., by oxidising benzyl chloride (p. 272) with lead nitrate. The chloride is boiled with water and the nitrate in a reflux apparatus, and carbon dioxide steadily passed through the vessel to remove the liberated oxides of nitrogen, which would otherwise oxidise the aldehyde. When the irritating odour of the benzyl chloride has completely disappeared, and the heavy oily product is free from chlorine, it is extracted with ether, and the aldehyde purified from benzyl alcohol, etc., (p. 273) by means of its crystalline bisulphite compound, which resembles that of acetone.

The pure aldehyde is liberated from the washed and dried bisulphite crystals with dilute sulphuric acid, and once more extracted with ether, and the solution is dried with calcium chloride and fractionated. Benzaldehyde can also be made by direct hydrolysis of benzal chloride (below), and by cautious oxidation of benzyl alcohol—

$$2C_6H_5.CH_2Cl+Pb(NO_3)_2=2C_6H_5.CHO+NO+NO_2+PbCl_2+H_2O.$$

Benzaldehyde, $C_6H_5.CHO$ (Liebig and Wöhler, 1832), is a colourless, highly refractive liquid, which boils at 179°, and has the characteristic odour of essence of almonds.

In most respects the aromatic aldehyde resembles its fatty analogues. It is oxidised to benzoic acid by boiling with dilute nitric acid, or even by exposure to air, crystals of the acid being slowly formed when it is kept in an imperfectly stoppered bottle; and it accordingly reduces ammoniacal silver nitrate. Conversely benzoic acid is easily reduced to the aldehyde by dry-distilling its calcium salt with calcium formate, in the same manner as acetic acid to acetaldehyde—

$$Ca(O.CO.C_6H_5)_2+Ca(O.CHO)_2=2CaCO_3+2C_6H_5.CHO.$$

Like acetaldehyde, benzaldehyde is reduced to the alcohol by sodium amalgam in acid solution, and colours bleached rosaniline. With phosphorus pentachloride, or better with carbonyl chloride, it yields a dichloride, benzal or benzylidene chloride, a liquid boiling at 213°, just as acetaldehyde yields ethylidene chloride—

$$C_6H_5.CHO + COCl_2 = C_6H_5.CHCl_2 + CO_2;$$

and this dichloride, which like ethylidene chloride is also formed by direct chlorination of the boiling monochloride, is reconverted into the aldehyde by boiling with water and powdered chalk. The radicle $C_6H_5.CH\!:$ is known as the benzylidene or benzal radicle, and benzaldehyde may thus be regarded either as benzoyl hydride, or as benzal oxide—

$$C_6H_5.CH_3 \rightarrow C_6H_5.CH_2Cl \rightarrow C_6H_5.CHCl_2 \longleftrightarrow C_6H_5.CHO.$$

Additive Compounds and Condensation Products of Benzaldehyde.—The additive compounds of benzaldehyde with sodium bisulphite and hydrocyanic acid are similar to those of acetaldehyde, but the bisulphite compound, as noted above, is much more readily formed. The ammonia compound is different, however, the aldehyde condensing with the ammonia and not forming an additive compound as in the case of the fatty aldehydes.

Hydrobenzamide,

$$\begin{matrix} C_6H_5.CH \\ C_6H_5.CH \\ C_6H_5.CH \end{matrix} \begin{matrix} >N \\ >N \end{matrix}$$

a crystalline substance melting at 110°, is formed as a white precipitate, when benzaldehyde is shaken with aqueous ammonia.

Benzaldehyde further differs from the aliphatic aldehydes in that it does not polymerise, and in its action with caustic soda (see below). The condensation products are similar, however, but more easily formed and better defined. The phenylhydrazone, $C_6H_5.CH\!:\!N.NH.C_6H_5$, is a crystalline substance, melting at 152°. A similar crystalline condensation product, benzylideneaniline, $C_6H_5.CH\!:\!N.C_6H_5$, is formed by heating the aldehyde with aniline for an hour at 100°. It can be recrystallised from water. The oxime, benzaldoxime, $C_6H_5.CH\!:\!N.OH$, formed with hydroxylamine hydrochloride and caustic soda, is a crystalline substance, melting at 35°. This compound is interesting in that it is converted by dilute acids into an isomeric, probably stereoisomeric, modification, melting at 125°, which is reconverted into the original substance by distillation under low pressure. Acetaldoxime forms a similar modification. Benzaldoxime, like acetaldoxime, is dehydrated by phosphorus pentoxide to the corresponding benzonitrile, and unlike the fatty aldehyde is also directly convertible into the corresponding amine, benzylamine, by reduction with sodium amalgam—

$$C_6H_5.CH\!:\!N.OH + 4H = C_6H_5.CH_2.NH_2 + H_2O.$$

Benzaldehyde, unlike acetaldehyde, does not condense with itself, but it condenses in the aldol-crotonaldehyde manner with many substances containing the methyl or methylene group. With acetic acid, for example, it forms cinnamic acid, $C_6H_5.CH{:}CH.COOH$ (p. 328) the aromatic analogue of crotonic acid, and with acetone, benzal- or benzylidene-acetone, $C_6H_5.CH{:}CH.CO.CH_3$. The latter, a crystalline substance melting at 42°, is precipitated by simply warming the aldehyde with acetone and a little caustic soda solution, which thus serves as a condensing agent. Condensation is usually preceded by addition, as in the aldol reaction. The usual agents are hydrogen chloride gas, sulphuric acid, anhydrous zinc chloride, and dilute soda or baryta (see also Cinnamic Acid).

The action of caustic soda on benzaldehyde is similar to its action on the higher fatty aldehydes (p. 73), half the aldehyde being reduced to the alcohol, and half oxidised to the acid—

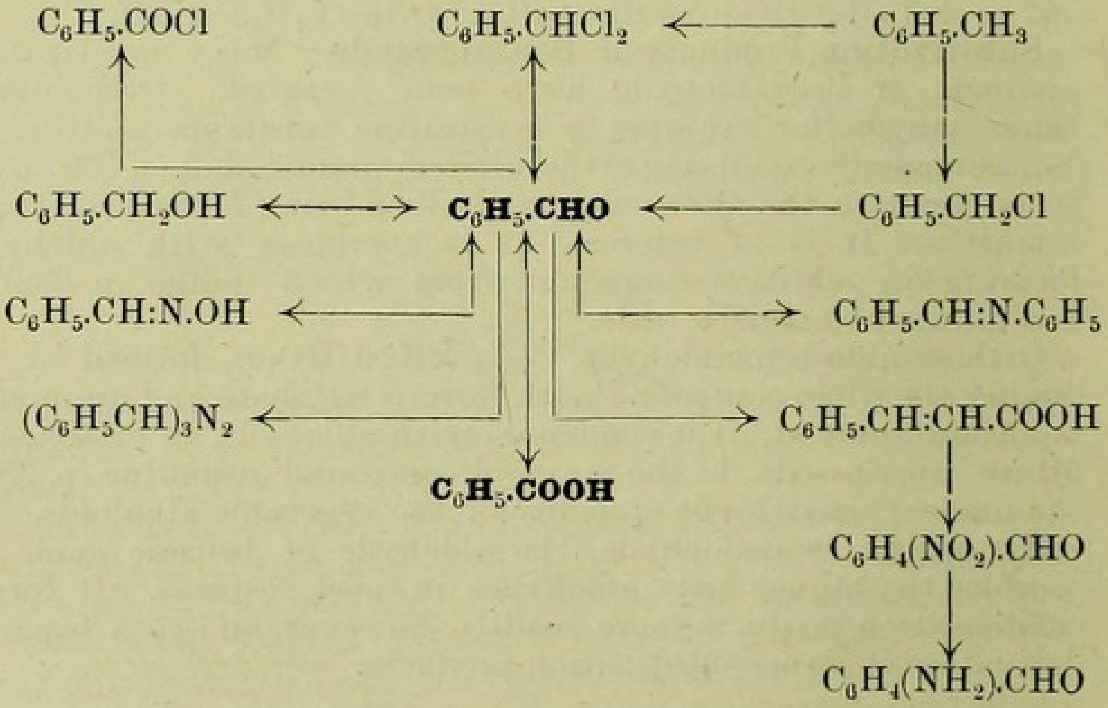
$$2C_6H_5.CHO + NaOH = C_6H_5.COONa + C_6H_5.CH_2OH.$$

Substitution Products of Benzaldehyde.—Many substitution products of benzaldehyde have been prepared. Ortho-nitrobenzaldehyde, for example, a crystalline substance melting at 46°, is made by oxidising ortho-nitro-cinnamic acid (p. 329) with permanganate, the meta-compound alone being formed by direct nitration. It is of interest, as it combines with aldehyde, forming an additive compound from which indigo (p. 332) is precipitated by caustic soda.

Ortho-amido-benzaldehyde, $C_6H_4(NH_2).CHO(o)$, formed by reducing the nitro-compound with ferrous sulphate and ammonia, is also of interest, as it condenses with aldehyde, in presence of dilute caustic soda, to the aminoid compound quinoline (p. 383), the nucleal constituent of many of the vegetable alkaloids.

Synopsis.—Benzaldehyde, the aldehyde of benzoic acid, resembles the higher fatty aldehydes in most respects. It forms condensation products more readily, however, and as a benzene derivative it forms substitution products.

BENZALDEHYDE.



CHAPTER XLV

TOLUENE: THE BENZYL RADICLE

Toluene.—Benzoic acid is not only related to benzene in the same way as acetic acid to methane, but it also bears to the homologous hydrocarbon, toluene or methyl-benzene, a relation parallel to that which acetic acid bears to ethane.

As already stated, the unfrozen mother-liquor which is drained from the benzene crystals, and constitutes about 30 per cent. of ordinary commercial benzene, contains this hydrocarbon. It is purified by fractional distillation, but can only be separated from paraffins of neighbouring boiling point by means of its sulphonic acid (p. 244).

Toluene, C_7H_8 (Pelletier, 1832), is a light, mobile and insoluble liquid which boils at 110°, but otherwise resembles benzene. It was first obtained in quantity by dry-distilling balsam of Tolu, and can also be formed from the toluic acids (p. 316), and from benzene. That it is a benzene derivative is proved by its slow oxidation to benzoic acid when boiled with chromic acid mixture or dilute nitric acid in a reflux apparatus, the acid being precipitated on pouring the product into water when the light insoluble oil has disappeared—

$$C_6H_5.CH_3 + 3O = C_6H_5.COOH + H_2O.$$

Toluene thus appears as methyl-benzene, and the presence of the paraffinoid, as well as of the benzenoid radicle is proved by two syntheses. In the first method, an equimolecular solution of bromobenzene and methyl iodide in dry ether is boiled in a reflux apparatus with the calculated amount of sodium. The addition of a few drops of ethyl acetate much accelerates the action. The sodium is gradually converted into the sodium bromide and iodide, and at the end of the operation the cooled product is poured off and fractionated. Some ethane first escapes, formed from the methyl iodide, and then the ether passes over, accompanied by a little benzene, produced by the reduction of the bromo-derivative. Finally, the crude toluene distils at about 110°, leaving a small residue of diphenyl (p. 348) in the flask. The toluene is then refractionated (Fittig, 1864)—

$$C_6H_5Br + Na_2 + CH_3I = C_6H_5.CH_3 + NaBr + NaI.$$

The second method consists in passing methyl chloride vapour into a boiling solution of anhydrous aluminium chloride in benzene, hydrogen chloride being evolved in abundance, and toluene and other methyl derivatives of benzene being formed.

The aluminium chloride remains unchanged and acts as a carrier, probably forming an intermediate additive compound with the benzene and methyl chloride (Friedel and Crafts, 1877)—

$$C_6H_6 + AlCl_3 + CH_3Cl \rightarrow C_6H_5.CH_3 + AlCl_3 + HCl.$$

When hydrogen chloride ceases to be evolved, and the weight of the product has increased by an amount corresponding with the conversion of the benzene into toluene, the product is poured into water, and the light layer of hydrocarbon dried, and fractionated to separate unchanged benzene and higher methyl-benzenes (p. 322).

Both methods are of wide applicability, bromo-benzene for example being thus convertible into ethyl-benzene and propylbenzene.

The Benzyl Radicle: Toluene as Phenyl-methane.—As toluene is both phenyl-methane and methyl-benzene, it shows the characters both of a benzenoid and of a paraffinoid hydrocarbon. It is readily nitrated and sulphonated, and when digested with chlorine in the cold forms substitution products (p. 309) homologous with and analogous in every respect to those of benzene. But on passing chlorine into the boiling hydrocarbon, the action is the same as with ethane, the hydrogen atoms of the methyl group being successively replaced by the halogen. Benzyl chloride, $C_6H_5.CH_2Cl$, and benzal chloride, $C_6H_5.CHCl_2$, are first formed, and finally, benzotrichloride, $C_6H_5.CCl_3$, identical with that formed from benzoyl chloride by the action of phosphorus pentachloride—

$$C_6H_5.CH_3 \rightarrow C_6H_5.CH_2Cl \rightarrow C_6H_5.CHCl_2 \rightarrow C_6H_5.CCl_3.$$

Benzyl and benzal chlorides correspond very closely with those of ethyl and ethylidene. The benzyl compound is readily prepared by passing chlorine into boiling toluene in a reflux apparatus until the necessary increase in weight is observed. The action proceeds best in presence of sunlight, but a carrier must not be used, or substitution is effected in the benzene nucleus. The product is simply fractionated to separate unchanged toluene and benzal chloride.

Benzyl chloride, $C_6H_5.CH_2Cl$ (Cannizzaro, 1853), is a colourless, insoluble liquid, boiling at 176°. Its odour is aromatic and pleasant, but its vapour extremely irritating to the eyes. The irritating odour of the bromobenzene made from commercial benzene containing toluene is due to the presence of benzyl bromide. Benzyl chloride is very easily oxidised to benzoic acid, and the chlorine is therefore in the methyl group or "side chain," as it is termed, and not in the benzene nucleus—

$$C_6H_5.CH_3 \rightarrow C_6H_5.CH_2Cl \rightarrow C_6H_5.COOH.$$

Benzyl chloride is thus the phenyl substitution product of methyl chloride, and it behaves in fact as an aliphatic chloride. Whilst chlorobenzene is unaffected by alkalies, benzyl chloride is hydrolysed by boiling with sodium carbonate solution, or even with water, and thus more easily than the aliphatic chlorides themselves. The benzyl alcohol thus formed occurs naturally in various aromatic balsams and resins—as benzyl benzoate, for example, in balsam of Peru, but it is most readily obtained from benzaldehyde (p. 267). On shaking the latter with strong caustic soda solution, heat is developed, and ultimately a permanent emulsion is formed with the liberated alcohol and benzoate. After a day or so, water is added to dissolve the benzoate, and the alcohol is extracted with ether and fractionated. It is unnecessary to dry the ethereal solution—

$$C_6H_5.CHO \rightarrow C_6H_5.CH_2OH \leftarrow C_6H_5.CH_2Cl.$$

Benzyl alcohol, $C_6H_5.CH_2OH$ (Cannizzaro, 1853), is a colourless, sparingly soluble liquid, which boils at 206°, and has only a faint aromatic odour. In its properties it resembles the aliphatic alcohols, and is a typical example of an aromatic alcohol. Thus it is reconverted into the chloride by phosphorus pentachloride, or even by prolonged boiling with concentrated hydrochloric acid, and on warming with acetic chloride or anhydride, it yields in the normal manner benzyl acetate. When boiled with boric anhydride it is dehydrated to the corresponding ether, benzyl ether, $(C_6H_5.CH_2)_2O$, an insoluble aromatic liquid, boiling at 296°; and a similar mixed ether is formed by heating benzyl chloride with sodium ethoxide, in the same way as common ether from ethyl iodide.

Finally, as a primary alcohol, benzyl alcohol is converted by mild oxidising agents, such as dilute nitric acid, into benzaldehyde and benzoic acid, *i.e.* an aldehyde and acid containing the same number of carbon atoms. It is thus clearly phenylcarbinol, the phenyl substitution-product of methyl alcohol—

$$C_6H_5.CH_2OH \rightarrow C_6H_5.CHO \rightarrow C_6H_5.COOH.$$

The benzyl radicle, $C_6H_5.CH_2$, resembles the paraffinoid radicles and combines with amidogen, cyanogen, etc., in precisely the same way as ethyl. Benzylamine can be formed in all the ways in which ethylamine is made. It is produced, together with di- and tribenzylamine, when benzyl chloride is heated with alcoholic ammonia. It can also be prepared by hydrolysis of benzyl isocyanate, $C_6H_5.CH_2.N{:}CO$, with strong caustic soda solution. It is formed by the reduction of benzonitrile, $C_6H_5.CN$, with sodium in alcohol, and finally can be made by the successive action of bromine and caustic soda on phenyl-acetamide, $C_6H_5.CH_2.CONH_2$ (p. 274), in the same way as methylamine from acetamide itself.

Benzylamine, $C_6H_5.CH_2.NH_2$ (Mendius, 1862), is a soluble alkaline liquid, boiling at 183°. It resembles the aliphatic amines, and is much more basic than aniline. Like all amines, it forms crystalline additive salts with acids, but unlike aniline it absorbs carbon dioxide. As an amine also it is unaffected by alkalies or acids, and is converted by nitrous acid in the normal manner, into benzyl alcohol, without the formation of a diazo-compound—

$$C_6H_5.CH_2Cl \rightarrow C_6H_5.CH_2.NH_2 \rightarrow C_6H_5.CH_2OH.$$

Phenyl-acetic and Mandelic Acids.—The difference in activity between benzyl chloride and chlorobenzene (p. 242) is equally well marked in its action with potassium cyanide, benzyl cyanide being formed by simply boiling the chloride in a reflux apparatus with a solution of the alkali cyanide in dilute alcohol. The insoluble product is simply washed with water and fractionated. Benzyl cyanide also occurs in combination in nasturtium seeds.

Benzyl cyanide, $C_6H_5.CH_2.CN$, is a liquid boiling at 232°. When boiled with caustic soda solution, or better, with moderately concentrated sulphuric acid, ammonia is set free in the normal manner, and on cooling the product, phenyl-acetic acid crystallises out, and may be purified by recrystallisation from hot water.

Phenyl-acetic or *a*-toluic acid, $C_6H_5.CH_2.COOH$ (Cannizzaro, 1855), is a crystalline substance, melting at 76°. When dry-distilled with soda-lime, it loses carbon dioxide in the normal manner, and is converted into toluene, but on boiling with dilute nitric acid it is oxidised to benzoic acid, the second carbon atom of the aliphatic chain breaking away, in accordance with the invariable rule—

$$\begin{tikzcd} C_6H_5.CH_3 \arrow[r] & C_6H_5.CH_2Cl \arrow[r] & C_6H_5.CH_2.CN \arrow[r] & C_6H_5.CH_2.COOH \arrow[r] \arrow[lll, bend left] & C_6H_5.COOH. \end{tikzcd}$$

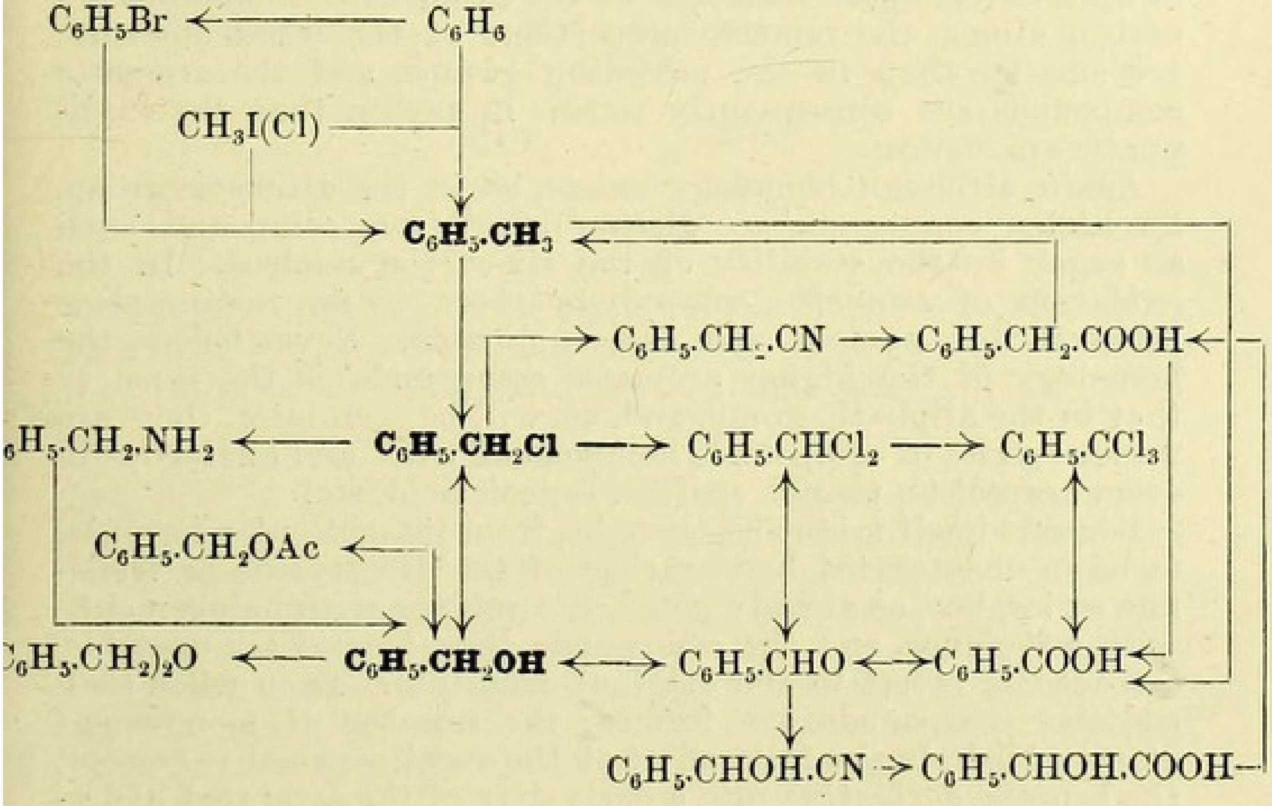
Phenyl-acetic acid is thus the aromatic analogue of propionic acid, and it forms in fact similar derivatives. Thus, mandelic acid, the hydroxy-compound analogous to lactic acid, is formed from benzaldehyde by the cyanhydrin synthesis, benzaldehyde hydrocyanide, $C_6H_5.CHOH.CN$, a yellow oil, which decomposes into its constituents when heated, being hydrolysed by concentrated hydrochloric acid in the usual way—

$$C_6H_5.CHO \rightarrow C_6H_5.CHOH.CN \rightarrow C_6H_5.CHOH.COOH.$$

Mandelic acid, $C_6H_5.CHOH.COOH$ (Winckler, 1834), is a crystalline substance, melting at 118°. As a synthetic compound it is of course optically inactive, but by fractional crystallisation of its strychnine salt, it can be resolved into two oppositely active isomerides, melting at 133°, which recombine when melted together. The relation of mandelic to phenyl-acetic acid is confirmed by its reduction to the latter when heated with hydriodic acid. The inactive acid is also formed by direct hydrolysis of amygdalin with concentrated hydrochloric acid, so that the glucoside is represented by the formula, $C_6H_5.CH(CN).O.C_{12}H_{21}O_{11}$.

Synopsis.—Toluene or phenyl-methane not only forms a series of products similar to those derived from benzene, but also a series in which the benzyl or phenylmethyl radicle plays the part of an alkylic radicle.

TOLUENE AND THE BENZYL COMPOUNDS.



CHAPTER XLVI

CONSTITUTION OF BENZENE

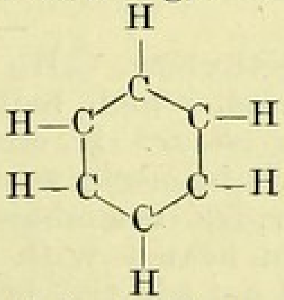
The Ring Formula.—A sufficient number of aromatic compounds have now been considered to show that whilst in some respects they are similar to those of the aliphatic group, in most respects they differ from them. Although the molecules of even the simplest members of the group contain at least six carbon atoms, the relative proportions of the other elements are smaller than in the preceding groups, and the aromatic compounds are consequently richer in carbon than their aliphatic analogues.

Again, although homology exists, as in the aliphatic group, the higher compounds are distinguished from compounds such as sugar by the stability of the six-carbon nucleus. In the oxidation of aromatic compounds there is no resting-place between this nucleus and carbon dioxide. Nevertheless, the homology of the higher aromatic compounds is the same as that in the aliphatic group, and, as will be seen later, there are various series of compounds homologous with, and analogous in every respect to, phenol, aniline, benzoic acid, etc.

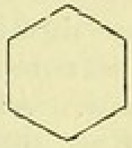
Benzene itself might be thought, from its molecular formula, to be an unsaturated hydrocarbon of the diacetylene or triolefine series, but, as already noted, it combines with halogen only with reluctance, and the compounds thus formed are unstable, and readily revert to the original condition. Even when such additive compounds are formed, the number of monovalent atoms added always falls short of the eight required to convert the benzene derivative into a derivative of the saturated hydrocarbon hexane. Benzene itself combines only with six atoms of halogen, and benzoic acid, under certain conditions, takes up six atoms of hydrogen, and no more.

Benzene cannot therefore be an olefine or acetylene hydrocarbon, and apart from the fact that acetylene hydrocarbons of the same formula are known (p. 279), and have quite different properties, it is evident that the carbon atoms in benzene and its derivatives must be arranged in some manner essentially different from the arrangements obtaining in the aliphatic group (Kekulé).

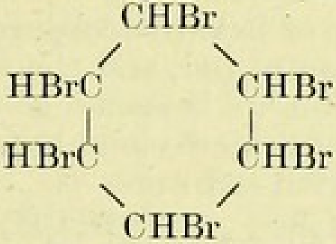
The assumption which best accounts for these peculiar properties of the aromatic compounds, is that in the six-carbon nucleus common to all of them, the carbon atoms are linked together in a closed chain or ring, and that in benzene, a hydrogen atom is linked to each carbon (Kekulé, 1865). This ring formula is usually symbolised by a hexagon, a carbon atom being imagined at each angle—



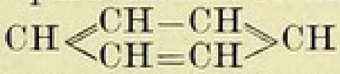
or



This formula satisfactorily accounts for the addition of only six halogen atoms to the benzene molecule, for the remaining two atoms cannot be introduced without breaking the ring, all the carbon valencies now being saturated—

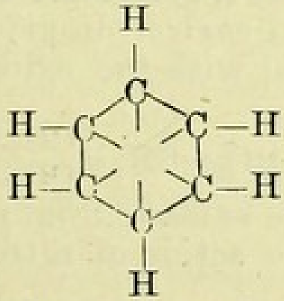


The only difficulty is in the disposal of the six free carbon valencies. It was originally suggested that the carbon atoms are united by alternate paraffin and olefine bonds—



$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH-CH}\\\mathrm{CH{=}CH}\end{matrix}{>}\mathrm{CH}$$

but this is hardly consistent with the virtually saturated character of benzene. Various modifications have been proposed to obviate the difficulty. In the centric or isodynamic formula (Armstrong, 1887), the surplus valencies are assumed to be directed towards the centre of the ring, each carbon atom exercising a general attraction over the others. This takes into account the great stability of the benzene nucleus, and the reluctance with which it forms additive compounds—

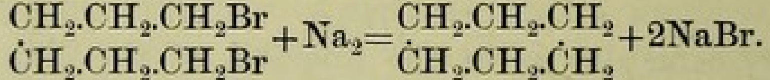


It is usual in practice, however, to ignore such considerations, and to use the plain hexagon.

Reduction Products of Benzene.—As will be seen presently, the strongest confirmation of the ring formula for benzene is the thorough manner in which it accounts for the isomerism of the di- and higher substitution products, but confirmation is also afforded by the nature of the reduction products, both of the hydrocarbon and of certain of its derivatives. When benzene, for instance, is heated in a sealed tube with hydriodic acid, it is converted into a hydrocarbon isomeric with the hexylenes.

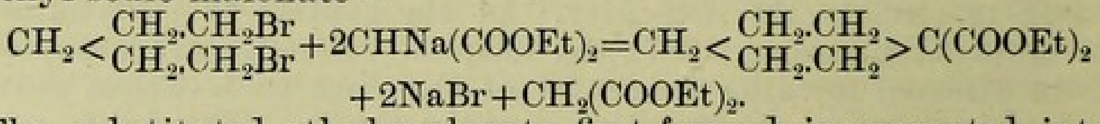
Hexahydrobenzene or hexamethylene, C_6H_{12} (Wreden, 1877), is a light and very mobile liquid, which boils at 70°, and resembles purified petroleum in odour. It occurs, in fact, in Caucasian petroleum. Although isomeric with the hexylenes, it has not the olefine character, but resembles the paraffins in its chemical behaviour. When heated with chlorine or bromine, it forms substitution and not additive products, and these behave like the haloid paraffins, and are hydrolysed by alkalies, etc. Neither is the hydrocarbon appreciably oxidised by nitric acid, as would be the case were it an olefine, and it cannot be further reduced.

The entire behaviour of hexahydrobenzene tends to show that it is a true saturated compound, and the saturated ring formula suggested by its relation to benzene is fully confirmed by its synthesis by heating hexamethylene bromide (see Pentamethylene bromide, below) with sodium—



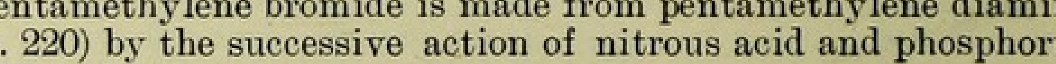
$$\begin{matrix}CH_2.CH_2.CH_2Br\\ \dot{C}H_2.CH_2.CH_2Br\end{matrix}+Na_2=\begin{matrix}CH_2.CH_2.\dot{C}H_2\\ \dot{C}H_2.CH_2.\dot{C}H_2\end{matrix}+2NaBr.$$

Benzoic acid itself is reducible in a similar manner, by means of sodium in amyl alcohol solution. Hexahydrobenzoic or hexamethylene-carboxylic acid, $C_6H_{11}.COOH$ (Aschan, 1891), is a crystalline substance, melting at 28°. Its constitution is fully proved by its synthesis from pentamethylene bromide and ethyl sodio-malonate—



$$CH_2<\begin{matrix}CH_2.CH_2Br\\ CH_2.CH_2Br\end{matrix}+2CHNa(COOEt)_2=CH_2<\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}>C(COOEt)_2$$
$$+2NaBr+CH_2(COOEt)_2.$$

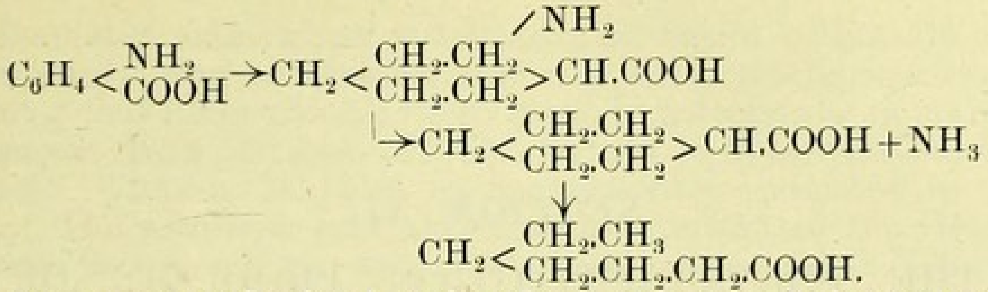
The substituted ethyl malonate first formed is converted into the corresponding crystalline derivative of malonic acid in the manner already described (p. 153), and this on heating splits up in the normal way into carbon dioxide and a hexamethylene carboxylic acid, identical with the reduction product of benzoic acid (Perkin, jun., 1893)—



$$CH_2<\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}>C(COOH)_2=CH_2<\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}>CH.COOH+CO_2.$$

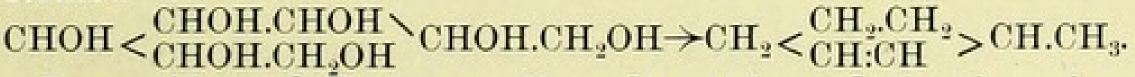
Pentamethylene bromide is made from pentamethylene diamine (p. 220) by the successive action of nitrous acid and phosphorus tribromide.

The same acid is formed, together with hexahydro-anthranilic acid, by reducing anthranilic acid with sodium in amyl alcohol solution, and in this case part is further reduced and hydrolysed to normal pimelic acid (p. 159), so that the ring compounds, benzene and benzoic acid, may in this way be directly converted into open-chain paraffin derivatives—



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{COOH}\end{matrix}\rightarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}>\overset{\diagup\mathrm{NH_2}}{\mathrm{CH.COOH}}$$
$$\rightarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}>\mathrm{CH.COOH}+\mathrm{NH_3}$$
$$\downarrow$$
$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2.CH_3}\\ \mathrm{CH_2.CH_2.CH_2.COOH.}\end{matrix}$$

A converse synthesis of a ring from an open-chain compound is effected, it will be remembered, by heating perseïtol or glucoheptitol (p. 193) with hydriodic acid, tetrahydrotoluene being formed—



$$\mathrm{CHOH}<\begin{matrix}\mathrm{CHOH.CHOH}\diagdown\\ \mathrm{CHOH.CH_2OH}\end{matrix}\mathrm{CHOH.CH_2OH}\rightarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH.CH_3}.$$

Isomerides of Benzene.—Two diacetylene derivatives isomeric with benzene have been prepared, and, as might be expected (Kekulé), their properties are entirely different from those of the aromatic hydrocarbon. Dipropargyl can be made synthetically from allyl iodide. The iodide is boiled with sodium in ethereal solution, and thus converted into diallyl, $\mathrm{CH_2{:}CH.CH_2.CH_2.CH{:}CH_2}$, a liquid diolefine, boiling at 59°, and having a garlic odour (Berthelot, 1856). This diallyl, as a diolefine, combines with bromine, forming a tetrabromide, a crystalline substance melting at 93°, and resembling camphor in odour. Finally, when this tetrabromide is boiled with alcoholic potash, it loses all its bromine as hydrogen bromide, and is converted into the diacetylene hydrocarbon, dipropargyl, in the same way as ethylene bromide into acetylene itself—

$$\mathrm{CH_2{:}CH.CH_2I}\rightarrow\mathrm{CH_2{:}CH.CH_2.CH_2.CH{:}CH_2}$$
$$\longrightarrow\mathrm{CH_2Br.CHBr.CH_2.CH_2.CHBr.CH_2Br.}$$
$$\longrightarrow\mathrm{CH\vdots C.CH_2.CH_2.C\vdots CH.}$$

Dipropargyl, $\mathrm{CH\vdots C.CH_2.CH_2.C\vdots CH}$ (Henry, 1873), is a colourless liquid, boiling at 86°. It has all the properties of a highly unsaturated hydrocarbon, and of an acetylene derivative. It combines readily with bromine and hydrobromic acid, forming respectively octobromo- and tetrabromo-hexane, both quite stable compounds. It forms explosive derivatives with copper and other metals, and is very easily oxidised. Permanganate converts it at once into carbon dioxide, and chromic acid mixture into carbon dioxide and oxalic acid.

A second isomeride of the formula $\mathrm{CH_3.C\vdots C.C\vdots C.CH_3}$, is known, which differs from dipropargyl only in that it does not form metallic compounds.

Synopsis.—To account for the unique properties of the aromatic compounds, it is assumed that in the six-carbon nucleus common to them, the carbon atoms are arranged in a closed chain or ring, instead of in an open chain, as in the aliphatic compounds.

SECTION XII

THE POLY-SUBSTITUTION PRODUCTS OF BENZENE

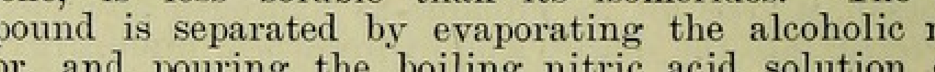
CHAPTER XLVII

COMPLEX NITRO- AND AMIDO-COMPOUNDS

The Poly-Nitrobenzenes.—It has been already noted that benzene, like ethane, forms poly-substitution products. If in its nitration the hydrocarbon is poured into the acid mixture, so that it is always surrounded by excess of the latter, and the mass is boiled instead of being kept cool, three isomeric dinitrobenzenes are formed; and the same compounds are produced in this way from nitrobenzene itself. The heavy oily product is poured into water, and as soon as it has set to a crystalline mass is well washed, and repeatedly recrystallised from hot alcohol in which the principal constituent, meta-dinitrobenzene, is less soluble than its isomerides. The ortho-compound is separated by evaporating the alcoholic mother liquor, and pouring the boiling nitric acid solution of the residue into a large excess of the cold acid. Finally, the para-compound is precipitated from the acid mother liquor with water. Very little of the latter is formed, however, and it is best made in other ways—

$$C_6H_6 \rightarrow C_6H_5.NO_2 \rightarrow C_6H_4(NO_2)_2.$$

Meta-dinitro-benzene, $C_6H_4(NO_2)_2(m)$ (Deville, 1841), crystallises in colourless needles, and melts at 90°. It is usually yellowish from impurity. Ortho-dinitro-benzene melts at 116°, the para-compound at 172°, and all three boil at about 300° without being decomposed. The dinitro-benzenes are neutral substances resembling the mono-nitro-compound in chemical character, and their hydrogen is not mobile. One of the nitro-groups in the ortho-compound, however, is detachable by hydrolysis with caustic soda, the sodium salt of ortho-nitro-phenol (p. 282) thus being formed—



$$C_6H_4 < {NO_2 \atop NO_2}(o) + NaOH = C_6H_4 < {NO_2 \atop OH}(o) + NaNO_2 + H_2O.$$

By further nitrating the dinitro-benzenes, a third nitro-group can with difficulty be introduced, but no more. The meta-compounds yields a tri-nitro-benzene, melting at 121°, and the ortho- and para-compounds an isomeric product, melting at 57° (p. 290). These are all the nitro-benzenes that are known.

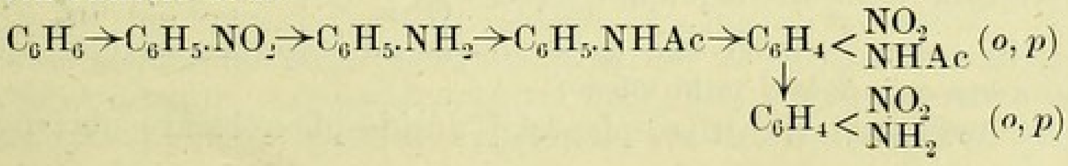
The Nitranilines: Protection of Amido-Groups.—By means of alcoholic ammonium sulphide, the agent originally used in the reduction of nitrobenzene, the dinitro-benzenes can be reduced to nitranilines, the second nitrogroup remaining intact as long as any of the original dinitro-compound is present. Meta-nitraniline is conveniently prepared in this way. The alcoholic and ammoniacal solution of the dinitrobenzene is alternately saturated with sulphuretted hydrogen and heated on a water bath in a reflux apparatus, until the requisite increase in weight, due to the sulphur and eliminated water, is noted. The product is poured into hot water, and the nitraniline dissolved out from the washed precipitate with dilute hydrochloric acid, and reprecipitated with ammonia. It may be recrystallised either from hot water, or from alcoholic ammonia.

Meta-nitraniline, $C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix}$ (*m*), (Muspratt and Hofmann, 1846), crystallises in yellow needles, and melts at 114°.

The corresponding ortho- and para-compounds may be made in the same way, but are more conveniently obtained by nitrating acetanilide. Aniline itself is decomposed by concentrated nitric acid, and can only be nitrated in presence of sulphuric acid, and then the meta-compound is principally formed. If however, an acetyl group be introduced into the amido-group, by heating the base with acetic chloride or acid, the group is protected from the action of the substituting agent, and substitution is effected in the benzene ring in the normal manner. In this way, acetanilide can be converted into ortho- and para-nitracetanilides, and from these the respective nitranilines can be readily obtained.

The acetanilide is slowly added to cold fuming nitric acid, the temperature not being allowed to rise, and the deep red solution is diluted by pouring on pounded ice. Water is then added, and the precipitated yellow nitro-compound, which consists principally of para-nitracetanilide, is well washed and dried, and purified from the ortho-compound by washing with cold chloroform. The two compounds are finally recrystallised from hot alcohol.

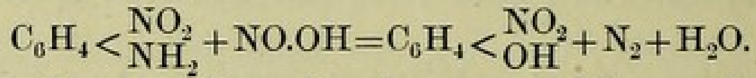
Para-nitracetanilide, $C_6H_4<\begin{matrix}NO_2\\NHAc\end{matrix}$ (*p*), (Grethen, 1875), crystallises in colourless needles, and melts at 207°, the ortho-compound in orange plates, and melts at 78°. Like the mother substance, both are readily hydrolysed by acids and alkalies, and after simply boiling for a short time with concentrated hydrochloric acid, the resulting nitranilines can be precipitated with caustic soda—



$$C_6H_6 \rightarrow C_6H_5.NO_2 \rightarrow C_6H_5.NH_2 \rightarrow C_6H_5.NHAc \rightarrow C_6H_4<\begin{matrix}NO_2\\NHAc\end{matrix}\ (o, p)$$
$$\downarrow$$
$$C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix}\quad (o, p)$$

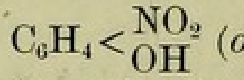
Ortho-nitraniline crystallises in orange needles, and melts at 71°; the para-compound in colourless needles, and melts at 147°. The nitranilines are much less basic than aniline, owing to the acidifying action of the nitro-group. Their salts are unstable, and the amido-groups of the ortho- and para-compounds are detachable by hydrolysis with caustic soda, nitrophenols again being formed. The nitranilines are thus less akin to the amines than aniline, and more akin to the amides.

The Nitro- and Amido-Phenols.—The nitranilines are also converted into the nitro-phenols by nitrous acid, in precisely the same way as aniline into phenol, and meta-nitro-phenol is best prepared in this manner. It crystallises on concentrating the product—

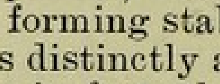


$$C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix}+NO.OH=C_6H_4<\begin{matrix}NO_2\\OH\end{matrix}+N_2+H_2O.$$

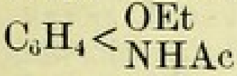
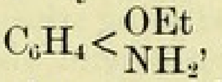
Ortho- and para-nitro-phenol are readily made by direct nitration of phenol. The latter is simply digested with cold dilute nitric acid for a few hours, and the oily product, after well washing with cold water, is distilled with steam. The ortho-compound passes over with the steam, and collects with the water in bright yellow crystals, whilst the colourless para-compound is extracted from the tarry residue with boiling water. The ortho-compound is simply dried and the para-compound is dissolved in caustic soda, and reprecipitated with dilute acid.

Ortho-nitro-phenol,  $C_6H_4<\begin{matrix}NO_2\\OH\end{matrix}$ (*o*) (Hofmann, 1857), is a golden yellow crystalline substance, which melts at 45°. It differs very remarkably from its isomerides. It has a peculiar and characteristic odour, is sweetish in taste, and, as has been seen, is volatile with steam. Meta-nitro-phenol forms only pale yellow crystals, and melts at 96°, whilst the para-compound is colourless, and melts at 114°. Neither is volatile with steam, nor odorous.

Just as the nitranilines are less basic than aniline, the nitro-phenols are more acid than phenol, and all three compounds decompose sodium carbonate, forming stable and characteristic salts. Their hydroxyl is thus distinctly acid, and by the action of phosphorus pentachloride, in fact, the compounds are converted into nitro-chloro-benzenes, which closely resemble acid chlorides. The ortho- and para-chloro-compounds, for example, are readily hydrolysed by caustic soda, and are converted by ammonia into the corresponding nitranilines, from which they may also be made by the diazo-reaction.

Sodium ortho-nitro-phenol,  $C_6H_4<\begin{matrix}NO_2\\ONa\end{matrix}$ (*o*), is intense crimson in colour, whilst the para-compound is golden yellow, and the meta-compound colourless.

By reducing the nitro-phenols, amido-phenols are obtained as colourless crystalline substances, which are unstable, and soon turn brown in the air. They are basic in character, and form salts with acids resembling the aniline salts.

Paramido-phenol melts at 184°, and the anilide of its ethyl ether, parethoxy-acetamidobenzene or phenacetin,  $C_6H_4<\begin{matrix}OEt\\NHAc\end{matrix}$ (*p*), is used as a febrifuge. It is made from the amido-phenol by first converting the latter into paramido-phenetole,  $C_6H_4<\begin{matrix}OEt\\NH_2\end{matrix}$, by heating with ethyl iodide and caustic soda, and then into the anilide by boiling with acetic acid. Phenacetin is a crystalline substance, melting at 242°.

Picric Acid.—The influence of nitro-groups on the activity of others is especially evident in trinitrophenol or picric acid. This compound is readily made by slowly adding a solution of phenol in concentrated sulphuric acid (phenol-sulphonic acid) to moderately concentrated nitric acid. The tarry, semi-crystalline product is drained and well washed with cold water, and finally recrystallised from hot water slightly acidified with sulphuric acid. When the acid is crystallised from benzene, it separates with benzene of crystallisation. Benzene "picrate," $C_6H_2(NO_2)_3.OH,C_6H_6$, is a yellow, crystalline substance, which soon loses its benzene by efflorescence. As will be seen later, most benzenoid hydrocarbons form such compounds.

Picric acid is also formed by oxidising with potassium ferricyanide the trinitrobenzene formed from meta-dinitro-benzene. It is produced also by the action of nitric acid on animal tissues and products, such as skin, silk, horn, etc., and was first made in this manner from silk.

Trinitrophenol or picric acid, $C_6H_2(NO_2)_3.OH$ (Welters, 1799), is a bright yellow, bitter, crystalline substance (*πικρος*=bitter), which melts at 122°, and sublimes when gently heated. It is only sparingly soluble in cold, but freely in hot water, and dyes animal fibres yellow (p. 354). Picric acid behaves in every way as an acid. It readily decomposes the alkali carbonates, forming stable yellow salts, and the crystalline trinitro-chloro-benzene or picryl chloride, $C_6H_2(NO_2)_3.Cl$, formed by the action of phosphorus pentachloride, has all the properties of an acid chloride. It is hydrolysed by cold water in the usual way, and is converted by ammonia in the normal manner into the corresponding amide.

Picramide or trinitraniline, $C_6H_2(NO_2)_3.NH_2$, is an orange crystalline substance, melting at 186°, which like acetamide, and unlike aniline, is readily hydrolysed by caustic soda, and reconverted into the hydroxy-compound by nitrous acid, without the intermediate formation of a diazo-compound. As a nitro-compound picric acid is reducible to the corresponding amido-compound, tri-amido-phenol, $C_6H_2(NH_2)_3.OH$, an unstable basic substance, which forms stable crystalline salts with acids.

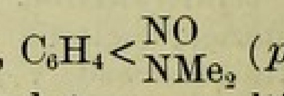
As stated above, the picrates are definite crystalline salts. Potassium picrate, for instance, is noteworthy as scarcely soluble in cold water. These salts are very explosive, however, detonating when suddenly struck or heated, and ammonium picrate is sometimes used in blasting. The acid interacts with potassium cyanide, forming a characteristic compound, potassium isopurpurate, $K.C_8H_4N_4O_6$, which can be used for the detection of small quantities of phenol.

The Diamido-Benzenes.—By reducing the dinitro-benzenes or nitranilines with iron and acetic acid, both nitro-groups are attacked, and diamido-benzenes formed. The meta-compound is conveniently made in this way by slowly adding meta-dinitro-benzene to excess of reduced iron suspended in the calculated quantity of very dilute acetic acid, and is extracted from the product with hot water. After evaporation, the semi-crystalline mass may finally be fractionated in a stream of coal-gas.

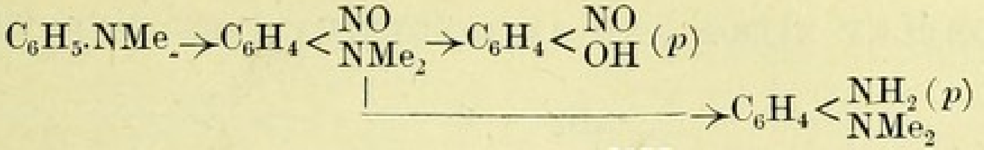
Metaphenylene-diamine, $C_6H_4(NH_2)_2$ (*m*) (Zinin, 1844), is a colourless, crystalline solid, which melts at 63°, and boils at 287°. It soon turns brown in the air from oxidation. The diamine is a powerful base, and forms a crystalline hydrochloride in the usual manner, but its behaviour with nitrous acid is anomalous, as is also the case with its isomerides. With the meta-compound, an intensely brown colouring matter, Bismarck brown, is formed (p. 379). The reaction affords a convenient test for traces and nitrites, such as occur in drinking water.

Ortho-phenylene-diamine is a similar crystalline substance, melting at 102°, and is best made from ortho-nitraniline. It is characterised by the red colour which it forms with ferric chloride in presence of hydrochloric acid. Para-phenylene-diamine melts at 147°, and is made from amido-azobenzene (p. 378). Its dimethyl derivative, paramido-dimethylaniline, is made from the corresponding azobenzene derivative, or from para-nitroso-dimethylaniline.

The latter compound is formed by the action of sodium nitrite on a solution of dimethyl-aniline in dilute hydrochloric acid. The reddish-brown crystalline hydrochloride separates at once from the product, and after recrystallisation, is decomposed with sodium carbonate solution, the free base being extracted with ether. The nitrous acid radicle here enters the benzene nucleus.

Para-nitroso-dimethylaniline, 

$C_6H_4<\begin{matrix}NO\\NMe_2\end{matrix}$ (*p*) (Baeyer, 1874), is a dark-green, crystalline substance, melting at 85°. It is hydrolysed by caustic soda to dimethylamine and para-nitroso-phenol $C_6H_4(NO).OH$, an unstable crystalline substance, and reduced by zinc and hydrochloric acid to the corresponding amido-compound, paramido-dimethyl-aniline—

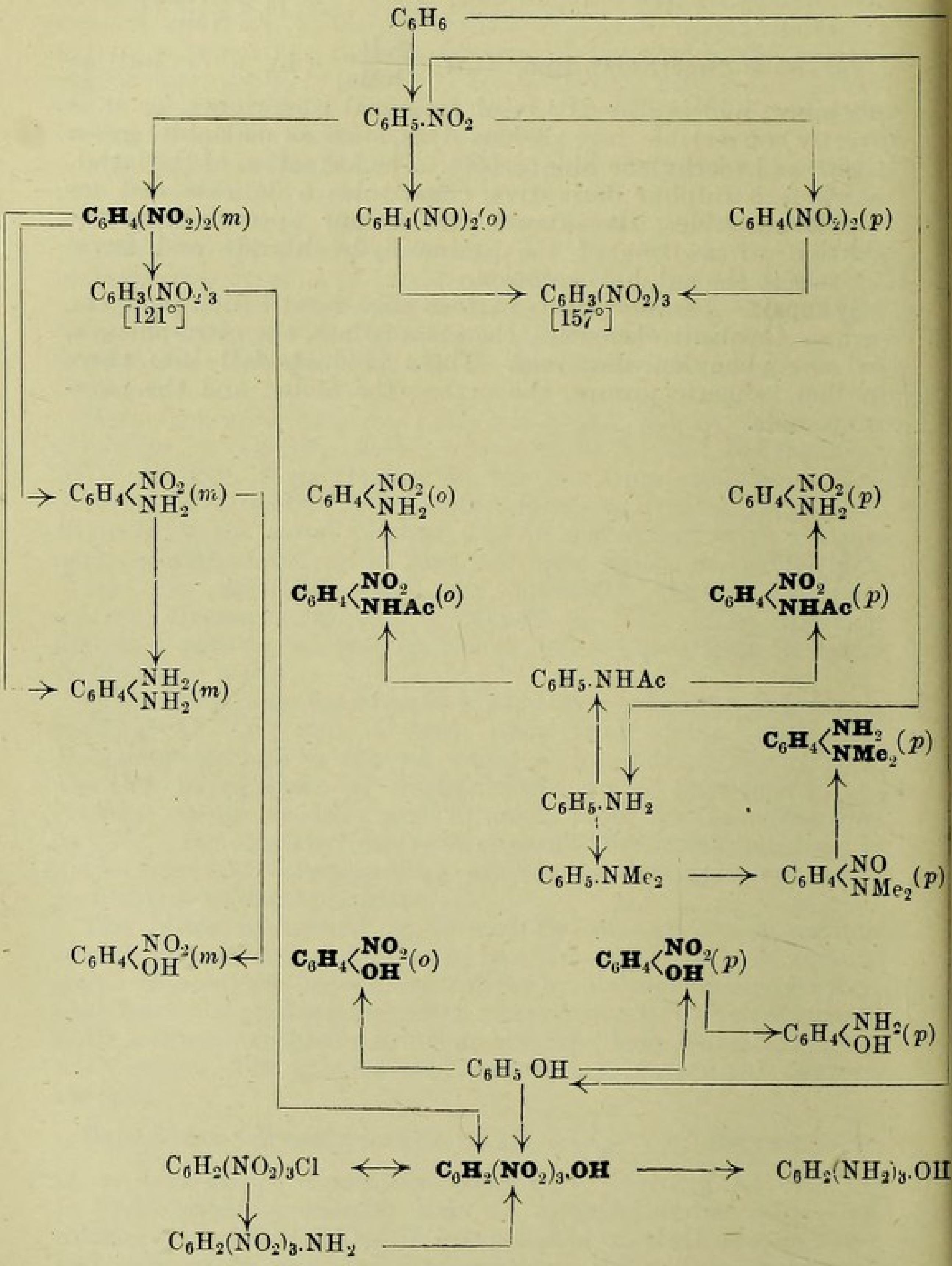


$$\begin{aligned} &C_6H_5.NMe_2 \rightarrow C_6H_4<\begin{matrix}NO\\NMe_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}NO\\OH\end{matrix}(p)\\ &\qquad\qquad\qquad\qquad\qquad\qquad \rightarrow C_6H_4<\begin{matrix}NH_2\\NMe_2\end{matrix}(p)\end{aligned}$$

Paramido-dimethylaniline, $C_6H_4<\begin{matrix}NH_2\\NMe_2\end{matrix}$ (*p*), a crystalline substance, melting at 41°, is of technical importance, as it is directly convertible into various dyes, such as malachite green (p. 359) and methylene blue (p. 359). The formation of the latter, which is a sulphur derivative, constitutes a delicate test for soluble sulphides, its intense blue colour appearing on the addition of a drop of the amine hydrochloride and ferric chloride to the sulphide solution.

Synopsis.—Benzene forms various poly-substitution products, such as the dinitrobenzenes, the nitranilines, the nitro-phenols, and the phenylene-diamines. These products fall into three distinct isomeric groups, the ortho-, the meta-, and the para-compounds.

THE COMPLEX NITRO- AND AMIDO-DERIVATIVES OF BENZENE.

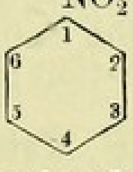


CHAPTER XLVII

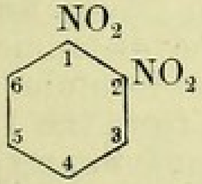
THE ISOMERISM OF THE BENZENE POLY-SUBSTITUTION PRODUCTS

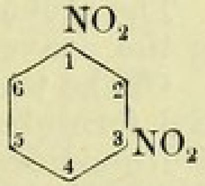
The Ring Formula and Position Isomerism.—Whilst the three classes of benzene di-derivatives are derived from the same hydrocarbon, the members of the separate classes are not interconvertible. Meta-dinitro-benzene, for example, can be converted into meta-nitraniline and meta-nitro-phenol, but not into compounds of the ortho- and para- series. Now compounds such as these cannot, of course, be metameric, neither can their isomerism be due to any alteration in the nucleus, since they are all derived from the same benzene. The only remaining hypothesis is that they are position isomerides.

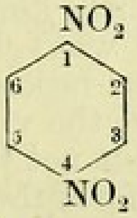
As already stated, the ring formula accounts in the most thorough manner for the existence of the three sets of products. The formula being symmetrical, the hydrogen atoms occupy equivalent positions, and only one set of mono-derivatives is to be expected, as is actually the case. But as soon as a hydrogen atom is replaced by a group or atom of another kind, the symmetry is destroyed. In nitrobenzene, for example, two of the hydrogen atoms (2, 6) are attached to carbon atoms, adjacent to that to which the nitro-group is linked: two others (3, 5) are situate at one remove, whilst the fifth (4) is placed at two removes from the central atom—



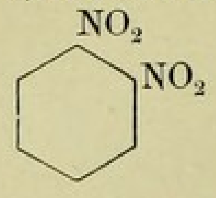
According to this hypothesis, therefore, the three di-nitrobenzenes are represented by the formulæ—



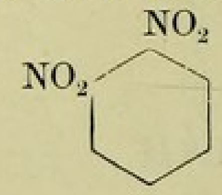




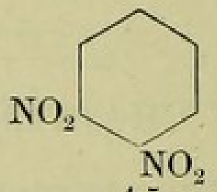
and may be termed 1:2, 1:3, and 1:4 di-nitro-benzenes. As the six positions in the formula of the hydrocarbon itself are equivalent, it does not matter where the numbering is started, but it is usual to commence as shown in the figure. It is to be noted that these positions may be represented by various other numbers. The 1:2 position is the same, for instance, as the 1:6, 4:5 and 2:3. It is the adjacent position, in fact—



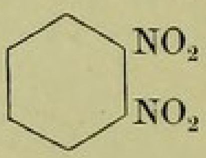
1:2



1:6



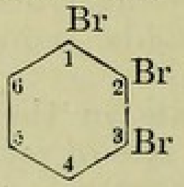
4:5

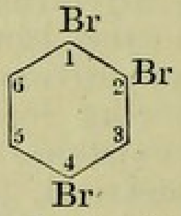


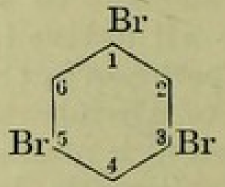
2:3

Similarly the 1:3 position is the same as the 1:5, 2:4, 3:5, etc., and the 1:4 as the 3:6 and 2:5 positions.

With regard to the higher substitution products, following the same reasoning as before, there should be three classes of tri-derivatives, and only three if the substituted groups are of the same kind, all conceivable arrangements being reducible to the positions 1:2:3, or vicinal, 1:2:4, or unsymmetrical, and 1:3:5, or symmetrical—



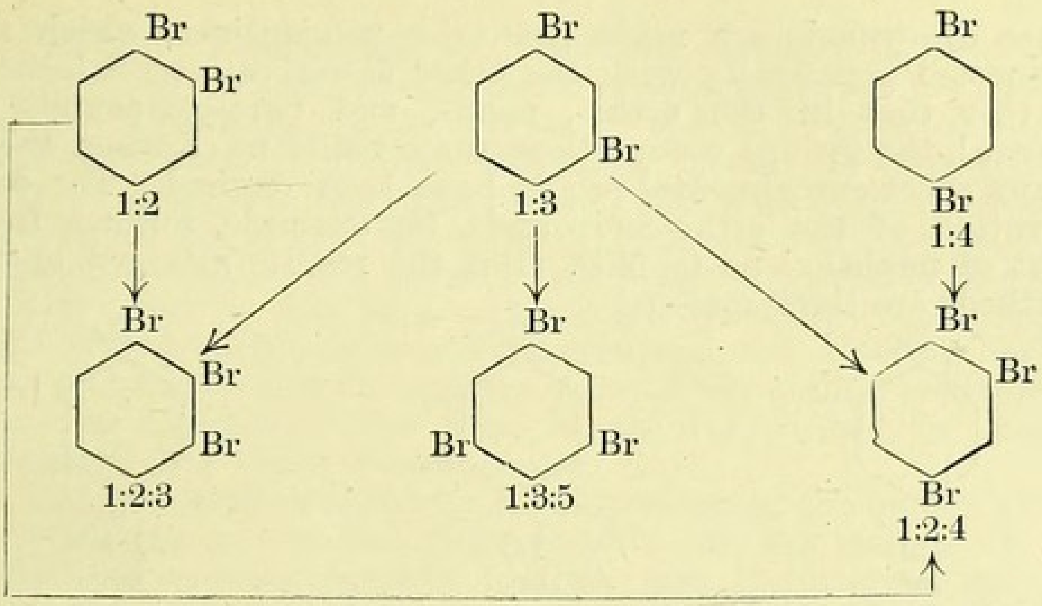




The isomerism of the tetra-derivatives, where such exist, will obviously be the same as that of the di-derivatives, and there will be no isomerism amongst the penta-derivatives, nor, of course, amongst the hexa-derivatives.

It has been proved experimentally, by somewhat complicated methods, that the six hydrogen atoms in benzene itself are really equivalent, and that in its mono-substitution products, four atoms are arranged in symmetrically disposed pairs, whilst the fifth is unique. But perhaps the most convincing proof of the position theory lies in the failure of all attempts to prepare more than one mono-substitution product and three di-substitution products of each kind.

Identification of the Ortho-, Meta- and Para- Positions.—The hypothesis thus being in line with the facts, it only remains to determine which constitution is to be assigned to each of the three known series. The problem has been solved, amongst other ways, by studying the conversion of the di-bromo- into the tri-bromo-benzenes. Of the three tri-bromo-formulæ shown above, the vicinal or 1:2:3 formula is derived from the 1:2 and 1:3, but not from the 1:4 di-modification, the unsymmetrical or 1:2:4 formula is derived from all three, whilst the symmetrical or 1:3:5 formula can obviously only result from the 1:3 modification. It follows, therefore, that the 1:4 di-bromo-benzene will yield on bromination only one tri-bromo-benzene, whilst the 1:2 modification will yield two, and the 1:3 modification, three—

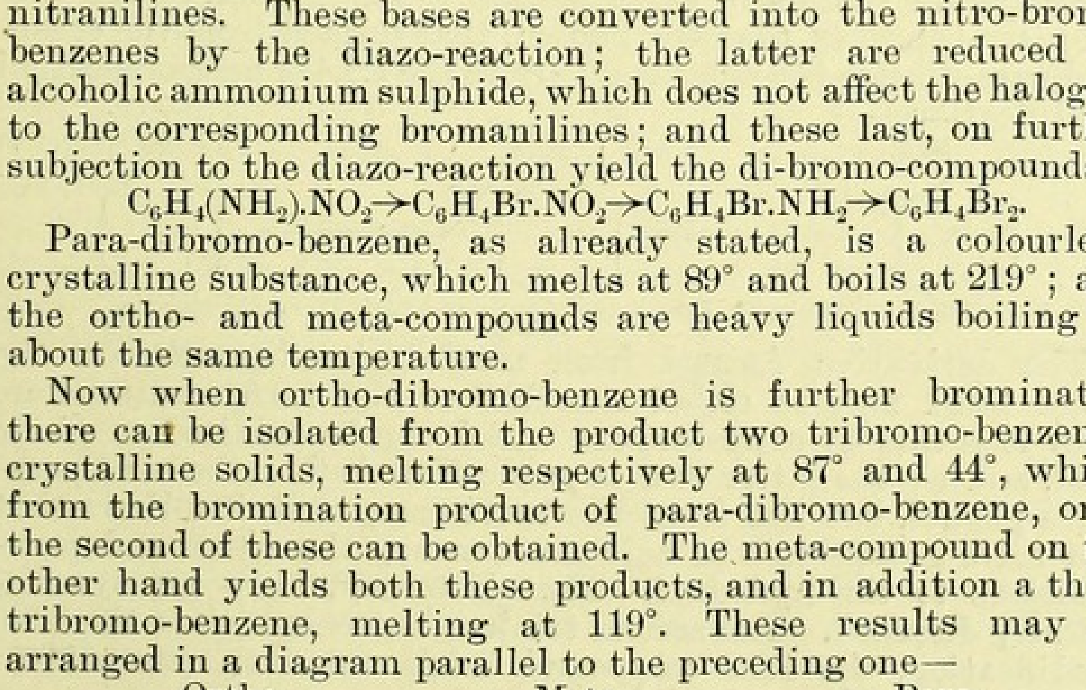


The three di-bromo-benzenes are all known, and can be brominated without much difficulty. The para- and ortho-compounds occur as bye-products in the preparation of bromo-benzene, but all three are best made from the corresponding nitranilines. These bases are converted into the nitro-bromo-benzenes by the diazo-reaction; the latter are reduced by alcoholic ammonium sulphide, which does not affect the halogen, to the corresponding bromanilines; and these last, on further subjection to the diazo-reaction yield the di-bromo-compounds—

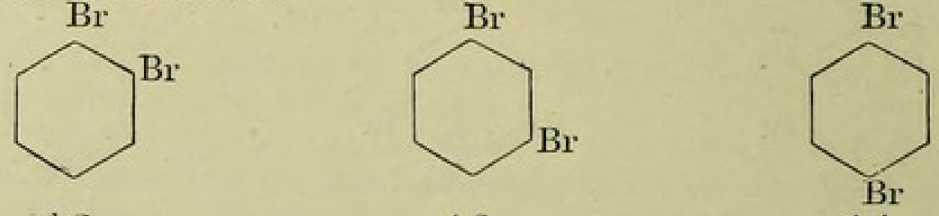
$$C_6H_4(NH_2).NO_2 \rightarrow C_6H_4Br.NO_2 \rightarrow C_6H_4Br.NH_2 \rightarrow C_6H_4Br_2.$$

Para-dibromo-benzene, as already stated, is a colourless, crystalline substance, which melts at 89° and boils at 219°; and the ortho- and meta-compounds are heavy liquids boiling at about the same temperature.

Now when ortho-dibromo-benzene is further brominated, there can be isolated from the product two tribromo-benzenes, crystalline solids, melting respectively at 87° and 44°, whilst from the bromination product of para-dibromo-benzene, only the second of these can be obtained. The meta-compound on the other hand yields both these products, and in addition a third tribromo-benzene, melting at 119°. These results may be arranged in a diagram parallel to the preceding one—



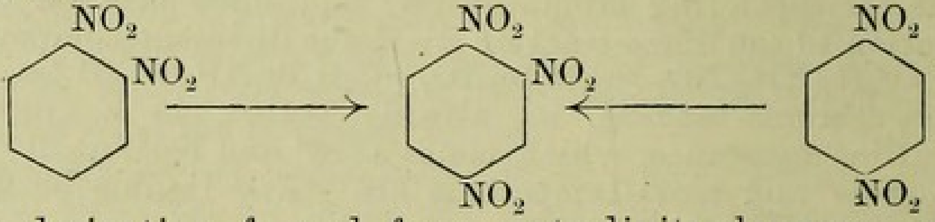
It follows, therefore, that in the ortho-compound, the bromine atoms occupy the 1:2 position, and in the meta- and para-compounds, the 1:3 and 1:4 positions respectively; and as these three compounds are made from the nitranilines, which are connected genetically with the other di-derivatives, it follows further that in the ortho-, meta-, and para-compounds in general, the groups occupy these same positions (Körner, 1874). Many other experimental proofs have been devised. The constitution of the ortho-compounds, for example, follows from that of naphthalene (p. 367). But the results attained by all methods are the same—



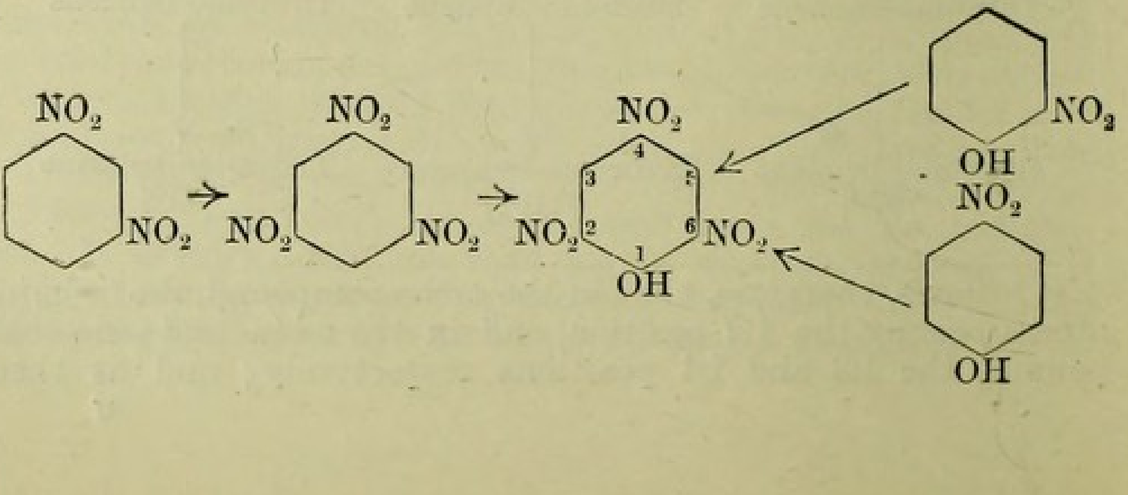
1:2 or ortho- 1:3 or meta- 1:4 or para-

Dibromo-benzenes.

The constitutions of the higher derivatives follow in the same way. Those of the tribromo-compounds, for example, follow, of course, from the above experimental data. Again, of the two tri-nitro-benzenes that are known, that formed from the ortho- and para-dinitro-benzenes can only be the 1:2:4 or unsymmetrical modification—



The derivative formed from meta-dinitro-benzene, on the other hand may be either the 1:2:3 or the 1:3:5 modification. Now it is this tri-nitro-benzene which can be oxidised to picric acid, and as the latter can be made from both ortho- and para-nitro-phenol, but not from the meta-compound, it follows that the nitro-groups in the acid must occupy the ortho- and para-positions to the hydroxyl. That is to say, they are symmetrically disposed. The second trinitro-benzene is thus the 1:3:5 modification, the 1:2:3 compound being unknown (see p. 280); and picric acid is 2:4:6-trinitro-phenol—

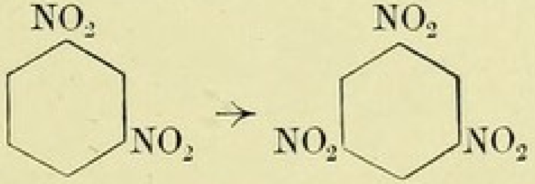


Positions Taken Up by Entering Groups.—It has been noticed that whilst nitrobenzene yields principally meta- or 1:2-dinitro-benzene, phenol and acetanilide are converted almost exclusively into para- and ortho-derivatives. It is a general rule, in fact, that the substituting group assumes either the meta-position, or the para- and ortho-positions to that already present, but never all three. The rule is not absolutely quantitative, for, as has been seen, small quantities of the para- and ortho-compounds usually accompany the meta-derivative, and *vice versâ*; but the greater part of the action proceeds in the one direction. The para- is usually formed in greater quantity than the ortho-compound.

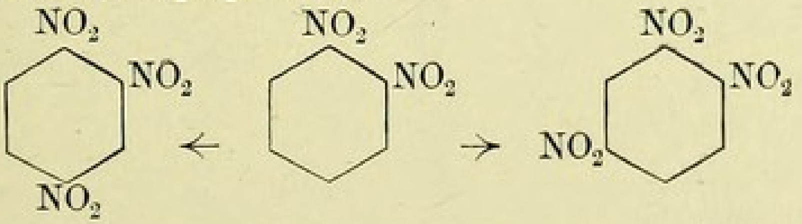
Now the position taken up is independent of the nature of the substituting group, and depends only on the nature of the radicle or radicles already present, and the matter may be summarised in the statement: that the substituting radicle—bromine, chlorine, or the nitro- or sulphonic group—takes up the para- (and ortho-) position, when the group already present is halogen, amidogen, acetamidogen, hydroxyl or methyl; and the meta-position, when the previously placed radicle is the nitro-, sulphonic, carboxyl or aldehyde group.*

Thus nitro-benzene always yields meta-compounds, the ortho- and para-compounds having to be prepared indirectly, whilst bromo-benzene yields, as already noted, para- and ortho-compounds.

The rule is well exemplified in the formation of the trinitrobenzenes from the dinitrobenzenes, and of picric acid from phenol. Metadinitrobenzene gives symmetrical trinitrobenzene because the 5-position is meta- to both the 1 and the 3 positions—



whilst ortho-dinitrobenzene gives the unsymmetrical compound because in both cases the 4 and 5 positions are meta- to one or other of the groups present—



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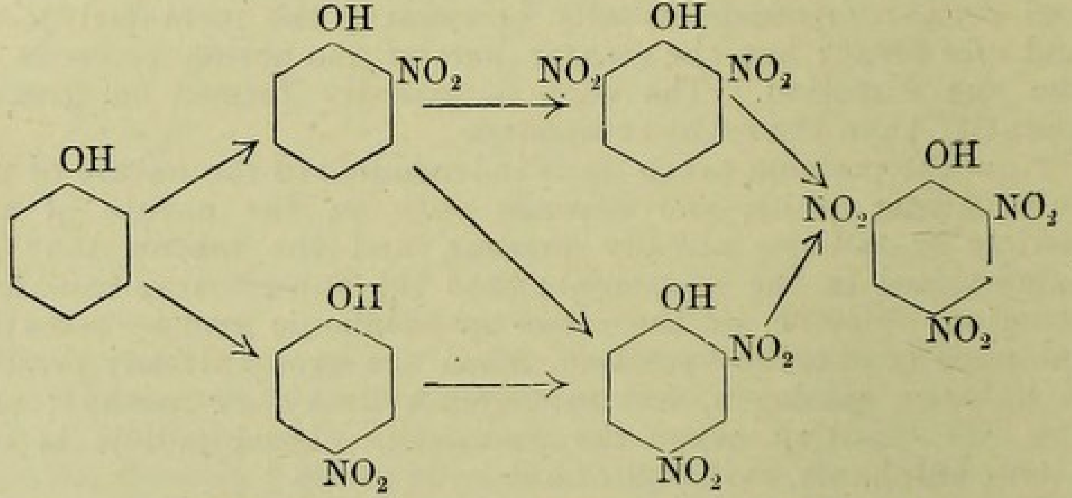
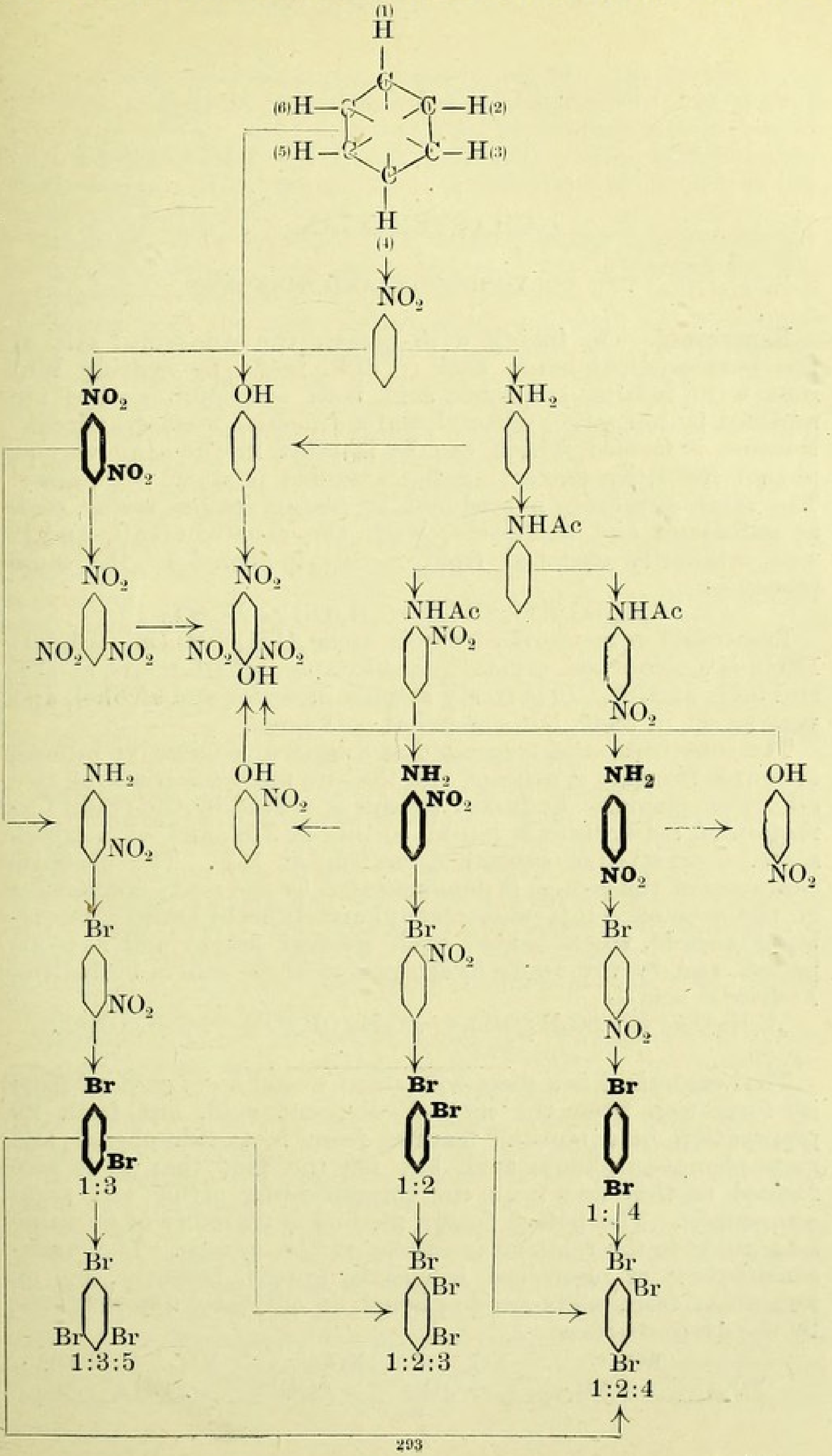
* The rule may be still more concisely stated by saying that if the compound formed by adding a hydrogen atom to the radicle already present is readily oxidised ($H-NO_2$, $H-COOH$), the new group takes up the meta-position, whilst if it is not readily oxidised ($H-Cl$, $H-OH$) the para- (and ortho-) position is taken up (Crum Brown, 1892).

Similarly phenol gives in the first place ortho- and para-nitrophenols. These then yield 1:2:4 and 1:2:6 dinitrophenols, in each case the nitro-group taking up the ortho- or para-position with regard to the hydroxyl, and the meta-position with regard to the nitro-group. Finally both dinitrophenols yield one and the same trinitrophenol, because the nitro-group again occupies the meta-position with regard to the two other nitro-groups, and the ortho- or para-position with regard to the hydroxyl—



Synopsis.—The isomeric substitution-products of benzene are position-isomerides, the groups in the ortho-, meta- and para-compounds occupying respectively the 1:2, 1:3 and 14: positions.

ISOMERISM OF THE BENZENE POLY-SUBSTITUTION-PRODUCTS.



CHAPTER XLIX

THE POLY-PHENOLS AND QUINONES

Resorcinol.—On fusing with potash the potassium salt of the benzene-disulphonic acid (p. 319), made by heating benzene with fuming sulphuric acid, both sulphonic groups are replaced by phenolic hydroxyl, and a diphenol, meta-dihydroxy-benzene, is formed, which can be isolated in the same way as phenol itself, by extracting the acidified product with ether. The same substance is produced by fusing various resins, such as galbanum and asafœtida, with the caustic alkali, and it was originally obtained from meta-iodo-phenol by the same process—

$$C_6H_4(SO_3K)_2 + 2KOH = C_6H_4(OH)_2 + 2K_2SO_3.$$

Resorcinol or meta-dihydroxy-benzene, $C_6H_4(OH)_2(m)$ (Körner, 1868), is a colourless, crystalline substance, which melts at 119° and boils at 276°. It is freely soluble in water and alcohol, and very sweet in taste, but somewhat poisonous.

The constitution of resorcinol as a benzene derivative follows of course from its synthesis, and that its molecule contains two alkylic or phenolic hydroxyl groups is proved by the ready formation of a diacetate, a liquid boiling at 278°, and of a dibenzoate, a crystalline substance melting at 117°. The phenolic character of the groups is demonstrated by the ready conversion of the substance into monomethyl and dimethyl ethers, resembling anisole, when heated with methyl iodide and aqueous potash, and by the ready hydrolysis of these ethers by boiling hydriodic acid—

$$\begin{tikzcd}
C_6H_4(OAc)_2 \arrow[r, leftrightarrow] & C_6H_4(OH)_2 \arrow[r, leftrightarrow] & C_6H_4(OH)(OMe) \arrow[r] & C_6H_4(OMe)_2. \arrow[ll, bend left]
\end{tikzcd}$$

That resorcinol is a meta-compound would seem evident from its formation from the meta-disulphonic acid, and from its preparation in a similar manner from meta-iodo-phenol and meta-phenol-sulphonic acid, but for the fact that it is also formed in this way from the corresponding ortho- and para-compounds. The potash fusion method is therefore of no value as a guide to the relative positions of the groups. The meta-constitution of resorcinol is clearly proved, however, by its formation from meta-amido-phenol, at ordinary temperatures, by the diazo-reaction—

Resorcinol is of technical importance, as when heated with phthalic anhydride it is converted into fluoresceïn, the mother substance of the eosin dyes (p. 361). Its aqueous solution is coloured dark violet by ferric chloride, and yields with bromine water a crystalline precipitate of a tribromo-compound in the same way as phenol.

Catechol.—The corresponding ortho-compound, pyrocatechin or catechol, occurs in catechu, and was first obtained by distilling this substance, but it is best prepared by distilling with hydriodic acid its monomethyl ether, guaiacol, a liquid occurring in quantity in beech-wood tar. Catechol may also be made by fusing phenol-ortho-sulphonic acid with caustic potash at a low temperature, although, as already stated, at a higher temperature resorcinol is formed. It is produced also by distilling protocatechuic acid (p. 305) with lime.

Catechol or ortho-dihydroxy-benzene, $C_6H_4(OH)_2(o)$ (Reinsch, 1839), is a crystalline substance, which resembles resorcinol, but melts at 104°, and boils at 245°. Its constitution is proved in the same way as that of its isomeride. As a phenol it forms a coloured product with ferric chloride, but the green colour thus produced is turned to violet and red by alkalies. The same reaction is given by its monomethyl ether, guaiacol, which still contains a phenolic group, but not by its dimethyl ether, veratrol. Catechol is very readily oxidised, and reduces silver in the cold. Its solution in alkali readily absorbs oxygen from the air also, forming dark coloured products.

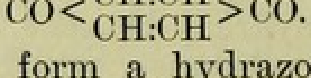
Quinol and Quinone.—Para-dihydroxy-benzene or quinol was first obtained by the dry-distillation of quinic acid (p. 307), but is best prepared by reducing quinone with sulphurous acid. The crude aqueous solution of the quinone is simply saturated with sulphur dioxide, and the quinol extracted from the product with ether. It is recrystallised from hot water containing a little sulphurous acid, and after decolourising its aqueous solution by digestion with animal charcoal, is finally again crystallised from water.

Quinol or hydroquinone, $C_6H_4(OH)_2(p)$ (Wöhler, 1844), is a crystalline substance, melting at 169°. Unlike its isomerides, it sublimes easily, and is only sparingly soluble in cold water. It is reduced to benzene when distilled with zinc dust, and that it is a para-compound follows from its relation to quinone. Like resorcinol and catechol, it forms a diacetate, etc., as well as mono- and di-methyl ethers. Quinol is a strong reducing agent, and is hence used as a developer in photography. Its solution is coloured green by ferric chloride, but the colour soon changes to yellow owing to re-oxidation to quinone.

Quinone was originally obtained by oxidation of quinic acid, but is best prepared by oxidation of aniline with cold chromic acid mixture. The powdered bichromate is slowly added to the ice-cold solution of the aniline in dilute sulphuric acid, and after twenty-four hours the quinone is extracted from the black product with ether, and purified by distillation with steam. It is formed also from various other para-compounds in this manner—from para-phenylene-diamine, and paramidophenol, for example—and it can be made synthetically from succinic acid (p. 299).

Quinone, $C_6H_4O_2$ (Woskresensky, 1838), is a golden yellow, volatile crystalline substance, which melts at 116°, and sublimes freely at a somewhat higher temperature. Its vapour, which is slowly given off, even at ordinary temperatures, possesses a characteristic irritating odour, and attacks the eyes and skin.

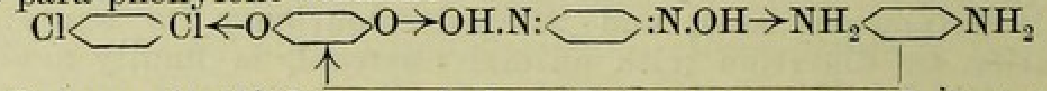
Quinone behaves in most respects as a diketone of the formula



$$CO<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CO.$$

Although it does not form a hydrazone, it condenses with hydroxylamine to a crystalline monoxime and dioxime, and this would be decisive, but that the monoxime is identical with para-nitroso-phenol, $NO.C_6H_4.OH$ (p. 284). Another difficulty is that quinone yields on reduction the ditertiary alcohol or phenol, quinol, instead of the secondary alcohol which might be expected from a compound of this formula; and that it is converted by phosphorus pentachloride not into a tetra-chloro-compound, but into para-dichloro-benzene. These anomalies, however, are probably accounted for by the influence of the benzene nucleus, compounds of the quinone type forming a special class, bearing much the same relation to the true ketones, as the phenols to the aliphatic and aromatic alcohols.

That quinone is a para-compound is proved by its conversion into para-dichloro-benzene, and by the reduction of its dioxime to para-phenylene diamine—

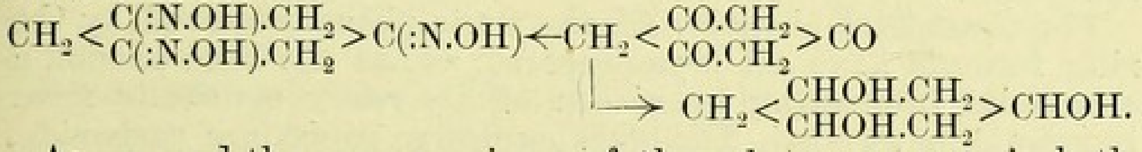


Quinone itself has marked oxidising powers, and its tetrachloro-derivative, chloranil, formed by directly chlorinating it, or more conveniently by boiling aniline or phenol with potassium chlorate and hydrochloric acid, is often used as an oxidiser in the preparation of dyes. Chloranil or tetrachloro-quinone, $CO{:}C_4Cl_4{:}CO$, is a golden-yellow, crystalline substance, which sublimes without melting, and is insoluble in water. The benzene nucleus in this compound is quite unstable, and the substance is resolved by caustic soda into dichloro-maleïc acid and trichlor-ethylene.

The Triphenols.—When resorcinol is fused with caustic soda, hydrogen is violently evolved, and on extracting the acidified solution of the brown melt with ether, a crystalline trihydroxybenzene is obtained. This phloroglucinol was first obtained from the glucoside phloridzin (p. 176), in which, as already stated, it exists in combination with phloretic acid; and it is also formed by fusing various resins with caustic potash.

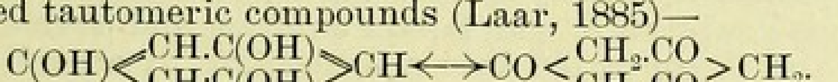
Phloroglucinol or symmetrical trihydroxy-benzene, $C_6H_3(OH)_3$ (*s*) (Hlasiwetz, 1855), is a sweet crystalline substance, which melts at 218°, and sublimes at a somewhat higher temperature. That it is trihydroxy-benzene is proved in much the same way as in the previous cases. It shows the usual properties of a phenol, gives a violet coloration with ferric chloride, and in alkaline solution absorbs oxygen and turns brown. It forms a crystalline triacetate and a trimethyl ether in the usual manner, and that it is a symmetrical compound follows from its conversion into symmetrical trichloro-benzene by phosphorus pentachloride.

But whilst phloroglucinol is thus obviously symmetrical trihydroxy-benzene, it condenses with hydroxylamine, with simple elimination of three molecules of water, to a crystalline trioxime of the formula $C_6H_6(:N.OH)_3$. It is therefore a triketone as well as a triphenol, and this is confirmed by its ready reduction by sodium amalgam to the corresponding secondary alcohol, phloroglucitol, $C_6H_9(OH)_3$, a sweet, soluble, crystalline substance, which melts at 184°, and resembles mannitol in character—



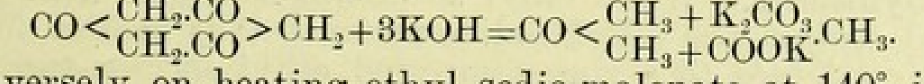
$$CH_2<\begin{matrix}C(:N.OH).CH_2\\C(:N.OH).CH_2\end{matrix}>C(:N.OH)\leftarrow CH_2<\begin{matrix}CO.CH_2\\CO.CH_2\end{matrix}>CO$$
$$\longrightarrow CH_2<\begin{matrix}CHOH.CH_2\\CHOH.CH_2\end{matrix}>CHOH.$$

As one and the same specimen of the substance reacts in both senses, it has been suggested that the phloroglucinol molecule, like that of hydrocyanic acid, assumes one form or the other according to external conditions, the hydrogen atoms oscillating between the oxygen and the vicinal carbon. Such compounds are termed tautomeric compounds (Laar, 1885)—



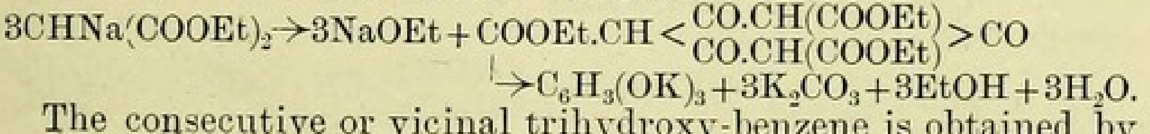
$$C(OH)<\begin{matrix}CH.C(OH)\\CH:C(OH)\end{matrix}>CH\longleftrightarrow CO<\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}>CH_2.$$

When phloroglucinol is chlorinated, it is broken up into dichloracetic acid and tetrachloracetone, and when it is heated at 160° with strong caustic alkali, it is similarly hydrolysed to acetone, acetic acid and carbon dioxide (Combes, 1892), the aromatic or ring compound being in both cases broken up into open-chain aliphatic compounds—



$$CO<\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}>CH_2+3KOH=CO<\begin{matrix}CH_3+K_2CO_3\\CH_3+COOK\end{matrix}.CH_3.$$

Conversely, on heating ethyl sodio-malonate at 140°, it condenses to the triethyl salt of phloroglucinol-tricarboxylic acid, a crystalline substance melting at 104°, from which the phenol is readily obtained by fusion with potash—



$$3CHNa(COOEt)_2\rightarrow 3NaOEt+COOEt.CH<\begin{matrix}CO.CH(COOEt)\\CO.CH(COOEt)\end{matrix}>CO$$
$$\rightarrow C_6H_3(OK)_3+3K_2CO_3+3EtOH+3H_2O.$$

The consecutive or vicinal trihydroxy-benzene is obtained by heating gallic acid (p. 305) at 210°, either alone, or with glycerol or water, and is formed synthetically by fusing chloro-phenol-sulphonic acid with potash.

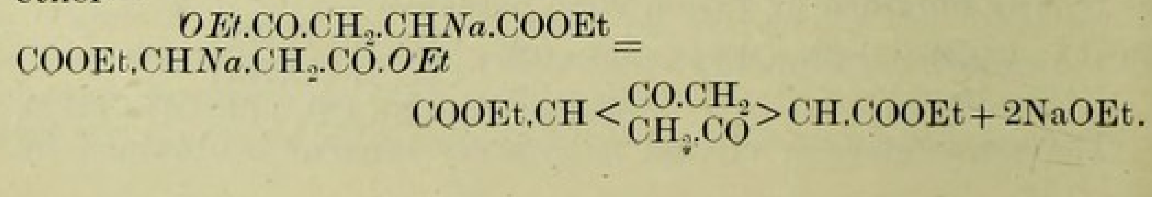
Pyrogallol or 1:2:3-trihydroxy-benzene, $C_6H_3(OH)_3$ (*v*) (Scheele, 1786), is a soft white crystalline substance, which melts at 132° and is very soluble in water and alkalies. It is a powerful reducing agent, and is hence used as a developer or precipitant of metallic silver, in photography. In alkaline solution it absorbs oxygen freely and completely, being itself oxidised to acetic acid, carbon dioxide and other products, and alkaline pyrogallol is thus used as an oxygen absorbent in gas analysis. As a phenol, pyrogallol forms coloured products with iron salts —red with ferric, and deep blue with partially oxidised ferrous salts. Its constitution is proved in the same way as that of phloroglucinol.

The third or unsymmetrical trihydroxy-benzene is formed by fusing quinol with potash, in the same way as phloroglucinol from resorcinol. Hydroxy-quinol or 1:2:3-trihydroxy-benzene, $C_6H_3(OH)_3$ (*a*), is a crystalline substance, melting at 141°; it resembles its isomerides in most respects, but absorbs oxygen even in aqueous solution, and is coloured greenish-brown by ferric salts.

The three tetra-phenols and the penta-phenol required by the ring formula have all been prepared, as has the hexa-phenol, a compound interesting by reason of its ready synthesis from inorganic materials. The black explosive potassium carboxide, $K_6C_6O_6$, formed by the direct union of the metal with carbon monoxide in the manufacture of potassium, is the potassium salt of this complex phenol, and is readily converted into the latter by hydrochloric acid.

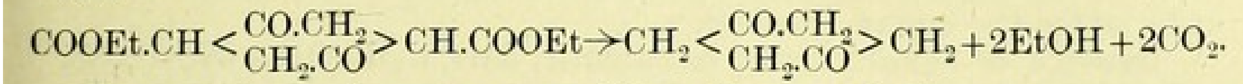
Hexa-phenol or hexahydroxy-benzene, $C_6(OH)_6$ (Nietzki, 1885), is a greyish substance, which soon oxidises and turns violet in the air, and is converted into a hexacetate by acetyl chloride. It is oxidised by nitric acid to the corresponding quinone, triquinoyl, $C_6O_6(+8H_2O)$, from which it is formed again by reduction with stannous chloride. The constitution of triquinoyl follows from its synthesis from tetrahydroxy-quinone, $C_6(OH)_4O_2$, by oxidation with concentrated nitric acid.

Reduction Products of the Polyphenols: the Succino-Succinic Synthesis.—When ethyl succinate is heated with finely divided sodium the ethyl sodio-succinate that is first formed slowly condenses to a ring compound, ethyl succino-succinate, which can be precipitated from the product with dilute sulphuric acid after some days, and recrystallised from alcohol and ether—



$$\begin{array}{l}\quad\quad\quad\mathit{OEt}.CO.CH_2.CH\mathit{Na}.COOEt \\ COOEt.CH\mathit{Na}.CH_2.CO.\mathit{OEt}\end{array} = \\ COOEt.CH<\begin{matrix}CO.CH_2\\CH_2.CO\end{matrix}>CH.COOEt+2NaOEt.$$

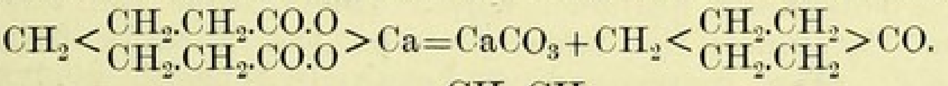
Ethyl succino-succinate, $C_6H_6O_2(COOEt)_2$ (Hermann, 1882), is a colourless or bright-green crystalline substance, melting at 127°, which is readily hydrolysed by caustic alkali to tetrahydro-quinone, both the ethyl and the carboxyl thus being eliminated—



$$\mathrm{COOEt.CH}<\genfrac{}{}{0pt}{}{\mathrm{CO.CH_2}}{\mathrm{CH_2.CO}}>\mathrm{CH.COOEt}\rightarrow\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CO.CH_2}}{\mathrm{CH_2.CO}}>\mathrm{CH_2}+2\mathrm{EtOH}+2\mathrm{CO_2}.$$

Tetrahydro-quinone or para-diketo-hexamethylene, $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2}}{\mathrm{CH_2.CH_2}}>\mathrm{CO}$ (Hermann, 1882), is a colourless, crystalline substance, melting at 78°. It is oxidised to yellow quinone by chromic acid mixture, and that it is a true ketone of the aliphatic type is shown by its reduction by sodium amalgam to the corresponding secondary alcohol, quinitol, $\mathrm{CHOH}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2}}{\mathrm{CH_2.CH_2}}>\mathrm{CHOH}$ (Baeyer, 1892), a bitter-sweet, crystalline substance, which melts at 144° and has all the properties of a paraffinoid alcohol.

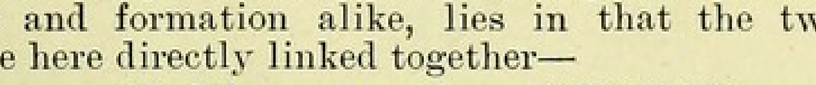
The corresponding monohydroxy-compound is formed from, and readily reconverted into the corresponding ketone, which is made in the same way as the aliphatic ketones, by dry-distilling the calcium salt of the corresponding acid, pimelic acid (p. 159)—



$$\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2.CO.O}}{\mathrm{CH_2.CH_2.CO.O}}>\mathrm{Ca}=\mathrm{CaCO_3}+\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2}}{\mathrm{CH_2.CH_2}}>\mathrm{CO}.$$

Keto-hexamethylene, $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2}}{\mathrm{CH_2.CH_2}}>\mathrm{CO}$ (Mager, 1893) is a liquid of peppermint odour, boiling at 155°, and the hydroxy-hexamethylene or hexahydro-phenol, $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2}}{\mathrm{CH_2.CH_2}}>\mathrm{CHOH}$ (Baeyer, 1894), is a liquid of fusel odour, boiling at 161°, and closely resembling the aliphatic alcohols. The alcohol is also formed by reducing with zinc dust and glacial acetic acid the iodhydrin, $C_6H_{10}I.OH$, made by boiling quinitol with dilute hydriodic acid.

The ketone resembles the aliphatic ketones in practically every respect, and when oxidised, its chain is broken at the carbonyl group in the normal manner, adipic acid being thus formed. The only difference from an aliphatic ketone, in the oxidation and formation alike, lies in that the two alkyl groups are here directly linked together—



$$\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.CH_2}}{\mathrm{CH_2.CH_2}}>\mathrm{CO}+3\mathrm{O}=\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2.COOH}}{\mathrm{CH_2.CH_2.COOH}}.$$

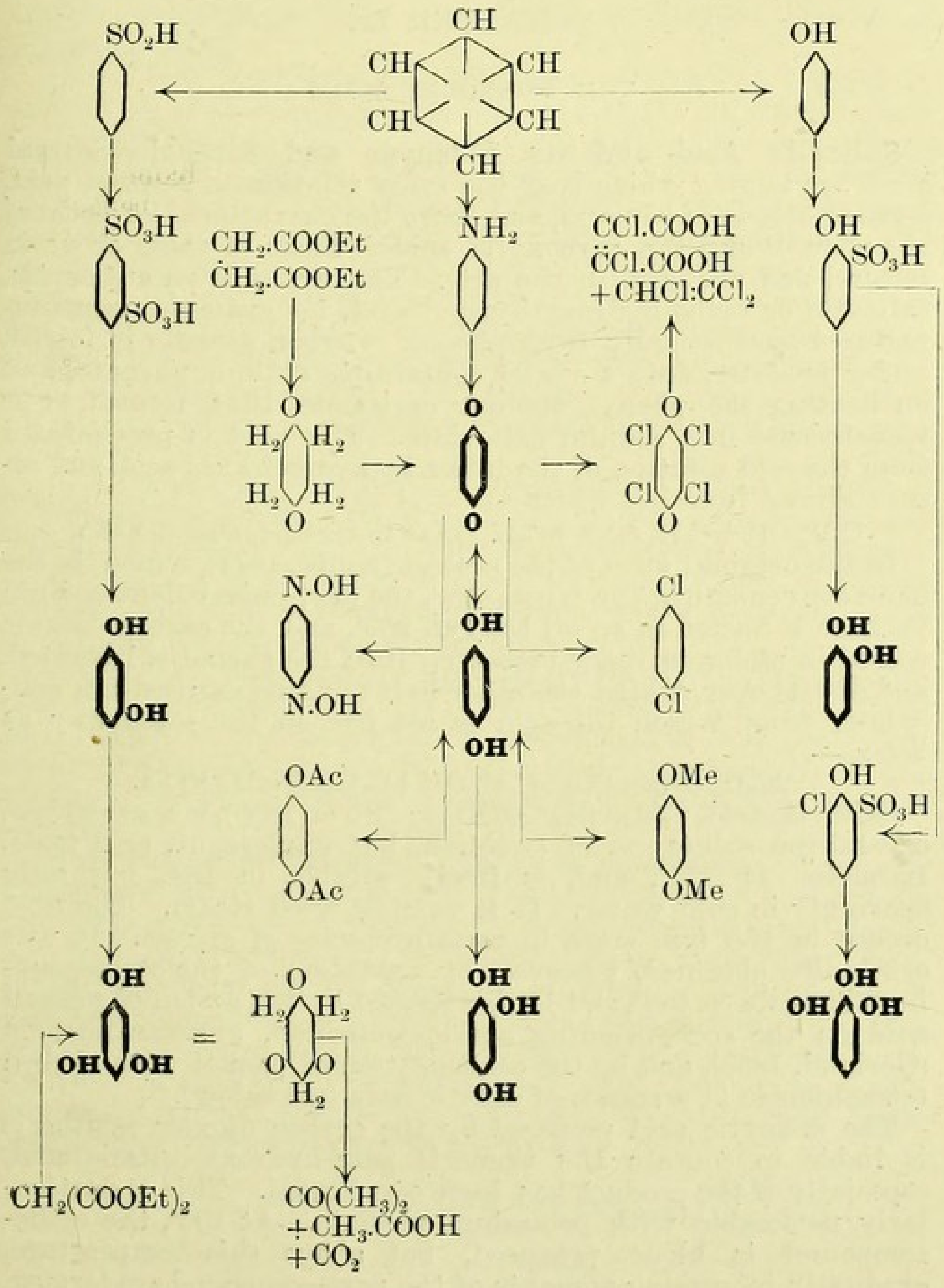
These reduced phenols and quinones, possessing all the characters of the aliphatic secondary alcohols and ketones, form the connecting links between the aliphatic and aromatic compounds. They are in fact saturated ring compounds, and differ from the open-chain saturated compounds only in that two carbon valencies are satisfied by the linkage of carbon to carbon instead of to hydrogen. Similarly, the hexamethylene from which they are derived, resembles, as already stated, the paraffins, and forms a connecting link between the latter and the aromatic hydrocarbons.

The penta- and hexa-hydroxy-derivatives of hexamethylene occur in nature, the former being the quercitol of acorns, and the latter the sugar, inositol.

Inositol or hexahydroxy-hexamethylene, $C_6H_6(OH)_6$ (Scheerer, 1850), is a sweet crystalline substance, which occurs in the heart muscles of animals and in unripe French beans. Although isomeric with, and physically like the hexoses, it has no reducing power, and does not form a hydrazone or osazone. That all its oxygen is hydroxylic, moreover, is proved by the ready conversion of the substance into a crystalline hexacetate. Its ring constitution is proved by its reduction to phenol and iodophenol when heated with hydriodic acid (Maquenne, 1892), and by its oxidation by nitric acid to tetrahydroxy-quinone. As an asymmetrical carbon compound, inositol occurs in three stereoisomeric modifications.

Synopsis.—The poly-hydroxy-benzenes resemble phenol in general characters, but are in most cases much more readily oxidised. The para-dihydroxy-compound is connected with a ketonic substance, quinone, which differs from the aliphatic ketones in much the same way as the phenols from the alcohols. The corresponding hexahydrobenzene derivatives closely resemble the aliphatic alcohols and ketones.

THE DI- AND TRI-PHENOLS AND QUINONE.



CHAPTER L

THE PHENOLIC ACIDS

Salicylic Acid and its Aldehyde and Alcohol.—Several acids are known which bear the same relation to benzoic acid, as the phenols to benzene, and share the characteristics both of the phenols and the carboxylic acids. Some of them occur in nature, and are used in the arts. The well-known antiseptic, salicylic or ortho-hydroxy-benzoic acid, for example, is manufactured synthetically from phenol. Carbon dioxide is forced, under pressure, into a vessel containing sodium phenate, and on heating the phenyl sodium carbonate thus formed, it is transformed into sodium salicylate. The acid is precipitated from the cold solution of the latter by hydrochloric acid, and recrystallised from hot water—

$$C_6H_5.OH \rightarrow C_6H_5.ONa \rightarrow C_6H_5.O.COONa \rightarrow C_6H_4(OH).COONa.$$

In the original form of the process (Kolbe, 1874), which is the more convenient in the laboratory, the dry, pulverulent sodium phenate is heated in an oil bath at 200°, and the carbon dioxide passed in under ordinary pressure. Half the phenol is liberated, and distils over, whilst the other half remains as disodium salicylate, from which the acid is set free in the same way as before—

$$2C_6H_5.ONa + CO_2 = C_6H_5.OH + C_6H_5(ONa).COONa.$$

Salicylic acid, $C_6H_4(OH).COOH$ (*o*) (Piria, 1838), is a colourless, crystalline substance, of sweetish, but unpleasant, acid taste. It melts at 155°, and, is freely soluble in hot, but only sparingly in cold water. It is volatile with steam. The acid occurs in the free state in certain species of spiræa. It was originally obtained, however, by oxidation of the corresponding aldehyde (p. 303), and is also formed by the action of nitrous acid on the corresponding amido-compound, anthranilic acid (Gerland, 1853), and by the condensation of phenol with carbon tetrachloride in presence of caustic soda (see below).

The salicylic acid prepared by the carbon dioxide synthesis is liable to contain the isomeric para-hydroxy-benzoic acid, especially if the product has been overheated. This is particularly noticeable with potassium phenate. At 150°, the ortho-compound is alone produced, but above this temperature, gradually increasing amounts of the para-compound are formed, until at 220° it is the sole product. Whilst the para-acid does not interfere with the use of the salicylic acid as an antiseptic, its physiological properties are different, and the corresponding cresotic acids, $C_6H_3Me(OH).COOH$, which are also formed, unless the phenol is first purified from cresols (p. 310), are poisonous. On this account, natural salicylic acid is preferred for medicinal purposes, and is prepared in quantity by the alkaline hydrolysis of oil of wintergreen, which, as already stated, contains a large proportion of methyl salicylate (Cahours, 1856).

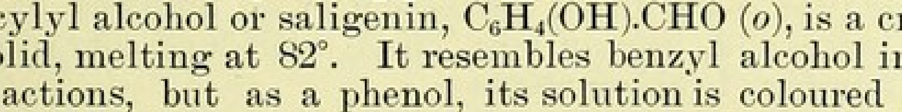
The aldehyde of salicylic acid was originally obtained by hydrolysis of the glucoside helicin, $C_6H_{11}O_5.O.C_6H_4.CHO$, which is formed by oxidation of the corresponding alcohol salicin, $C_6H_{11}O_5.O.C_6H_4.CH_2OH$, the natural glucoside of the willow bark (*salix*). It is best made synthetically, however, by boiling phenol with chloroform and caustic soda solution. The oil, which separates on acidifying the product with hydrochloric acid, consists of a mixture of salicylic aldehyde with the isomeric parahydroxy-benzaldehyde and unchanged phenol, but on distilling it with steam the phenol and salicylic aldehyde alone pass over, and can be separated by means of the crystalline bisulphite compound of the latter (Reimer, 1876)—

$$C_6H_5.ONa + CHCl_3 + 3NaOH = C_6H_5(ONa).CHO + 3NaCl + 2H_2O.$$

Salicylic aldehyde, $C_6H_4(OH).CHO$ (*o*), is a colourless liquid, which boils at 196°, and has the usual properties of aldehydes. It is readily oxidised to the acid by dilute nitric acid, and as an aromatic aldehyde is resolved by caustic soda into sodium salicylate and the corresponding primary alcohol.

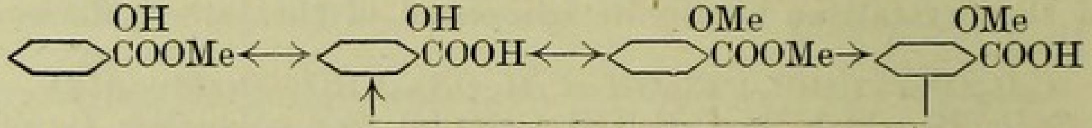
Salicylyl alcohol or saligenin, $C_6H_4(OH).CHO$ (*o*), is a crystalline solid, melting at 82°. It resembles benzyl alcohol in most of its actions, but as a phenol, its solution is coloured violet by ferric chloride. As stated above, it occurs naturally in the glucoside salicin, from which it is set free by hydrolysis with dilute acids.

Constitution of Salicylic Acid: its Isomerides.—The relationship of salicylic acid to phenol and benzoic acid is shown by many reactions. As stated above, it can be made from phenol, and it is reconverted into it by distillation with lime. It is formed also from *o*-amido-benzoic acid, and by fusing *o*-chloro- and *o*-sulpho-benzoic acids with potash. Conversely, it is converted into benzoic acid when heated in a sealed tube with hydriodic acid. That it is a carboxylic acid, moreover, is independently proved by its interconvertibility with the corresponding primary alcohol and aldehyde—



Salicylic acid behaves both as a phenol, and as a carboxylic acid. As a phenol, it gives a violet colour with ferric chloride (which is not destroyed by acetic acid), and is converted by bromine water into a flocculent tribromo-salicylic acid, resembling tribromo-phenol. On the other hand, as a carboxylic acid, it decomposes sodium carbonate, forming sodium salicylate, $C_6H_4(OH).COONa$, whilst as a phenol this salt dissolves in caustic soda, forming disodium salicylate, $C_6H_4(ONa).COONa$, a sweetish powder.

Similarly, the acid forms two sets of alkyl derivatives. Thus, when its alcoholic solution is saturated with hydrogen chloride gas, and the product poured into water, methyl salicylate, $C_6H_4(OH).COOMe$, separates, whilst when the solution is digested with methyl iodide and caustic soda, dimethyl salicylate, $C_6H_4(OMe).COOMe$, is formed. Both are colourless liquids. The first still shows phenolic properties, and as an ethereal salt is hydrolysed by caustic soda to the acid and methyl alcohol, but the second salt is no longer phenolic, and is hydrolysed only to *o*-methoxy-benzoic acid, $C_6H_4(OMe).COOH$, from which the methyl can only be removed by boiling with alcoholic potash or concentrated hydriodic acid—



When a solution of salicylic acid in amyl alcohol is digested with metallic sodium, the acid is reduced to a ketonic hexamethylene derivative (p. 291), which is then hydrolysed to normal pimelic acid (Einhorn, 1895). This is a very interesting instance of the direct conversion of an aromatic or closed-chain compound, into an open chain compound containing the same number of carbon atoms—

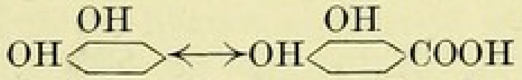
$$\begin{array}{lll} CH{=}CH.C.OH & CH_2.CH_2.CO & CH_2.CH_2.COOH \\ \dot{C}H{=}CH.\ddot{C}.COOH \nearrow & \dot{C}H_2.CH_2.\dot{C}H.COOH \nearrow & \dot{C}H_2.CH_2.CH_2.COOH. \end{array}$$

The meta and para-hydroxy-benzoic acids, isomeric with salicylic acid, can be formed from the corresponding amido- and chloro-benzoic acids, and, as already stated, the para-acid is produced by the action of carbon dioxide on potassium phenate at 220°. The meta-compound melts at 200°, and at a higher temperature distils unchanged, and the para-compound melts at 210°. Both are resolved into phenol when heated with lime. Neither acid forms a coloration with ferric chloride, and neither is volatile with steam. It is only the ortho-hydroxy-acids which have these properties. The methyl ether of para-hydroxy-benzoic acid occurs naturally as anisic acid, $C_6H_4(OMe).COOH$ (*p*), a crystalline substance, which melts at 185°, and like the corresponding ortho-compound, is resolved by heat into carbon dioxide and anisole.

Many homologues of salicylic acid are of course possible. There should be ten cresotic acids, $C_6H_3Me(OH).COOH$, for example, and all these have been made.

Protocatechuic Acid and its Derivatives.—The polyphenols also are connected with carboxylic acids, which bear the same relation to them, as salicylic acid to ordinary phenol. The chief of these are protocatechuic and gallic acids. Protocatechuic acid exists, in combination with phloroglucinol, in the mimosa and other plants, and is best prepared by fusing catechu, kino and like resins with potash.

Protocatechuic or 1:2:4-dihydroxy-benzoic acid, $C_6H_3(OH)_2.COOH$ (Stenhouse, 1861), is a crystalline substance, melting at 199°. When heated, it is decomposed into carbon dioxide and catechol, and that it is a catechol-carboxylic acid is confirmed by its synthesis, together with the isomeric acid, by heating the diphenol with solid ammonium carbonate—

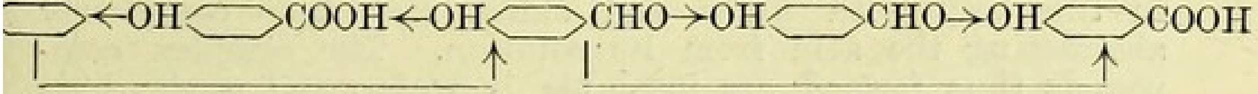


$$\text{OH}\overset{\text{OH}}{\langle\quad\rangle} \longleftrightarrow \text{OH}\overset{\text{OH}}{\langle\quad\rangle}\text{COOH}$$

As an ortho-diphenol, it gives a green coloration with ferric chloride, and, like most of the polyphenols, it reduces silver. As an acid, it forms salts, such as methyl protocatechuate, $C_6H_3(OH)_2.COOMe$, a crystalline solid, melting at 224°.

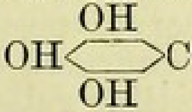
The flavouring matter of the vanilla fruit is one of the methyl-protocatechuic aldehydes. Vanillin, $C_6H_3(OH)(OMe).CHO$, is a crystalline solid, which melts at 80°, and sublimes easily. It is converted into protocatechuic acid by fusion with potash, and is hydrolysed to methyl chloride and protocatechuic aldehyde when heated with concentrated hydrochloric acid. This determines its constitution as a methyl-protocatechuic aldehyde, and since it is only the para-hydroxy-benzaldehydes which sublime easily, it follows that the uncombined phenol group is in the para-position to the aldehyde group.

Vanillin can be synthesised by boiling guaiacol or methyl-catechol with chloroform and caustic soda, in the same way as salicylic aldehyde from phenol. It has all the properties of an aromatic aldehyde, and is readily converted into the corresponding alcohol and acid—vanillic acid—in the usual manner—



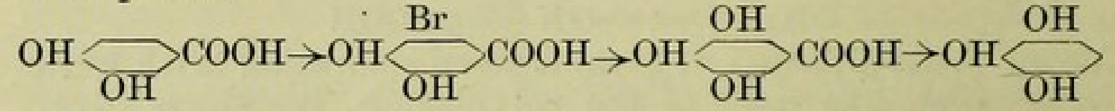
$$\overset{\text{OMe}}{\langle\quad\rangle} \longleftarrow \text{OH}\overset{\text{OMe}}{\langle\quad\rangle}\text{COOH} \longleftarrow \text{OH}\overset{\text{OMe}}{\langle\quad\rangle}\text{CHO} \longrightarrow \text{OH}\overset{\text{OH}}{\langle\quad\rangle}\text{CHO} \longrightarrow \text{OH}\overset{\text{OH}}{\langle\quad\rangle}\text{COOH}$$

Gallic Acid and Tannin.—The gallic acid from which pyrogallol is obtained is trihydroxy-benzoic or pyrogallol-carboxylic acid. It occurs in tea and in oak-galls, but is best prepared by hydrolysing tannin with hot dilute sulphuric acid.



Gallic acid, $\text{OH}\overset{\text{OH}}{\underset{\text{OH}}{\langle\quad\rangle}}\text{COOH}$, (Scheele, 1785), is a white silky, crystalline substance, which is freely soluble in water, and is astringent but only slightly acid in taste. It melts at 220°, and at the same time decomposes into pyrogallol and carbon dioxide. As a phenol, gallic acid forms a blue-black coloration or precipitate with iron salts, and as a polyphenol, it easily reduces silver and gold, and is hence used as a developer and intensifier in photography. The alkaline solution, like that of pyrogallol, absorbs oxygen, and turns brown in the air. When the acid is warmed with concentrated sulphuric acid it is condensed to rufigallic acid, a characteristic, insoluble, scarlet compound, which is an analogue of alizarin (p. 371)

As a triphenol, gallic acid forms a crystalline triacetyl derivative, and its constitution as pyrogallol-carboxylic acid is confirmed by its synthesis by fusing bromoprotocatechuic acid with potash—



The astringency of overdrawn tea and similar vegetable extracts, is due to tannin or digallic acid. Tannin constitutes half the weight of oak-galls ("oak-apples"), and as it is exceedingly soluble in water, but insoluble in alcohol and ether, is readily extracted from the powdered galls by shaking them with a mixture of ordinary alcohol and ether. The acid dissolves in the water of the alcohol, and separates as a heavy solution, from which it is reprecipitated on concentration. After several times redissolving and evaporating, the product becomes colourless.

Tannin, galloyl-gallic or gallotannic acid, $C_{14}H_{10}O_9 + 2H_2O$, is a light, amorphous substance, having a very characteristic, and not unfragrant, odour. As already stated, it is very soluble, and the solution is intensely astringent. Like gallic acid, tannin forms a blue-black coloration or precipitate with iron salts—ordinary ink. Infusion of galls was used in this way by the Romans to detect the adulteration of verdigris with green vitriol.

Tannin is distinguished from gallic acid, however, by forming a flocculent precipitate with cold gelatine solution. It combines in this way with hides and skins, raw hide completely abstracting the acid from its solution. The complex compounds thus formed are insoluble in water, and render hide resistent to the latter—leather. The tannic acid from oak-bark is mostly used for this purpose.

The constitution of tannin is proved by its hydrolysis to gallic acid by dilute sulphuric acid, and by its synthesis from this acid by heating it with phosphorus oxychloride. The presence of the five hydroxyl groups is confirmed by the formation of a pentacetyl derivative, a crystalline substance melting at 210°—

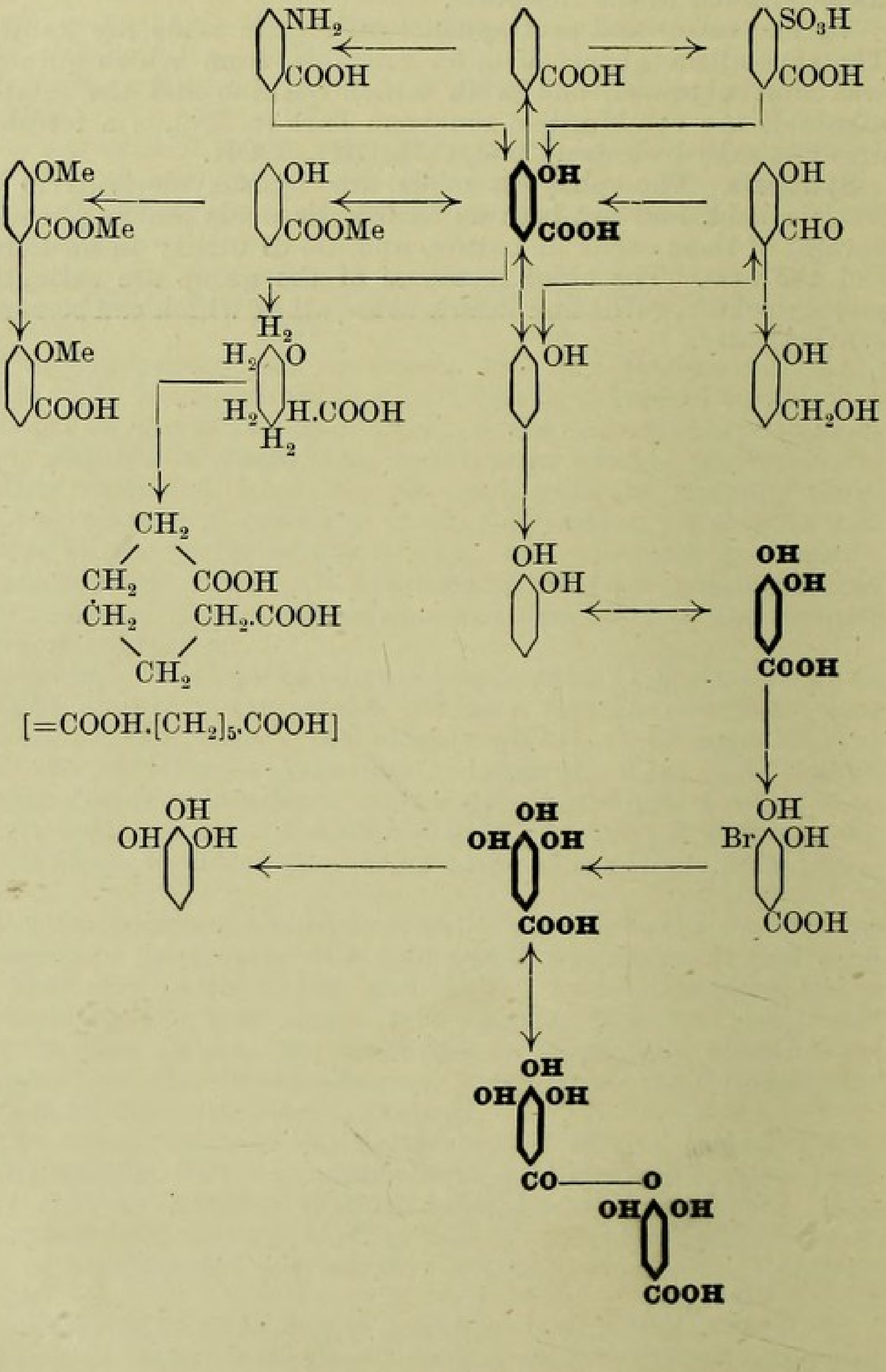
$$C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.COOH \longleftrightarrow 2C_6H_8(OH)_3.COOH.$$

There are many varieties of tannin, such as quercitannic and caffetannic acids. They are mostly derivatives of gallic acid, but in some cases are derived from the corresponding phloroglucinol acid. Most of the tannins occur as glucosides, and are obtained from these by hydrolysis, but gallotannic acid is usually found in the free state.

Various tetra- and penta-phenol-carboxylic acids are known. The crystalline quinic acid, for example, from which quinone was first obtained, and with which quinine and the related alkaloids are combined in cinchona bark (p. 396), is a tetrahydroxy-hexahydrobenzoic acid, $C_6H_7(OH)_4.COOH$.

Synopsis.—The phenolic acids are hydroxy-derivatives of benzoic acid, and act both as carboxylic acids and as phenols. Several of them occur in nature, and are of utility in medicine and the arts. The chief members of the group are salicylic, protocatechuic, gallic and tannic acids, all of which can be made synthetically.

THE PHENOLIC ACIDS.



SECTION XIII

THE METHYL-BENZENES AND THEIR DERIVATIVES

CHAPTER LI

THE CRESOLS AND TOLUIDINES : TOLUENE AS METHYL-BENZENE

The Chloro- and Bromo-toluenes.—Whilst boiling toluene functions with halogens as a paraffinoid compound, in the cold, especially in presence of a carrier such as ferric chloride, it behaves as a benzene derivative, the nucleal hydrogen atoms being successively replaced, and "aromatic" substitution effected.

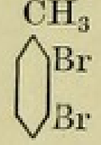
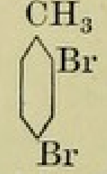
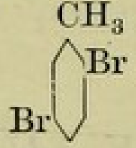
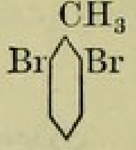
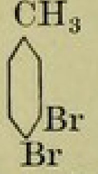
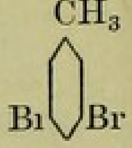
As the mono-substituted toluenes are di-substitution products of benzene, they exhibit the usual position isomerism, and in accordance with the rule previously noted, it is the para- and ortho-compounds which are formed by direct action, the meta-compounds having to be made indirectly, either from aceto-para-toluidide (p. 312), or from meta-toluidine (p. 313). In practice all three bromo-compounds are best made by this last method—

$$C_6H_4(CH_3).NH_2 \rightarrow C_6H_4(CH_3).N{:}N.Cl \rightarrow C_6H_4(CH_3).Br.$$

Ortho-bromo-toluene,  $\underset{Br}{CH_3\langle\quad\rangle}$ (Hübner, 1870), is a colourless liquid boiling at 180°. It resembles bromo-benzene in its actions, and is stable towards alkalies, and reducible to the hydrocarbon by sodium in alcohol. Like toluene it is oxidised to the corresponding carboxylic acid, ortho-bromo-benzoic acid, when boiled with dilute nitric acid. and it is thus clear that the halogen is attached to the benzene ring, and not to the side chain, as in the isomeric benzyl bromide. Meta-bromo-toluene boils at 184°, and has similar properties, and the para-compound differs only in that it solidifies in a freezing mixture to a crystalline solid, melting at 7°—

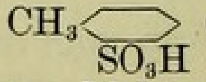
$$C_6H_5.CH_3 \rightarrow C_6H_4Cl.CH_3 \rightarrow C_6H_4Cl.COOH.$$

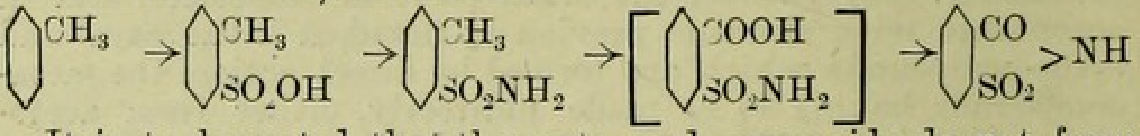
The isomerism of the di-substituted toluenes is more complex than that of the benzene derivatives, and not only are there six distinct dibromo-compounds, but there are also three bromo-benzyl bromides, isomeric with them. The dibromo-toluenes are distinguished from one another by their melting and boiling points, and by their yielding six distinct crystalline dibromobenzoic acids on oxidation—

1:2:3 [30°] 1:2:4 [– 25°] 1:2:5 (236°) 1:2:6 (240°) 1:3:4 (239°) 1:3:5 [39°]

The Toluene-Sulphonic Acids.—Toluene is sulphonated much more readily than benzene, and the para-compound thus formed is separated from the accompanying ortho-derivative by repeated crystallisation of its barium salt. The meta-compound is made from aceto-para-toluidide.

Toluene-ortho-sulphonic acid,  (Terry, 1873), is a well-defined crystalline substance, which resembles the corresponding benzene derivative in all essentials, and forms, for example, a sulphochloride, and a crystalline sulphonamide. It is not attacked by acid oxidising agents, but is converted by alkaline permanganate into the corresponding sulpho-benzoic acid (p. 265). The meta- and para-sulphonamides are similarly oxidised to the sulphobenzoic monamides, $C_6H_4(COOH).SO_2NH_2$, but the ortho-sulphonamide yields, as already noted, the imide or internal amide, saccharin—



It is to be noted that the meta- and para-acids do not form such internal anhydrides, and as will be seen later, it is a general rule that only ortho-groups interact in this manner. This is accounted for by the ring formula, in which the ortho-groups are attached to adjacent carbon atoms, as in succinic acid, and are therefore near one another in space.

The Cresols.—When fused with potash, as in making phenol from benzene-sulphonic acid, the toluene-sulphonic acids are hydrolysed to the cresols or toluene-phenols. These compounds occur also in coal and beech-wood tars, and can be formed from the corresponding amido-compounds, the toluidines, in precisely the same way as phenol from aniline—

$$C_6H_4(CH_3).SO_2OK \rightarrow C_6H_4(CH_3).OH \leftarrow C_6H_4(CH_3).NH_2.$$

Ortho-, meta- and para-cresol, $C_6H_4(CH_3).OH$ (Duclos, 1859), are crystalline substances of high boiling point, which resemble phenol in all essentials. The ortho-compound melts at 31°, and gives a blue colour with ferric chloride ; the meta-compound melts at 4°, and is therefore liquid at ordinary temperatures ; whilst the para-compound melts at 36°.

The resemblance of the cresols to phenol is very close. Their odour—that of commercial carbolic acid—is not so pleasant, but they are equally good disinfectants and antiseptics.

Creasote, the crude mixture of cresols and homologous compounds from wood tar, was formerly used as a meat preservative (*κρέας*, *σώζω*), and is still used as a disinfectant, and for rendering wood—railway sleepers, for example—more durable. The preservative action of wood smoke is largely due to creasote vapour.

The cresols form salts with bases, such as potassium cresylate, $C_6H_4Me.OK$, and with acids, such as tolyl sulphate and acetate, $C_6H_4Me.OAc$, and they are reduced to toluene when distilled with zinc dust. Unlike the toluene-sulphonic acids, however, they are either not affected by oxidising agents, or else broken up altogether, the methyl groups being to a certain extent protected by the hydroxyl. When, however, the latter is combined with acid groups, the methyl can be oxidised to carboxyl in the normal manner. The crystalline ortho-tolyl acetate, for example, formed by the action of acetic anhydride and sodium acetate on the phenol, is converted by chromic acid mixture into salicylic acid—

$$C_6H_4(OH).CH_3 \rightarrow C_6H_4(OH).COOH.$$

The cresols are converted by concentrated nitro-sulphuric acid into mono-, di- and tri-nitro-compounds, analogous to the nitrophenols and picric acid, and still more intensely coloured.

The Nitrotoluenes.—Whilst dilute nitric acid affects the toluene side-chain only, the hydrocarbon is nitrated by the concentrated acid in the same way as benzene, and as the nitro-toluenes are benzene di-substitution products, they exist of course in three isomeric forms. The product of direct nitration, obtained and isolated as in the preparation of nitrobenzene, consists of a mixture of the ortho- and para-varieties, into which, after washing and drying, it can be resolved by fractional distillation. The meta-compound is prepared from aceto-para-toluidide (p. 312).

Ortho-, meta- and para-nitro-toluene, $C_6H_4(CH_3).NO_2$ (Beilstein, 1870), are yellowish liquids, or crystalline solids, which resemble nitrobenzene in odour and chemical character. The ortho-compound melts at 10° and boils at 218°; the meta-compound melts at 16° and boils at 230°; whilst the para-compound melts only at 54°, and boils at 238°.

By further nitration, dinitro-toluenes, and with difficulty, trinitro-toluenes, can be formed, but, as in all cases, no more than three nitro-groups can be introduced into the benzene ring.

The Toluidines.—By reduction with tin and hydrochloric acid, or on the manufacturing scale with iron and hydrochloric acid, the nitro-toluenes are converted into the corresponding toluidines, of which the para-compound is extensively used in the colour industry.

The ortho- and para-compounds are best prepared together, however, from the mixed ortho- and para-nitro-toluenes, as they are more readily separated than the latter. After purifying the mixed bases, as in the preparation of aniline, they are separated by adding dilute sulphuric acid in amount insufficent to neutralise the whole—by fractional neutralisation, in fact. The acid combines preferentially with the more basic para-compound, and on steam distilling the product, the ortho-toluidine alone passes over. Meta-toluidine is made by reducing meta-nitro-toluene in the usual manner—

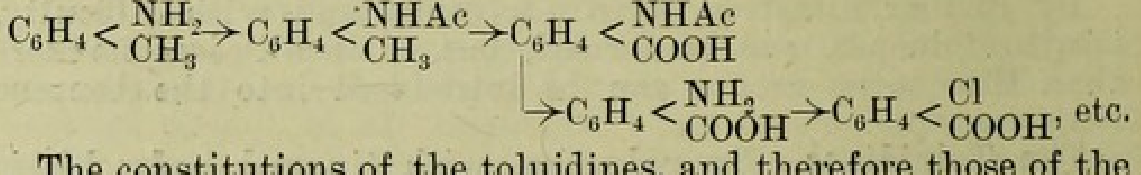
$$C_6H_5.CH_3 \rightarrow CH_3.C_6H_4.NO_2 \rightarrow C_6H_3.C_6H_4.NH_2.$$

Ortho- and meta-toluidine (Hofmann, 1845) are colourless liquids of high boiling point, resembling aniline in odour, but para-toluidine (Hofmann) is a crystalline substance, melting at 45°. It is noteworthy that in this, as in almost all cases, the melting point of the para-compound is considerably higher than those of its isomerides. The boiling points of the toluidines are singularly close—197°, 199°, 198°, but the three bases are readily identified by means of their acetyl compounds, which are prepared by the action of glacial acetic acid or acetyl chloride, in the same way as acetanilide.

Aceto-para-toluidide, $CH_3\left\langle\right\rangle NHAc$, is a crystalline substance resembling acetanilide, and melting at 153°, and the corresponding ortho- and meta-compounds are similar substances, melting respectively at 110° and 65°.

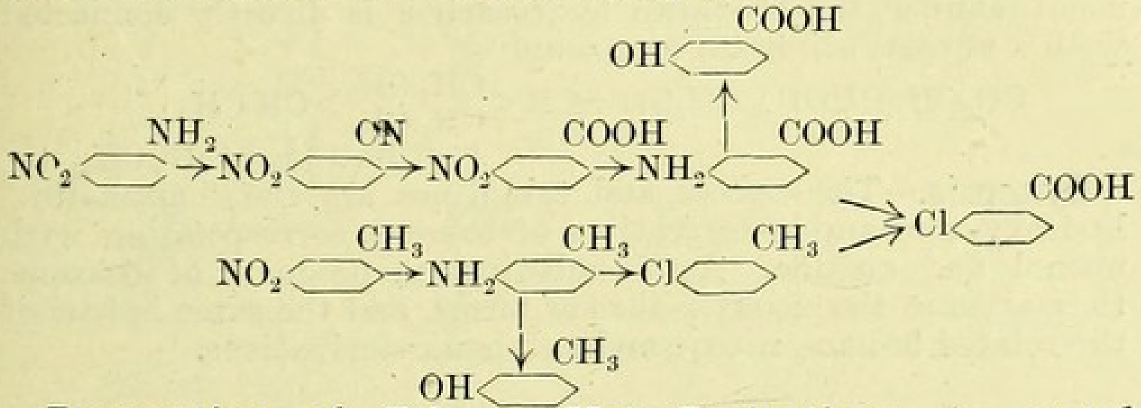
The toluidines are stronger bases than aniline, and resemble it in character, but they are much weaker than the isomeric benzylamine, in which the amido-group is in the side chain. Like aniline, they are readily convertible by the diazo-reaction into halogen derivatives, etc., and the hydrocarbon itself, the operations being identical with those already described.

Like the cresols, the toluidines are more or less broken up by oxidising agents. Ortho-toluidine, for example, forms a blue colouring matter with hypochlorites, in the same way as aniline. But the aceto-toluidides, in which the amido-groups are protected, are oxidised by acid permanganate in the normal manner, and the crystalline acetamido-benzoic acids thus formed are readily hydrolysed to the amido-benzoic acids, from which other substituted benzoic acids can then be obtained—



$$C_6H_4 < \begin{matrix} NH_2 \\ CH_3 \end{matrix} \rightarrow C_6H_4 < \begin{matrix} NHAc \\ CH_3 \end{matrix} \rightarrow C_6H_4 < \begin{matrix} NHAc \\ COOH \end{matrix}$$
$$\rightarrow C_6H_4 < \begin{matrix} NH_2 \\ COOH \end{matrix} \rightarrow C_6H_4 < \begin{matrix} Cl \\ COOH \end{matrix}, \text{ etc.}$$

The constitutions of the toluidines, and therefore those of the derived compounds, are readily proved by connecting the bases by means of the diazo and cyanide reactions with the nitranilines, whose constitutions are known. The meta-chloro-benzoic acid, for example, obtained by the diazo-cyanide synthesis from meta-nitraniline, is identical with that made from the toluidine prepared from aceto-para-toluidide; and this toluidine and its derivatives are therefore meta-compounds. The same applies to the ortho- and para-compounds. The constitutions of the toluene derivatives are also independently established by their genetic connection with the xylenes (p. 316)—



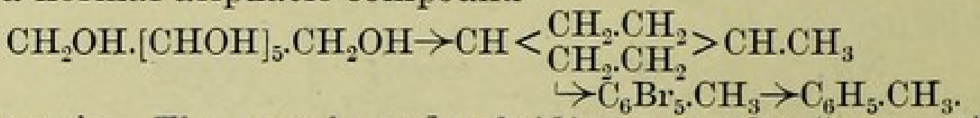
Preparation of Toluene Meta-Derivatives.—As stated above, the toluene meta-substitution products cannot be prepared directly, and are obtained amongst other sources from aceto-para-toluidide. The toluidide is here used in the same way as acetanilide, in the preparation of ortho- and para-nitranilines. The amido-group being protected by the acetyl, on nitrating the toluidide the nitro-group takes up the ortho-position to the acetamido-group, just as with acetamide (the para-position is already occupied), and therefore the meta-position to the methyl group; and on hydrolysing this 1:3:4-nitraceto-para-toluidide, which is a crystalline substance resembling the nitracetanilides, the corresponding nitro-toluidine is obtained. The order of the groups in such compounds are usually indicated in a bracket placed after the formula—

$$CH_3\langle\quad\rangle NH_2 \rightarrow CH_3\langle\quad\rangle NHAc \rightarrow CH_3\overset{NO_2}{\langle\quad\rangle} NHAc \rightarrow CH_3\overset{NO_2}{\langle\quad\rangle} NH_2$$

Nitro-para-toluidine, $NO_2.C_6H_4Me.NH_2[Me:NO_2:NH_2=1:3:4]$ is a crystalline substance resembling the nitranilines. Its value lies in that as its amido-group can be eliminated by the diazo-reduction method, in precisely the same way as with aniline (p. 256), it affords a source of meta-nitro-toluene, and thus of all the meta-toluene derivatives. Brom-aceto-para-toluidide and aceto-toluidide-sulphonic acid can be made in the same way, and meta-halogen and meta-sulphonic derivatives of toluene thus directly prepared—

$$CH_3\overset{NO_2}{\langle\quad\rangle} NH_2 \rightarrow CH_3\overset{NO_2}{\langle\quad\rangle} N{:}N.Cl \rightarrow CH_3\overset{NO_2}{\langle\quad\rangle}$$

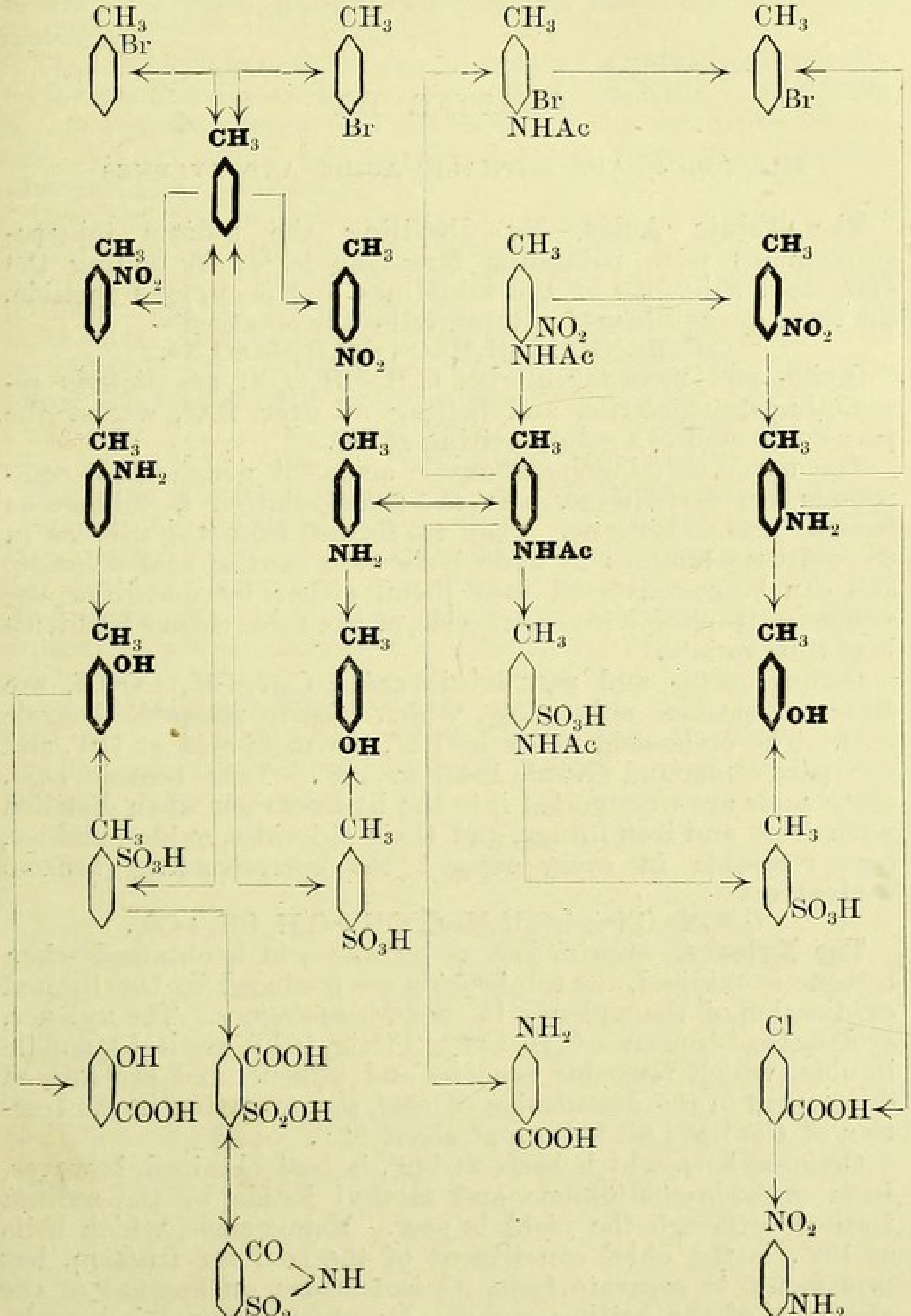
Additive Compounds of Toluene.—Toluene vapour combines with chlorine in sunlight in the same way as benzene, forming a similar crystalline hexachloride. It is also reduced by hydriodic acid, at a high temperature, to hexahydrotoluene, $C_6H_{11}.CH_3$, a liquid of paraffin odour, boiling at 100°, and closely resembling hexahydro-benzene. As already stated, hexahydrotoluene is also formed by the successive action of hydriodic and sulphuric acids on perseïtol, $\mathrm{CH_2OH.[CHOH]_5.CH_2OH}$. It is converted into penta-bromo-toluene by prolonged bromination in presence of aluminium bromide, and as this bromo-toluene is reducible to the hydrocarbon by sodium and alcohol in the usual manner, the aromatic hydrocarbon is directly connected with a normal aliphatic compound—



$$\mathrm{CH_2OH.[CHOH]_5.CH_2OH} \rightarrow \mathrm{CH}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}>\mathrm{CH.CH_3} \\ \hookrightarrow \mathrm{C_6Br_5.CH_3} \rightarrow \mathrm{C_6H_5.CH_3}.$$

Synopsis.—The cresols and toluidines are the "aromatic" hydroxy- and amido-derivatives of toluene, corresponding with phenol and aniline. As di-substitution products of benzene, they assume the usual isomeric forms, and the same is true of the related bromo-, nitro-, and sulphonic-derivatives.

THE CRESOLS AND TOLUIDINES.



CHAPTER LII

THE TOLUIC AND PHTHALIC ACIDS AND XYLENES

The Toluic Acids.—By distilling the sodium toluene-sulphonates with potassium ferrocyanide, or by adding the diazotized solutions of the toluidines to hot cuprous cyanide, the three cyanotoluenes or tolunitriles are obtained—

$$C_6H_4Me.NH_2 \rightarrow C_6H_4Me.CN \leftarrow C_6H_4Me.SO_3Na.$$

Ortho- and meta-tolunitrile, $C_6H_4(CH_3).CN$, are liquids resembling benzonitrile, and boiling at over 200°, whilst the para-compound is a solid, melting at 29°.

The toluic or toluene-carboxylic acids, of which these compounds are derivatives, bear the same relation to toluene as benzoic acid to benzene. They are formed from the nitriles in the ordinary manner by hydrolysis with caustic acid solution, and can be re-converted into them, either by distilling the amides with phosphorus pentoxide, or the acids themselves with lead thiocyanate.

Ortho-, meta- and para-toluic acids, $C_6H_4(CH_3).COOH$, are light, crystalline substances, which closely resemble benzoic acid. The ortho-acid melts at 102°, the meta-acid at 110°, and the para-compound (Noad, 1847) at 186°. Like benzoic acid, these acids are reconverted into the hydrocarbon when distilled with lime and iron filings, and their chlorides, oxides, amides, etc., resemble in every respect the corresponding benzoic derivatives—

$$C_6H_4Me.CN \longleftrightarrow C_6H_4Me.COOH \rightarrow C_6H_5.CH_3 + CO_2.$$

The Xylenes.—Again, just as benzoic acid is obtained when toluene is oxidised, the toluic acids are produced by the limited oxidisation of the xylenes, its next homologues. The xylenes, or dimethyl-benzenes, $C_6H_4(CH_3)_2$ (Fittig, 1870), are light, mobile liquids, which resemble benzene and toluene, and are formed with them in the distillation of coal, accumulating in the fraction of the light oil boiling at about 140°.

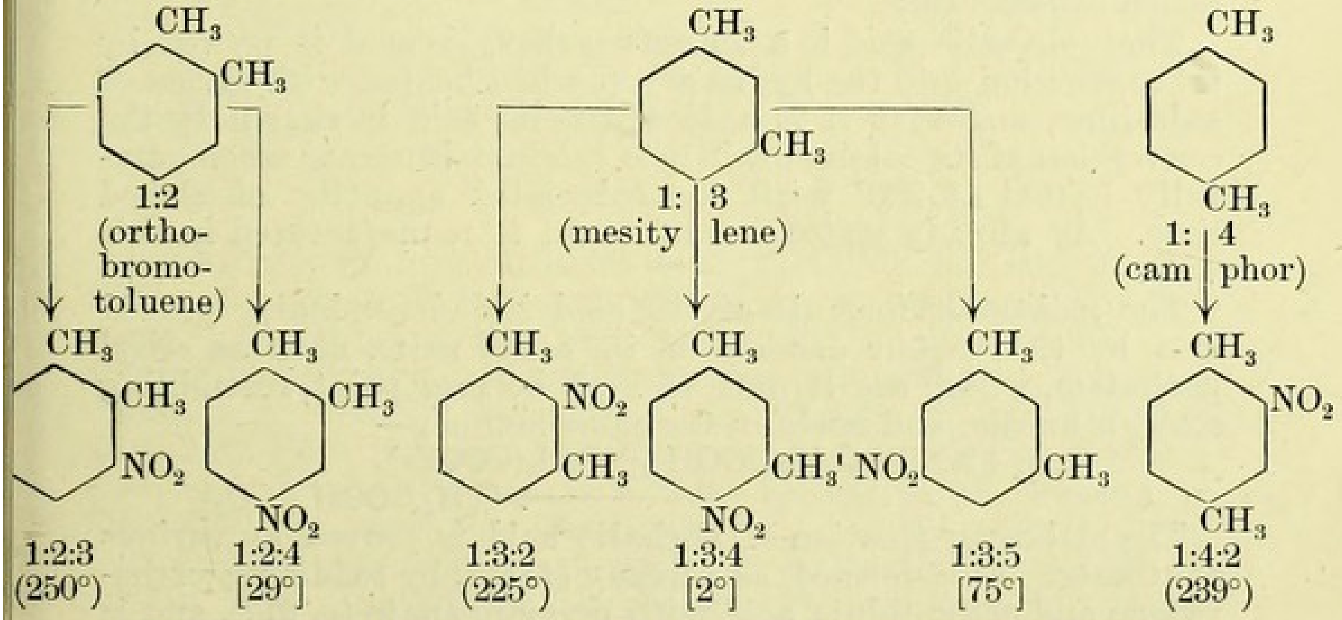
Ortho-xylene, which boils at 142°, is best obtained, however, from ortho-bromo-toluene and methyl iodide by the sodium method, although the yield is poor. Meta-xylene, which boils at 139°, is the chief constituent of the coal tar fraction, but is difficult to separate from its isomerides, on account of the closeness of the boiling points. It is best prepared indirectly, by distilling mesitylenic acid (p. 322) with lime. Para-xylene, which melts at 15° and boils at 138°, is easily made by distilling camphor with anhydrous zinc chloride, and is also formed synthetically, and with good yield, from para-dibromobenzene, or para-bromo-toluene, by the methyl-iodide-sodium method.

That the xylenes are dimethyl-benzenes is proved analytically by their successive oxidation to toluic and phthalic acids (p. 318), by appropriate agents, and synthetically by the direct formation of the ortho- and para-compounds from the dibromobenzenes and bromo-toluenes.

Ortho-xylene is burnt to carbon dioxide by chromic acid mixture, as is often the case with ortho-compounds, but it is converted into ortho-toluic acid by dilute nitric acid, and into phthalic acid by permanganate. Meta-xylene is oxidised to meta-toluic acid by dilute nitric acid, and to isophthalic acid by chromic acid, whilst para-xylene is converted into para-toluic and terephthalic acids by dilute nitric acid alone—

$$C_6H_4{<}\begin{matrix}CH_3\\CH_3\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CH_3\\COOH\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}COOH\\COOH\end{matrix}$$

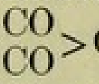
Relative Positions of Groups in the Xylenes.—The positions of the groups in the xylenes are directly ascertained by a method analogous to that used with the dibromo-benzenes. All three hydrocarbons are convertible under the ordinary conditions into mono-nitro-xylenes, of which there are six, similarly constituted to the dibromo-toluenes. But whilst the camphor xylene yields only one of these compounds, that from ortho-bromo-toluene gives two, and the xylene from coal tar and mesitylene, three. It follows, therefore, as in the former case, that the camphor xylene is the 1:4 or para-compound, and so on—



The constitution of meta-xylene, and thus of all the meta-derivatives of benzene, is confirmed also, as already stated, by its preparation from mesitylenic acid and mesitylene, which can be proved to be symmetrical compounds (p. 324), and it follows from this, and from the nitro-xylene relations, that in the alkyl-iodide-sodium synthesis the alkyl group takes up the position previously occupied by the halogen. This affords a means of determining the constitution of the higher methyl-benzenes (p. 325).

Phthalic Acid.—The acids obtained by the further oxidation of the xylenes and toluic acids, and termed the phthalic acids, from the genetic connection of the ortho-compound with the hydrocarbon naphthalene (p. 362), are of both theoretical and technical importance. As the ultimate oxidation products of all dialkyl-benzene derivatives, they serve to determine the constitutions of this class of compounds, and the ortho-acid is used in large quantities in the dye industry.

Ortho-phthalic or phthalic acid is made by boiling naphthalene (p. 366), or better, its tetra-chloride, in a reflux apparatus with concentrated nitric acid, until it is completely dissolved. The excess of the acid is then evaporated, and on distilling the residue, the acid anhydride passes over, and can be recrystallised from water. By boiling the anhydride with caustic soda solution, it is converted into sodium phthalate, and from this the acid is precipitated by hydrochloric acid.

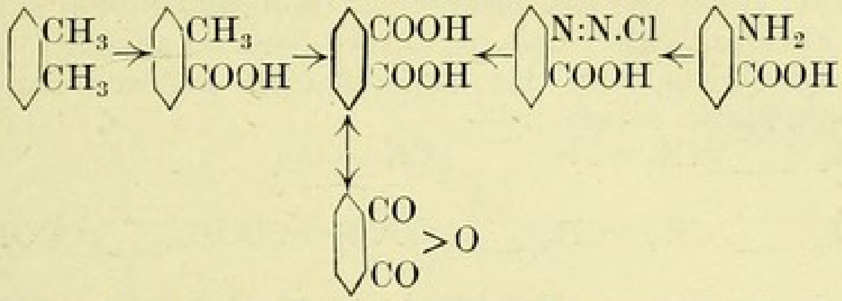
Phthalic or benzene-ortho-dicarboxylic acid, $C_6H_4(COOH)_2$ (*o*) (Laurent, 1836), is a crystalline substance, melting at 213°, and the phthalic anhydride,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O$ (*o*), obtained by distilling it, is a crystalline substance, melting at 128°. The same dehydration is partially effected by simple fusion, for on remelting the solidified acid, the melting point is found to have fallen considerably.

That phthalic acid is a benzene-carboxylic acid is proved by its conversion into the hydrocarbon when heated with excess of soda-lime, and that it is a dicarboxylic acid is shown by the conversion of its calcium salt into calcium benzoate when carefully heated at 230° with the calculated quantity of slaked lime. As already stated, benzoic acid is manufactured in this way.

The molecular formula of the acid is independently proved also by the vapour density of its alkyl salts, such as ethyl phthalate, which are liquids of high boiling point, resembling ethyl benzoate, and made in the same manner—

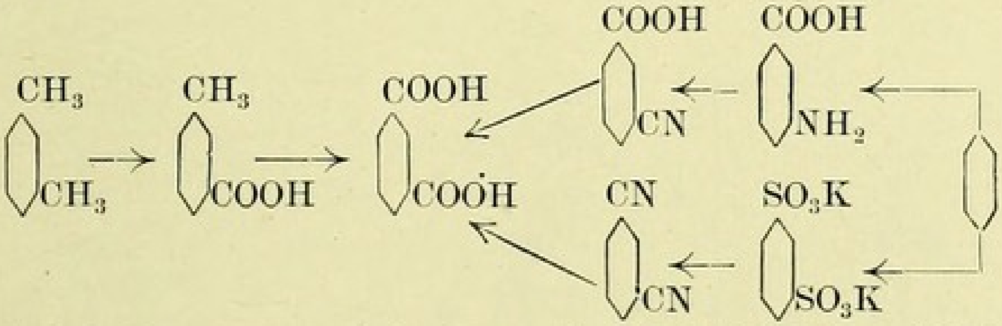
$$\begin{array}{l} C_6H_6+2CO_2 \leftarrow C_6H_4(COOH)_2 \rightarrow C_6H_4(COOEt)_2 \\ \qquad\qquad\qquad\qquad \llcorner\!\xrightarrow{\qquad\qquad\qquad} C_6H_5.COOH+CO_2 \end{array}$$

The ortho-constitution of phthalic acid is proved by various syntheses. It is formed, as already stated, by oxidising ortho-xylene and ortho-toluic acid with permanganate (p. 317), and is the product of the hydrolysis of the ortho-cyano-benzoic acid prepared from anthranilic acid by the diazo-reaction. Its conversion into an anhydride, moreover, is presumptive evidence that it is an ortho-compound, groups in the meta- and para-positions being too remote to interact, as has already been seen in the case of the amides of sulpho-benzoic acid (p. 265)—



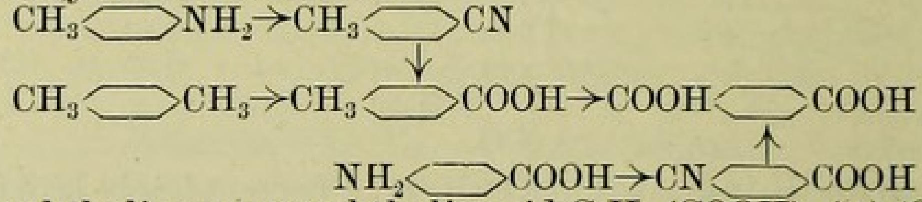
As previously indicated, phthalic acid is completely broken up by chromic acid mixture.

Isophthalic and Terephthalic Acids.—The isomeric meta- or iso-phthalic acid is formed, as already stated, by boiling meta-xylene or meta-toluic acid with chromic acid mixture, and can also be synthesised from meta-cyano-benzoic acid and dicyanobenzene, as already noted. On heating benzene with fuming sulphuric acid in a sealed tube at 200°, it is converted into benzene-meta-disulphonic acid, $C_6H_4(SO_3H)_2$ (*m*), a crystalline substance, which may be isolated in the same way as the monosulphonic acid, and resembles it in properties. By dry-distilling the potassium salt of this acid with anhydrous potassium ferrocyanide, meta-dicyanobenzene is formed, a crystalline solid, which when boiled with alkali, yields sodium metaphthalate, just as ethylene cyanide yields sodium succinate—



Isophthalic or metaphthalic acid, $C_6H_4(COOH)_2$ (*m*) (Fittig, 1868), is a crystalline substance, which is sparingly soluble, even in boiling water, and separates in fine needles on cooling the solution. It melts at above 300°, and then sublimes unchanged, without forming an anhydride. When distilled with soda-lime, it yields benzene, in the same way as phthalic acid, and its constitution as a meta-derivative of benzene is proved by the above cyanide syntheses.

The third benzene-dicarboxylic acid, terephthalic acid, is formed when turpentine (terebenthene), para-xylene, or any para-dialkyl derivative of benzene, is boiled with chromic acid mixture, but is best prepared by oxidising sodium para-toluate (made from para-toluidine) with permanganate. The permanganate solution is added to the boiling dilute solution of the toluate until it ceases to be decolourised, and after filtering off the precipitated manganese dioxide, the terephthalic acid is precipitated from the hot product with hydrochloric acid. The acid can also be made from paramido-benzoic acid by the diazo-cyanide synthesis, and its constitution follows from these various synthetic relations—

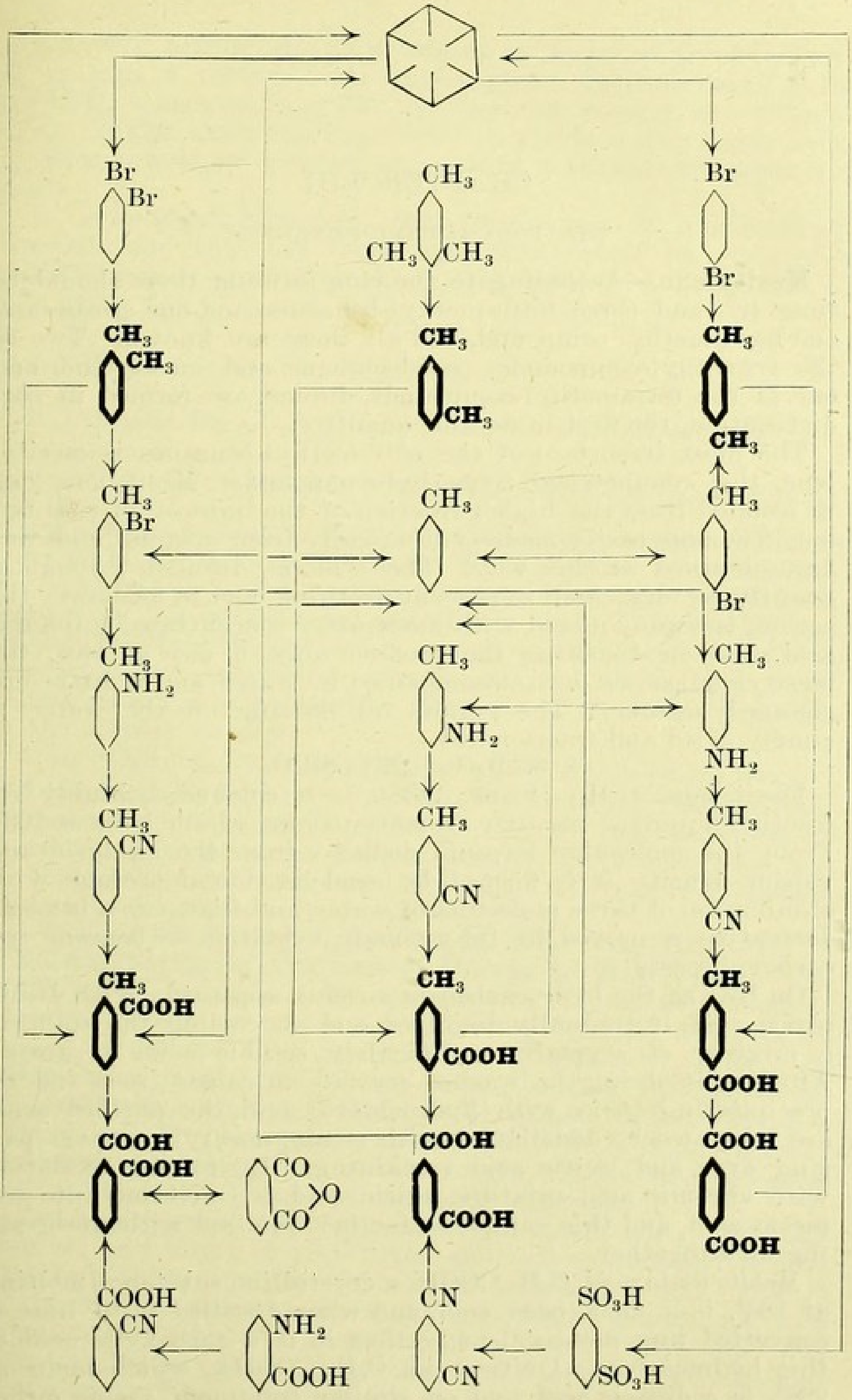


Terephthalic or para-phthalic acid $C_6H_4(COOH)_2$ (*p*) (Caillot, 1847) is a micro-crystalline substance, which is sharply distinguished from its isomerides by its insolubility in water, alcohol and ether, and by its subliming without melting and without forming an anhydride.

The phthalic acids yield an exceedingly large number of reduction products, many of which exist in stereoisomeric modifications analogous to maleïc and fumaric acids (Baeyer).

Synopsis.—The xylenes are the dimethyl-benzenes, and the toluic acids the corresponding mono- and di-carboxylic acids derived from them by oxidation.

THE TOLUIC AND PHTHALIC ACIDS AND THE XYLENES.



CHAPTER LIII

THE POLYMETHYL-BENZENES

Mesitylene.—According to the ring formula there should be three tri- and three tetra-methyl-benzenes, and one penta- and one hexa-methyl compound, and all these are known. Two of the trimethyl-compounds, pseudocumene and mesitylene, and one of the tetramethyl-compounds, durene, are formed in coal distillation, the first in notable quantity.

The most important of the poly-methyl-benzenes is mesitylene, the symmetrical trimethyl-compound. Mesitylene can be isolated from the higher fraction of the light oil of coal tar, but it is more easily made synthetically from acetone, and was first obtained in this way. The acetone, diffused through a quantity of dry sand, to prevent frothing, and to moderate the action, is simply mixed with moderately concentrated sulphuric acid, and on distilling the product after a day or two, the mesitylene passes over, accompanied by water and a little unchanged acetone. The yellow oil floating on the water is simply dried and fractionated—

$$3C_3H_6O = C_9H_{12} + 3H_2O.$$

Mesitylene, C_9H_{12} (Kane, 1838), is a colourless, highly refractive liquid, of peculiar aromatic odour, which boils at 163°. From the molecular formula deduced from the analysis and vapour density it is formed by condensation of acetone with elimination of three molecules of water, and that it is a benzene derivative is proved by its ultimate oxidation to benzene tricarboxylic acid.

On boiling the hydrocarbon in a reflux apparatus with dilute nitric acid, it gradually dissolves, and on cooling the solution a mixture of crystalline, difficultly soluble acids separates. After redissolving the washed crystals in caustic soda and reprecipitating them with hydrochloric acid, the purified acids are separated by distillation with steam, mesitylenic acid passing over and uvitic acid remaining. By further oxidation with chromic acid mixture, uvitic acid is converted into trimesic acid, and this cannot be further oxidised without breaking up altogether.

Mesitylenic acid, $C_8H_9.COOH$, a crystalline substance melting at 166°, is a mono-basic acid, and when distilled with lime is converted into meta-xylene, so that it is a carboxylic acid of this hydrocarbon. Uvitic acid, $C_7H_6(COOH)_2$, which melts at 288°, is a dibasic acid, and on similar treatment yields either meta-toluic acid or toluene, according to the proportion of alkali. It is thus a toluene-dicarboxylic acid. Trimesic acid, $C_6H_3(COOH)_3$, which melts at 300° and sublimes readily, is a tribasic acid. Under the same conditions it yields either isophthalic or benzoic acid, or benzene, and is thus a benzene-tricarboxylic acid.

It is evident, therefore, that mesitylene is a trimethyl-benzene, and that the three acids are formed by successive oxidation of its methyl groups (Fittig, 1867)—

$$\begin{tikzcd}
C_6H_3(CH_3)_3 \arrow[d] & & & \\
C_6H_3(CH_3)_2.COOH \arrow[r] \arrow[d] & C_6H_4(CH_3)_2+CO_2 & & \\
C_6H_3(CH_3)(COOH)_2 \arrow[r] \arrow[d] & C_6H_4(CH_3).COOH+CO_2 \arrow[r] & C_6H_5.CH_3+2CO_2 & \\
C_6H_3(COOH)_3 \arrow[r] & C_6H_4(COOH)_2+CO_2 \arrow[r] & C_6H_5.COOH+2CO_2 \arrow[r] & C_6H_6+3CO_2.
\end{tikzcd}$$

This result is confirmed by a synthesis of trimesic acid from benzene by the cyanide method. When sodium benzene-meta-disulphonate is boiled with concentrated sulphuric acid, it is converted into a benzene-trisulphonic acid, $C_6H_3(SO_3H)_3$, and by dry-distilling the potassium salt of this acid with potassium ferrocyanide a crystalline tricyano-benzene, $C_6H_3(CN_3)$, is obtained, which is hydrolysed by caustic soda to sodium trimesate in the normal manner—

$$C_6H_6 \rightarrow C_6H_4(SO_3H)_2 \rightarrow C_6H_3(SO_3K)_3 \rightarrow C_6H_3(CN)_3 \rightarrow C_6H_3(COOH)_3.$$

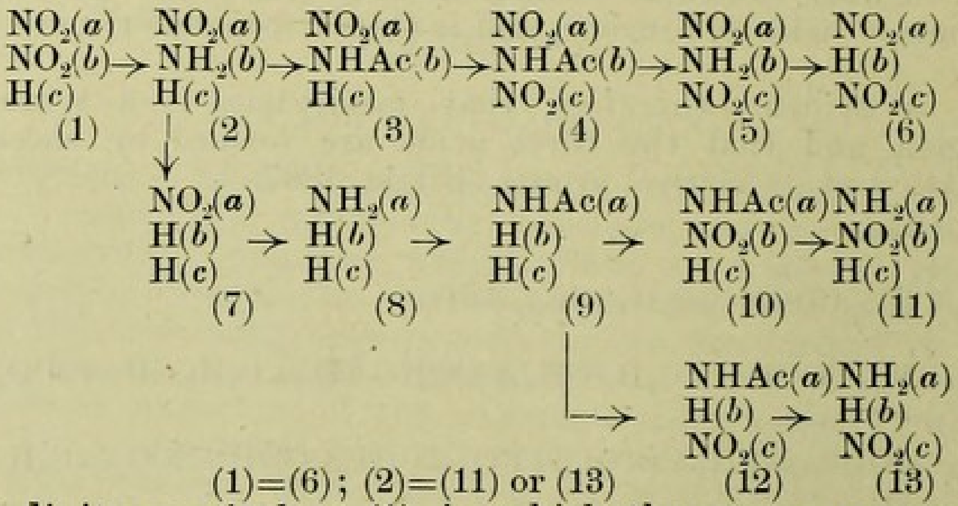
Additional confirmatory evidence is afforded by the synthesis of mesitylene from allylene, $CH_3.C \vdots CH$, by polymerisation at a red heat, in the same way as benzene from acetylene, and by that of trimesic acid from propiolic acid by polymerisation in direct sunlight—

$$3CH_3.C \vdots CH \rightarrow C_6H_3(CH_3)_3 \rightarrow C_6H_3(COOH)_3 \leftarrow 3CH \vdots C.COOH.$$

Determination of Position of Groups in Mesitylene.—The synthesis of mesitylene by condensation of acetone renders it probable that it is a symmetrical compound, for there is no reason to believe that the condensing molecules behave in different ways, as would have to be the case to produce an unsymmetrical product (Baeyer, 1867). This, however, is not a rigid proof, for benzene hexabromide, which is necessarily symmetrical, yields, when heated, unsymmetrical and not symmetrical tribromo-benzene, as might be expected.

A complete proof of the symmetry of mesitylene is afforded however by a study of its dinitro- and nitro-amido-derivatives. Although there are three replaceable hydrogen atoms (*a*, *b*, *c*) in the benzene nucleus, it is obvious that if mesitylene is a symmetrical compound, there can be only one dinitro- and one nitro-amido-derivative. Now only one dinitro-mesitylene and one nitro-amido-mesitylene are known, and more than this, each compound can be prepared in such a way that the groups replace different hydrogen atoms, whilst the properties remain unchanged—

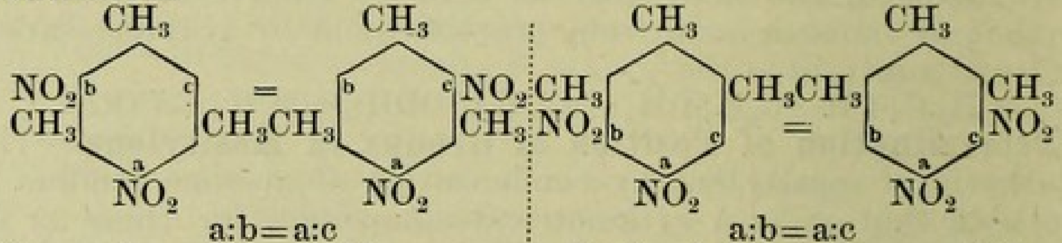
PROOF OF THE SYMMETRY OF MESITYLENE.



$$\begin{array}{cccccc}
NO_2(a) & NO_2(a) & NO_2(a) & NO_2(a) & NO_2(a) & NO_2(a) \\
NO_2(b) \rightarrow & NH_2(b) \rightarrow & NHAc(b) \rightarrow & NHAc(b) \rightarrow & NH_2(b) \rightarrow & H(b) \\
H(c) & H(c) & H(c) & NO_2(c) & NO_2(c) & NO_2(c) \\
(1) & (2)\ \downarrow & (3) & (4) & (5) & (6) \\
 & NO_2(a) & NH_2(a) & NHAc(a) & NHAc(a) & NH_2(a) \\
 & H(b) \rightarrow & H(b) \rightarrow & H(b) \rightarrow & NO_2(b) \rightarrow & NO_2(b) \\
 & H(c) & H(c) & H(c) & H(c) & H(c) \\
 & (7) & (8) & (9) & (10) & (11) \\
 & & & \lfloor \rightarrow & NHAc(a) & NH_2(a) \\
 & & & & H(b) \rightarrow & H(b) \\
 & & & & NO_2(c) & NO_2(c) \\
\multicolumn{4}{c}{(1)=(6);\ (2)=(11) \text{ or } (13)} & (12) & (13)
\end{array}$$

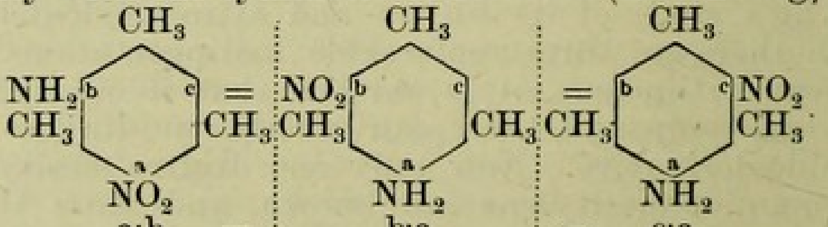
The dinitro-mesitylene (1), in which the groups occupy the positions (say) *a*, *b*, can be converted by the stages indicated into a second dinitro-compound (6), in which, whilst one of the groups retains its original position (*a*), the other takes up the third available position (*c*). But the actual substances are identical, and so, therefore, are their formulæ—(1)=(6).

The positions *b* and *c* are therefore similarly situated with regard to *a*, that is, they are both ortho or both meta to the *a* position (they cannot both, of course, be para). This result is in harmony with the symmetrical and vicinal trimethylbenzene formulæ, but irreconcilable with the asymmetrical modification—



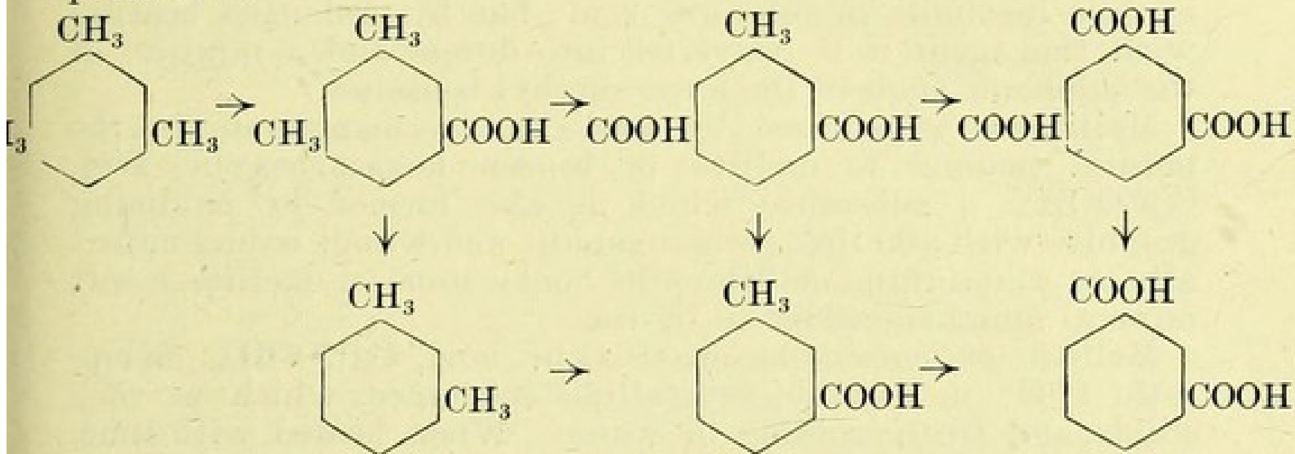
a:b=a:c a:b=a:c

Now the nitro-amido-compound (2), formed by partial reduction of the dinitro-compound (1), can be converted by a similar process into a second nitro-amido compound (11) or (13), in which the amido-group occupies the position *a*, whilst the new nitro-group takes up the position *b* or *c*. But the two substances are again identical, and this second result is consistent only with the symmetrical formula (Ladenburg, 1875)—



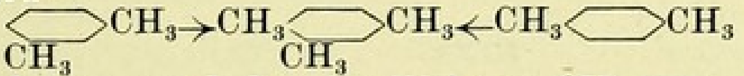
a:b = b:a = c:a

Since mesitylene is thus symmetrical or 1:3:5 trimethylbenzene, it is obvious that the xylene and meta-toluic and isophthalic acids obtained from it must be 1:3 compounds. That is, in the meta-compounds the groups occupy the 1:3 position—



The Higher Methyl-Benzenes.—Of the two trimethyl-benzenes isomeric with mesitylene, the unsymmetrical compound, pseudo-cumene, occurs, as already stated, in considerable quantity in coal-tar oil.

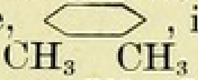
Pseudocumene, or 1:2:4 trimethyl-benzene,  $\underset{CH_3}{CH_3\langle\quad\rangle}CH_3$, is a liquid which resembles mesitylene, but boils at 170°. Its constitution is proved by two direct syntheses from bromo-para-xylene and bromo-meta-xylene by the methyl-iodide-sodium method—



$$\underset{CH_3}{\langle\quad\rangle}CH_3 \rightarrow \underset{CH_3}{CH_3\langle\quad\rangle}CH_3 \leftarrow CH_3\langle\quad\rangle CH_3$$

The vicinal compound, hemimellithene,  $\underset{CH_3\ \ CH_3}{CH_3\langle\quad\rangle}$, is a similar liquid.

Of the three tetra-methyl-benzenes, the symmetrical compound, durene, occurs with the trimethyl-compounds in coal-tar.

Durene, or 1:2:4:5 tetra-methyl-benzene,  $\underset{CH_3\ \ CH_3}{\overset{CH_3\ \ CH_3}{\langle\quad\rangle}}$, is a crystalline compound of camphor odour, melting at 79°. Its constitution follows from its synthesis from di-bromo-xylene and methyl iodide by the sodium method, and from its oxidation to symmetrical dimethylisophthalic and dimethylterephthalic acids. Durene can also be made from hexa-methyl-benzene.

Hexamethyl-benzene or mellithene can be synthesised both from benzene and methyl chloride by the aluminium chloride method, and from crotonylene by polymerisation, in the same way as benzene and mesitylene—

$$C_6H_6+6CH_3Cl \rightarrow C_6(CH_3)_6 \leftarrow 3CH_3.C\vdots C.CH_3.$$

Most of the intermediate polymethyl-benzenes can be made by the aluminium chloride method, but it is difficult to stop the action at a definite intermediate point, mixtures being usually obtained.

Hexamethyl-benzene or mellithene, $C_6(CH_3)_6$, is a crystalline substance, melting at 164°. As there is no hydrogen in the benzene nucleus, mellithene does not form a sulphonic acid, and is thus insoluble in sulphuric acid; but by prolonged heating with this agent it is converted into durene and a mixture of the sulphonic acids of the lower methyl-benzenes.

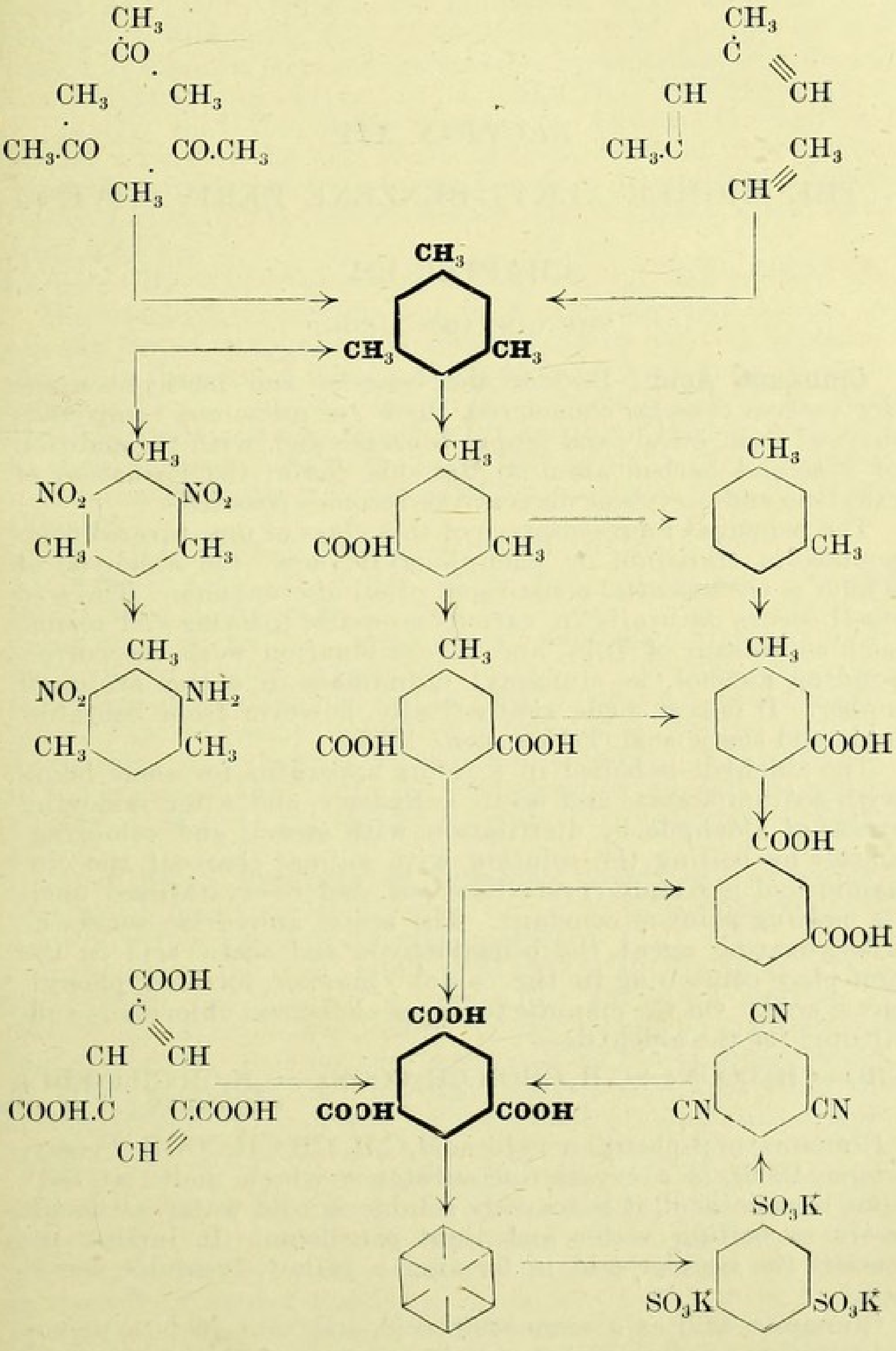
Mellithene is oxidised by potassium permanganate in the normal manner to mellitic or benzene-hexacarboxylic acid, $C_6(COOH)_6$, a substance which is also formed by oxidising graphite with alkaline permanganate, and which occurs naturally, as aluminium mellitate, in honey stone or mellite, a soft mineral found embedded in lignite.

Mellitic or benzene-hexacarboxylic acid, $C_6(COOH)_6$, (Klaproth, 1799), is a silky, crystalline substance, which is very stable, and freely soluble in water. When heated with lime, it is converted into benzene in the normal manner—

$$C_6(CH_3)_6 \rightarrow C_6(COOH)_6 \rightarrow C_6H_6 + 6CO_2.$$

Synopsis.—All the polymethyl-benzenes required by the ring formula are known. Mesitylene, the symmetrical tri-derivative, prepared synthetically from acetone, affords an independent proof of the position of the groups in meta-xylene and its oxidation products

MESITYLENE.


CH$_3$
CO
CH$_3$
CH$_3$
CH$_3$.CO
CO.CH$_3$
CH$_3$
CH$_3$
C
CH
CH
CH$_3$.C
CH$_3$
CH
CH$_3$
CH$_3$
CH$_3$
CH$_3$
NO$_2$
NO$_2$
CH$_3$
CH$_3$
CH$_3$
COOH
CH$_3$
CH$_3$
CH$_3$
CH$_3$
NO$_2$
NH$_2$
CH$_3$
CH$_3$
CH$_3$
COOH
COOH
CH$_3$
COOH
COOH
COOH
COOH
C
CH
CH
COOH.C
C.COOH
CH
COOH
COOH
COOH
CN
CN
CN
SO$_3$K
SO$_3$K
SO$_3$K

SECTION XIV

THE HIGHER ALKYL-BENZENE DERIVATIVES

CHAPTER LIV

THE CINNAMIC GROUP

Cinnamic Acid.—Besides the benzene and methyl-benzene derivatives thus far considered, there are numerous compounds derived from ethyl- and propyl-benzene, and, with the addition of a second carbon atom to the side chain, the formation of ethylene and acetylene derivatives becomes possible.

The principal representative of this class of unsaturated compounds is cinnamic or phenyl-acrylic acid, the aldehyde of which is the essential constituent of oil of cinnamon. The acid itself occurs naturally in various aromatic balsams and resins, such as balsam of Tolu, and, in combination with the corresponding alcohol, as cinnamyl cinnamate in storax or liquid amber. It is best made synthetically, however, from benzaldehyde and acetic acid (Perkin, sen., 1875).

The aldehyde is boiled in a reflux apparatus for some hours with sodium acetate and acetic anhydride, and, after removing excess of aldehyde by distillation with steam, and colouring-matter by boiling the solution with animal charcoal, the cinnamic acid is simply crystallised out, and re-crystallised until its melting point is constant. The acetic anhydride serves as a dehydrating agent, the benzaldehyde and acetic acid in the first place combining in the "aldol" manner, forming phenyl-lactic acid. On the manufacturing scale benzal chloride is substituted for the aldehyde—

$$C_6H_5.CHO + CH_3.COONa \rightarrow C_6H_5.CHOH.CH_2.COONa \rightarrow C_6H_5CH{:}CH.COOH + CH_3.COONa + CH_3.COOH$$

Cinnamic or β-phenyl-acrylic acid, $C_6H_5.CH{:}CH.COOH$ (Frémy, Simon, 1839), is a crystalline substance which melts at 133°. Like benzoic acid, it is scarcely soluble in cold water, although freely in boiling water and light petroleum. It further resembles the simpler acid in forming a yellow, insoluble ferric salt.

Cinnamic acid is a monobasic acid, and that it is a mono-substitution product of benzene is proved not only by its synthesis from benzaldehyde, but also by its successive conversion into benzaldehyde and benzoic acid when boiled with chromic acid mixture. That it is an ethylene derivative is proved in the usual manner by its direct combination with bromine to a crystalline dibromide, $C_6H_5.CHBr.CHBr.COOH$, and by its oxidation by alkaline permanganate to the corresponding dihydroxy-compound, β-phenyl-glyceric acid, $C_6H_5.CHOH.CHOH.COOH$.

Finally, that the olefine linkage is between the first and second atoms of the side chain is confirmed, not only by the synthesis of the acid from benzaldehyde and acetic acid, but by its resolution into potassium acetate and benzoate when fused with potash—

$$C_6H_5.CHO + CH_3COOH \rightarrow C_6H_5.CH:CH.COOH \rightarrow C_6H_5.COOK + CH_3.COOK.$$

The aldehyde corresponding with cinnamic acid occurs, as already stated, in oil of cinnamon, and can be isolated by steam-distilling the washed bisulphite crystals with sodium carbonate solution. It is formed also in the normal manner by dry-distilling calcium cinnamate with calcium formate, and may be made synthetically in the same way as the acid, by saturating a mixture of benzaldehyde and acetaldehyde with hydrogen chloride—

$$C_6H_5.CHO + CH_3.CHO \rightarrow C_6H_5.CH:CH.CHO + H_2O.$$

Cinnamic aldehyde, $C_6H_5.CH:CH.CHO$ (Dumas and Péligot, 1833), is a liquid which boils unchanged only under low pressure, and, unlike its aliphatic analogue, crotonic aldehyde, is particularly fragrant in odour. It has the usual properties of an aldehyde, and is readily oxidised and reduced, whilst as an ethylene derivative it forms a crystalline additive dibromide. By reduction with sodium amalgam, it is converted in the normal manner into the corresponding alcohol, cinnamyl alcohol, $C_6H_5.CH:CH.CH_2OH$, a crystalline substance melting at 33°.

Substitution Products of Cinnamic Acid.—As a benzene derivative, cinnamic acid forms many substitution products, some of which are of technical importance.

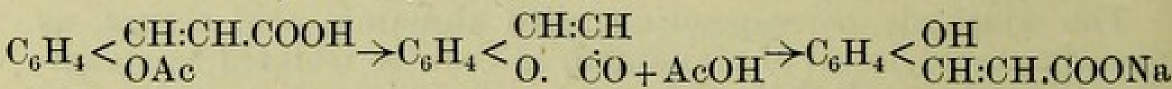
Ortho-nitro-cinnamic acid, $C_6H_4(NO_2).CH:CH.COOH$ (Beilstein, 1872), for example, a crystalline substance melting at 238°, is an intermediate product in the technical synthesis of indigo (p. 332). It is formed, together with the para-compound, by direct nitration, and its ethyl salt is separated from the sparingly soluble para-salt by fractional crystallisation from alcohol.

By the action of nitrous acid on the *o*-amido-acid, the hydroxy-acid is formed, a product which occurs naturally in clover and other plants. It may also be made synthetically by condensing salicylic aldehyde with sodium acetate and acetic anhydride, in the same way as cinnamic acid, the acetyl derivative formed in the first instance being then hydrolysed by dilute alkali—

$$C_6H_4(OH).CHO + Ac_2O + CH_3.COONa \rightarrow C_6H_4(OAc).CH:CH.COOH.$$

Ortho-cumaric or *o*-hydroxy-cinnamic acid $C_6H_4(OH).CH{:}CH.COOH$ (Delalande, 1842), is a crystalline substance melting at 208°. On fusion with potash it is resolved into salicylic and acetic acids, in a parallel manner to cinnamic acid itself. Acetyl-*o*-cumaric acid is manufactured for the sake of its internal anhydride or lactone, coumarin, into which it is converted by simply heating.

o-Cumaric lactone or coumarin, $C_6H_4{<}\begin{matrix}CH{:}CH\\ O. \quad \dot{C}O\end{matrix}$ (Boullay, 1826), is a crystalline substance melting at 66°, which occurs naturally in the common woodruff, and on account of its fragrant odour is used as the basis of many perfumes. When boiled with alcoholic soda, it is hydrolysed to sodium cumarate—



$$C_6H_4{<}\begin{matrix}CH{:}CH.COOH\\ OAc\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CH{:}CH\\ O. \quad \dot{C}O\end{matrix} + AcOH \rightarrow C_6H_4{<}\begin{matrix}OH\\ CH{:}CH.COONa\end{matrix}$$

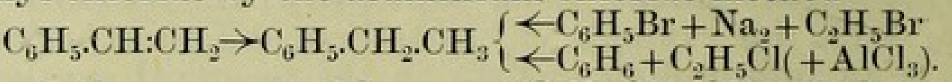
Phenyl-Ethane, Phenyl-Ethylene, and Phenyl-Acetylene.—On heating cinnamic acid with lime, the carboxyl is eliminated in the normal manner, and the corresponding hydrocarbon styrene formed. Styrene also occurs free in storax, from which it may be separated by distillation with steam, and it can be synthesised in various ways—

$$C_6H_5.CH{:}CH.COOH = C_6H_5.CH{:}CH_2 + CO_2.$$

Styrene or phenylethylene, $C_6H_5.CH{:}CH_2$ (Simon, 1839), is a highly refractive liquid of pleasant odour, boiling at 144°. As an ethylene derivative it absorbs bromine, forming styrene dibromide, $C_6H_5.CHBr.CH_2Br$, a crystalline substance melting at 74°, and it is resolved by fusion with potash, in the normal manner, into benzoic and carbonic acids—

$$C_6H_5.CH{:}CH_2 + 3KOH \rightarrow C_6H_5.COOK + K_2CO_3.$$

On heating styrene in a sealed tube with concentrated hydriodic acid, it is reduced in the usual way to the corresponding saturated hydrocarbon, phenyl-ethane. This compound can also be formed synthetically, both from bromo-benzene and ethyl bromide by the sodium method, and from benzene itself and ethyl chloride by the aluminium chloride method—



$$C_6H_5.CH{:}CH_2 \rightarrow C_6H_5.CH_2.CH_3 \begin{cases} \leftarrow C_6H_5Br + Na_2 + C_2H_5Br \\ \leftarrow C_6H_6 + C_2H_5Cl (+ AlCl_3). \end{cases}$$

Phenyl-ethane or ethyl-benzene, $C_6H_5.CH_2.CH_3$ (Tollens and Fittig, 1864), is a liquid resembling toluene, and boiling at 134°. Like its homologue, it yields benzoic acid when boiled with dilute nitric acid, the side chain being disintegrated. As stated before, this is always the case, however long the chain. When phenyl-ethane is brominated at its boiling point, the halogen enters the side-chain, as in toluene, and phenyl-ethyl bromide is formed.

Phenyl-ethyl bromide, $C_6H_5.CH_2.CH_2Br$, is a liquid which resembles benzyl bromide, and boils at 200°, at the same time partially decomposing into hydrogen chloride and styrene; with alcoholic potash this decomposition becomes quantitative, as in the case of ethyl bromide—

$$C_6H_5.CH_2.CH_3 \rightarrow C_6H_5.CH_2.CH_2Br \rightarrow C_6H_5.CH{:}CH_2.$$

Similarly, on heating styrene dibromide with alcoholic potash, it is decomposed in precisely the same way as ethylene bromide. At the boiling point, bromo-styrene, $C_6H_5.CBr{:}CH_2$, is formed, an unstable liquid analogous to vinyl bromide, whilst at 120° the whole of the bromine is eliminated, and phenyl-acetylene produced—

$$C_6H_5.CHBr.CH_2Br \rightarrow C_6H_5.CBr{:}CH_2 \rightarrow C_6H_5.C \vdots CH.$$

Phenyl-acetylene, $C_6H_5.C \vdots CH$ (Glaser, 1870), is a colourless liquid, of pleasant, aromatic odour, which boils at 142°, and resembles acetylene in its actions. It forms a white silver and a yellow cuprous compound, for example, and hot sodium absorbs it, forming a spontaneously inflammable sodium derivative, $C_6H_5.C \vdots CNa$, which, like sodium crotonylene, absorbs carbon dioxide, and is converted into sodium phenyl-propiolate (p. 332).

Phenyl-acetylene is reduced to phenyl-ethylene when its glacial acetic acid solution is boiled with zinc, and when heated with moderately concentrated sulphuric acid, it is hydrated to acetophenone, in the same way as allylene to acetone—

$$C_6H_5.CH{:}CH_2 \rightarrow C_6H_5.C \vdots CH \rightarrow C_6H_5.C \vdots C.Na \rightarrow C_6H_5.C \vdots C.COONa.$$

Hydrocinnamic Acid: Tyrosine.—On digesting cinnamic acid with sodium amalgam in aqueous solution, it is reduced to the corresponding saturated acid, phenyl-propionic or hydrocinnamic acid, which may also be made from benzyl chloride and acetic acid by the acetoacetic synthesis—

$$C_6H_5.CH{:}CH.COOH \rightarrow C_6H_5.CH_2.CH_2.COOH \leftarrow CH_3.CO.CH(CH_2.C_6H_5)COOEt.$$

Hydrocinnamic or phenyl-propionic acid, $C_6H_5.CH_2.CH_2.COOH$ (Erlenmeyer, 1862), is a crystalline substance melting at 49°. It is oxidised to benzoic acid when boiled with chromic acid mixture, the side-chain being disintegrated in the normal manner; and when heated with lime it is converted into phenyl-ethane, in the same way as butyric acid into propane—

$$C_6H_5.CH_2.CH_2.COOH \rightarrow C_6H_5.CH_2.CH_3 + CO_2.$$

The pathological product tyrosine, which is formed in liver disease, and in the putrefaction and hydrolysis of albumen, is a derivative of hydrocinnamic acid. It is best prepared by boiling cheese with potash, or horn-shavings with dilute sulphuric acid.

Tyrosine, or para-hydroxy-phenyl-alanine, $C_6H_4(OH).CH_2.CH(NH_2).COOH$ (Liebig, 1846), is a crystalline substance, which melts at 235°, and is sparingly soluble in boiling water. It has all the characters of an amido-acid; forms salts with acids and bases; is converted by nitrous acid into a hydroxy-acid; and is resolved by heat into carbon dioxide and the corresponding amine, hydroxyphenyl-ethylamine, $C_6H_4(OH).CH_2.CH_2.NH_2$.

On fusing tyrosine with potash, it is converted into para-hydroxybenzoic-acid, acetic acid, and ammonia, and it can be synthesised from phenyl-acetaldehyde in the same way as alanine from acetaldehyde itself.

The phenyl-acetaldehyde, made from phenylacetic acid by the formate method, is converted into phenyl-alanine, $C_6H_5.CH_2.CH(NH_2).COOH$, in the same way as acetaldehyde into alanine, and the phenyl-alanine is then nitrated, and the nitro-group reduced and converted into hydroxyl—

$$C_6H_5.CH_2.CHO \rightarrow C_6H_5.CH_2.CH(NH_2).COOH$$

$$\downarrow$$

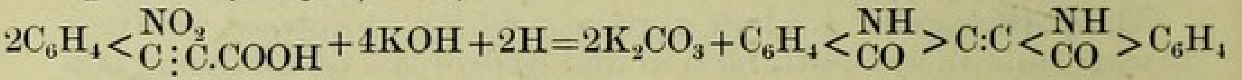
$$C_6H_4(NO_2).CH_2.CH(NH_2).COOH \rightarrow C_6H_4(OH).CH_2.CH(NH_2).COOH.$$

Phenyl-Propiolic Acid.—On heating cinnamic acid dibromide, or better, the dibromide of ethyl cinnamate, with alcoholic potash, it is converted first into bromocinnamic acid, $C_6H_5.CH{:}CBr.COOH$, and finally into phenyl-propiolic acid, $C_6H_5.C{\vdots}C.COOH$.

Phenyl-propiolic acid, $C_6H_5.C{\vdots}C.COOH$ (Glaser, 1870), is a crystalline substance, which melts at 136°, and resembles propiolic acid in its actions. When heated with water at 120°, it is resolved into carbon dioxide and phenyl-acetylene, from the sodium salt of which, as indicated above, it may also be directly synthesised. Phenyl-propiolic acid is reduced to cinnamic acid by zinc and acetic acid, and to hydrocinnamic acid by sodium amalgam. It does not form metallic compounds, because like crotonylene, and unlike propiolic acid, it does not contain "acetylene" hydrogen.

The acid is of technical importance, as its ortho-nitro-derivative, made by boiling the dibromide of ethyl *o*-nitro-cinnamate with alcoholic potash, is directly convertible into indigo.

Ortho-nitro-phenyl-propiolic acid, $C_6H_4(NO_2).C{\vdots}C.COOH$ (*o*), is a crystalline substance, which does not melt when heated, but decomposes into carbon dioxide and *o*-nitro-phenyl-acetylene. When boiled with aqueous potash, it is converted into isatin, the first oxidation product of indigo, but if a mild reducing agent, such as grape sugar, is also present, indigo itself is precipitated (Baeyer, 1880)—



$$2C_6H_4<{}^{NO_2}_{C{\vdots}C.COOH}+4KOH+2H=2K_2CO_3+C_6H_4<{}^{NH}_{CO}>C{:}C<{}^{NH}_{CO}>C_6H_4$$

This process is used in dyeing, and especially in printing the better kinds of cloth, the fabric being impregnated with the cold, colourless alkaline solution, and the dye precipitated in the body of the fibre by steaming.

Indigo and Isatin.—The well-known dye indigo (ἰνδικόν, the Indian dye) has been used from very early times. It occurs in the various indigofera as a glucoside, indican, from which it is set free by the hydrolytic action of the accompanying enzyme, or by dilute acids. The indigo leaves are simply macerated with water and left to rot, and the crude indigo which settles at the bottom of the vat is collected and washed, and finally purified by sublimation. The essential constituent of indigo is the dye indigo-blue, but related colouring matters such as indigo-red and indigo-purple are also present.

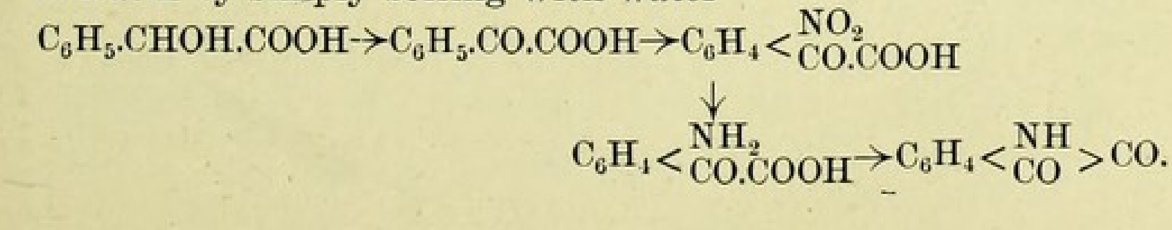
Indigo blue, $C_6H_4<\substack{NH\\CO}>C{:}C<\substack{NH\\CO}>C_6H_4$, is a dark blue, insoluble powder, which can be crystallised by sublimation under low pressure, or from boiling aniline or turpentine. Both the vapour and solution are intensely blue, and the crystals and polished powder show a fine copper-red lustre.

The molecular formula of indigo-blue follows from its vapour density; and its constitution from its relation to isatin, anthranilic acid and aniline, and from a synthesis from the dinitro-derivative of di-phenyl-diacetylene, $C_6H_5.C\vdots C.C\vdots C.C_6H_5$, a hydrocarbon formed by oxidising copper phenyl-acetylene with alkaline ferrocyanide (Baeyer, 1882).

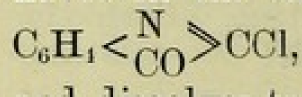
As indigo-blue itself is insoluble in water, it cannot be used directly as a dye, but must first be converted into soluble derivates, such as can either combine with the fibre, or can be precipitated in its substance. A compound of the first class, indigo-sulphonic acid, is formed by dissolving indigo-blue in fuming sulphuric acid. It retains the blue colour of the indigo, and dyes wool directly—Saxony blue. Indigo-white, $C_{16}H_{12}N_2O_2$, a colourless substance formed by reducing indigo-blue with grape sugar and warm dilute caustic soda, is a compound of the second class. The alkaline solution is readily absorbed by the fibre, and on exposing the fabric to air the indigo-white is re-oxidised, and the indigo precipitated—vat dyeing.

On account of its technical importance, indigo-blue has been synthesised in many ways, but as yet the synthetic is more expensive than the natural product, and the phenyl-propiolic synthesis described above is the only one much used. A quick laboratory synthesis of the dye is effected by fusing bromacetic anilide with potash in small quantities, the indigo being precipitated on adding ammonia to the solution of the reddish-brown melt in water. The yield, however, is very small (Flimm, 1890).

When indigo is boiled with dilute nitric acid, it is converted into isatin, a coloured crystalline substance, which separates on cooling the product. It may also be made synthetically, both from nitro-phenyl-propiolic acid, as mentioned above, and by a separate method from mandelic acid. The mandelic acid is oxidised to phenyl-glyoxylic acid, and on nitrating and reducing the latter, an amido-acid is obtained, which is dehydrated to isatin by simply boiling with water—

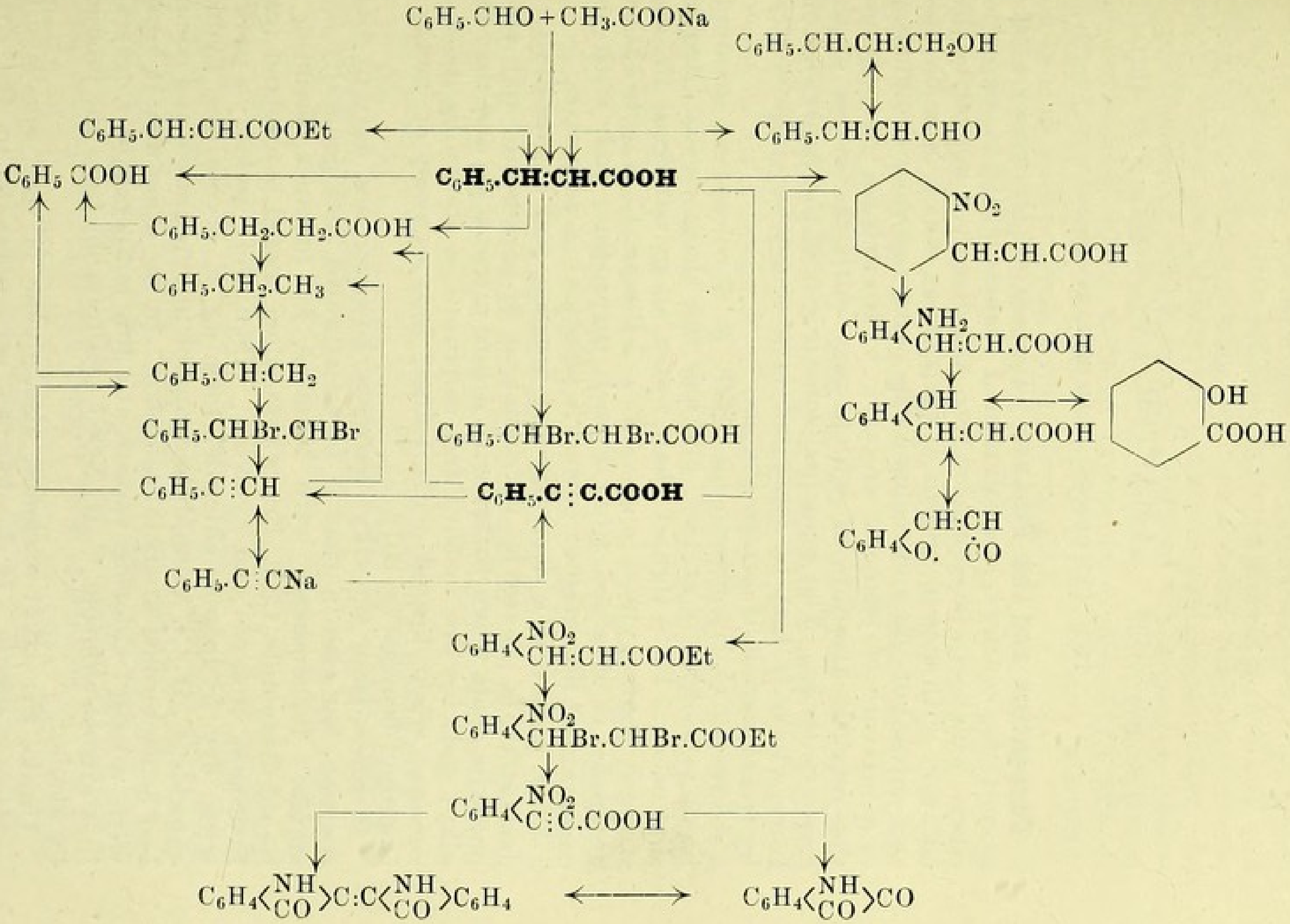


$$\begin{array}{l} C_6H_5.CHOH.COOH \rightarrow C_6H_5.CO.COOH \rightarrow C_6H_4<\substack{NO_2\\CO.COOH} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ C_6H_4<\substack{NH_2\\CO.COOH} \rightarrow C_6H_4<\substack{NH\\CO}>CO. \end{array}$$

o-Amido-phenylglyoxylic lactame or isatin,  $C_6H_4<\substack{NH\\CO}>CO$ (Erdmann, Laurent, 1841), is an orange crystalline substance, melting at 201°. In most respects it behaves as a ketone, but with phosphorus pentachloride in benzene solution it behaves in the same way as quinone, forming isatin chloride,  $C_6H_4<\substack{N\\CO}>CCl$, a crystalline substance which melts at 180°, and dissolves to a blue solution in ether. Isatin is hydrolysed to potassium *o*-amido-phenylglyoxylate when boiled with potash, whence the above synthesis, and on warming its chloride with zinc dust and water, it is reconverted into indigo.

Synopsis.—Cinnamic acid is the phenyl derivative of acrylic acid, and a true unsaturated compound. The pathological product tyrosine is derived from hydrocinnamic acid, and the dye indigo from the related acetylene derivative, phenyl-propiolic acid. The corresponding unsaturated hydrocarbons are also known.

CINNAMIC ACID AND ITS DERIVATIVES.



CHAPTER LV

THE TERPENES: CAMPHANE GROUP

Turpentine and the Pinenes.—Turpentine, the sticky exudation of the conifers, is a solution of resin (p. 345) in an oil or spirit, which can be separated from the dissolved matter by distillation with steam. Spirit of turpentine, which is much used as a solvent of oils and resins in the paint and varnish industry, is a mixture of isomeric aromatic hydrocarbons, the terpenes, the relative amounts of which vary with the source of the crude material. The principal constituent of the American oil, from which it may be separated in a somewhat impure state by fractionation, is dextro-pinene.

d-Pinene, $C_{10}H_{16}$ (Berthelot, 1850), is a colourless, insoluble liquid, which boils at 155°, and has the characteristic turpentine odour. It is lighter than water, sp. gr.$=0{\cdot}858$ at 15°, and strongly dextrogyrate, $[\alpha]_D = +21°$. l-Pinene, $C_{10}H_{16}$, its optical antipode, is obtained from French turpentine, and, with the exception of its rotatory power, is identical in properties.

That pinene is a derivative of benzene, and a para-dialkyl-derivative, is proved by its oxidation to para-toluic and terephthalic acids when boiled with dilute nitric acid; and that the alkyl radicles are methyl and isopropyl is shown by its conversion, when heated with iodine, into cymene or methyl-isopropyl-benzene (p. 337).

It differs from the alkyl-benzenes, however, not only in composition, but also in that it is unsaturated, and generally less stable. It combines with bromine, for instance, forming a liquid dibromide, $C_{10}H_{16}Br_2$, which when heated is resolved into hydrogen bromide and cymene. When well cooled, it unites with dry hydrogen chloride, forming a crystalline hydrochloride, $C_{10}H_{17}Cl$, resembling camphor in appearance and odour, and hence termed artificial camphor. In the same way it forms with nitrosyl chloride vapour, at a low temperature, a crystalline nitroso-chloride, $C_{10}H_{16}NOCl$, precipitable from the product by alcohol.

Unlike the alkyl-benzenes, also, pinene is very sensitive to oxidising agents. It decolourises permanganate in the cold, and when hot moist air is blown through it, resinous peroxides are formed, accompanied by ozone and hydrogen peroxide, so that the product has marked antiseptic properties.

On account of the ease with which it is transformed into isomerides, the hydrocarbon cannot be recovered from its compounds. When, for example, the nitroso-chloride is heated with aniline, the corresponding inactive pinene is obtained, and similarly on heating pinene itself in a sealed tube, it is transformed into a second inactive isomeride, camphene (p. 338), the hydrochloride of which is also produced when pinene hydrochloride is heated with sodium acetate. With concentrated sulphuric acid, again, a third isomeride, dipentene (p. 342), is produced, the hydrochloride of which is also formed by digesting pinene with aqueous hydrochloric acid.

l-Pinene behaves throughout in precisely the same way.

Cymene and Carvacrol.—The hydrocarbon cymene, from which the pinenes and most of the terpenes are derived, occurs naturally in carraway and eucalyptus oils, and may be prepared directly from oil of turpentine by oxidation with concentrated sulphuric acid.

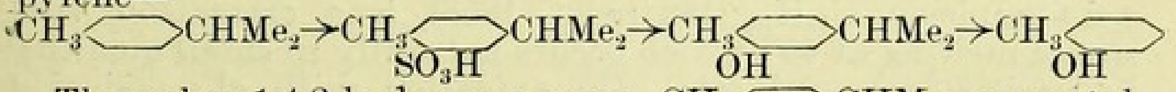
Cymene or *p*-methyl-isopropylbenzene, $CH_3.C_6H_4.CH(CH_3)_2$ (*p*), (Gerhardt, 1839), is a light, insoluble liquid of pleasant odour, boiling at 175°. In its chemical behaviour it resembles the lower alkyl-benzenes, forming a sulphonic acid, nitro-compound, etc., and that it is a para-dialkyl-benzene, follows from its oxidation to para-toluic and terephthalic acids when boiled with dilute nitric acid.

The proof of the constitution of cymene is completed by direct synthesis. On boiling benzene with isopropyl and aluminium chlorides, cumene or isopropyl-benzene, $C_6H_5.CHMe_2$, is formed, a liquid resembling cymene, and boiling at 153°, and on brominating this hydrocarbon, a monobromo-derivative is obtained, which is convertible into cymene by the methyl-iodide-sodium synthesis—

$$C_6H_6 \rightarrow C_6H_5.CHMe_2 \rightarrow CH_3.C_6H_4.CHMe_2 \rightarrow COOH.C_6H_4.COOH(p).$$

Of the twenty methyl-propyl-phenols, two only, carvacrol and thymol are derivatives of cymene.

Carvacrol or 1:4:2-hydroxy-cymene,  $CH_3\underset{OH}{\langle\quad\rangle}C_3H_7$ (Müller, 1869), a liquid boiling at 236°, occurs naturally in garden-cress oil, and is easily made by boiling camphor with iodine in a reflux apparatus. That it is a cymene derivative is proved by its conversion into this hydrocarbon by heating with phosphorus pentasulphide, and by its synthesis by fusing cymene-sulphonic acid with potash; and that the hydroxyl group is in the ortho-position to the methyl is demonstrated by the conversion of the substance into ortho-cresol when heated with phosphorus pentoxide, the isopropyl being eliminated as propylene—



$$CH_3\langle\quad\rangle CHMe_2 \rightarrow CH_3\underset{SO_3H}{\langle\quad\rangle}CHMe_2 \rightarrow CH_3\underset{OH}{\langle\quad\rangle}CHMe_2 \rightarrow CH_3\underset{OH}{\langle\quad\rangle}$$

Thymol or 1:4:3-hydroxy-cymene,  $CH_3\underset{OH}{\langle\quad\rangle}CHMe_2$, a crystal-

Z

line substance melting at 51°, occurs with cymene in oil of thyme, from which, as a phenol, it can be extracted with caustic soda. Thymol smells strongly of thyme, and is used in medicine, and as an antiseptic. Its constitution follows from its conversion in the above manner into cymene and meta-cresol.

When cymene is taken internally, it is excreted in the urine as cuminic or cumene-carboxylic acid, $CHMe_2.C_6H_4.COOH$, a crystalline substance, which is also formed by oxidising its aldehyde, cuminal, $CHMe_2.C_6H_4.CHO$, the essential constituent of oil of carraway.

Camphor, Camphene, and Camphane.—The hydrocarbon camphene, formed by isomerisation of the pinenes, is genetically connected with the natural product, camphor, and this in turn with cymene. Dextro-camphor is found in the camphor laurel, a tree indigenous to Japan, from the chopped wood of which it is extracted by distillation with steam. The corresponding laevo- and inactive modifications are also known.

d-Camphor, $C_{10}H_{16}O$, is a transparent, tough, crystalline substance, having the well-known, characteristic odour. It melts at 175°, and boils at 204°, but readily sublimes even at the ordinary temperature. Its specific rotatory power in alcoholic solution is $[\alpha]_D = +44°$.

When heated with phosphorus pentoxide, camphor is converted into cymene, whilst on distillation with iodine, carvacrol is obtained, in much the same way as cymene itself from the pinenes—

$$CH_3.C_6H_3(OH).CHMe_2 \leftarrow C_{10}H_{16}O \rightarrow CH_3.C_6H_4.CHMe_2.$$

The oxygen of camphor is ketonic, for the substance forms a crystalline oxime, $C_{10}H_{16}{:}N.OH$, and is reduced by sodium and alcohol to a secondary alcohol, borneol.

d-Borneol or Borneo camphor, $C_{10}H_{17}.OH$ (Pelouze, 1836), is a crystalline substance, which also occurs naturally in the wood of a tree indigenous to Borneo. It resembles camphor in appearance, but is more pungent in odour, and melts at 207°. Ordinary borneol is dextrogyrate, but the corresponding laevo- and inactive modifications are known, the first being that which is formed by reducing camphor.

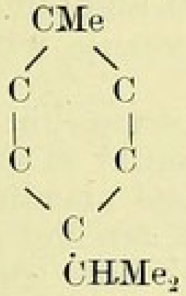
That borneol is an alcohol is proved by its conversion into a liquid acetate by acetic chloride, and into a crystalline chloride, bornyl chloride, $C_{10}H_{17}.OH$, by phosphorus pentachloride. It is reoxidised to camphor by boiling nitric acid, and when heated with phosphorus pentoxide, or its chloride with aniline, it is converted into camphene—

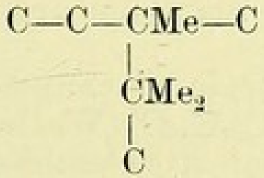
$$C_9H_{16}{:}CO \rightarrow C_9H_{16}{:}CHOH \rightarrow C_9H_{16}{:}CHCl \rightarrow C_{10}H_{16}.$$

d-Camphene, $C_{10}H_{16}$ (Berthelot, 1858), is a crystalline substance melting at 48°, which occurs naturally in small quantity in various essential oils. On oxidation with chromic acid mixture, it is reconverted into camphor, which, as the hydrocarbon can be prepared from pinene hydrochloride, may thus be made from ordinary turpentine.

On boiling camphor or camphene with concentrated nitric acid, it is oxidised to d-camphoric acid, $C_8H_{14}(COOH)_2$, a crystalline and optically active dibasic acid, melting at 187°. This on further oxidation yields a variety of products, prominent amongst which are camphoronic or α-β-trimethyl-carballylic acid, $CH_2(COOH).CMe(COOH).CMe_2(COOH)$, and the products of oxidation of this substance.

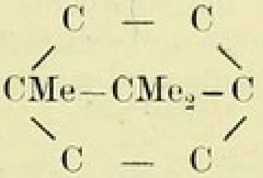
Constitution of Camphor and the Pinenes.—The camphor molecule thus not only contains the cymene nucleus, but also that of the tricarballylic acid—



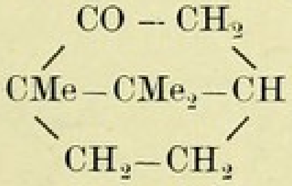


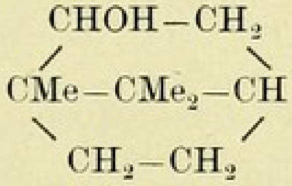
$$\mathrm{C{-}C{-}\underset{\begin{array}{c}|\\CMe_2\\|\\C\end{array}}{CMe}{-}C}$$

Now the two nuclei can be combined in one by assuming that the isopropyl group of the cymene nucleus is linked to both paracarbon atoms—

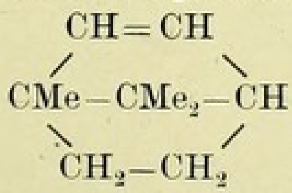


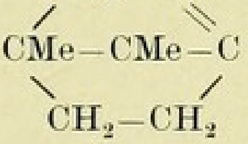
and as from the relation of camphor to carvacrol, the ketonic group is in the ortho-position to the methyl, camphor and borneol may be represented by formulæ—



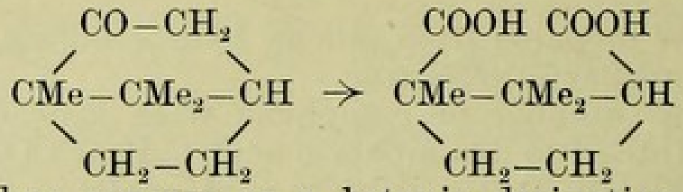


in which they appear as derivatives both of hexamethylene or hexahydrobenzene, and of pentamethylene; camphene and the pinenes being the corresponding olefines (Bredt, 1893)—

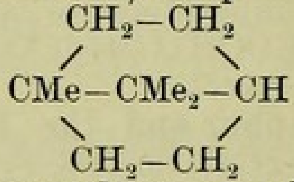




These formulæ show camphor as a saturated compound, and interpret its conversion into camphoric acid as the normal oxidation of a ketone by breaking chain at the carbonyl group—



Camphor thus appears as a ketonic derivative of a hypothetical saturated hydrocarbon, camphane—

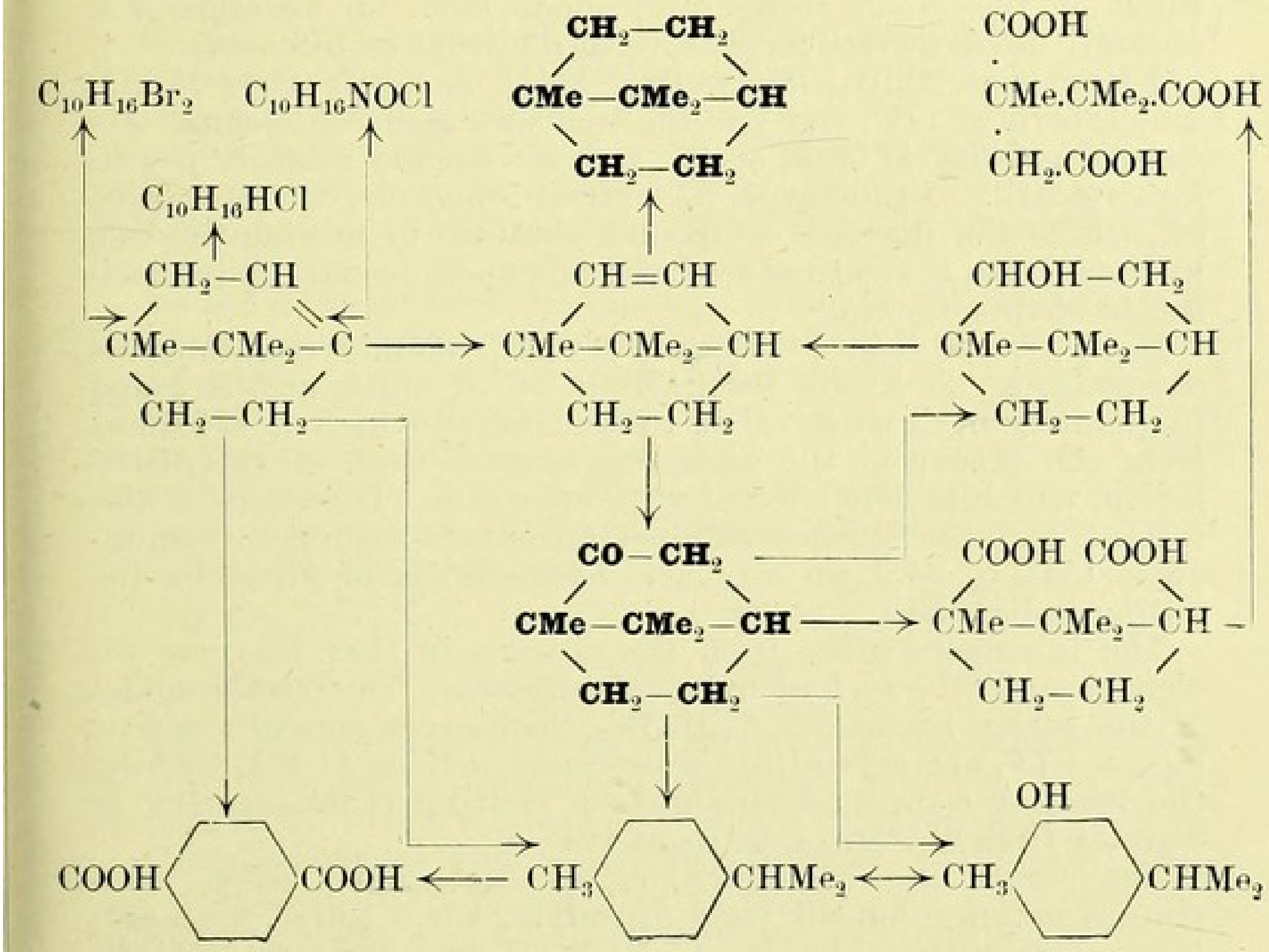


borneol being the corresponding secondary alcohol. The constitution of camphor, however, is not yet absolutely proved, as some of its reactions are difficult to reconcile with the above formula.

An isomeride of camphor, fenchone, occurs in fenchel oil. Fenchone, $C_{10}H_{16}O$ (Wallach, 1890), is liquid at ordinary temperatures, but it resembles camphor in its chemical relations, and is convertible into fenchyl alcohol, fenchyl chloride, and fenchene, in the same way as camphor into borneol, bornyl chloride, and camphene. It bears the same relation to meta-cymene as camphor to para-cymene.

Synopsis.—The pinenes and camphene are olefinic derivatives of a complex saturated hydrocarbon camphane, derived from cymene or paramethyl-isopropyl-benzene. Camphor and borneol are the corresponding ketone and secondary alcohol.

THE CAMPHANE GROUP.



CHAPTER LVI

THE TERPENES: MENTHANE AND OLEFINE GROUPS

The Limonenes.—The terpenes of turpentine are by no means the only representatives of the class. The chief constituent of the oil of orange and lemon rind, for example, is a strongly dextrogyrate terpene, termed citrene or limonene.

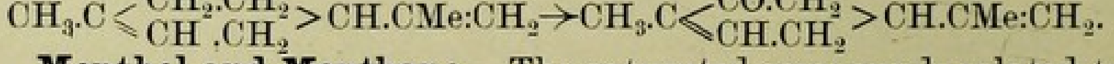
d-Limonene, $C_{10}H_{16}$ (Schweizer, 1841), is a colourless liquid, which boils at 177°, and has the fragrant odour of lemons. Its specific gravity is 0·856 at 15°, and its specific rotatory power, $[\alpha]_D = +106°$. l-Limonene, its optical isomeride, occurs in pine oil, whilst the inactive compound, obtained by mixing the two hydrocarbons, is identical with the dipentene formed by isomerisation of the pinenes.

Dipentene or inactive limonene, $C_{10}H_{16}$, closely resembles its components. It occurs naturally in oil of cinea, and is found in quantity in Swedish oil of turpentine, in which it is formed from the pinene at the high temperature used in the distillation, which is here effected without steam. Dipentene is also formed by spontaneous polymerisation of isoprene or pentadiene, C_5H_8 (p. 345), an aliphatic hydrocarbon obtained by distilling indiarubber.

The limonenes differ from the pinenes in that they are diolefines, and take up four monovalent atoms. The tetrabromides of the active limonenes, $C_{10}H_{16}Br_4$, themselves optically active, $[\alpha]_D = +73°$, are crystalline substances melting at 104°; whilst the inactive compound obtained by melting them together, or directly from dipentene, melts at 124°.

The crystalline dihydrochlorides, $C_{10}H_{16},2HCl$, differ in a similar manner, but all yield dipentene when boiled with aniline. The nitrosochlorides, $C_{10}H_{16}NOCl$, however, are isomeric with those of the camphane group.

On heating the limonene nitroso-chlorides with alcoholic potash they lose hydrogen chloride, and are converted into the oximes of a ketonic substance, carvone, $C_{10}H_{14}O$, the dextrogyrate modification of which, a fragrant liquid boiling at 225°, occurs naturally in carraway and dill oils. Carvone is converted into the isomeric carvacrol when heated with phosphorus pentachloride, and it is thus probable that the hydrocarbons and ketone are derivatives of dihydrocymene—



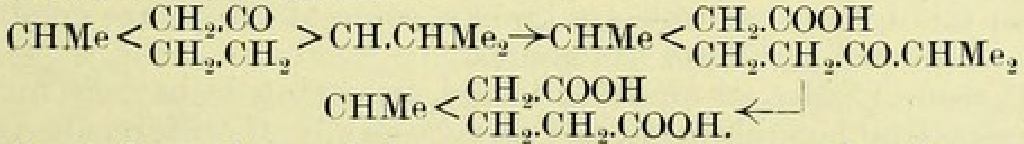
$$CH_3.C{<}\begin{matrix}CH_2.CH_2\\CH.CH_2\end{matrix}{>}CH.CMe{:}CH_2 \rightarrow CH_3.C{<}\begin{matrix}CO.CH_2\\CH.CH_2\end{matrix}{>}CH.CMe{:}CH_2.$$

Menthol and Menthane.—The saturated compounds related to the limonenes and carvones are prepared from menthol, the essential constituent of peppermint.

Menthol or mint camphor, $C_{10}H_{19}.OH$ (Dumas, 1830), is a crystalline substance melting at 42°. When heated with anhydrous copper sulphate, it is converted into cymene, whilst by oxidation with dilute nitric acid it yields the corresponding ketone, menthone, $C_9H_{18}:CO$, a liquid which is also present in peppermint oil. Menthone forms an oxime, etc., and by further oxidation is successively converted into the saturated paraffin derivatives, oxomenthylic acid, $C_9H_{17}O.COOH$, a monobasic ketonic acid, and β-methyl-adipic-acid, $COOH.CH_2.CH_2.CHMe.CH_2.COOH$.

On heating menthol with concentrated sulphuric acid, it is dehydrated to the corresponding olefinic compound, menthene, $C_{10}H_{18}$, a liquid which forms a dibromide in the same way as the pinenes; but on reducing menthyl chloride with hydriodic acid, it is converted into menthane or hexahydro-cymene, $CH_3.C_6H_{10}.CHMe_2$, a liquid hydrocarbon resembling the hexahydro-benzenes.

As the compounds of the limonene group do not yield products of the type of camphoric acid on oxidation, their molecules do not contain a para-linkage, and it is probable that they are all derivatives of menthane. The formation of oxomenthylic acid from menthone is thus parallel to that of camphoric acid from camphor, in each case the chain being broken at the carbonyl group. The methyl-adipic acid, also, is formed from the ketonic acid in a similar manner—

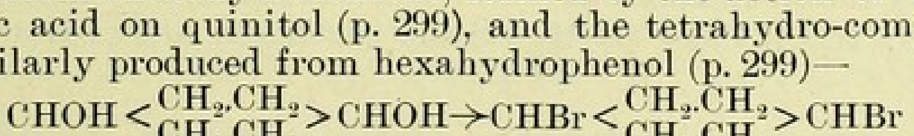


$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2.CO}\\ \mathrm{CH_2.CH_2}\end{matrix}>\mathrm{CH.CHMe_2}\rightarrow\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2.COOH}\\ \mathrm{CH_2.CH_2.CO.CHMe_2}\end{matrix}$$

$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2.COOH}\\ \mathrm{CH_2.CH_2.COOH.}\end{matrix}\leftarrow$$

The hydrocarbons of the menthane group may thus be termed the hydro-aromatic terpenes or terpanes, in distinction to the more complex compounds of the camphane group (Baeyer, 1896).

Dihydrobenzene and Tetrahydrobenzene.—From this point of view menthene is tetrahydrocymene, and the limonenes, dihydrocymenes, and, as a matter of fact, reduced benzenes can be obtained which very closely resemble these terpenes. Dihydrobenzene is made by boiling with alcoholic potash the paradibromo-hexahydrobenzene, formed by the action of hydrobromic acid on quinitol (p. 299), and the tetrahydro-compound is similarly produced from hexahydrophenol (p. 299)—



$$\mathrm{CHOH}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}>\mathrm{CHOH}\rightarrow\mathrm{CHBr}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}>\mathrm{CHBr}$$

$$\mathrm{CH}\lessdot\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2-CH}\end{matrix}\gtrdot\mathrm{CH.}\leftarrow$$

Dihydrobenzene, C_6H_8 (Baeyer, 1892), is a liquid which boils at 81°, and closely resembles the limonenes, in particular a related terpene, sylvestrene, occurring in Swedish turpentine. It resinifies in air, decolourises permanganate, forms a crystalline tetrabromide, and, like sylvestrene, gives a blue coloration with concentrated sulphuric acid. Similarly tetrahydrobenzene, C_6H_{10}, a similar liquid boiling at 84°, forms, like the limonenes, a dibromide and a crystalline nitroso-chloride, and in addition, a crystalline nitrosate like terpinene (below)

Dihydrocymene, $CH_3.C_6H_6.CHMe_2$ (Baeyer, 1893), prepared synthetically in much the same way, not only shows the chemical characters of the terpenes, but actually has the turpentine odour.

Terpinene and Phellandrene.—There are two terpenes, which differ from those of the camphane and menthane groups in that they do not form bromides or nitroso-chlorides, but, like tetrahydrobenzene, unite with nitrous anhydride, forming crystalline nitrosites.

Terpinene, $C_{10}H_{16}$, a liquid boiling at 180,° occurs naturally in cardamom oil, and is formed also by boiling dipentene and other terpenes with dilute alcoholic sulphuric acid. Its nitrosite, $C_{10}H_{16}(NO).O.NO$, a crystalline substance melting at 155°, is formed by the addition of potassium nitrite to its solution in glacial acetic acid.

The similar, but optically active terpene, phellandrene, occurs naturally in fenchel and eucalyptus oils, and is converted into terpinene by dilute alcoholic sulphuric acid, but terpinene itself cannot be converted into any of its isomerides, and is thus the most stable of the terpenes. The constitutions of terpinene and phellandrene have not yet been determined.

Olefinic (Open-Chain) Terpenes.—Several terpenes of open-chain tri-olefine structure are known, some of which are genetically connected with the limonenes.

Myrcene, $C_{10}H_{16}$, an unstable liquid, occurring in bay oil, forms a crystalline hexabromide, and is necessarily, therefore, an open-chain compound. It is readily hydrated by dilute sulphuric acid to a tertiary alcohol, linaloöl, whose constitution is proved by oxidation.

Linaloöl, $C_{10}H_{17}.OH$ (Morin, 1881), which occurs naturally in lavender oil and oil of "lignum aloë," is a liquid boiling at 195°. On gentle oxidation it yields an olefinic ketone, methylheptenone, whose constitution follows from its forming a dibromide, and from its conversion into acetone and levulinic acid by further oxidation—

$$CMe_2{:}CH.CH_2.CH{:}CMe.CH{:}CH_2 \rightarrow CMe_2{:}CH.CH_2.CH_2.CMe(OH).CH{:}CH_2$$

$$\downarrow$$

$$CMe_2{:}CH.CH_2.CH_2.CO.CH_3 + 2CO_2 \rightarrow COMe_2 + COOH.CH_2.CH_2.CO.CH_3.$$

On heating linaloöl with dilute sulphuric acid, it is converted into terpin hydrate, $C_{10}H_{18}(OH)_2+H_2O$, a crystalline substance, which is formed in the same way from pinene and the limonenes, and is resolved into dipentene or inactive limonene when heated with concentrated hydrochloric acid.

Linaloöl is also connected with the limonenes by another path. On heating it with acids under certain conditions, it is transformed into the isomeric primary alcohol geraniol, and this is directly convertible into d-limonene by distillation with phosphorus pentoxide.

Geraniol or rhodinol, $\text{CMe}_2\text{:CH.CH}_2\text{.CH}_2\text{.CMe:CH.CH}_2\text{OH}$ (Jacobsen, 1871), the essential constituent of Indian geranium oil and attar of roses, is a fragrant liquid, which can be distilled unchanged under low pressure. As a primary alcohol it yields, on oxidation, the corresponding aldehyde, geranial or citral, a liquid boiling at 228°, which occurs naturally in lemon oil. On distilling geranial with potassium bisulphate it is dehydrated to para-cymene, confirming the constitutional formula of the alcohol—

$$\text{CMe}\left<\begin{matrix}\text{CH}_2\text{.CH}_2\text{.}\\ \text{CH.CHO}\end{matrix}\right.\text{CH:CMe}_2 = \text{CMe}\left<\begin{matrix}\text{CH}=\text{CH}\\ \text{CH}-\text{CH}\end{matrix}\right>\text{C.CHMe}_2 + \text{H}_2\text{O}.$$

The Polyterpenes and Hemiterpenes.—Caoutchouc, $(\text{C}_5\text{H}_8)_x$, the solidified milky sap of the indiarubber plant, is polymeric with and closely related to the terpenes. It cannot be crystallised, but is precipitated by alcohol in white curds from its chloroform solution. The molecular weight of indiarubber is unknown, but from its colloid nature is undoubtedly very high.

As is well known, caoutchouc combines readily with sulphur, forming vulcanised indiarubber, vulcanite, etc., substances of all grades of hardness, which retain their elasticity over very wide ranges of temperature.

When indiarubber is distilled, it is converted into a hemiterpene, isoprene. Isoprene, C_5H_8, which is most probably identical with the synthetic open-chain diolefine, methyl-butadiene, $\text{CH}_2\text{:CMe.CH:CH}_2$ (Ipatieff, 1897), is a mobile liquid boiling at 35°, but it is unstable, and when kept gradually polymerises to dipentene and caoutchouc.

In addition to this hemiterpene and complex polyterpene, sesquiterpenes, $\text{C}_{15}\text{H}_{24}$, are known, such as occur naturally in hop oil, etc, as well as diterpenes, $\text{C}_{20}\text{H}_{32}$.

The Resins.—The residue which remains in the still after the steam distillation of turpentine solidifies to the well-known glassy resin or "colophony." Common resin dissolves almost entirely in caustic alkalies, and on neutralising the clear solution with hydrochloric acid is reprecipitated in white curds, from which a crystallisable acid, abietic acid, is extracted by boiling alcohol.

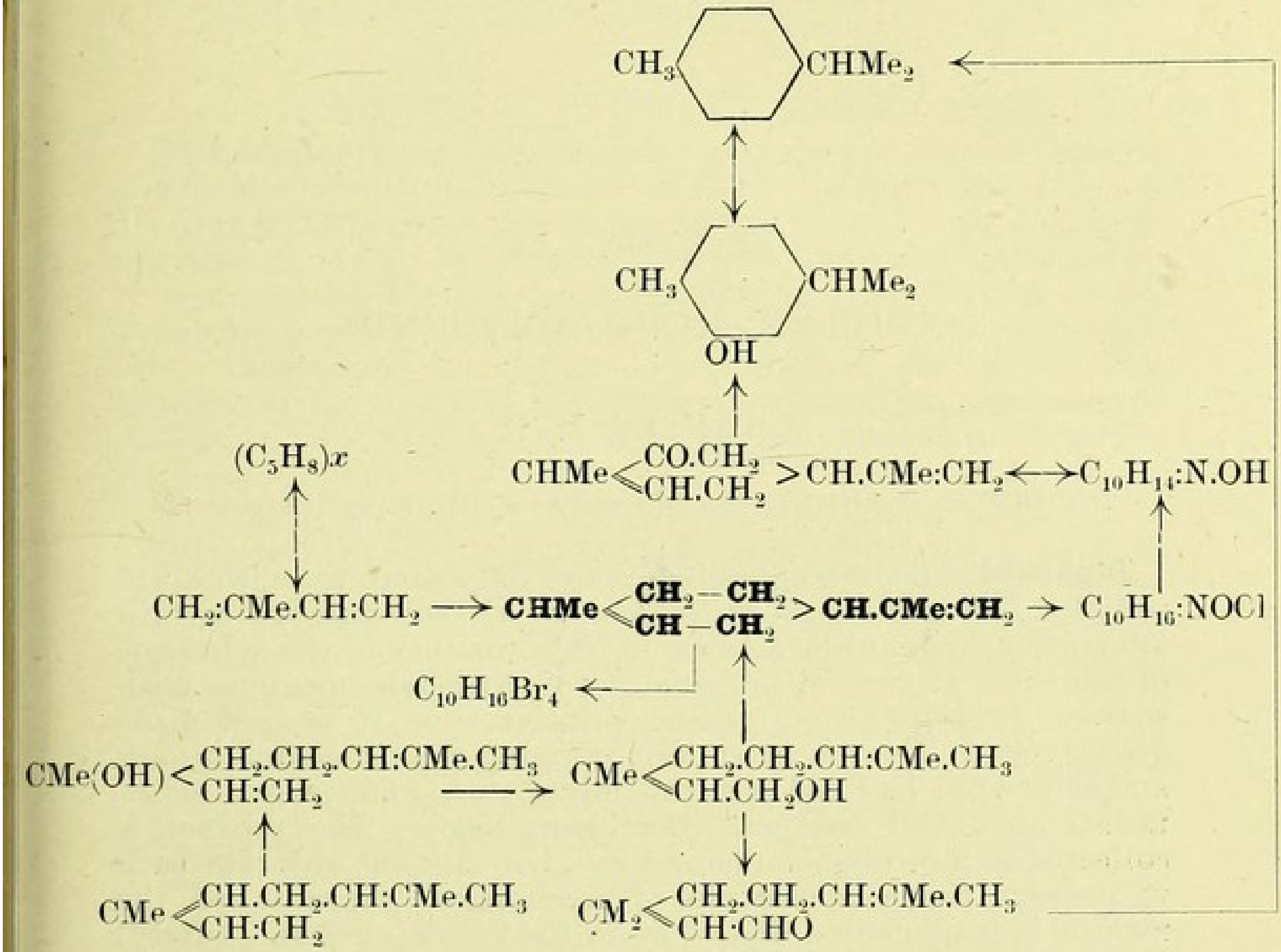
Abietic acid, $\text{C}_{18}\text{H}_{27}\text{.COOH}$, is a crystalline substance, melting at 146°. It is a benzene derivative, for it yields resorcinol, protocatechuic acid, etc., when fused with potash, and it is closely related to the terpenes, as it yields isophthalic and terebic acids on oxidation.

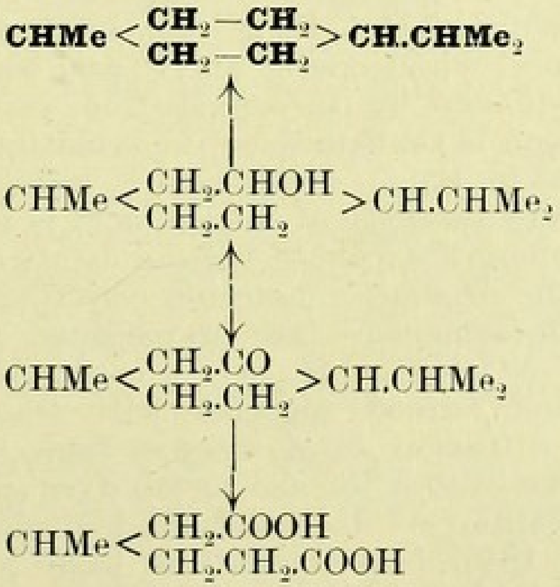
As an acid, melted resin dissolves metallic oxides, and is hence used in soldering, and the solution of resin in alkali is used in paper making for rendering the fibres ink-proof. The solution is mixed with the pulp, and the insoluble resin acid precipitated on the fibres by the addition of alum.

The ordinary varnishes are simply solutions of various resins —colophony, copal, mastic, etc.—in turpentine, and the natural balsams, such as Canada balsam, are similar more or less viscid solutions. Amber is a fossil resin, which yields resin acids and volatile terpenes when distilled, as well as succinic acid. The lacs are similar substances.

Synopsis.—The limonenes are probably dihydro-cymenes, diolefinic derivatives of hexahydro-cymene or menthane. Analogous synthetic terpenes are known, as well as a few open-chain tri-olefinic isomerides.

THE MENTHANE AND OPEN-CHAIN TERPENES.





SECTION XV

COMPLEX RING COMPOUNDS

CHAPTER LVII

DIPHENYL, DIPHENYL-METHANE AND DIPHENYL-ETHANE

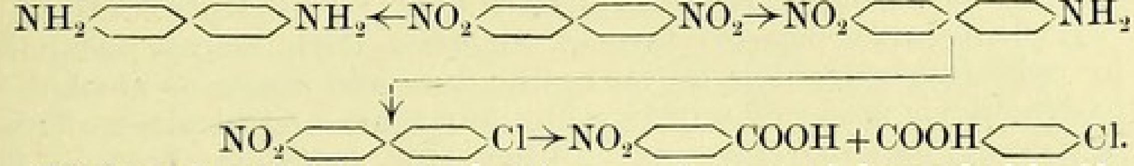
Diphenyl.—Benzenoid radicles not only combine with alkyl radicles, but with each other, and, as already noted, a certain amount of diphenyl is formed in this manner in the synthesis of toluene. It can be prepared by boiling bromobenzene with sodium, in benzene or toluene solution, but it is best made directly from benzene by slowly dropping the latter into a long and somewhat inclined iron tube filled with pumice, and maintained at a dull red heat (Berthelot, 1866). The product is collected in a receiver immersed in a hot calcium chloride bath to prevent the condensation of unchanged benzene, and the residue is fractionated and recrystallised from alcohol. Ditolyl and other analogous compounds are known—

$$2C_6H_6 - H_2 \rightarrow C_6H_5.C_6H_5 \leftarrow 2C_6H_5Br + Na_2.$$

Diphenyl, $C_6H_5.C_6H_5$ (Fittig, 1862), is a colourless, crystalline substance, which melts at 71°, and boils at 254°. The constitution indicated by its composition, vapour density and mode of formation is confirmed by its oxidation to benzoic acid, when its solution in glacial acetic acid is boiled with chromic anhydride. A minute quantity of benzoic acid is formed in this manner by the prolonged action of boiling dilute nitric acid on benzene.

As the diphenyl molecule contains two benzene rings, the position-isomerides are numerous. The di-para-dinitro-compound, $NO_2.C_6H_4.C_6H_4.NO_2$, a crystalline substance melting at 233°, and formed, together with the ortho-para-derivative, by direct nitration, is of interest from its connection with benzidine, the base of the azo cotton dyes (p. 380).

Benzidine or di-para-diamido-diphenyl, $NH_2.C_6H_4.C_6H_4.NH_2$ (Zinin, 1845), is a crystalline basic substance melting at 122°. It is manufactured from azobenzene derivatives (p. 377), but its constitution is proved by its formation by reduction of the nitro-compound, and by the conversion of the latter, through the nitro-amido and nitro-bromo-compounds, into para-nitro- and para-bromo-benzoic acids—



Diphenylmethane.—On boiling a mixture of benzyl chloride and benzene with aluminium chloride, the benzyl radicle is introduced into the benzene ring in the normal manner, and diphenylmethane or benzyl-benzene is formed. The same hydrocarbon is produced by heating benzophenone in a sealed tube with hydriodic acid and red phosphorus, and can be extracted from the cold product with ether. It is formed also by heating benzene with methylal (*i.e.* formaldehyde) and concentrated sulphuric acid; and by distilling diphenylacetic acid (p. 350) with soda-lime—

$$C_6H_5.CH_2Cl + C_6H_6 \rightarrow C_6H_5.CH_2.C_6H_5 \leftarrow C_6H_5.CO.C_6H_5.$$

Diphenylmethane, $C_6H_5.CH_2C_6H_5$ (Jena, 1870), is a crystalline substance which melts at 27°, and boils at 261°. It resembles oranges in odour. Like diphenyl, it forms nitro- and other substitution-products, but on oxidation with chromic acid mixture is reconverted into benzophenone.

As already stated, on reducing benzophenone with sodium amalgam, the intermediate secondary alcohol is formed, and the same compound is obtained by heating diphenyl-methyl bromide, $C_6H_5.CHBr.C_6H_5$, in a sealed tube with water.

When diphenyl-methane vapour is passed through a red-hot tube, it is converted into fluorene or diphenyl-methylene, $\underbrace{C_6H_4.CH_2.C_6H_4}$, in the same way as benzene into diphenyl.

Dibenzyl and Benzoïn.—On boiling a benzene solution of benzyl chloride with sodium, the benzyl radicles unite in the normal manner, and dibenzyl or diphenyl-ethane, the phenyl analogue of normal butane, is formed—

$$C_6H_5.CH_2Br + Na_2 + CH_2Br.C_6H_5 \rightarrow C_6H_5.CH_2.CH_2.C_6H_5 + 2NaBr.$$

Dibenzyl, or symmetrical diphenylethane, $C_6H_5.CH_2.CH_2.C_6H_5$ (Cannizzaro, 1862), a crystalline substance melting at 52°, is the mother substance of a group of paraffinoid alcohols and ketones. The alcohol-ketone, benzoïn, is polymeric with benzaldehyde. It is formed by heating a dilute alcoholic solution of the latter at 100° with a little potassium cyanide, and crystallises out on cooling—

$$C_6H_5.CHO + CHO.C_6H_5 = C_6H_5.CHOH.CO.C_6H_5.$$

Benzoïn, $C_6H_5.CHOH.CO.C_6H_5$ (Liebig and Wöhler, 1830), is a crystalline substance melting at 137°. It is reduced by hydriodic acid at a high temperature to dibenzyl, of which it is thus a derivative, and that it is an alcohol-ketone is proved by its oxidation by concentrated nitric acid to the corresponding diketone, benzil (below), and its reduction to the corresponding glycol, hydrobenzoïn, by sodium amalgam—

$$C_6H_5.CHOH.CHOH.C_6H_5 \leftarrow C_6H_5.CHOH.CO.C_6H_5 \rightarrow C_6H_5.CO.CO.C_6H_5.$$

Hydrobenzoïn is also formed, together with benzyl alcohol, by reducing benzaldehyde with zinc dust and acetic or alcoholic hydrochloric acid; or with sodium amalgam and alcohol. This is a very general reaction. When, for instance, acetone is reduced with sodium amalgam, not only is isopropyl alcohol formed, but also the intermediate tetramethyl-glycol or pinacone. Such condensations are hence termed pinacone condensations—

$$C_6H_5.CHO + 2H + CHO.C_6H_5 = C_6H_5.CHOH.CHOH.C_6H_5 + H_2O.$$

Hydrobenzoïn or symmetrical diphenyl-glycol, $C_6H_5.CHOH.CHOH.C_6H_5$ (Zinin, 1862), is a crystalline substance, which melts at 138°, and boils at a high temperature. As its molecule contains two asymmetrical carbon atoms, it should exist in four stereoisomeric forms, like the tartaric acids, but as yet only three of these are known. Hydrobenzoïn is reoxidised to benzoïn by dilute nitric acid, but is resolved into benzaldehyde by chromic acid mixture.

Benzil.—The benzil formed by heating benzoïn on a water-bath with concentrated nitric acid, separates as a yellow oil, which solidifies after washing away the acid. It is purified by crystallisation from alcohol.

Benzil or diphenyl-glyoxal, $C_6H_5.CO.CO.C_6H_5$ (Laurent, 1834), is a bright yellow, crystalline substance, melting at 90°. As an *a*-diketone, it forms with phenyl-hydrazine acetate a crystalline osazone, NHPh.N:CPh.CPh:N.NHPh, whilst with hydroxylamine it forms no less than three monoximes and three dioximes. These are distinct crystalline substances of the usual constitution, and must therefore be stereoisomerides.

Benzil is dissolved by cold potash solution to a violet solution, from which it is reprecipitated by alkalies, but when fused with the alkali it is hydrated to the potassium salt of benzilic acid, which is also formed by boiling benzoïn with aqueous potash—

$$COPh.COPh \rightarrow CPh_2(OH).COOH \leftarrow C(OH)Ph.COPh.$$

Benzilic or diphenyl-glycollic acid, $CPh_2(OH).COOH_2$, (Liebig, 1837), is a crystalline substance melting at 148°. Its connection with diphenyl-methane is proved by its reduction to diphenyl-acetic acid, $CHPh_2.COOH$, when heated with hydriodic acid, and by the conversion of the latter into the hydrocarbon by distillation with lime—

$$CPh_2(OH).COOH \rightarrow CHPh_2.COOH \rightarrow CH_2Ph_2 + CO_2.$$

Stilbene and Tolane.—The ethylene and acetylene derivatives corresponding with dibenzyl are known, and the former was in fact the first of the group prepared. It is obtained by distilling benzyl sulphide and other benzyl compounds, and may also be prepared by dechlorinating benzal chloride with sodium—

$$C_6H_5CHCl_2 + 2Na_2 + CHCl_2.C_6H_5 \rightarrow C_6H_5.CH:CH.C_6H_5 + 4NaCl.$$

Stilbene or symmetrical diphenyl-ethylene, $C_6H_5.CH{:}CH.C_6H_5$ (Laurent, 1844), forms large, colourless, brilliant crystals (στιλβειν), melting at 124°. As an ethylene derivative it forms an additive bromide, stilbene dibromide, $C_6H_5.CHBr.CHBr.C_6H_5$, a crystalline substance melting at 237°, and it is reduced by hydriodic acid to the corresponding ethane derivative, dibenzyl. It is oxidised to benzoïc acid by chromic acid mixture, and to phenanthrene (p. 373) when passed through a red-hot tube—

$$C_6H_5.CH_2.CH_2.C_6H_5 \leftarrow C_6H_5.CH{:}CH.C_6H_5 \rightarrow C_6H_5.CHBr.CHBr.C_6H_5.$$

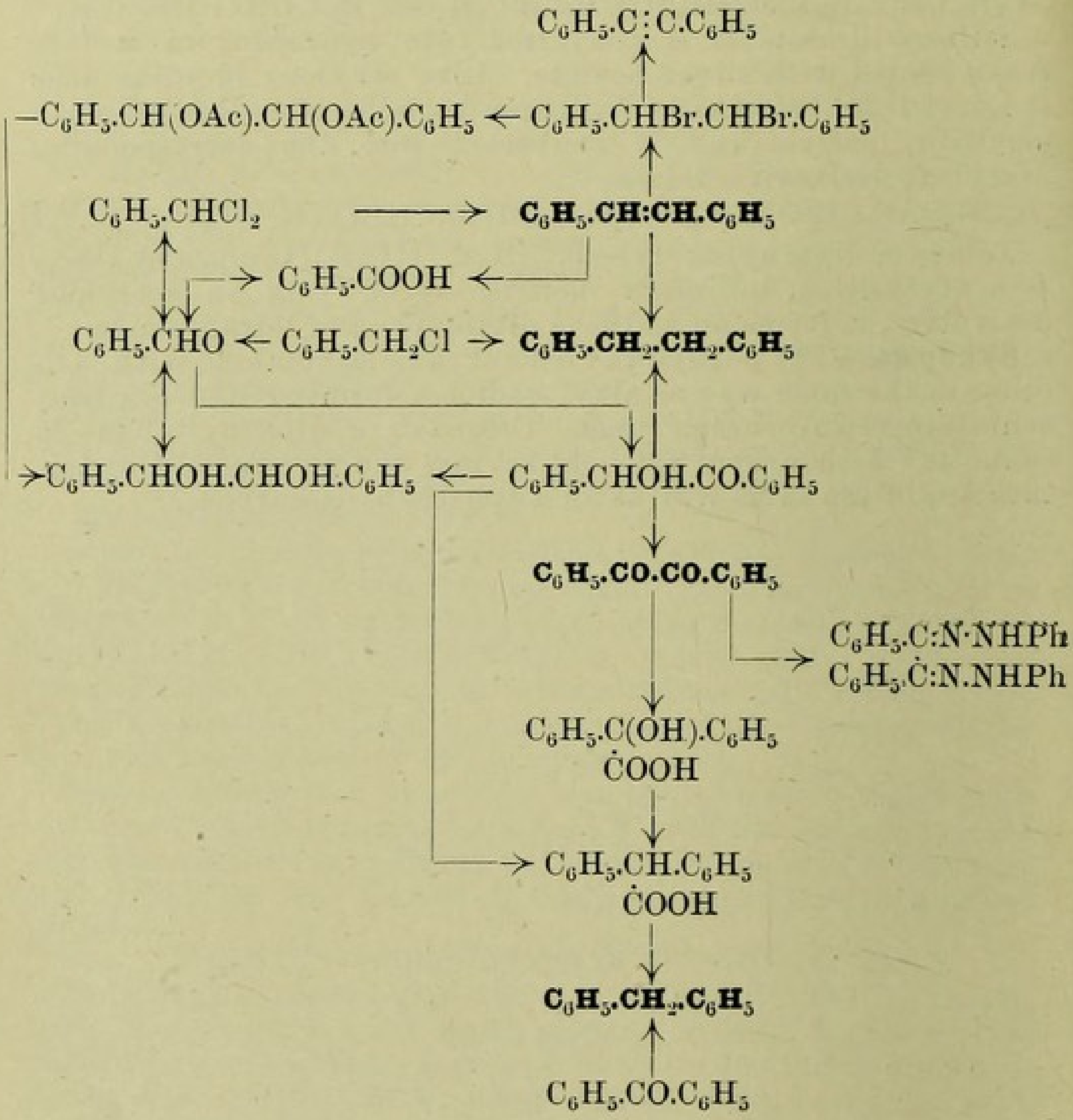
Stilbene dibromide is converted into hydrobenzoïn acetate when heated with silver acetate. Like ethylene bromide also, it loses all its bromine as hydrogen bromide when heated with alcoholic potash, and is converted into the corresponding acetylene derivative, tolane—

$$C_6H_5CH(OAc).CH(OAc).C_6H_5 \leftarrow C_6H_5.CHBr.CHBr.C_6H_5 \rightarrow C_6H_5.C \vdots C.C_6H_5.$$

Tolane or diphenyl-acetylene, $C_6H_5.C \vdots C.C_6H_5$ (Limpricht, 1868), is a crystalline substance melting at 60°. As an acetylene derivative, it forms an additive dibromide and tetrabromide.

Synopsis.—The phenyl and benzyl radicles combine with each other in the same way as alkyl radicles, forming hydrocarbons containing two benzene rings. Dibenzyl or diphenylethane is connected with a set of alcohols, ketones and unsaturated hydrocarbons, in the same way as an aliphatic hydrocarbon.

DIBENZYL AND ITS DERIVATIVES.



CHAPTER LVIII

THE TRIPHENYL-METHANE GROUP: THE ROSANILINES

The Rosanilines.—The well-known dye magenta is a derivative of the complex hydrocarbon, triphenyl-methane. With the exception of a few such compounds as picric acid and murexide, the dye-stuffs in use up to the middle of the present century—indigo, madder, cochineal, etc.—were of natural origin, but they are now to a large extent supplanted by the artificial aniline dyes. Mauve, the first such dye made (Perkin, 1856), is a complex substance formed by oxidising crude aniline with chromic acid mixture, and magenta is synthesised in a similar manner, by boiling aniline with mercuric chloride solution or arsenic acid. Pure aniline does not yield any of the dye, nor do the ortho- and para-toluidines with which it is associated in the commercial base, but a mixture of the three amines in molecular proportions gives even better results than the crude material. In the same way, a mixture of aniline and para-toluidine yields para-rosaniline chloride, a base homologous with magenta. The corresponding acetates, sulphates, etc., are also used as dyes.

Magenta is usually manufactured by oxidising the mixed amines with nitrobenzene in presence of ferric chloride. The hydrochloric acid solution is heated at 190° with the requisite amount of nitrobenzene, and small quantities of iron filings periodically added. After several hours' heating, unchanged aniline, etc., is distilled off with steam, and the rosaniline hydrochloride extracted with boiling water and precipitated with salt. The ferrous chloride initially formed acts as a carrier, being alternately oxidised by the nitrobenzene, and reduced by the mixed amines.

Rosaniline chloride or magenta, $C_{20}H_{20}N_3Cl$ (Verquin, 1860), is an almost black crystalline substance, having a green pseudo-metallic lustre. It is freely soluble in water and alcohol to an intense crimson solution, which dyes silk and wool a fast purple-red. Pararosaniline chloride, $C_{19}H_{18}N_3Cl$ (Rosenstiehl, 1876), differs from magenta only in that its colour is of a less bluish shade. Both compounds are basic in character.

Dyes and Mordants.—As just stated, both rosaniline and para-rosaniline salts dye silk and wool purple red, and the colour is fast, that is to say, is not washed out by soap and water. But on treating cotton fabrics in this manner, the colours obtained, although of much the same hue and depth, are not permanently fixed and can be washed out of the material. Similarly, picric acid dyes silk, wool, and cotton alike a bright yellow, but the silk and wool colours are alone permanent.

Now, as noted in the case of indigo, the permanency of a dye depends either on its being precipitated in the body of the fibre, or on its forming an insoluble compound with some constituent of the latter. In both silk and wool there are constituents of the nature of amido-acids, with which acid dyes like picric acid, and basic dyes like the rosanilines probably form such compounds, but the cellulose of cotton is practically a neutral substance, and only in rare cases (p. 380) combines with colouring matters.

In order to dye cotton, therefore, a mordant must be introduced into the fibre, that is to say, a substance which will form an insoluble compound with the dye. With picric acid, for example, the calico, etc., is soaked in a solution of alum, and then in dilute ammonia, by which the alum, diffused through the substance of the fibre, is converted into insoluble alumina. On now immersing the fabric in the dye-bath, the picric acid combines with the base, forming a yellow insoluble compound, which cannot be washed out of the fibre. The colour produced in this manner is of course that of the mordant compound, and is often different from that of the dye itself (p. 371).

To dye cotton with basic dyes such as the rosanilines, an acid mordant is obviously requisite, and for this purpose tannin or a metallic tannate are usually employed. In some cases silk and wool have themselves to be mordanted.

Constitution of the Rosanilines: Triphenyl-methane.—As indicated above, rosaniline chloride is a somewhat basic substance. It combines with concentrated hydrochloric acid, for instance, forming rosaniline trichloride, $C_{20}H_{20}N_3Cl,2HCl$. This is practically colourless, but very unstable, and is reconverted into the monochloride by simple dilution with water. On the other hand, it is also decolourised by caustic alkalies, and in this case the highly basic "colour base," rosaniline, $C_{20}H_{21}N_3O$, is precipitated as a white, crystalline substance. This again is unstable, and is at once reconverted into the dye by dilute acids.

But on reducing rosaniline chloride with zinc dust and hydrochloric acid, it undergoes a more permanent transformation, similar to the conversion of indigo into indigo-white, and its colour disappears owing to the formation of a colourless or "leuco-base," leucaniline, which can be set free with caustic soda, and extracted with ether.

Leucaniline, $C_{20}H_{21}N_3$ (Hofmann, 1862), is a colourless, crystalline substance, melting at 148°. Unlike free rosaniline, it is stable in air, but it is reconverted into the dye by mild oxidising agents. It is highly basic, though less so than the colour base, and that it is a primary triamine is proved by its forming a crystalline additive trihydrochloride, $C_{20}H_{21}N_3$, 3HCl, and by its conversion by the diazo-reaction into the corresponding trihydroxy-compound, $C_{20}H_{15}(OH)_3$ (p. 357).

It is thus the triamido-derivative of a hydrocarbon, $C_{20}H_{18}$, and it is in fact convertible into this by the diazo-method, the amido-groups being eliminated by warming the acid alcoholic solution of the amine with sodium nitrite, as in the conversion of aniline into benzene (E. and O. Fischer, 1878)—

$$C_{20}H_{21}(OH)_3 \leftarrow C_{20}H_{15}(NH_2)_3 \rightarrow C_{20}H_{15}(N{:}N.Cl)_3 \rightarrow C_{20}H_{15}{:}H_3.$$

Pararosaniline behaves in a precisely similar manner, yielding a colour-base, leuco-base, and hydrocarbon, homologous with those derived from its higher homologue. Now this second hydrocarbon, $C_{19}H_{16}$, the mother-substance of the rosaniline group, may also be made synthetically from chloroform and benzene by the aluminium chloride method, and is thus triphenyl-methane. The anhydrous and freshly prepared chloride is added to the dry mixture of benzene and chloroform, and after the action has ceased the product is poured into water, and the heavy insoluble layer fractionated. The fractions distilling below 300° contain diphenyl-methane, etc., but the higher fractions solidify on cooling, and after crystallisation from benzene, and drying at 100° to drive off benzene of crystallisation, are recrystallised from alcohol—

$$CHCl_3 + 3C_6H_6 + AlCl_3 = CH(C_6H_5)_3 + 3HCl + AlCl_3.$$

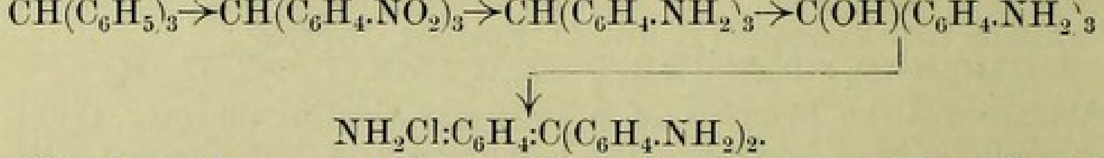
Triphenyl-methane, $CH(C_6H_5)_3$ (Kekulé, 1872), is a colourless, crystalline substance, melting at 92°. Its constitution is obvious from its composition and mode of formation.

Para-leucaniline is thus triamido-triphenylmethane. Now on oxidising triphenyl-methane with chromic anhydride in acetic acid, it is converted into the corresponding tertiary alcohol, triphenyl-carbinol, $CPh_3.OH$, a crystalline substance melting at 159° (the benzene hydrogen would not of course be attacked); and as this is also formed by eliminating the amido-groups from para-rosaniline by the diazo-method, it follows that the latter is tri-amido-triphenyl-carbinol, $C(OH)(C_6H_4.NH_2)_3$, or rather, its anhydride—

$$CH(C_6H_5)_3 \rightarrow C(OH)(C_6H_5)_3 \leftarrow C(OH)(C_6H_4.NH_2)_3.$$

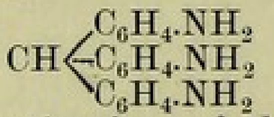
Rosaniline is proved in a similar manner to be the corresponding derivative of diphenyltolyl-methane (E. and O. Fischer, 1878). The determination of the positions of the amido-groups is involved, and it can only be stated here that they can be proved to occupy the para-positions in the three benzene rings.

Synthesis of Para-rosaniline from Triphenyl-methane.—The above results are fully confirmed by a direct synthesis of para-rosaniline from the parent hydro-carbon. On dissolving triphenyl-methane in fuming nitric acid and pouring the product into water, a crystalline trinitro-derivative, $C_{19}H_{13}(NO_2)_3$, is obtained, which on reduction with zinc dust in glacial acetic acid solution is reduced to the corresponding triamido-compound, $C_{19}H_{13}(NH_2)_3$. This can be precipitated from the diluted and filtered product with ammonia. On heating the dry triamido-triphenylmethane with a little concentrated sulphuric acid on platinum foil, it is oxidised to the corresponding carbinol, and this on acidification with dilute hydrochloric acid yields a dye identical with para-rosaniline (Fischer)—

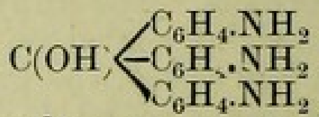


$$CH(C_6H_5)_3 \rightarrow CH(C_6H_4.NO_2)_3 \rightarrow CH(C_6H_4.NH_2)_3 \rightarrow C(OH)(C_6H_4.NH_2)_3 \rightarrow NH_2Cl{:}C_6H_4{:}C(C_6H_4.NH_2)_2.$$

The leuco-base, para-leucaniline, is thus para-triamido-triphenylmethane, and the colour base, pararosaniline, para-triamido-triphenylcarbinol; leucaniline and rosaniline themselves being the corresponding derivatives of diphenyl-tolylmethane—

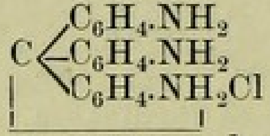


$$CH\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases}$$



$$C(OH)\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases}$$

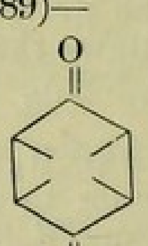
The constitutions of the dyes themselves are matters of controversy. It was originally suggested that they are internal ammonium salts of the betaïne type (Hofmann), and others regard them as the alkylic chlorides of the carbinols (Rosenstiehl)—

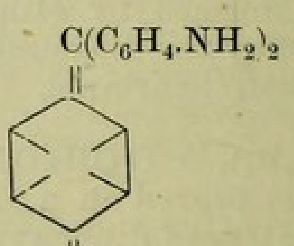


$$C\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2Cl\end{cases}$$

$$CCl\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases}$$

The more recent view, however, is that their structure is quinonoid. All the para-quinones, including those of naphthalene (p. 367) and anthracene (p. 370), are highly coloured substances, and it has been found possible to arrange the formulæ of practically all coloured organic compounds on the quinone model (Armstrong, 1889)—





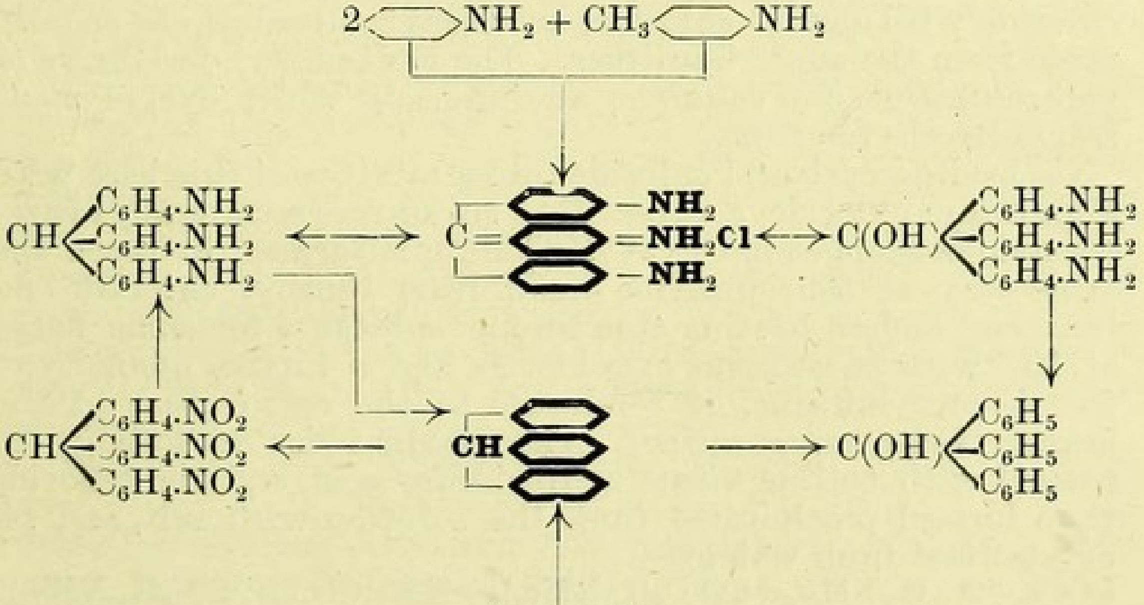
Pararosaniline is reconverted into aniline and para-toluidine when heated with hydriodic acid at 200°, and its leuco-base is probably formed from these substances in the same way as that of malachite green (p. 359), by condensation of the aniline with para-amido-benzaldehyde, formed by oxidation of the para-toluidine—

$$NH_2.C_6H_4.CH_3 \rightarrow NH_2.C_6H_4.CHO \rightarrow NH_2.C_6H_4.CH(C_6H_4.NH_2)_2.$$

The phenolic or hydroxy-compounds, aurin and rosolic acid, corresponding with the rosanilines, and formed from them by the diazo-reaction, can also be made by heating phenol or a mixture of phenols with oxalic or arsenic acid and concentrated sulphuric acid. Aurin, $O:C_6H_4:C(C_6H_4.OH)_2$ (Kolbe, 1861), is a dark red crystalline substance, having a metallic lustre like the rosanilines. It dissolves freely in alcohol and alkalies—in the latter to dark red solutions; but is of no use as a dye, as it cannot be satisfactorily fixed. It is reconverted into pararosaniline by ammonia.

Synopsis.—The rosaniline colour-bases are the triamido-derivatives of triphenyl-carbinol and its next homologue: the leuco-bases are similarly related to the hydrocarbons; and the dyes themselves are carbinol ammonium salts.

PARAROSANILINE.



CHAPTER LIX

THE TRIPHENYL-METHANE GROUP: ROSANILINE DERIVATIVES AND PHTHALEÏNS

The Alkyl Rosanilines.—On introducing alkyl and phenyl radicles into the rosaniline amido-groups, the colour of the dye gradually changes through violet to blue, and by further addition of methyl chloride or iodide to these derived substances, green ammonium salts are produced. A mixture of such violet methyl-pararosanilines is obtained on heating pararosaniline chloride with methyl chloride, but these compounds are usually made from the methyl-anilines. The hexamethyl-derivative of pararosaniline, for example, an intensely violet dye, is made from dimethyl-aniline.

On leading carbonyl chloride into a mixture of this base with aluminium chloride, a crystalline substance, tetramethyl-para-diamido-benzophenone, $CO(C_6H_4.NMe_2)_2$ is formed, in much the same way as benzophenone itself from benzoyl chloride and benzene; and on heating this ketonic substance for some hours at 100° with phosphorus oxychloride and a further quantity of the dimethylaniline, it condenses to the colour base of the hexamethyl-pararosaniline. The product is repeatedly extracted with boiling dilute hydrochloric acid, and the chloride thus formed precipitated from the solution with salt, and recrystallised from water—

$$COCl_2+2C_6H_5.NMe_2 \rightarrow CO(C_6H_4.NMe_2)_2 \rightarrow NMe_2Cl{:}C_6H_4{:}C(C_6H_4.NMe_2)_2.$$

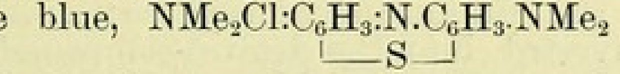
Hexamethyl-pararosaniline chloride or crystal violet, $NMe_2Cl{:}C_6H_4{:}C(C_6H_4.NMe_2)_2$ (Hofmann, 1873), is an almost black crystalline substance, which, like most of the aniline dyes, shows a marked metallic lustre. It dissolves in water and alcohol to a deep violet solution, and dyes silk and wool, and, as a basic dye, cotton mordanted with tannin, violet. When heated with methyl iodide it is converted into the corresponding methiodide, iodine green, $NMe_2Cl{:}C_6H_4{:}C(C_6H_4.NMe_2)_2,CH_3I$.

The pure hexamethyl dye is not much used in practice, as methyl-violet, a similar and much less expensive mixture of hexa- and lower methyl-pararosanilines, can be obtained by direct oxidation of dimethyl-aniline. The latter is simply warmed with potassium chlorate and copper sulphate for some hours, and the dye extracted from the product with hot water, and precipitated with salt, after removing dissolved copper with sulphuretted hydrogen. The corresponding methochloride, methyl green, is made by passing methyl chloride vapour into a warm alcoholic solution of methyl violet.

The Phenyl Rosanilines.—Whilst the introduction of alkyl groups into the rosanilines gives all shades of violet, pure blues can only be obtained by introducing phenyl. By heating rosaniline, for example, with aniline and benzoic acid for several hours at 180°, triphenyl-rosaniline or aniline blue is obtained. The product is extracted with dilute hydrochloric acid, and the chloride precipitated with the concentrated acid.

Aniline blue, or triphenyl-rosaniline, $NHPhCl{:}C_6H_3Me{:}C(C_6H_4.NHPh)_2$ (Girard and De Laire, 1862), is an almost black substance, which is freely soluble in alcohol to a dark blue solution, and dyes silk and wool a pure blue. The dye is insoluble in water, but as in the case of indigo is readily converted into a soluble sulphonic acid. The sodium sulphonate, water blue, is only faintly coloured, whilst the acid itself is as intensely blue as the original dye. After dyeing the fabric therefore, mordanted with tannin in the case of cotton, it is passed through a bath of dilute acid.

The corresponding para-rosaniline derivative can be made by heating diphenylamine with oxalic acid, the latter supplying the nucleal carbon. In this connection the important basic dye methylene blue may be mentioned, as it is a derivative of diphenylamine, although not of triphenyl-methane. It is formed by passing sulphuretted hydrogen into a solution of paramido-dimethylaniline (p. 285), in presence of ferric chloride. The product assumes an intense blue colour, and the double zinc chloride of the dye is precipitated by adding zinc chloride and common salt to the aqueous extract.

Methylene blue,  $NMe_2Cl{:}\underbrace{C_6H_3{:}N.C_6H_3}_{S}.NMe_2$ (Caro, 1876), is freely soluble in water, and dyes cotton mordanted with antimony tannate a fine indigo blue.

Malachite Green.—The important green dye, malachite green, is related to the rosanilines, being the methyl derivative of diamido-triphenylmethane. It is manufactured from benzaldehyde and dimethyl-aniline. The mixed liquids are heated with anhydrous zinc chloride on a water-bath for some hours, and after removing any unchanged dimethyl-aniline by distillation with steam, the leuco-compound, $C_6H_5.CH(C_6H_4.NMe_2)_2$, is dissolved in dilute hydrochloric acid, and oxidised with freshly precipitated lead peroxide. The dissolved lead is precipitated with sodium sulphate, and the carbinol converted into the double zinc chloride of the dye by the addition of zinc chloride—

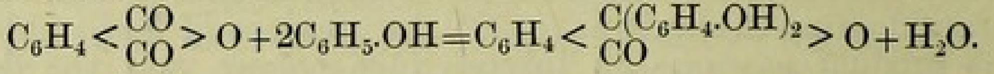
$$CHPh.CH(C_6H_4.NMe_2)_2 \rightarrow CPh(OH)(C_6H_4.NMe_2)_2$$

$$\longrightarrow NMe_2.C_6H_4.CPh{:}C_6H_4{:}NMe_2Cl.$$

Malachite green, or tetramethyl-diamido-triphenyl-methane chloride, $NMe_2.C_6H_4.CPh{:}C_6H_4{:}NMe_2Cl$ (O. Fischer, 1877), is an almost black crystalline substance, which dissolves in water to a dark green solution. It dyes silk and wool, and, as a basic dye, cotton mordanted with tannin, a dark green. The carbinol or colour base precipitated from the solution by caustic alkalies, is a colourless crystalline substance, like the corresponding rosaniline compound. It is more stable than free rosaniline, however, and even on acidifying its solution is only slowly converted into the dye. The colour appears, however, immediately the solution is warmed.

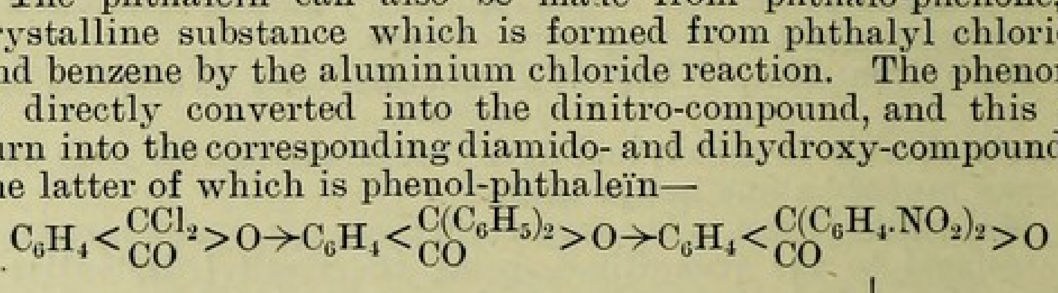
Malachite green, like the rosanilines, forms various alkyl derivatives, and the colour, as in the previous cases, is shifted towards the red end of the spectrum by the introduction of alkyl groups. The corresponding ethyl compound, for example, "brilliant green," is a bright yellowish green in hue.

The Phthaleïns.—The last group of triphenyl-methane derivatives to be considered comprises a number of coloured and other compounds formed by heating the various phenols with phthalic anhydride. By heating ordinary phenol at 120° for several hours with phthalic anhydride and concentrated sulphuric acid, the well known alkali indicator, phenol phthaleïn, is obtained. After boiling the product with water, to remove phthalic and sulphuric acids, and distilling it with steam, to remove the phenol, the phthaleïn is extracted from the insoluble portion with dilute caustic soda, and precipitated from the crimson solution with acetic acid—



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O+2C_6H_5.OH=C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4.OH)_2}{CO}>O+H_2O.$$

The phthaleïn can also be made from phthalo-phenone, a crystalline substance which is formed from phthalyl chloride and benzene by the aluminium chloride reaction. The phenone is directly converted into the dinitro-compound, and this in turn into the corresponding diamido- and dihydroxy-compounds, the latter of which is phenol-phthaleïn—

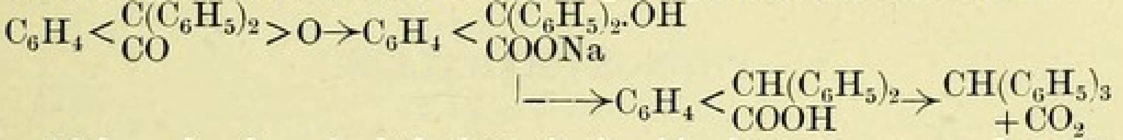


$$C_6H_4<\genfrac{}{}{0pt}{}{CCl_2}{CO}>O\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_5)_2}{CO}>O\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4.NO_2)_2}{CO}>O$$

$$\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4.NH_2)_2}{CO}>O\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4.OH)_2}{CO}>O.$$

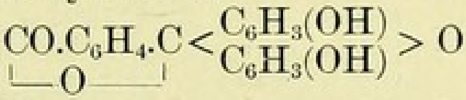
Phenol phthaleïn, $C_6H_4<\genfrac{}{}{0pt}{}{C(C_6H_4.OH)_2}{CO}>O$ (Baeyer, 1880), is a sandy crystalline substance melting at 250°. It is freely soluble in alcohol to a colourless or yellowish solution, and is insoluble in water. But it dissolves in alkalies to a deep crimson solution, the colour of which is discharged by all acids, and even by carbon dioxide and many acid salts. The phthaleïn can therefore be used as an alkali indicator in many cases where litmus and methyl orange are unsuitable. It is of no use as a dye, as its colour cannot be fixed.

The relation of the phthaleïns to triphenyl- methane is traced through phthalo-phenone. When the latter is boiled with concentrated alcoholic potash, it is hydrolysed to sodium triphenylcarbinol-carboxylate, and this is reduced by zinc dust and caustic soda to triphenylmethane-carboxylic acid. On distilling the latter with lime, triphenyl-methane is obtained—



$$C_6H_4<\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}>O\rightarrow C_6H_4<\begin{matrix}C(C_6H_5)_2.OH\\COONa\end{matrix}$$
$$\longrightarrow C_6H_4<\begin{matrix}CH(C_6H_5)_2\\COOH\end{matrix}\rightarrow\begin{matrix}CH(C_6H_5)_3\\+CO_2\end{matrix}$$

Although phenol-phthaleïn is itself of no use as a dye, the corresponding resorcinol derivative, which is made in precisely the same way, furnishes some valuable dye-stuffs.

Fluoresceïn or resorcinol-phthaleïn,  $\underbrace{CO.C_6H_4.C}_{O}<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>O$ (Baeyer, 1876), is a dark red crystalline substance, which is insoluble in water, but soluble in alcohol and alkalies. The alkali solution is red, and shows a fine green fluorescence. Fluoresceïn itself dyes silk and wool yellow with green fluorescence, but the colour is not fast to light. The disodium salt, however, is used as a dye—uranin.

The halogen substitution-products of fluoresceïn are important dyes. On slowly adding bromine to an alcoholic solution of fluoresceïn, a brick-red precipitate of a tetrabromo-derivative is eventually formed, which is purified by washing with alcohol, and drying at 100° to remove alcohol of crystallisation.

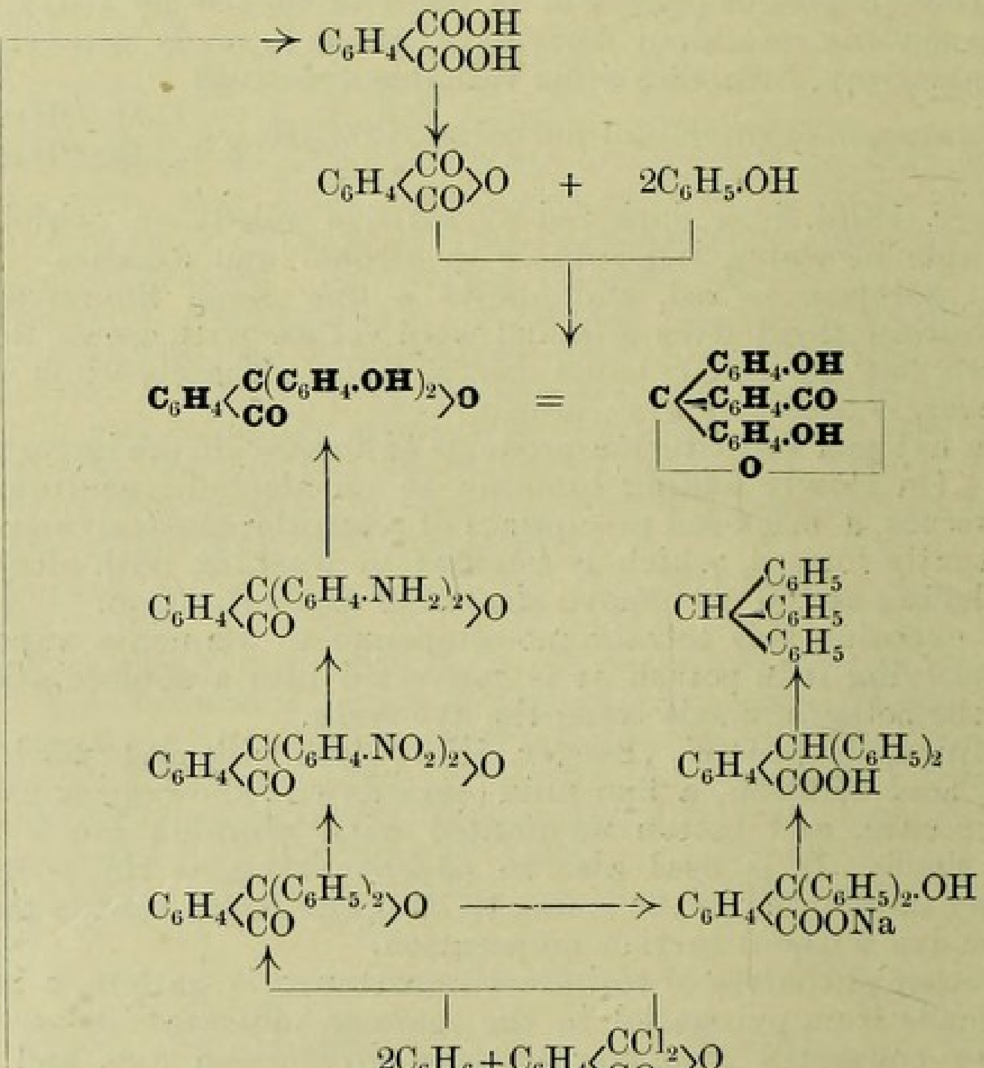
On exposing this tetrabromo-compound to ammonia vapour, or dissolving it in potash, it is converted into a soluble alkali salt, the potassium salt being the dye eosin.

Eosin, $C_{20}H_6Br_4O_5K_2$ (Baeyer, 1876), dyes silk and wool, in acetic acid solution, a fine pink (ἠώς=dawn), showing a green fluorescence, and cotton mordanted with alumina much the same shade. It is used also in paper-making, as the pulp is already mordanted in the sizing (p. 346), and hence readily takes up the dye without further preparation.

Another phthaleïn of technical importance is galleïn, a blue dye, made from pyrogallol in the manner indicated above. It can be converted into cœruleïn, an olive-green dye, and an anthracene derivative.

Synopsis.—By introducing alkyl or phenyl groups into the amido-groups of rosaniline and other amido-triphenyl methanes, blue, violet, and green dyes are produced. The phthaleïns, formed by condensation of phthalic anhydride with phenols, are carboxylic anhydrides of the hydroxy-triphenylmethanes.

PHENOL-PHTHALEÏN.



CHAPTER LX

NAPHTHALENE

Naphthalene and its Halogen and Alkyl Derivatives.—Naphthalene, the crystalline hydrocarbon which is deposited in gas mains in cold weather, is formed, together with benzene, etc., when the simple gaseous hydrocarbons are heated to redness, and its presence in coal gas and tar is doubtless due to this synthesis. Its chief source is the middle oil of coal tar (p. 251), from which, as already stated, it crystallises on cooling. After draining under pressure, and washing away phenols with alkali, it is purified by sublimation.

Naphthalene, $C_{10}H_8$ (Kidd, 1816), forms large, colourless, leafy crystals, having a characteristic tarry odour. It melts at 78°, and boils at 218°, but sublimes very easily at much lower temperatures, and is volatile with steam. The hydrocarbon has marked antiseptic properties, and destroys moth and the like; but its chief use is in the local enrichment of coal gas, and in the manufacture of phthaleïn and azo dyes.

Naphthalene resembles benzene in most of its actions, and forms chloro-, nitro-, and sulphonic substitution products even more readily, but the isomerism of its derivatives is much more complex. Two sets of mono-substitution products are known, and of di-substitution products no less than ten, or, if the substituting groups are dissimilar, fourteen.

Of the mono-chloro-derivatives, α-chloro-naphthalene, $C_{10}H_7Cl$ (α) (Laurent, 1831), a liquid boiling at 263°, is formed by direct chlorination of the boiling hydrocarbon, whilst the β-compound, a crystalline solid melting at 56°, is prepared from the corresponding amido-compound, $C_{10}H_7.NH_2$, by the diazo-reaction, or from the sulphonic acid by the action of phosphorus pentachloride (p. 365). The chloro-naphthalenes closely resemble chloro-benzene. Their chlorine is not displaced by boiling with alkalies, but can be exchanged for hydrocarbon radicles by the aluminium chloride or sodium methods, in the same way as with the benzene derivative. The ten dichloro-naphthalenes are crystalline substances, which for the most part are prepared by indirect means.

Like benzene, naphthalene behaves on occasion as an unsaturated compound. By the action of chlorine, for example, at the ordinary temperature, naphthalene tetrachloride, $C_{10}H_8Cl_4$, a crystalline substance melting at 182°, is formed, which on boiling with alcoholic potash is converted into one of the dichloro-naphthalenes, in much the same way as benzene hexachloride into trichloro-benzene.

Naphthalene resembles benzene also in forming alkyl derivatives, such as *α*- and *β*-methyl-naphthalenes, $C_{10}H_7.CH_3$, liquids which, like methyl-benzene, are present in coal tar. The naphthyl radicle unites similarly with phenyl and analogous radicles, and with itself, forming such hydrocarbons as the two phenyl-naphthalenes and the three dinaphthyls. *ββ*-Dinaphthyl, for example, is formed in the same way as diphenyl, by the action of sodium on *β*-chloro-naphthalene in boiling xylene solution in presence of ethyl acetate—

$$C_{10}H_7Cl + Na_2 + C_{10}H_7Cl = C_{10}H_7.C_{10}H_7 + 2NaCl.$$

Like benzene also, naphthalene forms an additive compound with picric acid, which is precipitated on mixing the alcoholic solutions of the two substances. Naphthalene picrate, $C_{10}H_8$, $C_6H_2(NO_2)_3.OH$, is a red crystalline substance, which melts unchanged at 149°, but is readily decomposed into its components by alkalies.

The Nitro-Naphthalenes and Naphthalene-Sulphonic Acids.—Naphthalene is nitrated as easily as benzene. On digesting it with nitro-sulphuric acid at the ordinary temperature, or better, on heating its solution in glacial acetic acid with nitric acid on a water-bath, it is converted into *α*-nitro-naphthalene, which can be purified in the same way as dinitro-benzene.

α-Nitro-naphthalene, $C_{10}H_7.NO_2(\alpha)$ (Laurent, 1848), is a yellow crystalline substance, melting at 59°. It resembles nitrobenzene in most of its actions, and is thus reducible to the corresponding naphthylamine (p. 365), but on the other hand it is oxidised by chromic acid mixture to nitrophthalic acid, $C_6H_3(NO_2)(COOH)_2$, a crystalline substance resembling the nitro-benzoïc acids.

β-Nitro-naphthalene, $C_{10}H_7.NO_2(\beta)$, a similar yellow substance melting at 79°, can only be obtained indirectly. *α*-Naphthylamine is digested with dilute nitric acid, and the amido-group eliminated from the *β*-nitro-*α*-naphthylamine thus formed by warming its solution in alcoholic hydrogen chloride with sodium nitrite—

$$C_{10}H_8 \rightarrow C_{10}H_7.NH_2(\alpha) \rightarrow C_{10}H_6(NH_2\alpha)(NO_2\beta) \rightarrow C_{10}H_7.NO_2(\beta).$$

Both naphthalene-sulphonic acids are formed by direct sulphonation of the hydrocarbon, but they can be separated by fractionally crystallising their calcium salts, the *α*-salt being much the more soluble. At 160°, however, the *α*-acid is transformed into the *β*-acid, and the latter is therefore alone produced by sulphonating the hydrocarbon above this temperature.

α- and *β*-Naphthalene-sulphonic acids, $C_{10}H_7.SO_3H$ (Faraday, 1826), are deliquescent, crystalline substances, resembling benzene-sulphonic acid in their actions. They are converted into sulphonic chlorides by phosphorus pentachloride, and these by ammonia into crystalline sulphonamides, $C_{10}H_7.SO_2.NH_2$. The chlorides differ from the benzene sulphochlorides, however, in that they are resolved into the corresponding chloro-naphthalenes by the further action of phosphorus pentachloride—

$$C_{10}H_7.SO_2.OH \rightarrow C_{10}H_7.SO_2Cl \rightarrow C_{10}H_7.Cl + SOCl_2 + POCl_3.$$

By the action of fuming sulphuric acid on naphthalene, di- and tri-sulphonic acids are formed, in the same way as with benzene.

The Naphthylamines and Naphthols.—As indicated above, by reducing the nitro-naphthalenes with iron filings and acetic acid, they are converted into naphthylamines, bases which can be liberated with caustic soda and extracted with ether. The bases are also formed by heating the naphthols with zinc-chloride-ammonia (p. 253), and the β-compound is best prepared in this way, the action taking place much more readily than with phenol, and at a lower temperature—

$$C_{10}H_7.NO_2 \rightarrow C_{10}H_7.NH_2 \leftarrow C_{10}H_7.OH.$$

a-Naphthylamine, $C_{10}H_7.NH_2(a)$ (Zinin, 1842), is a colourless crystalline substance of unpleasant fæcal odour, which melts at 50°, and boils at 300°, but readily sublimes at a lower temperature. It resembles aniline in its actions, and forms salts with acids, but its basic properties are less marked, and its salts are decomposed by sodium carbonate. It is still more easily oxidised, turning reddish-brown in the air, and like aniline is converted into colouring matters—red and blue—by weak oxidising agents, such as ferric chloride. When boiled with chromic acid mixture it is converted first into naphthoquinone (p. 367) in the same way as aniline into quinone, but on further oxidation phthalic acid is formed.

β-Naphthylamine, $C_{10}H_7.NH_2(\beta)$, is a similar crystalline substance, melting at 112°. It is odourless, however, and not coloured by oxidising agents, but directly converted into phthalic acid.

The naphthylamines are reduced by sodium in alcohol to tetrahydro-compounds, which more resemble the aliphatic amines; and they are convertible by the diazo-reaction into the naphthols and hydrocarbon, as well as into the chloro- and cyano-naphthalenes, and naphthoic acids, the naphthalene analogues of benzoic acid.

The naphthols or naphthalene phenols occur in small quantities in coal tar, but are usually made from the naphthalene-sulphonic acids, in the same way as phenol from benzene-sulphonic acid (p. 253)—

$$C_{10}H_8 \rightarrow C_{10}H_7.SO_3K \rightarrow C_{10}H_7.OH.$$

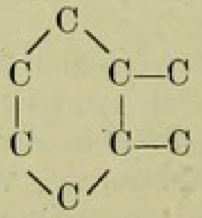
a-Naphthol, $C_{10}H_7.OH$ (Griess, 1866), is a colourless, crystalline substance, having a slight phenolic odour. It melts at 94°, and is only sparingly soluble in water. The β-compound is similar, but melts at 122°, and is more freely soluble. The naphthols give coloured precipitates with ferric chloride, and they otherwise resemble phenol, although distinctly more reactive. Their hydroxyl, as has been seen, is easily exchanged for amidogen, and they are converted into ethers, such as naphthyl ethyl ether, by simply warming with alcoholic hydrogen chloride.

Like phenol, the naphthols are converted by nitric acid into yellow nitro-compounds, having marked acid properties. Dinitro-*a*-naphthol, $C_{10}H_5(NO_2)_2.OH$, for example, is a brilliant yellow crystalline substance, resembling picric acid in almost every respect. Its sodium salt, Martius' yellow, is used as a dye, and the potassium salt of its sulphonic acid is similarly used as naphthol yellow.

The sulphonic acids of the naphthylamines are much used in the preparation of azo dyes (p. 380). Fourteen are theoretically possible, and the majority of these are known and manufactured. The most important is naphthionic or *a*-naphthylamine-sulphonic acid, $C_{10}H_6(SO_3H).NH_2(a)$, which is formed by direct sulphonation of *a*-naphthylamine at 130°. It is a sparingly soluble compound which is isolated in the ordinary manner.

Constitution of Naphthalene.—The actions of naphthalene being so closely parallel to those of benzene, it may be expected to be a benzene derivative, and as previously indicated, it is oxidised to phthalic acid when boiled with nitric acid. The oxidation is more readily effected with naphthalene tetrachloride, or, as already stated, with the impure dichloride formed by warming the hydrocarbon with potassium chlorate and hydrochloric acid.

This action shows not only that naphthalene is a benzene derivative, but also that two of the additional carbon atoms are attached to the ring in the ortho-position, whilst the other two are only indirectly connected—

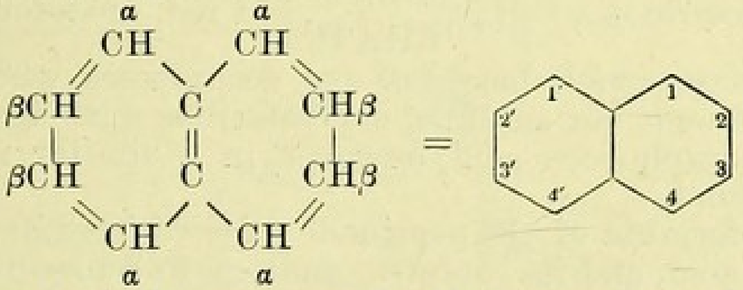


Now these four atoms cannot form an open chain, or a hexachloride would be formed by addition of chlorine. They must therefore be arranged in a ring. There are several ways in which this may be effected, but from the general nature of the hydrocarbon it would seem probable that this second ring is also a benzene ring (Erlenmeyer, 1866), and this can be proved the case.

As stated above, whilst *a*-nitro-naphthalene yields nitrophthalic acid on oxidation, the *a*-naphthylamine obtained by reducing this nitro-compound yields phthalic acid itself. Now no instance is known in which an amido-group is replaced by hydrogen by the action of oxidising agents, and it follows therefore that a benzene ring exists in the amido-naphthalene and nitro-naphthalene molecules distinct from that containing the amido and nitro-groups (Graebe, 1880; Noelting, 1883)—

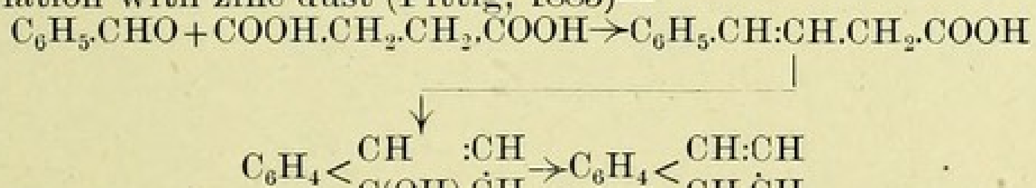
$$C_6H_3(NO_2)(COOH)_2 \leftarrow C_6H_3(NO_2):C_4H_4 \rightarrow C_6H_3(NH_2):C_4H_4$$
$$C_6H_3(NH_2):C_4H_4 = C_6H_4:C_4H_3.NH_2 \rightarrow C_6H_4(COOH)_2.$$

The naphthalene molecule thus consists of two benzene rings, which have two carbon atoms in common, and necessarily therefore adjacent. This affords an independent proof of the position of the groups in phthalic acid—



This formula fully accounts for the isomerism of the naphthalene substitution-products. There should be two sets of mono-substitution products, for the positions next to the central carbon atoms (*α*) are differently situated from the other four (*β*); and in the di-substitution products the positions 1:2,1:3,1:4,1:1′,1:2′,1:3′,1:4′,2:3,2:2′,2:3′, are all different.

A synthetic confirmation of the formula is afforded by the preparation of naphthalene from benzaldehyde and succinic acid. On heating these substances with sodium succinate, they condense, losing water and carbon dioxide, and on boiling the crystalline product, phenyl-isocrotonic acid, thus formed, either alone or with water, it suffers further condensation to *α*-naphthol. This is converted into the hydrocarbon by distillation with zinc dust (Fittig, 1883)—

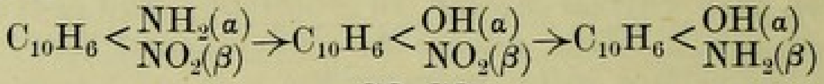


$$C_6H_5.CHO + COOH.CH_2.CH_2.COOH \rightarrow C_6H_5.CH:CH.CH_2.COOH$$
$$\downarrow$$
$$C_6H_4<\genfrac{}{}{0pt}{}{CH\quad :CH}{C(OH):\dot{C}H} \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CH:CH}{CH:\dot{C}H}$$

The Naphthoquinones.—As already stated, when *α*-naphthylamine is boiled with chromic acid mixture it is converted into *α*-naphthoquinone. This compound is more conveniently prepared by directly oxidising the hydrocarbon itself with chromic anhydride in glacial acetic acid solution, and in either case is isolated by distillation with steam.

α-Naphthoquinone, $C_6H_4<\genfrac{}{}{0pt}{}{CO.CH}{CO.\ddot{C}H}$ (Groves, 1873), is a yellow crystalline substance, melting at 125°, which resembles ordinary benzoquinone in appearance and odour, and in the readiness with which it sublimes. Like quinone also, it is reduced by sulphurous acid to the corresponding hydroxy-compound, 1:4-dihydroxy-naphthalene, a crystalline substance resembling quinol; but, as already stated, it is further oxidised to phthalic acid when boiled with chromic acid mixture.

A second naphthoquinone is formed by similarly oxidising the β-amido-α-naphthol, formed from β-nitro-α-naphthylamine by the successive action of nitrous acid and tin and hydrochloric acid—



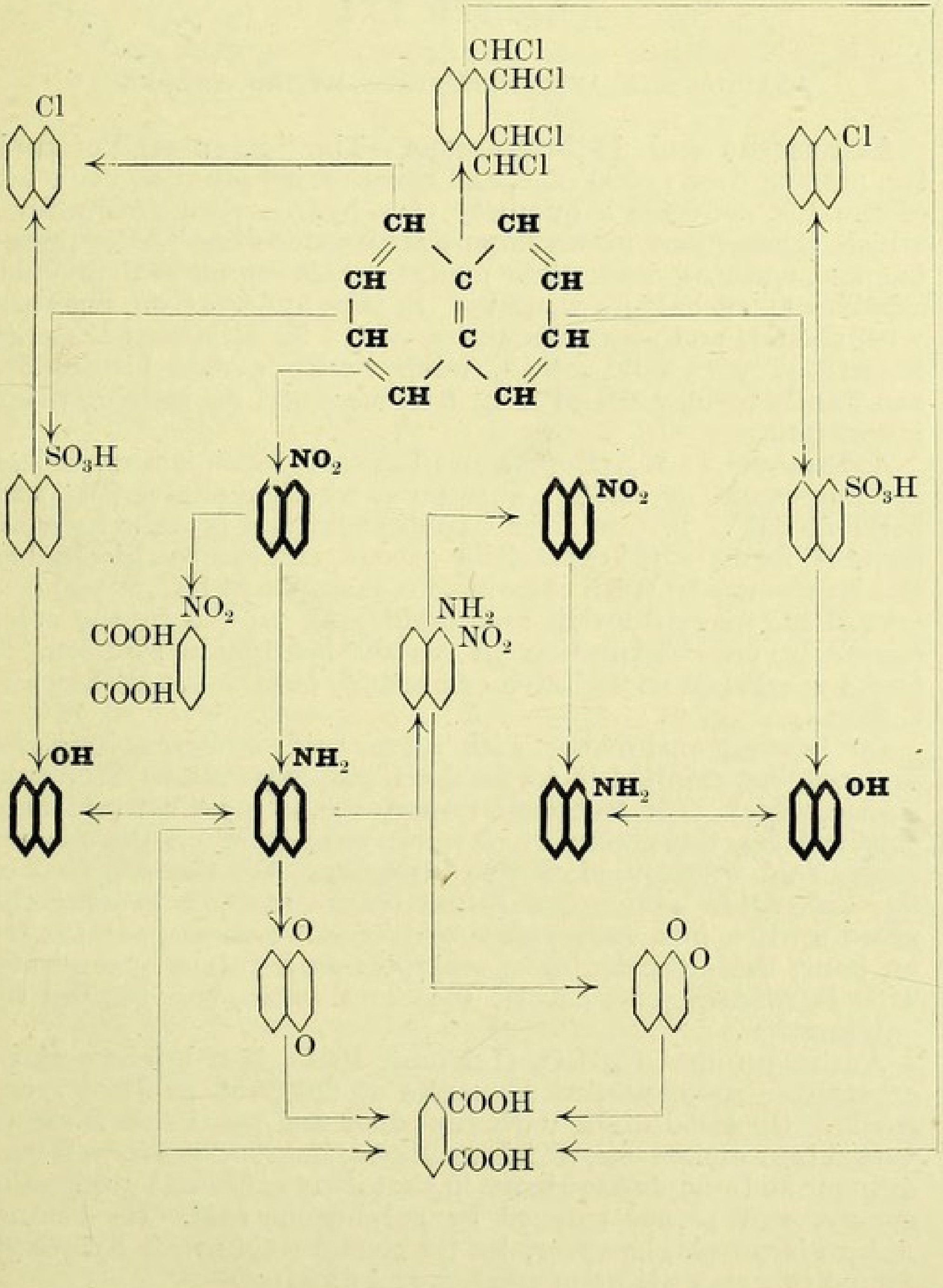
$$C_{10}H_6 < \begin{matrix} NH_2(\alpha) \\ NO_2(\beta) \end{matrix} \rightarrow C_{10}H_6 < \begin{matrix} OH(\alpha) \\ NO_2(\beta) \end{matrix} \rightarrow C_{10}H_6 < \begin{matrix} OH(\alpha) \\ NH_2(\beta) \end{matrix}$$

β-Naphthoquinone, $C_6H_4 < \begin{matrix} CO.CO \\ \vdots \\ CH.CH \end{matrix}$, is a red, inodorous, crystalline substance, which blackens and decomposes when heated, and does not melt nor sublime, nor volatilise with steam. It is reduced by sulphurous acid, however, in a similar manner to the α-compound.

The para-formula of the α-quinone follows from its oxidation to phthalic acid, and its complete analogy to benzoquinone, and as the β-compound is also convertible into phthalic acid, it must be represented by the only alternative or ortho-quinone formula.

Synopsis.—Naphthalene is a hydrocarbon which resembles benzene and forms similar derivates, but as its molecule consists of two benzene rings having two carbon atoms in common, the isomerism of its substitution products is more complex.

NAPHTHALENE.



CHAPTER LXI

ANTHRACENE AND ANALOGOUS HYDROCARBONS

Anthracene and Anthraquinone.—The "green oil" of coal tar, passing over at 300–350°, and constituting about 20 per cent. of the tar, contains a quantity of a hydrocarbon anthracene, which crystallises in an impure state on cooling. After pressing and washing with light naphtha, this commercial product contains about half its weight of the pure hydrocarbon, together with phenols and phenanthrene (p. 373). To eliminate these, it is distilled with solid potash, washed with carbon bisulphide, and finally re-crystallised from benzene until its melting point is constant.

Anthracene, $C_{14}H_{10}$ (Dumas and Laurent, 1832), is a colourless but fluorescent crystalline substance, which melts at 201°, and boils at 351°. It resembles naphthalene and benzene in most respects, forms a red crystalline picrate, and can be chlorinated and sulphonated. With chlorine, for example, at 100°, it yields a crystalline monochloride and dichloride, whilst in the cold, especially on chlorination in carbon bisulphide solution, it forms a crystalline additive compound, anthracene dichloride, $C_{14}H_{10}Cl_2$.

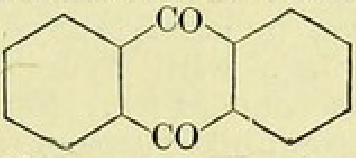
On heating anthracene with nitric acid, however, it is not nitrated, but oxidised to its quinone, anthraquinone. This substance, which is of technical importance, is more conveniently obtained by the action of chromic anhydride on the glacial acetic acid solution of the hydrocarbon. On the addition of the anhydride a vigorous action occurs, and on pouring the green product into water, after boiling in a reflux apparatus for an hour, the anthraquinone separates as a yellow precipitate. This is washed with caustic soda and water, and purified by sublimation.

Anthraquinone, $C_{14}H_8O_2$ (Laurent, 1834), is a bright yellow, crystalline substance, which melts at 285°, and sublimes very easily. On distillation with zinc dust and pumice, it is reconverted into anthracene, which sublimes; but it differs from benzoquinone and α-naphthoquinone in that it is unaffected by oxidising agents, and is not reduced by sulphurous acid. Its ketonic nature is proved, however, by its condensation with hydroxylamine to a crystalline monoxime and dioxime.

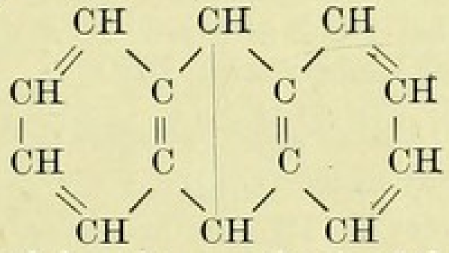
On fusing anthraquinone with potash, it is converted into potassium benzoate, and conversely, it is formed, together with benzophenone, by the dry distillation of calcium benzoate. It is produced also by distilling with phosphorus pentoxide the crystalline *o*-benzoyl-benzoic acid, $C_6H_4<\genfrac{}{}{0pt}{}{CO.C_6H_5}{COOH}$, formed from phthalic acid and benzene by the dehydrating action of aluminium chloride.

These decompositions and syntheses lead to the assumption that anthraquinone is a double ketone of benzoic acid—

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4, \text{ or}$$



But if this is the case, the anthracene molecule must contain three benzene rings—



and this is confirmed by the synthesis of the hydrocarbon from acetylene tetrabromide and benzene by the aluminium chloride method—

$$C_6H_6+\genfrac{}{}{0pt}{}{Br-CH-Br}{Br\ -\dot{C}H-Br}+C_6H_6\rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CH}{\dot{C}H}>C_6H_4+4HBr.$$

Alizarin.—The chief interest of anthracene and anthraquinone lies in their relation to alizarin, which is the essential constituent of madder, one of the most important and longest known of the natural dye-stuffs of the East. Alizarin occurs in the madder root as a crystalline glucoside, ruberythric acid, $C_{26}H_{23}H_{14}$, which on macerating the root with water is hydrolysed by an accompanying enzyme to glucose and the dye, which may be purified by sublimation. As usual, the hydrolysis may also be effected by dilute acids—

$$C_{26}H_{28}O_{14}+2H_2O=C_{14}H_8O_4+2C_6H_{12}O_6.$$

Alizarin, $C_{14}H_8O_4$ (Rochleder, 1870), is a red crystalline substance, which melts at 290°, and easily sublimes. It is scarcely soluble in water, but dissolves in alkalies to a purple solution, from which insoluble, highly coloured salts, the "lakes," are precipitated by metallic hydroxides. The aluminium and stannic lakes, for example, are crimson, the ferric lake dark violet, and the chromic lake purple brown.

By mordanting fabrics with the hydroxides these lakes can be precipitated within the fibres, and very fast and brilliant colours produced. Thus, on steaming a fabric soaked in aluminium acetate, the salt is dissociated, and on passing the fabric, thus mordanted with alumina, through hot water in which alizarin is suspended, it is dyed a fast purple-red. In Turkey red dyeing, by which a brilliant scarlet is produced on cotton, the fabric is mordanted with the aluminium salt of ricinoleïc acid, an acid related to oleïc acid, and occurring as a glyceride in castor-oil. All "acid" dyes are mordanted with hydroxides in this manner.

Constitution and Synthesis of Alizarin.—That alizarin is either an acid or a phenol, is obvious from the formation of these salts, and that it is a phenol, and not an acid, is proved by its conversion by acetic anhydride into a diacetate, which no longer combines with hydroxides. This leaves two oxygen atoms to be accounted for. Now on distilling the dye with zinc dust in a current of hydrogen, it is reduced to anthracene, and as anthraquinone is itself reduced in an identical manner, and all phenols yield their hydrocarbon when treated in this way, it may be concluded that alizarin is a diphenol of anthraquinone (Graebe and Liebermann, 1870)—

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OH)_2.$$

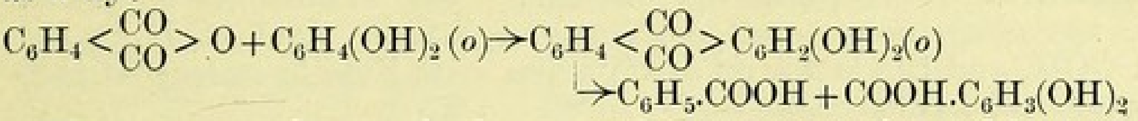
This view is thoroughly confirmed by synthesis. On brominating anthraquinone at 160° in presence of a little iodine, a crystalline dibromo-compound is obtained, and on fusing this with potash in the same way as in converting benzene-sulphonic acid into phenol, a purple potassium salt is formed, from which a red dye, subliming in red crystals, and in every respect identical with natural alizarin, is precipitated by acids (Graebe and Liebermann, 1870)—

$$C_{14}H_{10} \rightarrow C_{14}H_8O_2 \rightarrow C_{14}H_6O_2Br_2 \rightarrow C_{14}H_6O_2(OH)_2.$$

A more economical method consists in fusing potassium anthraquinone-disulphonate with potash (Perkin, 1876), and the dye is now usually made from the sodium mono-sulphonate by a modification of this process. The crude anthraquinone, prepared by oxidising crude anthracene with chromic acid mixture, is converted into the mono-sulphonic acid by heating with fuming sulphuric acid at 180°; and on fusing the sparingly soluble sodium sulphonate—termed silver salt, technically, from its lustrous appearance—with caustic soda and potassium chlorate, sodium alizarin is obtained, from which the dye is precipitated with dilute sulphuric acid. It is usually used in paste form. The alizarin thus synthesised has practically supplanted the natural dye—

$$C_{14}H_8O_2 \rightarrow C_{14}H_7O_2.SO_3H \rightarrow C_{14}H_7O_2.OH \rightarrow C_{14}H_6O_2(OH)_2.$$

On fusing alizarin with potash at a high temperature, it is resolved into benzoic and protocatechuic acids, so that the phenolic groups are in the same benzene ring, and in the ortho-position relatively to one another. A similar proof is afforded by the synthesis of the dye by heating a mixture of catechol and phthalic anhydride with sulphuric acid. The tinctorial power is dependent on the relative positions of the phenolic groups, for the quinazarin formed in this way from quinol is of no value as a dye—



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O + C_6H_4(OH)_2\,(o) \rightarrow C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2(OH)_2(o) \rightarrow C_6H_5.COOH + COOH.C_6H_3(OH)_2$$

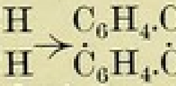
The corresponding trihydroxy-anthraquinones, formed by oxidising alizarin with manganese dioxide and dilute sulphuric acid, or by fusing anthraquinone disulphonic acid with potash (hydrogen being evolved, as in the oxidation of of resorcinol), are also used as dyes, and produce yellower reds than alizarin. The vicinal compound, purpurin, is associated with alizarin as a glucoside in madder.

Phenanthrene, Chrysene, and Picene.—As already indicated, crude anthracene contains a quantity of an isomeric hydrocarbon, phenanthrene, which is freely soluble in the carbon bisulphide used in the purification. The product obtained on evaporating the solution is converted into the picrate, and the latter, after several recrystallisations from alcohol, by which any anthracene picrate is dissociated, is decomposed with ammonia, and the hydrocarbon recrystallised.

Phenanthrene, $C_{14}H_{10}$ (Fittig, 1873), is a colourless, crystalline substance, melting at 205°, and is fluorescent only in alcoholic solution. It resembles anthracene in general properties, and on oxidation with chromic acid mixture is converted into a quinonic derivative, which, however, resembles β-naphthaquinone rather than the other quinones.

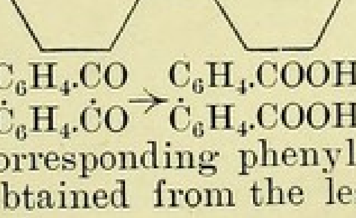
Phenanthrene-quinone, $C_{14}H_8O_2$, is an orange crystalline substance, melting at 99°. Like benzoquinone, it forms a dioxime, but it is also convertible into a bisulphite compound, like the aliphatic ketones, and is odourless, and not volatile with steam.

Now by further oxidation, phenanthrene-quinone is converted into a crystalline dibasic acid, diphenic acid, $C_{12}H_8(COOH)_2$, and that this is diphenyl-dicarboxylic acid is proved by its conversion into diphenyl when distilled with lime. Phenanthrene is thus a derivative of this hydrocarbon, and since, as already noted, it is formed by passing stilbene vapour through a red-hot tube, it is also a derivative of the latter hydrocarbon, and is represented by a formula analogous to that of naphthalene—



$$\begin{matrix}C_6H_4.CH\\ \dot{C}_6H_4.\ddot{C}H\end{matrix}$$

or



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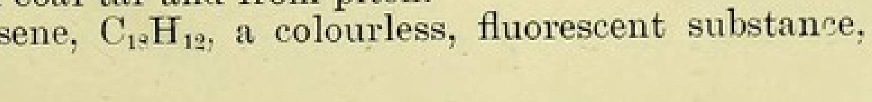
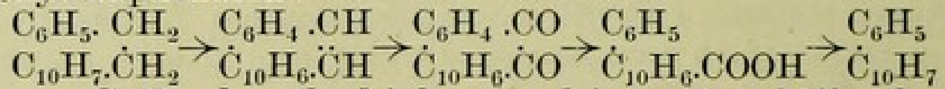


$$\begin{matrix}C_6H_5.CH\\ C_6H_5.\ddot{C}H\end{matrix} \rightarrow \begin{matrix}C_6H_4.CH\\ \dot{C}_6H_4.\ddot{C}H\end{matrix} \rightarrow \begin{matrix}C_6H_4.CO\\ C_6H_4.\dot{C}O\end{matrix} \rightarrow \begin{matrix}C_6H_4.COOH\\ \dot{C}_6H_4.COOH\end{matrix} \rightarrow \begin{matrix}C_6H_5\\ \dot{C}_6H_5\end{matrix}$$

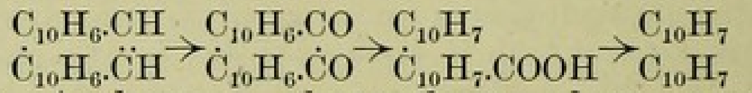
Chrysene and picene, the corresponding phenyl-naphthyl and dinaphthyl compounds, are obtained from the less volatile portions of coal tar and from pitch.

Chrysene, $C_{18}H_{12}$, a colourless, fluorescent substance, which melts at 250° and boils at 448°, is also formed synthetically by distilling phenyl-naphthyl-ethane. On oxidation it yields chrysene-quinone and β-phenyl-naphthoic acid, $C_6H_5.C_{10}H_6.COOH$, and the latter on distillation with lime is converted into β-phenyl-naphthalene—



$$\begin{array}{l}C_6H_5.CH_2\\ C_{10}H_7.\dot{C}H_2\end{array} \rightarrow \begin{array}{l}C_6H_4.CH\\ \dot{C}_{10}H_6.\ddot{C}H\end{array} \rightarrow \begin{array}{l}C_6H_4.CO\\ \dot{C}_{10}H_6.\dot{C}O\end{array} \rightarrow \begin{array}{l}C_6H_5\\ \dot{C}_{10}H_6.COOH\end{array} \rightarrow \begin{array}{l}C_6H_5\\ \dot{C}_{10}H_7\end{array}$$

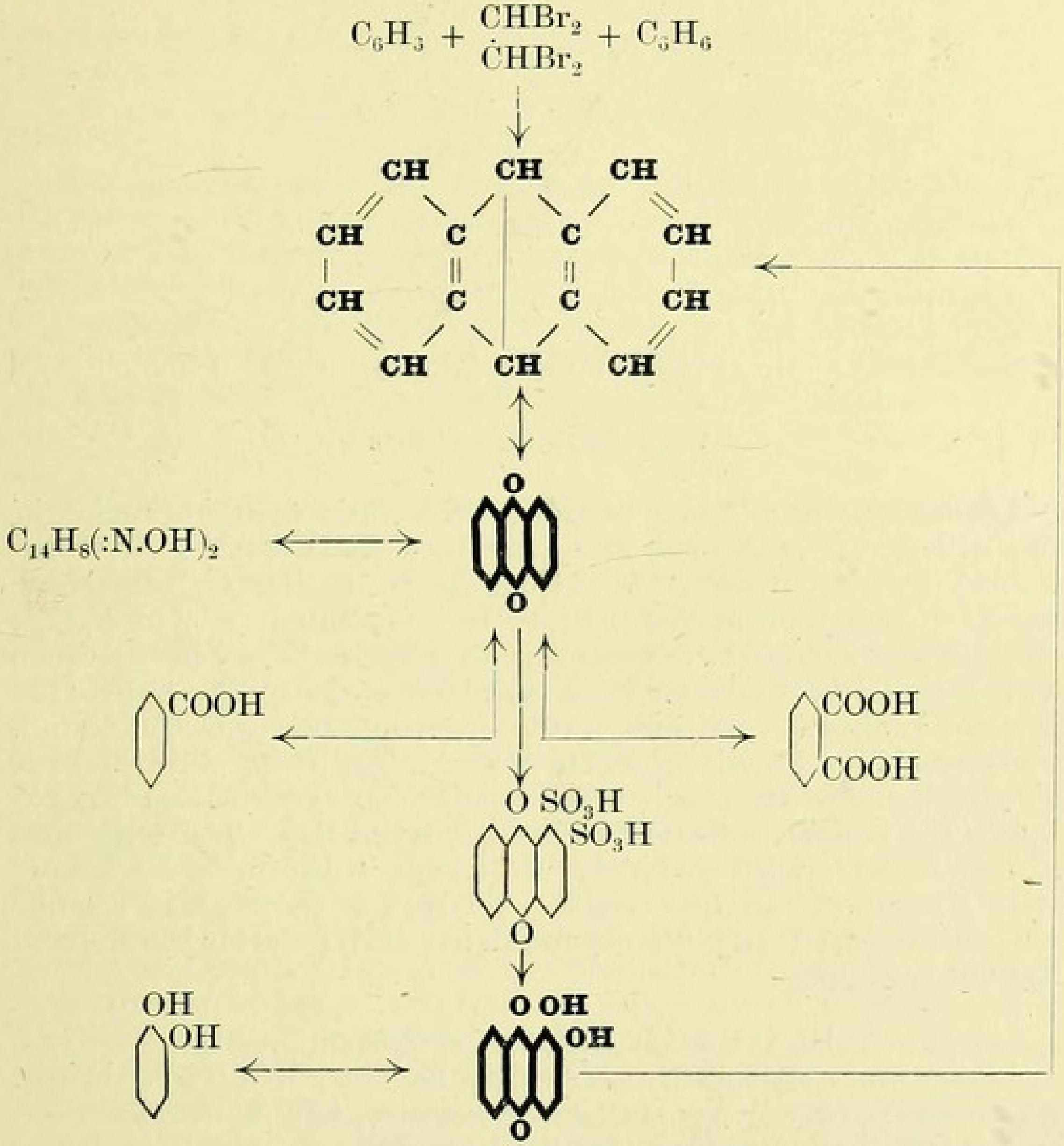
Picene, $C_{22}H_{14}$, has the highest melting point, 364°, of all the hydrocarbons, and boils only at a dull red heat. It behaves on oxidation in the same way as chrysene, being converted into picene-quinone, and picenic or β-naphthyl-naphthoic acid, from which ββ-dinaphthyl (p. 364), is obtained by distillation with lime—



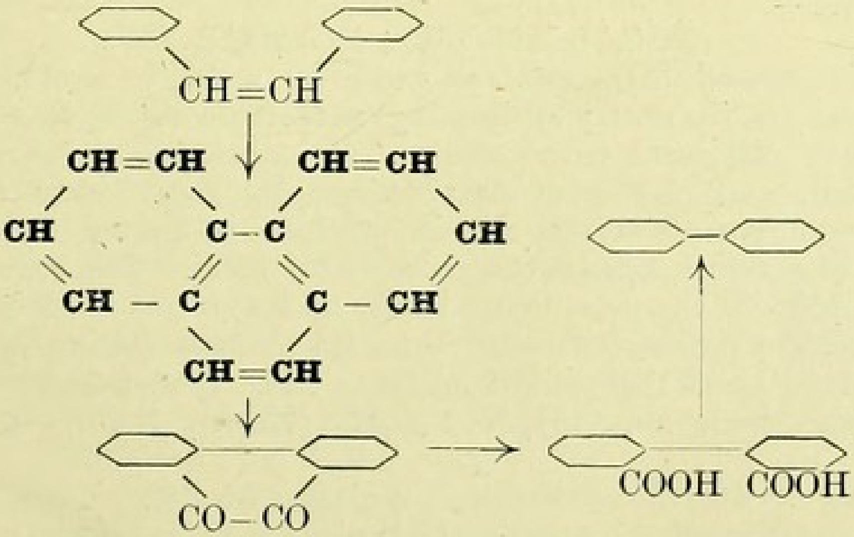
$$\begin{array}{l}C_{10}H_6.CH\\ \dot{C}_{10}H_6.\ddot{C}H\end{array} \rightarrow \begin{array}{l}C_{10}H_6.CO\\ \dot{C}_{10}H_6.\dot{C}O\end{array} \rightarrow \begin{array}{l}C_{10}H_7\\ \dot{C}_{10}H_7.COOH\end{array} \rightarrow \begin{array}{l}C_{10}H_7\\ \dot{C}_{10}H_7\end{array}$$

Synopsis.—Anthracene, phenanthrene, chrysene and picene are coal tar hydrocarbons which resemble naphthalene, but contain three or more benzene rings in their molecules. Anthracene is the mother substance of the natural dye alizarin, which is made synthetically from it.

ANTHRACENE.



PHENANTHRENE.



CHAPTER LXII

THE AZO-COMPOUNDS

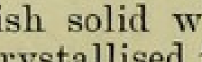
Azobenzene and Azoxybenzene.—The only transformation of the nitro-group that has thus far been dealt with is that involved in its reduction to the amido-group, but an important group of compounds has now to be considered, in which this reduction is arrested at intermediate stages. When for instance nitrobenzene is shaken with a solution of stannous hydroxide in caustic alkali, a red precipitate of an intermediate compound, azobenzene, is slowly thrown down. The same substance is obtained, and with much better yield, by dry-distilling azoxybenzene, a second intermediate compound of this class, with iron filings, or by simply reducing the crude substance (see below) with zinc dust. In any case the product is thoroughly washed with dilute acid and water, and dried and recrystallised from light petroleum—

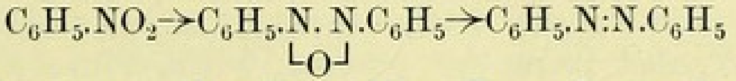
$$C_6H_5.NO_2 \rightarrow C_6H_5.N{:}N.C_6H_5 \leftarrow C_6H_5.\overbrace{N.\ N}^{O}.C_6H_5$$

Azobenzene, $C_6H_5.N{:}N.C_6H_5$ (Mitscherlich, 1834), is a bright orange-red, coarsely crystalline substance, which melts at 68°, and at 293° boils to a deep red vapour. It is chemically indifferent and combines neither with acids nor alkalies, but on further reduction with zinc dust and acetic acid is broken up into aniline—

$$C_6H_5.N{:}N.C_6H_5 + 4H = 2C_6H_5.NH_2.$$

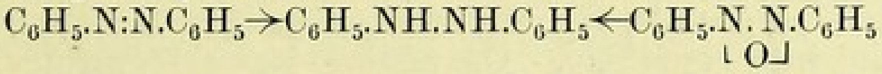
The second intermediate product, azoxybenzene, is readily formed in quantity by boiling nitrobenzene with a solution of sodium ethoxide in alcohol. The metal is dissolved in the alcohol, and the mixture obtained by cautiously adding the nitro-compound to the viscid product is heated for an hour or two in a reflux apparatus on a water-bath. The alcohol is then distilled off from a brine-bath, and the product poured into water, the yellowish solid which separates being well washed and dried, and recrystallised from light petroleum.

Azoxy-benzene,  $C_6H_5.\underbrace{N.N}_{O}.C_6H_5$ (Zinin, 1845), is a bright-yellow crystalline substance, melting at 36°. Like azobenzene it is indifferent to acids and alkalies, and as already mentioned is reduced to the azo-compound when distilled with iron filings—



$$C_6H_5.NO_2 \rightarrow C_6H_5.\underbrace{N.\,N}_{O}.C_6H_5 \rightarrow C_6H_5.N{:}N.C_6H_5$$

Hydrazobenzene: the Benzidine Transformation.—Whilst in acetic acid solution azobenzene is resolved into aniline, in boiling alkaline or alcoholic solution, with zinc dust, it is converted into hydrazo-benzene, a third product intermediate to nitrobenzene and aniline, which is precipitated by the addition of water to the colourless alcoholic solution; it is also obtained by reducing azoxy-benzene with ammonium sulphide—



$$C_6H_5.N{:}N.C_6H_5 \rightarrow C_6H_5.NH.NH.C_6H_5 \leftarrow C_6H_5.\underbrace{N.\,N}_{O}.C_6H_5$$

Hydrazo-benzene or symmetrical diphenyl-hydrazine, $C_6H_5.NH.NH.C_6H_5$ (Hofmann, 1863), is a colourless crystalline substance, which melts at 131°, and resembles camphor in odour. Like azobenzene, it is indifferent to acids and alkalies, and is reduced to aniline by zinc dust and acetic acid, but it is less stable than the coloured product and is readily reoxidised to it, even by the air.

Itself indifferent, hydrazo-benzene is converted by simple digestion with concentrated hydrochloric acid into its highly basic isomeride, benzidine or para-diamido-diphenyl, $NH_2.C_6H_4.C_6H_4.NH_2$ (p. 348). The same transformation is effected by reducing alcoholic azobenzene with tin and hydrochloric acid, the hydrazobenzene at first formed at once undergoing conversion. After distilling off the alcohol, the sparingly soluble benzidine sulphate is precipitated with dilute sulphuric acid, and the base precipitated from this with ammonia. The homologous compounds derived from the nitro-toluenes, etc., are transformed in a similar manner, except when one or both para-positions are already occupied, in which case derivatives of diphenylamine are formed—

$$C_6H_5.N{:}N.C_6H_5 \rightarrow C_6H_5.NH.NH.C_6H_5 \rightarrow NH_2C_6H_4.C_6H_4.NH_2.$$

The constitutions of azobenzene and its relatives rest partly on their relations to nitrobenzene and aniline, and partly on the synthesis of their derivatives from diazo-compounds (below).

Amido-Azobenzene and Diazo-Amidobenzene.—The importance of the azo-compounds lies in that they are the mother substances of a large class of valuable dyes. Although, as already stated, azobenzene is itself intensely coloured, it is of no use as a dye, for being indifferent to acids and bases it does not combine with fibres nor mordants, and cannot be made fast. But by introducing acid or basic groups—hydroxyl, amidogen, etc.—colouring matters are obtained, which, as in the case of indigo, combine with mordants, etc., and can thus be fixed in the fabric. These are the azo-dyes, and azobenzene is on this account termed a chromogen.

The amido-azobenzenes or chrysoidines can be made by nitrating and reducing azobenzene. Amido-azobenzene itself for example is obtained by reducing with ammonium sulphide the nitro-azobenzene made by nitrating the azo-compound. It can be extracted from the product with dilute hydrochloric acid, and after reprecipitating with caustic soda, and washing and drying, can be purified by recrystallisation from light petroleum—

$$C_6H_5.N:N.C_6H_5 \rightarrow C_6H_5.N:N.C_6H_4.NO_2 \rightarrow C_6H_5.N:N.C_6H_4.NH_2.$$

But this and the related dyes are much more easily prepared from diazobenzene and the various amido-benzenes, the diazo-amido-compounds initially formed being converted into the amido-azo-compounds, by a transformation akin to that of hydrazobenzene into benzidine. On adding ice-cold aniline hydrochloride solution, for example, to a similar solution previously diazotised (p. 256), the diazobenzene chloride behaves as an acid chloride, and the crystalline diazo-amidobenzene thus formed can be salted out with sodium acetate. On warming this compound for an hour or so with aniline hydrochloride and aniline, it is converted into amido-azobenzene—

$$C_6H_5.N:N.Cl + NH_2.C_6H_5 \rightarrow C_6H_5.N:N.NH.C_6H_5 \rightarrow C_6H_5.N:N.C_6H_4NH_2.$$

In preparing the amido-azobenzene directly, the process can be much simplified. A concentrated solution of sodium nitrite is simply added to the solution of aniline hydrochloride in the requisite amount of aniline, and after warming the mixture until the change is complete, and no nitrogen is evolved on heating a sample of the product with a little concentrated hydrochloric acid, the dye is precipitated by adding sufficient hydrochloric acid to combine with the excess of aniline. It is then purified as before.

Amido-azobenzene, $C_6H_5.N:N.C_6H_4.NH_2$ (Griess, 1866), is an orange crystalline substance, melting at 123°. Its oxalate, aniline yellow, a steel-blue crystalline substance which dissolves in water to a yellow solution, was one of the first azo-dyes manufactured (Nicholson, 1863). It dyes silk and wool directly, and cotton after mordanting with stannic tannate—stannic chloride and tannin in succession (p. 254). The colour is in all cases a dull and fugitive yellow, but a purer and faster colour, acid yellow, is given by the sodium salt of the corresponding sulphonic acid.

The intermediate diazo-amidobenzene, or diazobenzene-anilide, $C_6H_5.N:N.NH.C_6H_5$ (Griess, 1862), is a golden-yellow, crystalline substance, which melts at 96°, and explodes at a somewhat higher temperature. Like azobenzene, it is practically neutral. As a diazo-compound, however, it is resolved into chlorobenzene, nitrogen and aniline by concentrated hydrochloric acid, and similarly is reduced to aniline and phenyl-hydrazine in the normal manner by zinc dust and alcoholic acetic acid—

$$C_6H_5Cl + N_2 + NH_2.C_6H_5 \leftarrow C_6H_5.N:N.NH.C_6H_5$$
$$\rightarrow C_6H_5.NH.NH_2 + NH_2.C_6H_5.$$

The constitution of amido-azobenzene follows both from its direct formation from azobenzene (p. 377), and from its quantitative resolution into aniline and paraphenylene-diamine when boiled with a solution of stannous chloride in concentrated hydrochloric acid—

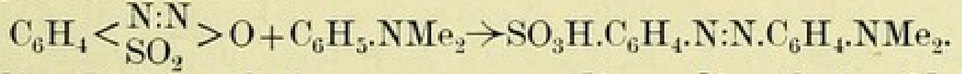
$$C_6H_5.N{:}N.C_6H_4.NH_2 + 4H = C_6H_5.NH_2 + NH_2.C_6H_4.NH_2.$$

Other Azobenzene Derivatives.—By introducing more amido-groups into the azobenzene molecule, browner tints are obtained, whilst by alkylating the amido-groups, the colour is as usual shifted towards the red end of the spectrum. The diamido-compound is made from the diazo-salt and metaphenylene-diamine, whilst the triamido-compound is formed by the direct action of nitrous acid on the same diamine, half the latter being converted into the diazo-amido-compound, with which the other half then interacts—

$$NH_2.C_6H_4.N{:}N.NH.C_6H_4.NH_2 \rightarrow NH_2.C_6H_4.N{:}N.C_6H_3(NH_2)_2.$$

Diamido-azobenzene hydrochloride or chrysoidine, $C_6H_5.N{:}N.C_6H_3(NH_2)_2, HCl$, is a deep red crystalline substance, which dyes silk and wool yellow, and cotton mordanted with tannin a dark yellow. Triamido-azobenzene hydrochloride, $NH_2.C_6H_4.N{:}N.C_6H_3(NH_2)_2,HCl$ (Caro and Griess, 1867)—Bismarck or Manchester brown—is a crystalline substance which dyes leather and mordanted cotton dark brown.

The alkyl-amido-azobenzenes are formed by the direct action of the diazo-chlorides on the alkyl-anilines, the formation of an intermediate diazo-amido-compound here being impossible, as both amido-hydrogen atoms are replaced. Methyl orange, for example, is made from diazobenzene sulphonate and dimethyl-aniline. The sulphonate is made by diazotising sodium sulphanilate in the usual manner with the exact amount of sodium nitrite and hydrochloric acid, and on adding the solution of the amine hydrochloride followed by a slight excess of caustic soda, the dye is formed, and can be precipitated with salt—



$$C_6H_4 < \genfrac{}{}{0pt}{}{N{:}N}{SO_2} > O + C_6H_5.NMe_2 \rightarrow SO_3H.C_6H_4.N{:}N.C_6H_4.NMe_2.$$

Helianthin, methyl orange, or sodium dimethylamido-azobenzene sulphonate, $NMe_2.C_6H_4.N{:}N.C_6H_4.SO_3Na$ (Griess, 1877), is an orange crystalline powder, which dissolves in water to a yellow solution. The free acid is dark red in colour, and thus serves as an indicator in alkalimetry. It is especially valuable as it is not liberated by carbonic nor hydrosulphuric acids, nor as a rule by acid salts. Methyl orange is not used as a dye on account of this sensitiveness.

Its constitution is proved by its reduction to sulphanilic acid and paramido-dimethylaniline, when a hydrochloric acid solution of stannous chloride is added to its hot concentrated solution. The acid crystallises out, and the diamine can be liberated from the residue with caustic soda and extracted with ether. The constitutions of all azo-compounds are determined by reduction in this manner.

The hydroxy-azo-benzenes or tropœolines are made in much the same way as the amido-azo-compounds, the diazotised solution being slowly run into the cold slightly alkaline solution of the phenol, and the product precipitated with salt.

Sodium dihydroxy-azobenzene-sulphonate, $SO_3Na.C_6H_4.N{:}N.C_6H_4(OH)_2$, or tropœolin O dyes silk and wool deep yellow in an acid bath.

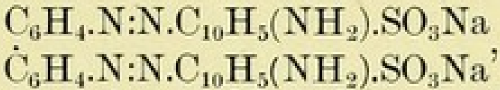
Naphthalene Azo-Compounds. — Naphthalene forms azo-compounds of the same character as those of benzene, the azo-group in some cases being linked to two naphthyl radicles, and in others to a naphthyl and a benzenoid radicle. On passing nitrous anhydride into *α*-naphthylamine, for example, the diazo-naphthalene nitrite interacts with a further quantity of the base, just as with aniline, and diazo-amidonaphthalene is formed, an unstable crystalline substance resembling the corresponding benzene compound; and similarly when this is heated with naphthylamine, it is transformed into amido-azonaphthalene.

Amido-azonaphthalene, $C_{10}H_7.N{:}N.C_{10}H_6.NH_2$, is a brownish-red crystalline substance, and its sulphonic acids, which are formed in the same way from the naphthylamine sulphonic acids, are used as dyes. The hydroxy-sulphonate, roccellin, or sodium hydroxy-azonaphthalene-sulphonate, $SO_3Na.C_{10}H_6.N{:}N.C_{10}H_6.OH$, formed from diazo-naphthionic acid and β-naphthol, is a cochineal red dye, and has largely supplanted natural cochineal; whilst the mixed azo-compound, Orange II, $SO_3Na.C_6H_4.N{:}N{:}C_{10}H_6.OH$, made from β-naphthol and diazo-benzene-sulphonic acid, dyes a deep yellow.

Pure red dyes are obtained by the action of the diazo-alkyl-benzenes on the naphthylamines and their derivatives, the scarlet dye "Ponceau 2R," $C_6H_3Me_2.N{:}N.C_{10}H_4(SO_3Na)_2.OH$, for example, being made from diazo-xylene chloride and β-naphthol-sulphonic acid. Many such dyes have been made, of all shades from brown to scarlet.

The Disazo-Compounds.—The simple azo-dyes are fast only on mordanted cotton, but a series of more complex compounds have been made which dye vegetable fibres directly. They all contain two azo-groups, and most of them are made from benzidine. When the latter is diazotised, it forms a double diazo-compound, tetrazo-diphenyl chloride, $Cl.N{:}N.C_6H_4.C_6H_4.N{:}N.Cl$, and this unites with phenyl, etc., in the same way as the simple diazo-salts, but with two radicles, instead of with one.

The benzidine azo-dyes are termed Congo dyes, from the first of the class, Congo red, a dye made by the action of diazotized benzidine on naphthionic acid.

Congo red,  $\begin{array}{l}C_6H_4.N:N.C_{10}H_5(NH_2).SO_3Na \\ | \\ C_6H_4.N:N.C_{10}H_5(NH_2).SO_3Na\end{array}$, is a scarlet powder, which dyes cotton a fast reddish brown. The free acid is blue, and the colour is thus apt to become dull on exposure to the atmosphere.

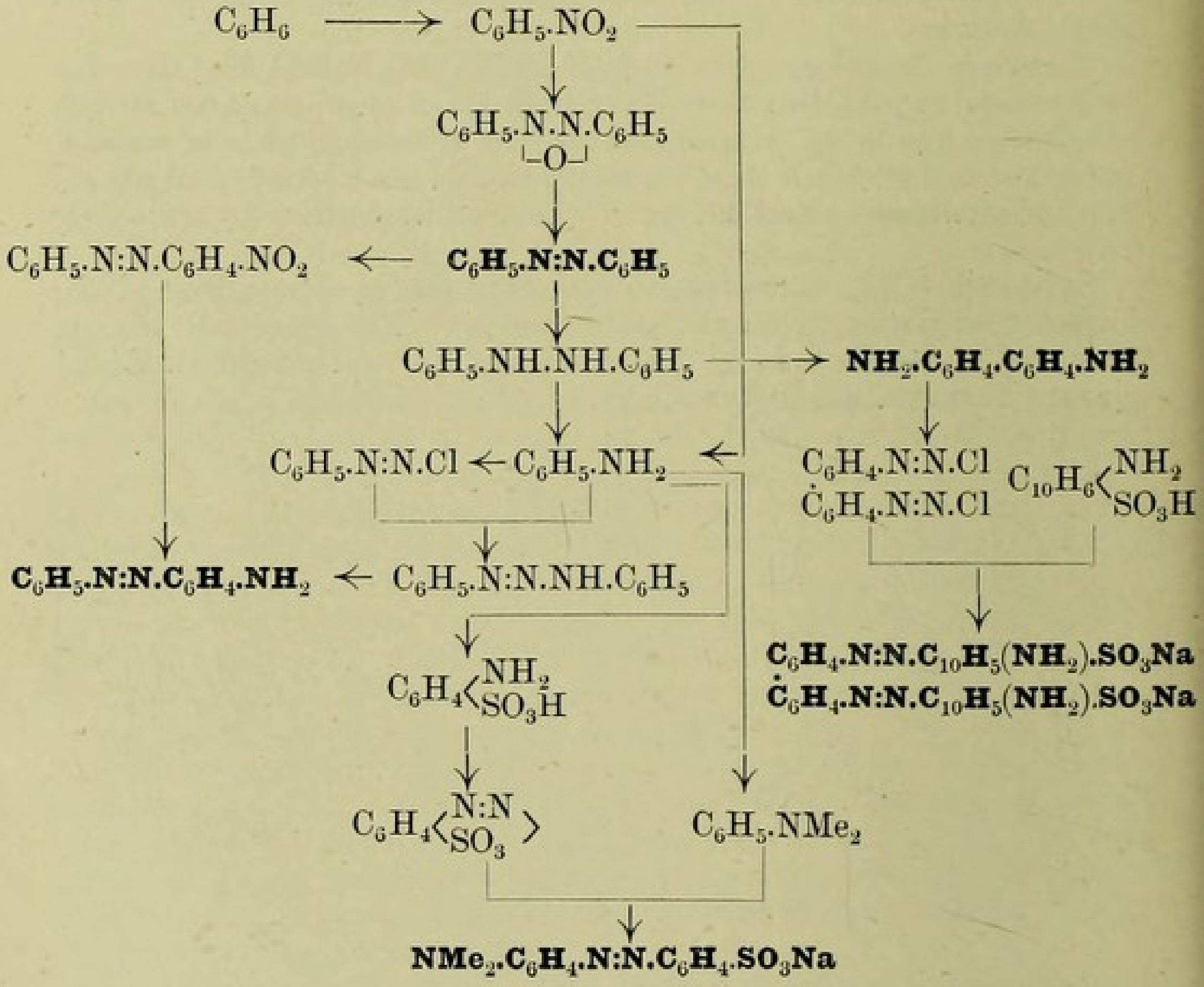
Benzopurpurin, from tolidine (the toluene analogue of benzidine) and β-naphthylamine sulphonic acid, dyes unmordanted cotton scarlet, whilst chrysamine, from benzidine and sodium salicylate, is a pure yellow dye.

Another class of dis-azo-compounds are formed by diazotising the amido-azo-compounds, and then combining them with fresh radicles.

Biebrich scarlet, $SO_3Na.C_6H_4.N:N.C_6H_4.N:N.C_{10}H_6.OH$, for instance, a crystalline powder which dyes unmordanted cotton scarlet, is made by the action of the diazo-chloride of amido-azobenzene-sulphonic acid on β-naphthol. As already indicated, the constitutions of these products are determined by reducing them.

Synopsis.—The azo-compounds contain in the group N:N, linked to benzene or naphthalene nuclei. They are all highly coloured substances, and in combination with acid or basic groups form valuable dye-stuffs.

THE AZO-COMPOUNDS.



SECTION XVI

RING COMPOUNDS OF NITROGEN AND OTHER ELEMENTS

CHAPTER LXIII

PYRIDINE AND THE QUINOLINES

Quinoline.—In addition to the alkaloids of the uric acid group, such as caffeïne, and the open-chain animal alkaloids, such as neurine and the ptomaïnes, there are a number of basic nitrogenous substances occurring in plants, which also have very marked physiological actions. These are the vegetable alkaloids. They are derivatives either of the quinolines, or of the simpler base pyridine.

Quinoline is formed when quinine is distilled with solid potash (Gerhardt, 1842), and also occurs in coal tar, and in the tar or oil made by distilling bones. It was originally obtained from the second source; the tar-oil being extracted with dilute sulphuric acid, and the quinoline sulphate purified by repeated crystallisation. The base, however, is best prepared synthetically from aniline and glycerol (Skraup, 1880).

On mixing these two liquids with concentrated sulphuric acid and nitrobenzene, a vigorous action sets in, after which the mixture is boiled for some hours. The diluted acid product is distilled with steam to remove excess of nitrobenzene, and after making strongly alkaline with caustic soda, the quinoline and excess of aniline are distilled off in the same manner. Sodium nitrite is next added to the dilute sulphuric acid solution of the distillate, and the liquid warmed to convert the aniline into phenol, and on now rendering the product strongly alkaline with caustic soda, and again distilling with steam, the quinoline passes over alone. It is extracted from the distillate with ether and simply re-distilled, drying being unnecessary on account of the high boiling point of the liquid. The nitro-benzene serves merely as an oxidising agent, and is reduced to aniline—

$$C_6H_5.NH_2+C_3H_8O_3+O=C_9H_7N+4H_2O.$$

Quinoline, C_9H_7N (Runge, 1834), is a colourless, highly refractive liquid of aniseed odour. It boils at 239°, and is slightly heavier than water, in which it is only sparingly soluble. It is a powerful antiseptic, and highly basic. That it is an aminoid compound is shown by its forming crystalline additive salts with acids, such as the hydrochloride, C_9H_7N,HCl; and double metallic salts, such as the orange, crystalline platinochloride, $(C_9H_7N,HCl)_2,PtCl_4$. Further, it is a tertiary amine, for when heated with methyl iodide it is converted into quinoline methiodide, C_9H_7N,CH_3I, a crystalline compound analogous to tetramethyl-ammonium iodide, NMe_3,CH_3I.

Quinoline is only partially resistent to oxidising agents, and when boiled with neutral permanganate solution for many hours, it is oxidised to quinolinic acid (p. 390), a crystalline substance which can be extracted from the acidified product with ether.

Pyridine.—When quinolinic acid is distilled with lime, it is resolved in the normal manner into carbon dioxide and pyridine, of which it is thus the dicarboxylic acid—

$$C_9H_7N \rightarrow C_5H_3N(COOH)_2 \rightarrow C_5H_5N + 2CO_2.$$

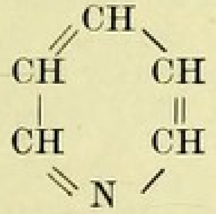
Pyridine occurs in quantity in bone-oil, from which it was first obtained by extraction with dilute acid, and it can be directly synthesised also from acetylene and hydrogen cyanide by passing the mixed vapours through a red-hot tube—

$$2C_2H_2 + HCN = C_5H_5N.$$

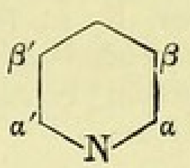
Pyridine, C_5H_5N (Anderson, 1849), is a colourless liquid, which boils at 114°, and soon oxidises and turns brown in the air. Its odour is rank and unpleasant. Like quinoline it is a tertiary amine, as it forms a similar hydrochloride, platinochloride and methiodide. It is a stronger base however, and is miscible with water, and it is much more stable and scarcely affected by oxidising agents.

As the nucleal constituent of the vegetable alkaloids, pyridine is a substance of great importance. Although a tertiary amine, and highly basic, in its general behaviour it bears a strong resemblance to benzene. There is far less hydrogen present than is required to saturate the carbon and nitrogen, yet the substance does not form additive compounds with halogen, nor is it oxidised by nitric acid. Like benzene, it is either resistant to oxidising agents, or else entirely broken up by them, and in its behaviour with reducing agents it also resembles the aromatic hydrocarbon. Thus when digested with sodium amalgam in alcoholic solution, pyridine takes up hydrogen in exactly the same proportion as benzene, forming hexahydropyridine, or piperidine, $C_5H_{11}N$, just as benzoic acid is reduced to hexahydro-benzoic acid. Conversely piperidine can be reconverted into pyridine by oxidising it with concentrated sulphuric acid at 300°.

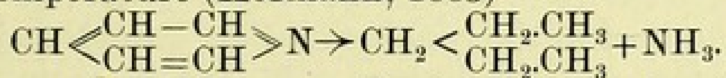
This general analogy to benzene suggests that pyridine is a ring compound, analogous to the hydrocarbon in constitution, and that its formula is derived from that of benzene by the substitution of a nitrogen atom for a methine group (Körner 1869)—



or



This view is borne out by the conversion of pyridine into ammonia and normal pentane when heated with hydriodic acid at a high temperature (Hofmann, 1883)—



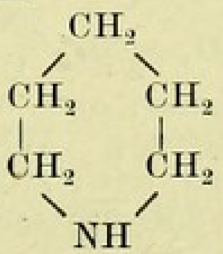
$$\mathrm{CH}{<}\begin{array}{l}\mathrm{CH-CH}\\ \mathrm{CH=CH}\end{array}{>}\mathrm{N}\rightarrow\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CH_2.CH_3}\\ \mathrm{CH_2.CH_3}\end{array}+\mathrm{NH_3}.$$

and is fully confirmed by a synthesis through piperidine.

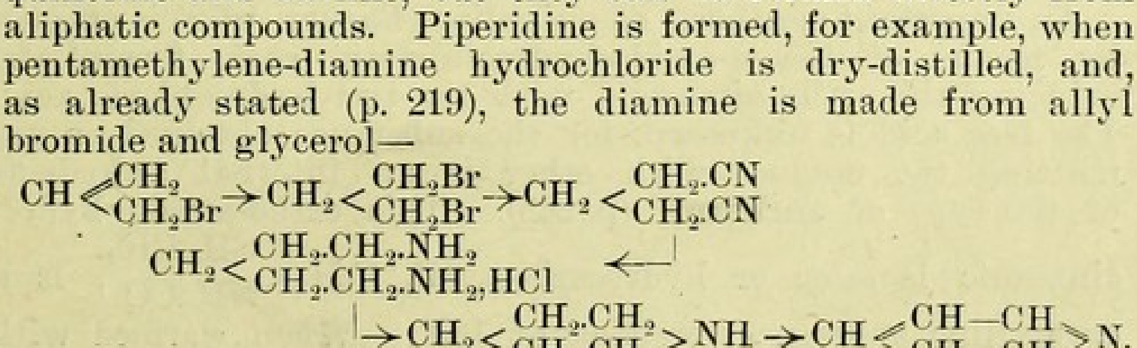
Piperidine.—Piperidine, $C_5H_{11}N$ (Cahours, 1853), is a colourless liquid, which boils at 106°, and has a sharp odour, akin to that of pepper, but ammoniacal. It was originally obtained by hydrolysis of the alkaloid piperine, the crystalline active constituent of black pepper. When piperine is distilled with soda-lime, it is resolved into piperic acid, a complex derivative of cinnamic acid, and the volatile piperidine, with which the acid is combined in amide form.

Piperidine forms a crystalline, additive hydrochloride and a platinochloride, and is thus an amine, but unlike pyridine and quinoline it is a secondary amine, for it forms a yellow, oily nitroso-compound, nitroso-piperidene, $C_5H_{10}N.NO$, when mixed with nitrous acid. With methyl iodide, again, it interacts violently, forming methyl-piperidine, $C_5H_{10}N.CH_3$, a basic liquid boiling at 107°, and a tertiary amine.

Piperidine is thus represented by a ring formula analogous to that of hexahydrobenzene—



Pyridine and piperidine can not only be synthesised from quinoline and aniline, but they can be formed directly from aliphatic compounds. Piperidine is formed, for example, when pentamethylene-diamine hydrochloride is dry-distilled, and, as already stated (p. 219), the diamine is made from allyl bromide and glycerol—

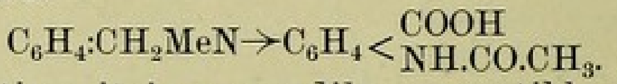


$$\mathrm{CH}{\ll}\begin{array}{l}\mathrm{CH_2}\\ \mathrm{CH_2Br}\end{array}\rightarrow\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CH_2Br}\\ \mathrm{CH_2Br}\end{array}\rightarrow\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CH_2.CN}\\ \mathrm{CH_2.CN}\end{array}$$

$$\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CH_2.CH_2.NH_2}\\ \mathrm{CH_2.CH_2.NH_2,HCl}\end{array}\leftarrow$$

$$\rightarrow\mathrm{CH_2}{<}\begin{array}{l}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{array}{>}\mathrm{NH}\rightarrow\mathrm{CH}{<}\begin{array}{l}\mathrm{CH-CH}\\ \mathrm{CH=CH}\end{array}{>}\mathrm{N}.$$

Constitution of Quinoline.—The constitution of quinoline follows from its dual relation to benzene and pyridine. Since it is formed from benzene by means of ordinary agents and at low temperatures, it is practically certain that the benzene nucleus is intact, and that this is actually so is proved by the oxidation of *a*-methyl-quinoline (p. 391) to acetyl-anthranilic acid by nitric acid—

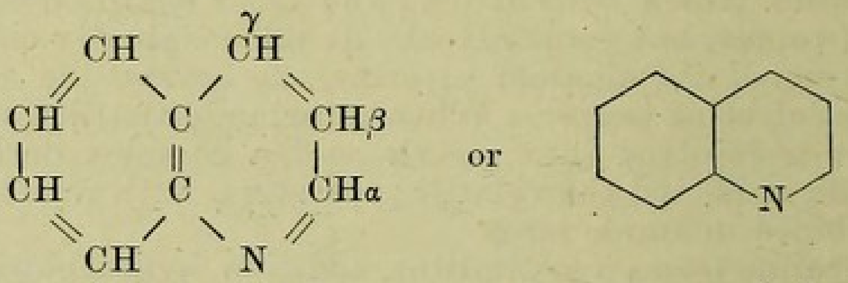


$$C_6H_4{:}CH_2MeN \rightarrow C_6H_4<\begin{matrix}COOH\\NH.CO.CH_3.\end{matrix}$$

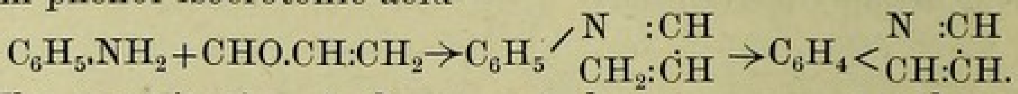
At the same time it is so readily convertible into pyridine that it must be a derivative of the latter—

$$C_5H_3N{:}C_4H_4 \rightarrow C_5H_3N(COOH)_2 \rightarrow C_5H_5N + 2CO_2.$$

These facts lead to the conclusion that quinoline is analogous in constitution to naphthalene, and that its molecules consist of benzene and pyridine nuclei having two carbon atoms in common—

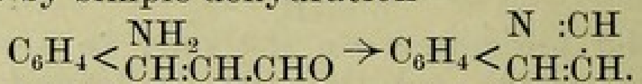


Quinoline thus bears the same relation to naphthalene as pyridine to benzene. The mechanism of its synthesis from aniline and glycerol can now be understood. Acroleïn is formed by the dehydration of the glycerol and condenses with the aniline to acroleïn-aniline, $C_6H_5.N{:}CH.CH{:}CH_2$. This is then oxidised by the nitrobenzene, the end carbon uniting with the benzene ring in the same way as in the synthesis of *a*-naphthol from phenol-isocrotonic acid—

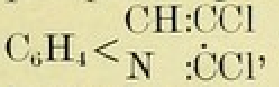


$$C_6H_5.NH_2 + CHO.CH{:}CH_2 \rightarrow C_6H_5\diagup\begin{matrix}N\ \ {:}CH\\CH_2{:}CH\end{matrix} \rightarrow C_6H_4<\begin{matrix}N\ \ {:}CH\\CH{:}\dot{C}H.\end{matrix}$$

The constitution is borne out by numerous syntheses of quinoline and its derivatives. When, for instance, *o*-amido-cinnamaldehyde is heated with zinc chloride it is converted into quinoline by simple dehydration—

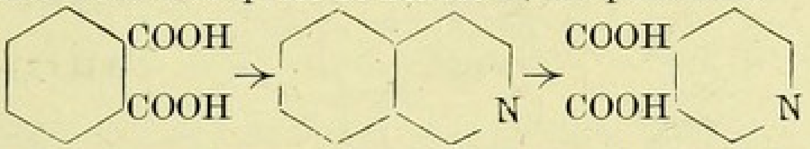


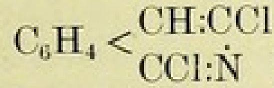
$$C_6H_4<\begin{matrix}NH_2\\CH{:}CH.CHO\end{matrix} \rightarrow C_6H_4<\begin{matrix}N\ \ {:}CH\\CH{:}\dot{C}H.\end{matrix}$$

An important synthesis of quinoline (Baeyer, 1879) is effected by means of the *o*-amido-hydrocinnamic acid, formed by reducing the ortho-nitro-acid with tin and hydrochloric acid. The free acid is unknown, for the substance obtained on extracting the product with ether is an internal anhydride of the type of anthranil (p. 265). This ortho-amido hydrocinnamic lactame or hydrocarbostyril, $C_6H_4<\begin{matrix}CH_2.CH_2\\NH\ .\dot{C}O\end{matrix}$, is a crystalline substance, melting at 163°. When warmed with phosphorus pentachloride it is converted into dichloroquinoline,  $C_6H_4<\begin{matrix}CH:CCl\\ N\ \ :\dot{C}Cl\end{matrix}$, a crystalline substance, which is reduced to the base when heated with hydriodic acid.

Isoquinoline.—Since the nitrogen in quinoline is in the β-position of the naphthalene ring, an isomeric compound may be expected in which it occupies the α-position. This compound is known in isoquinoline.

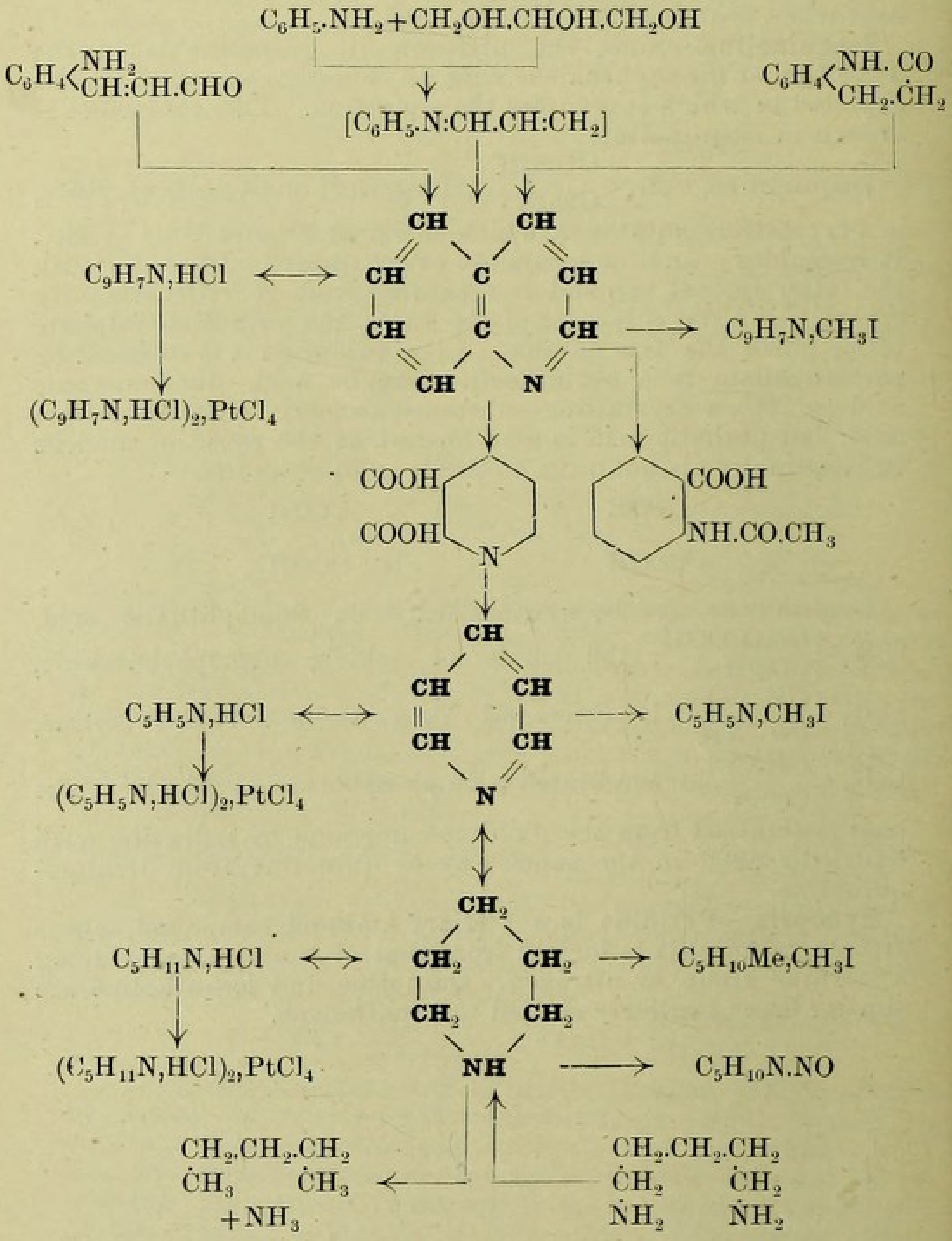
Isoquinoline,  $C_6H_4<\begin{matrix}CH:CH\\ CH:\dot{N}\end{matrix}$ (Hoogewerf and Van Dorp, 1885), is a crystalline substance, which melts at 23° and boils at 240°. It resembles quinoline in almost every respect. It occurs with the latter in coal tar, and is separated from it by fractionally crystallising the sulphates of the bases, the quinoline sulphate being much the less soluble. Like quinoline it is oxidised by permanganate to a pyridine-dicarboxylic acid, cinchomeronic acid (p. 390), a crystalline substance isomeric with quinolinic acid; but phthalic acid is also formed, as the pyridine nucleus in isoquinoline is not quite so stable as in quinoline—



Isoquinoline can be synthesised from homophthalic acid,  $C_6H_4<\begin{matrix}CH_2.COOH\\ COOH\end{matrix}$, the imide of which, homophthalimide,  $C_6H_4<\begin{matrix}CH_2.\dot{C}O\\ CO\ .\dot{N}H\end{matrix}$, is converted into a dichlor-isoquinoline,  $C_6H_4<\begin{matrix}CH:CCl\\ CCl:\dot{N}\end{matrix}$, when heated with phosphorus oxychloride. The base is obtained from the dichloro-compound by reduction with hydriodic acid, in the same way as quinoline from dichloroquinoline.

Synopsis.—Pyridine is a tertiary aminoid compound, whose structural formula is formed from that of benzene by replacing a methine group by nitrogen. Quinoline and isoquinoline are similar bases similarly related to naphthalene.

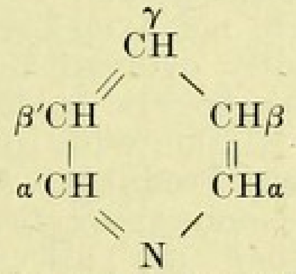
PYRIDINE AND QUINOLINE.



CHAPTER LXIV

DERIVATIVES OF PYRIDINE AND QUINOLINE

The Methyl-Pyridines.—The isomerism of the substitution products of pyridine resembles that of the benzene derivatives of the next higher order. Thus there are three methyl-pyridines, the positions $\alpha\alpha'$, $\beta\beta'$, and γ being differently situate with regard to the nitrogen atom—

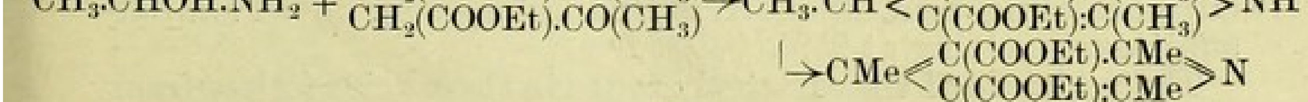


The mono-, di- and tri-methyl-pyridines, which are known respectively as the picolines, lutidines, and collidines, are liquids resembling pyridine. Some of them accompany it in bone-tar, but they are for the most part made in other ways.

α-Picoline, for example, is formed by heating pyridine methiodide, in much the same way as *o*-toluidine from methylaniline. β-Picoline can be isolated from bone-tar, but it is also formed when strychnine is dry-distilled, and can be synthesised by heating acroleïn-ammonia with a dehydrating agent, such as zinc chloride.

Symmetrical or $\alpha\alpha'\gamma$-collidine is readily synthesised from ethyl acetoacetate and aldehyde ammonia, and the synthesis is of importance on account of its general applicability (Hantzsch, 1882). On warming the aldehyde derivative with the acetoacetate, it dissolves, and much heat is evolved, the liquid boiling. The action is completed by boiling the product for a few minutes. Ethyl dihydrocollidine-dicarboxylate is thus formed, and may be isolated as a crystalline substance melting at 131°.

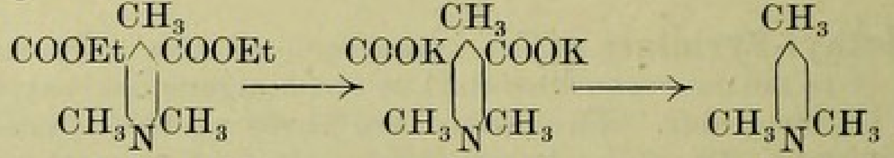
To obtain the collidine, however, the crude product is dissolved in alcohol, and oxidised by passing nitrous anhydride into the cooled solution, until a sample is entirely soluble in hydrochloric acid—



$$CH_3.CHOH.NH_2 + \begin{matrix} CH_2(COOEt).CO(CH_3) \\ CH_2(COOEt).CO(CH_3) \end{matrix} \rightarrow CH_3.CH < \begin{matrix} C(COOEt):C(CH_3) \\ C(COOEt):C(CH_3) \end{matrix} > NH$$

$$\rightarrow CMe \lessgtr \begin{matrix} C(COOEt).CMe \\ C(COOEt):CMe \end{matrix} \gtrless N$$

The ethyl collidine-dicarboxylate, a liquid boiling at 309°, which separates on making the product alkaline with sodium carbonate, is extracted with ether, and purified by fractionation. It is then hydrolysed by boiling with concentrated alcoholic potash on a water bath for some hours. The potassium salt, which crystallizes out on cooling, is distilled with lime, and the collidine passes over, and is purified by fractioning its dry ethereal solution. It is a liquid resembling pyridine, and boiling at 172°—



The methyl-pyridines resemble the methyl-benzenes in their behaviour with oxidising agents, but are somewhat more resistent. Thus they are not attacked by nitric or chromic acids, but they are readily oxidised by permanganate to the corresponding pyridine-carboxylic acids, from which pyridine itself is obtained by distillation with lime.

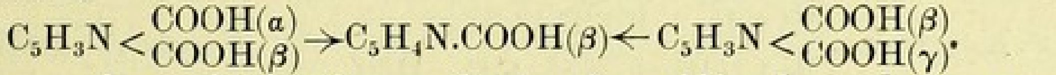
Pyridine Substitution Products.—According to the ring formula, three pyridine-mono-carboxylic acids are possible, and three are known. They are all crystalline substances. Picolinic acid, formed by the oxidation of α-picoline, melts at 135°. Nicotinic acid, formed by the oxidation of β-picoline and nicotine (p. 395), and also by direct synthesis from pyridine, melts at 229°. Isonicotinic acid, which is formed by oxidation of γ-picoline, sublimes when heated under ordinary pressure, but melts at 309° when heated in a closed tube. These acids, which are of frequent occurrence amongst the oxidation products of the alkaloids, are thus readily identified. The pyridine mono-carboxylic acids resemble the amido-acids in general behaviour, and form salts with both metals and acids.

The synthesis of nicotinic or pyridine-β-carboxylic acid from pyridine is precisely parallel to that of benzoic acid from benzene. When pyridine is heated with concentrated sulphuric acid, pyridine-β-sulphonic acid is formed, which may be isolated in the usual manner; and on dry-distilling the sodium sulphonate with potassium cyanide, it is converted into the corresponding β-cyano-pyridine, $C_5H_4N.CN$. From this crystalline substance, the nicotinic acid can be obtained by the usual hydrolysis—

$$C_5H_5N \rightarrow C_5H_4.SO_3H \rightarrow C_5H_4.SO_3Na \rightarrow C_5H_4N.CN \rightarrow C_5H_4N.COOH$$

The six dicarboxylic acids, the isomerism of which resembles that of the bromo-xylenes, are crystalline substances resembling the mono-carboxylic acids. Quinolinic, or pyridine-αβ-dicarboxylic acid, is a crystalline substance melting at 190°, and cinchomeronic acid, the corresponding βγ-acid, is a similar substance, melting at 259°.

The positions of the carboxyl groups in these acids follow from their formation from quinoline and isoquinoline, and those of the groups in the mono-acids, and thus in the other mono-substitution products, are determined by the genetic relations of the two sets of acids. By distilling the dicarboxylic acids with a single equivalent of alkali, they are converted into the mono-carboxylic acids, in the same way as phthalic into benzoic acid. Now quinolinic acid yields nicotinic acid alone, whilst cincho-meronic acid yields both nicotinic and isonicotinic acid. The nicotinic carboxyl is thus common to both dicarboxylic acids, and is therefore in the β-position. The isonicotinic carboxyl is therefore in the γ-position, and that of picolinic acid in the α-position—



$$C_5H_3N<\begin{matrix}COOH(\alpha)\\COOH(\beta)\end{matrix}\rightarrow C_5H_4N.COOH(\beta)\leftarrow C_5H_3N<\begin{matrix}COOH(\beta)\\COOH(\gamma)\end{matrix}.$$

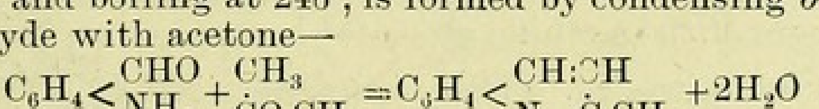
Many other substitution products of pyridine have been prepared, such as the chloro-pyridines, and the hydroxy-pyridines, or pyridine phenols. β-Hydroxypyridine, for example, is formed from the sodium β-sulphonate, in the same way as phenol from the benzene-sulphonate, and possesses the phenol character.

Pyridine cannot be nitrated, and the amido-pyridines have therefore to be made indirectly. Dihydroxypyridine, however, is directly convertible into a nitro-compound resembling the nitro-phenols. The corresponding trihydroxy-compound is a powerful reducing agent like pyrogallol.

Derivatives and Analogues of Quinoline.—Quinoline can be chlorinated, sulphonated and nitrated, and on account of the asymmetry of its molecule, the isomerism of its substitution products is very complex.

Thus there are seven monocarboxylic acids. Cinchoninic or quinoline-γ-carboxylic acid, for example (see p. 398), is a crystalline substance which is formed by the oxidation of cinchonine, and which is resolved into carbon dioxide and quinoline by distillation with lime.

Some of the methyl-quinolines can be formed synthetically. Thus quinaldine, or α-methylquinoline, a liquid resembling quinoline, and boiling at 246°, is formed by condensing *o*-amidobenzaldehyde with acetone—



$$C_6H_4<\begin{matrix}CHO\\NH_2\end{matrix}+\begin{matrix}CH_3\\\dot{C}O.CH_3\end{matrix}=C_6H_4<\begin{matrix}CH:CH\\N\ \ :\dot{C}.CH_3\end{matrix}+2H_2O$$

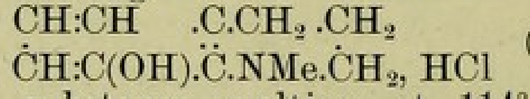
On oxidation with permanganate it yields quinoline-carboxylic acid, whilst with nitric acid, as already stated, acetamido-benzoic acid is formed.

Other quinoline substitution products can be formed synthetically. Thus carbostyril, or α-hydroxyquinoline, a white crystalline substance melting at 199°, is formed by reducing the *o*-nitro-cinnamic acid with tin and hydrochloric acid, the amido-group of the amido-acid at once condensing with the carboxyl—

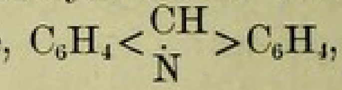
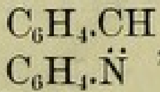
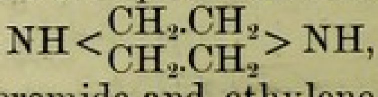
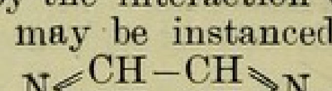
$$C_6H_4<\begin{matrix}NO_2\\CH:CH.COOH\end{matrix}\rightarrow C_6H_4<\begin{matrix}NH_2\\CH:CH.COOH\end{matrix}\rightarrow C_6H_4<\begin{matrix}N\ \ :C(OH)\\CH:\dot{C}H\end{matrix}$$

Quinoline, as already noted, is a tertiary amine, and, like pyridine, can be reduced to a secondary amine. When it is digested with tin and hydrochloric acid, for example, the pyridine ring alone is reduced, the benzene ring only being affected by more powerful agents. The tetrahydroquinoline which is thus formed, can be isolated in the usual manner.

Tetrahydroquinoline,  $C_6H_4<\begin{array}{l}CH_2.CH_2\\ NH\,.\dot{C}H_2\end{array}$, is a crystalline substance which melts at a low temperature, and, as a secondary amine, forms a nitroso-compound, etc. The phenolic derivative of methyl-tetrahydroquinoline is used as an antipyretic, the hydrochloride being known as kairine.

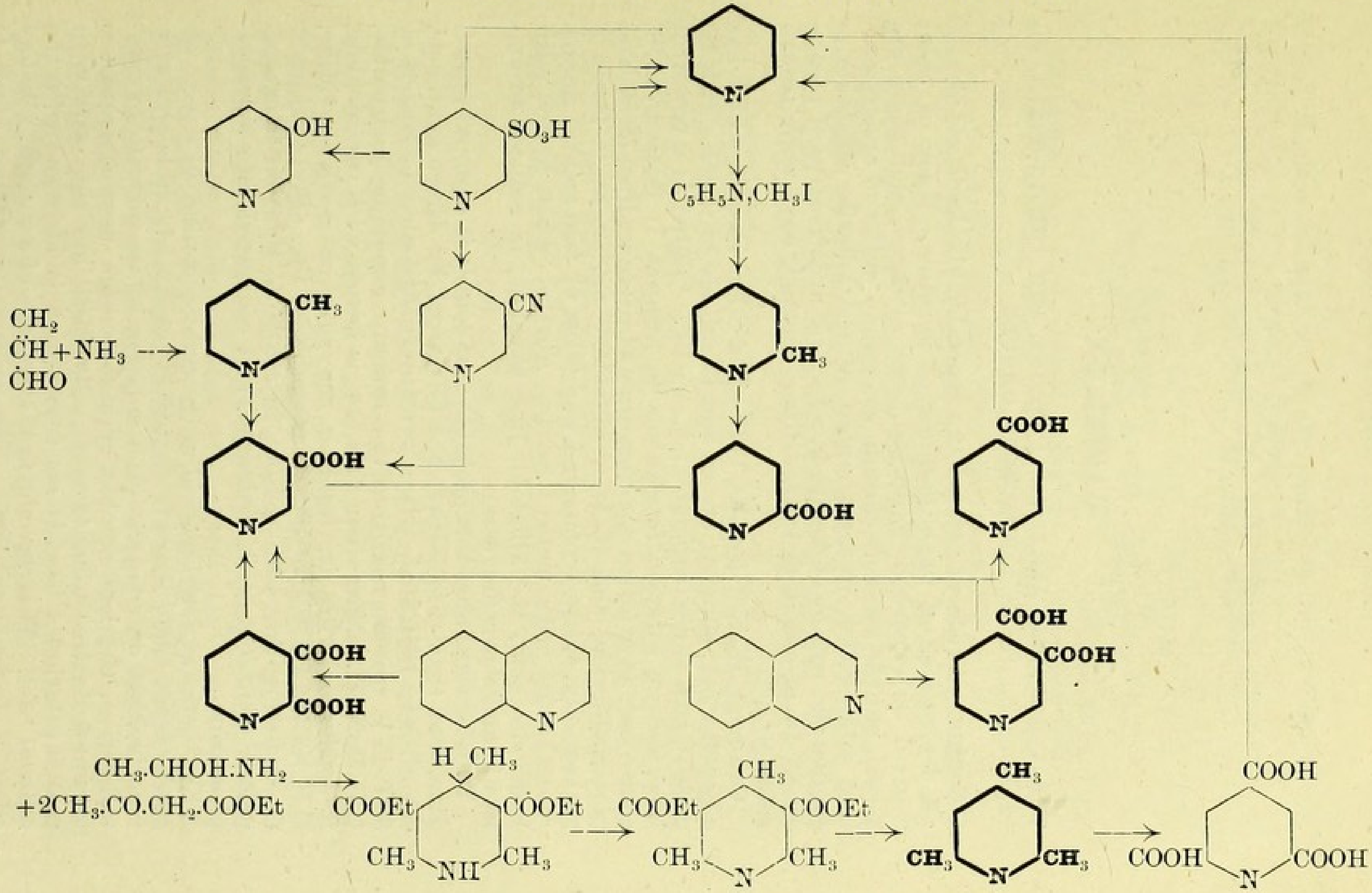
Kairine,  $\begin{array}{l}CH{:}CH\quad .C.CH_2\,.CH_2\\ \dot{C}H{:}C(OH).\ddot{C}.NMe.\dot{C}H_2,\ HCl\end{array}$ (O. Fischer, 1883), a crystalline substance melting at 114°, is made from the hydroxy-quinoline prepared from *o*-amidophenol by the glycerol synthesis. The hydroxy-quinoline is reduced to the tetrahydro-derivative, and this secondary base is heated with methyl iodide. The methyl-derivative is then dissolved in hydrochloric acid, and the hydrochloride recrystallised.

The glycerol synthesis is of very general applicability, and most ring amido-compounds, provided an ortho-position is unoccupied, condense in the same way as aniline. Naphthylamine and anthramine, for example, thus form naphthoquinoline and anthraquinoline, which are substances analogous to quinoline in their chemical behaviour. The first substance prepared in this way was alizarine blue, a blue dye made from amido-alizarine (Prud'homme, 1877).

Many ring compounds have been synthesised analogous to quinoline and pyridine. Acridine,  $C_6H_4<\begin{array}{c}CH\\ \dot{N}\end{array}>C_6H_4$, and phenanthridine,  $\begin{array}{l}C_6H_4.CH\\ C_6H_4.\ddot{N}\end{array}$, for example, are bases which bear much the same relation to anthracene and phenanthrene as quinoline to naphthalene. Ring compounds have also been made, in which two or more of the methine groups of benzene or naphthalene are replaced by nitrogen. The piperazine,  $NH<\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}>NH$, formed by the interaction of ethylene dibromide and ethylene diamine, may be instanced, and the related ditertiary amine, pyrazine,  $N<\begin{array}{l}CH-CH\\ CH=CH\end{array}>N$, a similar crystalline compound.

Synopsis.—Pyridine and quinoline form substitution products, alkyl derivatives, and reduction products, which resemble those of benzene and naphthalene in constitution, but owing to the presence of the nitrogen differ from them in isomerism and general properties.

PYRIDINE AND QUINOLINE SUBSTITUTION-PRODUCTS.



CHAPTER LXV

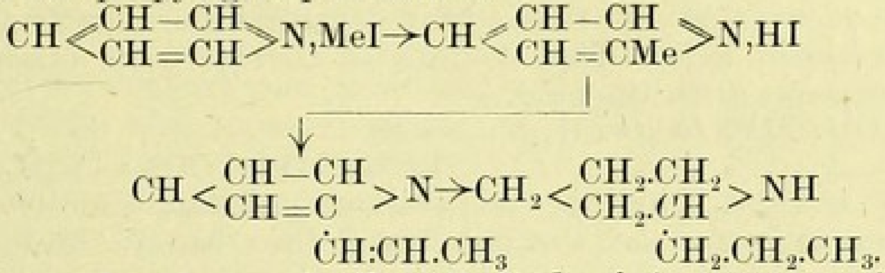
THE VEGETABLE ALKALOIDS: CONINE AND THE TROPINE AND CINCHONA GROUPS

Conine.—As already stated, the vegetable alkaloids are almost all derivatives of the quinolines or pyridine. Some of them contain only carbon, hydrogen, and nitrogen, and these are liquid, but the majority contain oxygen as well, and are crystalline solids. One of the simplest of the volatile alkaloids is conine, the poison of hemlock, which is a derivative of piperidine. It is obtained by distilling hemlock seed with potash solution.

Conine, $C_8H_{17}N$ (Giesecke, 1827), is a colourless oil, which has a penetrating, pungent odour, and is soluble in water. It boils at 167°, and is dextrogyrate, $[\alpha]_D = +18°$. Conine is a powerful base, and its solution is alkaline to litmus. It is an aminoid compound, as it forms a crystalline additive hydrochloride and platinochloride, and it is a secondary amine, as it forms a yellow, oily, nitroso-compound, and takes up two methyl groups when heated with methyl iodide. Further, when heated with hydriodic acid, the alkaloid, like pyridine, is reduced to ammonia and a paraffin, octane.

These actions render it probable that conine is *α*-propyl-piperidine, and that this is the case is proved by direct synthesis. As already indicated, when pyridine methiodide is heated at 300°, it is transformed into the isomeric *α*-picoline hydriodide, C_5H_4MeN,HI. Now when this base is heated with paraldehyde, it condenses with it, forming conyrine, or *α*-allyl-pyridine, $C_5H_4N.CH{:}CH.CH_3$, a liquid resembling the alkyl-pyridines. On reducing this with sodium in alcoholic solution it is completely saturated with hydrogen, and converted into *α*-propyl-piperidine.

Synthetic *α*-propyl-piperidine resembles conine in every respect except that, like all synthetic compounds, it is optically inactive, but on evaporating a solution of its tartrate to crystallisation, the less soluble crystals which first separate are those of dextroconine tartrate. By distilling this salt with potash solution a base is set free which is identical with the natural base. This was the first synthesis of a natural alkaloid effected (Ladenburg, 1886). The asymmetric carbon atom to which the optical activity of the coniine is due is the *α*-atom, to which the propyl group is linked—



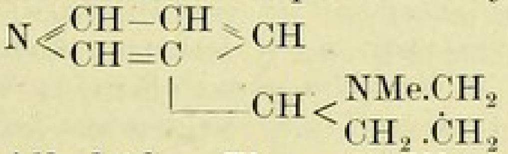
$$\mathrm{CH}<\begin{matrix}\mathrm{CH-CH}\\ \mathrm{CH=CH}\end{matrix}>\mathrm{N,MeI}\rightarrow\mathrm{CH}<\begin{matrix}\mathrm{CH-CH}\\ \mathrm{CH=CMe}\end{matrix}>\mathrm{N,HI}$$

$$\rightarrow\mathrm{CH}<\begin{matrix}\mathrm{CH-CH}\\ \mathrm{CH=C}\\ \dot{\mathrm{C}}\mathrm{H{:}CH.CH_3}\end{matrix}>\mathrm{N}\rightarrow\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.}\mathit{CH}\\ \dot{\mathrm{C}}\mathrm{H_2.CH_2.CH_3.}\end{matrix}>\mathrm{NH}$$

Nicotine.—Another volatile alkaloid of importance is the nicotine of tobacco, which can be obtained by distilling with lime the aqueous infusion of tobacco leaves, in which the base is present as the malate. The pure alkaloid is obtained by making the concentrated solution of the crude hydrochloride strongly alkaline with caustic soda, and fractionating the ethereal extract in a current of hydrogen.

Nicotine, $C_{10}H_{14}N_2$ (Posselt, 1820), is a colourless liquid of very rank and unpleasant odour. It boils at 247°, and, like conine, soon oxidises and turns brown in the air. It is also formed in the dry-distillation of tobacco, and thus accumulates in an impure form in the stems of tobacco pipes. Good tobacco contains, as a rule, less nicotine than the commoner varieties.

Nicotine is a ditertiary base, for it forms a dimethiodide, $C_{10}H_{14}N_2,2CH_3I$, as well as a crystalline dihydrochloride, $C_{10}H_{14}N_2,2HCl$. When oxidised with chromic acid mixture it is converted into nicotinic acid, so that it is a pyridine *β*-derivative. The second nitrogen atom probably forms part of a methyl-pyrrolidine ring (compare p. 407), in which case the constitution of the alkaloid is represented by the formula—



$$\mathrm{N}<\begin{matrix}\mathrm{CH-CH}\\ \mathrm{CH=C}\end{matrix}>\mathrm{CH}\qquad \mathrm{C}\text{—}\mathrm{CH}<\begin{matrix}\mathrm{NMe.CH_2}\\ \mathrm{CH_2\,.\dot{C}H_2}\end{matrix}$$

The Tropine Alkaloids.—The crystalline alkaloids fall naturally into several distinct classes, according to their origin and derivation. Atropine, hyoscyamine and cocaine, are derived from tropine, a somewhat complex derivative of piperidine.

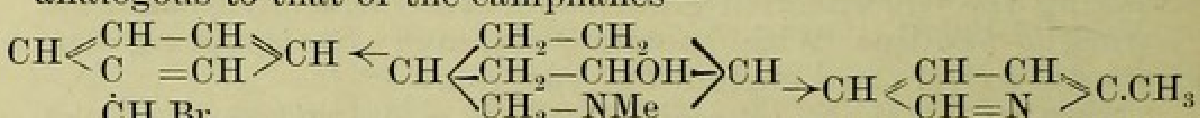
Atropine, the poison of the deadly nightshade, is not present as such in the plant, but is formed by the action of acids or alkalies on an isomeric alkaloid, hyoscyamine. The expressed juice is simply made alkaline with potash, and the crude atropine extracted with ether and purified by crystallising its sulphate. The molecular formulæ of this and the other crystalline alkaloids is best determined by the platinum method.

Atropine, $C_{17}H_{23}NO_3$ (Geiger, 1830), is a crystalline alkaline substance, and a powerful base, the sulphate having the formula $C_{17}H_{23}NO_3,H_2SO_4$. Its salts are exceedingly poisonous, but the sulphate is used in eye operations as a mydriatic.

When atropine is boiled with baryta water, it is hydrolysed to tropic or *a*-phenyl-hydracrylic acid, $CH_2OH.CHPh.COOH$, and a basic substance tropine, $C_8H_{15}NO$, and it is reproduced when a mixture of these two components is warmed with hydrochloric acid. The tropine is therefore in ethereal salt combination with the acid—

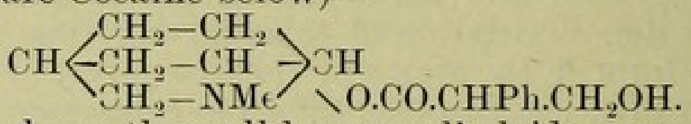
$$CH_2OH.CHPh.CO.OC_8H_{15}N + NaOH = CH_2OH.CHPh.COONa + C_8H_{14}N.OH.$$

Now tropine, which is a crystalline substance melting at 82°, can be converted on the one hand into benzyl bromide, and hence contains a benzyl nucleus, and on the other hand into picolinic acid, so that it is an *a*-alkyl derivative of pyridine. Further, it contains an alkylic hydroxyl group, and is a tertiary amine. These results are epitomised by a structural formula analogous to that of the camphanes—



$$\mathrm{CH}\left<\begin{array}{l}\mathrm{CH-CH}\\ \mathrm{C\ \ =CH}\\ \dot{\mathrm{C}}\mathrm{H_2Br.}\end{array}\right>\mathrm{CH}\leftarrow\mathrm{CH}\left<\begin{array}{l}\mathrm{CH_2-CH_2}\\ \mathrm{CH_2-CHOH}\\ \mathrm{CH_2-NMe}\end{array}\right>\mathrm{CH}\rightarrow\mathrm{CH}\left<\begin{array}{l}\mathrm{CH-CH}\\ \mathrm{CH=N}\end{array}\right>\mathrm{C.CH_3}$$

The structural formula of atropine is therefore in all probability (compare Cocaïne below)—

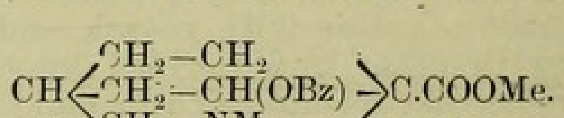


$$\mathrm{CH}\left<\begin{array}{l}\mathrm{CH_2-CH_2}\\ \mathrm{CH_2-CH}\\ \mathrm{CH_2-NMe}\end{array}\right>\mathrm{CH}\diagdown\mathrm{O.CO.CHPh.CH_2OH.}$$

As stated above, the well-known alkaloid cocaïne is a derivative of tropine. It is found in coca leaves, and extracted from their alkaline infusion with ether, after precipitating tannin, etc., with basic lead acetate.

Cocaïne, $C_{17}H_{21}NO_4$ (Niemann, 1860), is a crystalline substance, melting at 98°. It has marked basic properties, and forms well-defined crystalline salts, such as the hydrochloride, $C_{17}H_{21}NO_4,HCl$. The latter salt is used in dental and ophthalmic surgery for deadening pain, as it has the power of paralysing superficial nerves. It has the same effect on the coats of the stomach, and is sometimes used to deaden hunger; but it is an active poison.

Cocaïne is readily hydrolysed by alkalies to methyl alcohol and benzoyl-ecgonine, a crystalline substance, of which it is thus the ethereal salt, and the benzoyl-ecgonine is further hydrolysable to benzoic acid and ecgonine, of which it is thus the benzoate. Ecgonine, $C_9H_{15}NO_3$, can be proved to be tropine-carboxylic acid, so that the structural formula of cocaïne is probably—



$$\mathrm{CH}\left<\begin{array}{l}\mathrm{CH_2-CH_2}\\ \mathrm{CH_2-CH(OBz)}\\ \mathrm{CH_2-NMe}\end{array}\right>\mathrm{C.COOMe.}$$

The Cinchona Alkaloids.—Perhaps the most important of the vegetable alkaloids is quinine, which, together with cinchonine and other related alkaloids, such as quinidine and cinchonidine, is found in cinchona bark, combined with tannin and quinic acid, $C_5H_7(OH)_4.COOH$ (p. 307).

The associated alkaloids are extracted from the finely-divided bark with dilute sulphuric acid, and precipitated with soda, and the mixture of sulphates, obtained by neutralising the alcoholic solution with dilute sulphuric acid, is fractionally crystallised from water. Quinine sulphate is the least soluble, and therefore crystallises out first, and cinchonine sulphate is next in order, and separates from the quinine mother liquor. The free bases can be precipitated from the solutions of the sulphates by ammonia, and crystallised from alcohol.

Quinine, $C_{20}H_{24}N_2O_2$ (Pelletier, 1820), forms colourless, silky crystals, and melts when anhydrous at 173°. It is insoluble in water, but soluble in alcohol and ether, and of course in dilute acids. The salts of quinine most used in medicine are the sulphate and monohydrochloride, the intensely bitter solutions of which have the well-known antipyretic and tonic properties. The dilute solutions of the sulphate show a fine blue fluorescence.

Quinine in solution is readily identified by means of the coloured oxidation products it yields with chlorine and ammonia. When ammonia is added to a mixture of a quinine solution with chlorine or bromine water, a green precipitate is formed, which dissolves in excess of the alkali to a clear dark-green solution, whilst if potassium ferrocyanide is added before the ammonia, but after the halogen, a crimson coloration is obtained. The nature of these products is unknown.

Cinchonine, $C_{19}H_{22}N_2O_2$ (Pelletier, 1820), is a silky substance resembling quinine, but melting at 250°. It is less bitter also, and not so valuable therapeutically, its antipyretic properties being less marked. Its solutions are not fluorescent, and do not give the colour reactions with chlorine. The only characteristic salt of cinchonine is the ferrocyanide, which is very sparingly soluble, and is hence precipitated in small crystals on adding potassium ferrocyanide to a strong solution of the alkaloid. Cinchonine may be detected, however, by means of the general alkaloid tests.

All alkaloids, and most aminoid compounds, are characterised by forming certain insoluble compounds, from which they are set free by caustic or carbonated alkalies. The phosphomolybdates, for example, are buff or yellowish powders, which are precipitated by adding sodium phosphomolybdate to the neutral solutions, and the mercuriodides are similarly precipitated, by a solution of mercuric iodide in potassium iodide. Similarly, brown periodides are precipitated by a solution of iodine in potassium iodide. The mercuriodide test (Mayer) is very sensitive.

Constitution of Quinine and Cinchonine.—As quinine forms two classes of salts, it is a di-acid base, and that it is an aminoid compound is proved by the additive character of these salts, and by the formation of double salts, such as the platinochloride, $(C_{20}H_{24}N_2O_2,HCl)_2,PtCl_4$. Both the nitrogen atoms are thus basic, and that they are in tertiary amine combination is proved by the successive formation of quinine methiodide, $C_{20}H_{24}N_2O_2$, CH_3I, and dimethiodide, $C_{20}H_{24}N_2O_2,2CH_3I$, when the alkaloid is heated with methyl iodide. The same applies to cinchonine.

Both quinine and cinchonine are thus tertiary diamines. Both substances also contain an alkylic hydroxyl group, for when boiled with acetic anhydride they are converted into crystalline monacetyl-compounds. Further, quinine contains a methoxyl group, OCH_3, for when it is boiled with concentrated hydriodic acid, methyl iodide is volatilised in the proportion of one methyl group for each molecule of the alkaloid. The action is effected in a reflux apparatus in a stream of carbon dioxide, and the condenser water is warmed in order that the iodide vapour may pass whilst the water is returned. After washing the vapour free from hydriodic acid and iodine, by passing it through some warm water containing red phosphorus it is led into alcoholic silver nitrate, by which it is absorbed, and decomposed, silver iodide being precipitated. The latter is then collected and weighed (Zeisel, 1886)—

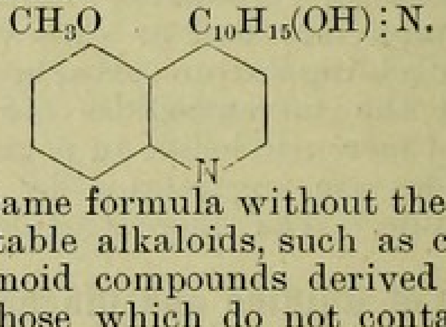
$$M(OCH_3)_x + xHI = M(OH)_x + xCH_3I \rightarrow xAgI.$$

Now, as already stated, when cinchonine is distilled with lime, it yields quinoline, and quinine under the same conditions yields γ-methoxy-quinoline. The above results may therefore be expressed in the partial constitutional formulæ—

$$CH_3O.C_9H_5N.C_{10}H_5(OH) : N \text{ and } C_9H_6N.C_{10}H_5(OH) : N.$$

Further, the second main group is linked to the γ-carbon of the quinoline, for by oxidising cinchonine and quinine with nitric acid, cinchoninic or quinoline-γ-carboxylic acid, and the corresponding methoxy-acid, are formed. The γ-position of the carboxyl in both these acids follows from their convertibility into cinchomeronic acid (p. 390), which is known to contain a γ-carboxyl group.

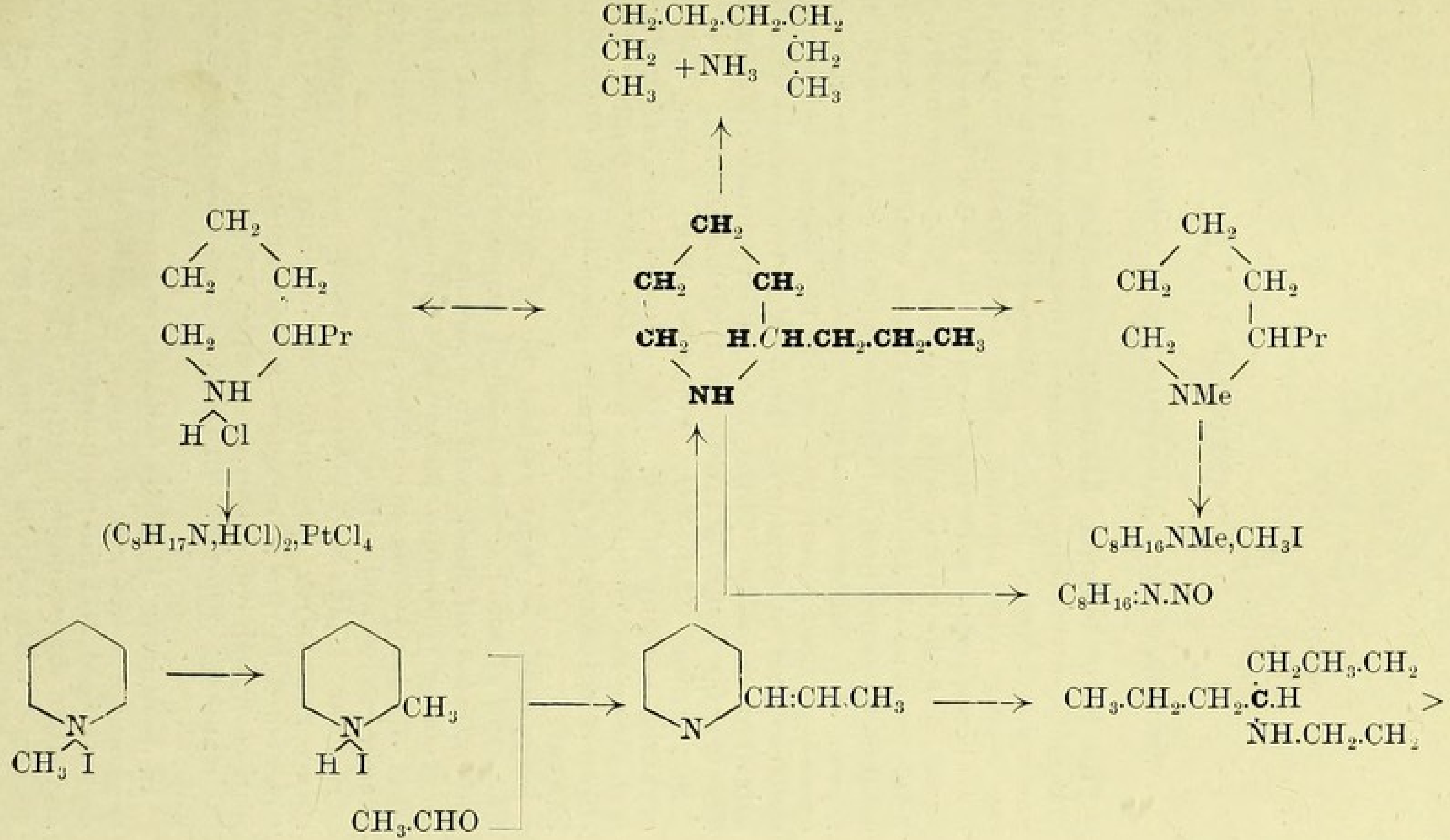
The exact nature of the second group, however, has not yet been determined. It is possibly a derivative of hexahydroquinoline, or it may be constituted analogously to tropine. For the present, therefore, quinine can only be represented by a partial structural formula—



and cinchonine by the same formula without the methoxyl.

Synopsis.—The vegetable alkaloids, such as conine and quinine, are complex aminoid compounds derived from pyridine and the quinolines. Those which do not contain oxygen are liquid, whilst the others are colourless, crystalline solids.

CONSTITUTION AND SYNTHESIS OF CONINE.



CHAPTER LXVI

THE VEGETABLE ALKALOIDS : NUX VOMICA AND OPIUM

The Nux Vomica Alkaloids.—Another pair of quinoline alkaloids, strychnine and brucine, are associated in the poisonous nux vomica bean. They are extracted from the powdered beans by boiling with alcohol. The accompanying tannin having been precipitated with lead acetate, the mixed bases are thrown down from the filtrate with magnesia, and fractionally crystallised from alcohol. The strychnine, which is much the less soluble, separates first, whilst the brucine remains in the mother liquor. The latter is purified by evaporating to dryness with excess of acetic acid, the strychnine acetate being thus dissociated, and on extracting the residue with water the brucine salt alone dissolves, whilst the free strychnine remains behind. The brucine is finally precipitated with ammonia.

Strychnine, $C_{21}H_{22}N_2O_2$ (Pelletier, 1810), forms well-defined crystals, melting at 268°. Its solutions are extremely bitter and poisonous, but in dilute form are used as tonics. The only effective antidotes for strychnine poisoning are chloroform and chloral.

Strychnine is characterised by a striking colour reaction. The solid alkaloid or salt is gently warmed with a few drops of concentrated sulphuric acid in a porcelain basin, and on drawing a crystal of potassium bichromate through the cold solution a trail of a dark violet oxidation product is left, which gradually changes to red and yellow.

Brucine, $C_{23}H_{25}N_2O_4$ (Pelletier, 1812), is a crystalline substance resembling strychnine, but melting at 178°. It is distinguished by its conversion by cold concentrated nitric acid into an orange-red colouring matter, which is changed to violet by stannous chloride. Brucine is less poisonous than strychnine.

In separating alkaloids from an organic mixture, such as the contents of a stomach, the mass is acidified with tartaric acid and strained, and the fluid shaken with ether to dissolve out fat and other objectionable matter. The acid solution is then made alkaline with sodium carbonate, and the liberated alkaloid extracted with a mixture of ether and chloroform. The filtered extract is evaporated at a low temperature, and examined, first by the general tests (p. 397), and then, if an alkaloid be present, by the special tests (Stas). Any ptomaïnes that may be present will of course be found in the final product.

Both strychnine and brucine are tertiary monamines, as they form only one class of salts, and take up only one methyl group. The second nitrogen atoms are therefore not in aminoid combination. Strychnine is oxidised by nitric acid to picric acid and a derivative of dihydro-quinoline, whilst brucine yields on fusion with potash, methyl-pyridines and tetrahydroquinoline. Beyond the fact, however, that both alkaloids are tertiary quinoline derivatives, little is known of their constitution.

The Opium Alkaloids: Morphine and Codeïne.—The narcotic properties of opium, the dried sap of green poppy capsules, are mainly due to morphine, which in company with other alkaloids, such as codeïne, papaverine, and narcotine, exists in the sap combined with meconic and other acids.

To isolate morphine, opium infusion is boiled with milk of lime, in which the principal alkaloid alone is soluble, and the filtered solution is saturated with ammonium chloride. The lime is thus converted into calcium chloride, and the morphine, deprived of its solvent, is slowly precipitated. The dry precipitate is recrystallised from fusel oil.

Morphine, $C_{17}H_{19}NO_2$ (Sertürner, 1817), is a crystalline substance, which is much less bitter than most of the alkaloids. The silky crystalline hydrochloride is much used in medicine. When injected beneath the skin in small doses it acts as a stimulant, whilst in larger doses it is narcotic, and relieves the severest pain. In somewhat larger amounts it is poisonous.

Morphine differs from the other alkaloids in that it is soluble in caustic alkalies, and gives in neutral solution a blue coloration with ferric chloride. It has reducing properties also, so that if a solution is shaken with some iodic acid and chloroform the latter is coloured violet with liberated iodine. Many reducing agents, however, have this action. The morphine in opium extracts, such as laudanum, is always associated with meconic acid, which is readily recognised by the intense purple-red coloration it forms with ferric chloride, even in presence of dilute hydrochloric acid.

Morphine is a tertiary monamine, and as it forms a diacetyl-compound, the molecule contains two hydroxyl-groups. One of these groups is phenolic, for when the alkaloid is heated with methyl iodide and caustic potash, it is converted into a methoxy-derivative, codeïne, $C_{17}H_{17}(OH)(OCH_3)NO$, which is reconverted into morphine by boiling with hydriodic acid. The presence of this phenolic group accounts for the solubility of morphine in alkalies, and for the colour reaction with ferric chloride. The second hydroxyl group is alkylic, for although codeïne forms a monacetyl-derivative with acetic anhydride, it is insoluble in alkalies, and is not coloured by ferric chloride.

Codeïne, or methyl-morphine, is a crystalline substance which melts at 150°. It may be extracted from the lime precipitate obtained in the isolation of morphine.

Little is known of the nucleal constitution of morphine and codeïne. When morphine is distilled with zinc dust it yields a relatively large amount of phenanthrene, so that it is a derivative either of this hydrocarbon, or of the simpler hydrocarbons, such as dibenzyl and stilbene, from which phenanthrene is formed pyrogenically.

The Opium Alkaloids : Papaverine and Narcotine.—Whilst little is thus known of the constitutions of morphine and codeïne, those of papaverine and narcotine have been fully established.

Papaverine, $C_{20}H_{21}NO_4$ (Merck, 1848), a crystalline substance melting at 148°, can be extracted from the lime precipitate in the extraction of morphine from opium.

Papaverine is a monamine, as it forms only one class of salts, and it is a tertiary amine, as it combines directly with one molecule of methyl iodide. Further, the molecule contains four methoxyl-groups, for the substance yields four equivalents of methyl iodide when boiled with hydriodic acid. The formula may therefore be written as $C_{16}H_9(OCH_3)_4 \vdots N$. There thus remain sixteen carbon atoms to be accounted for.

Now when the alkaloid is fused with potash it is resolved into dimethoxy-isoquinoline, $C_9H_5N(OCH_3)_2$, and veratric or dimethyl-protocatechuic acid, $C_6H_3(OMe)_2.COOH$, which suggests that papaverine is dimethoxy-benzyl-dimethoxy-isoquinoline—

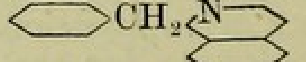
$$C_6H_3(OMe)_2.CH_2.C_9H_4N(OMe)_2 + 2O = C_6H_3(OMe)_2.COOH + C_9H_5N(OMe)_2.$$

This is supported by its oxidation by permanganate to the corresponding crystalline ketonic compound, papaveraldine—

$$C_6H_3(OMe)_2.CH_2.C_9H_5N(OMe)_2 \rightarrow C_6H_3(OMe)_2.CO.C_9H_5N(OMe)_2.$$

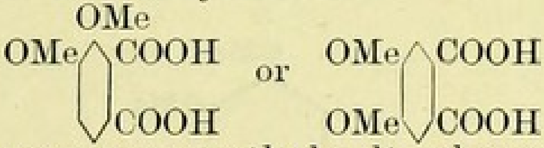
It remains to determine the relative positions of the two nucleal groups, and the positions of the methoxyl-groups in the isoquinoline part of the molecule.

Now when papaveraldine is oxidised it yields several products, amongst which is pyridine-αβγ-tricarboxylic acid. This is obviously formed by the breaking down of the isoquinoline part of the molecule; and as isoquinoline itself yields the βγ-dicarboxylic acid, it follows that the benzyl group is in an α-position, adjacent to the nitrogen atom, and to the benzene nucleus of the isoquinoline—



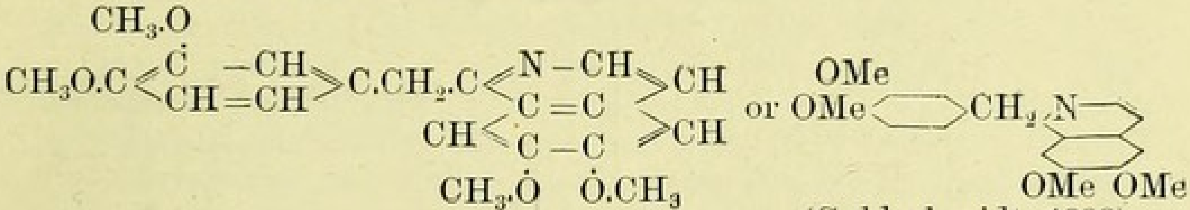
The position of the methoxyl groups follows from the occurrence of a dimethoxy-phthalic acid amongst the oxidation products of the papaveraldine. Metahemipinic acid, $C_8H_8O_2.(COOH)_2$, is a dibasic acid, which forms an anhydride, and therefore contains two adjacent carboxyl groups. When boiled with hydriodic acid it yields two equivalents of methyl iodide, and thus contains two methoxyl groups. It is therefore dimethoxyphthalic acid, $C_6H_2(OMe)_2(COOH)_2$, and is obviously formed by the breaking down of the pyridine half of the isoquinoline molecule.

Now metahemipinic acid is converted into protocatechuic acid when fused with potash, and the methoxyl groups are therefore adjacent. It is therefore either 1:2:3:4 or 1:2:4:5 dimethoxybenzene-dicarboxylic acid—



But it forms only one monomethyl salt, whereas an acid having the unsymmetrical formula would form two. The carboxyl groups are therefore symmetrically placed as in the second formula.

The structural formula of papaverine as dimethoxybenzyl-dimethoxy-isoquinoline is thus—

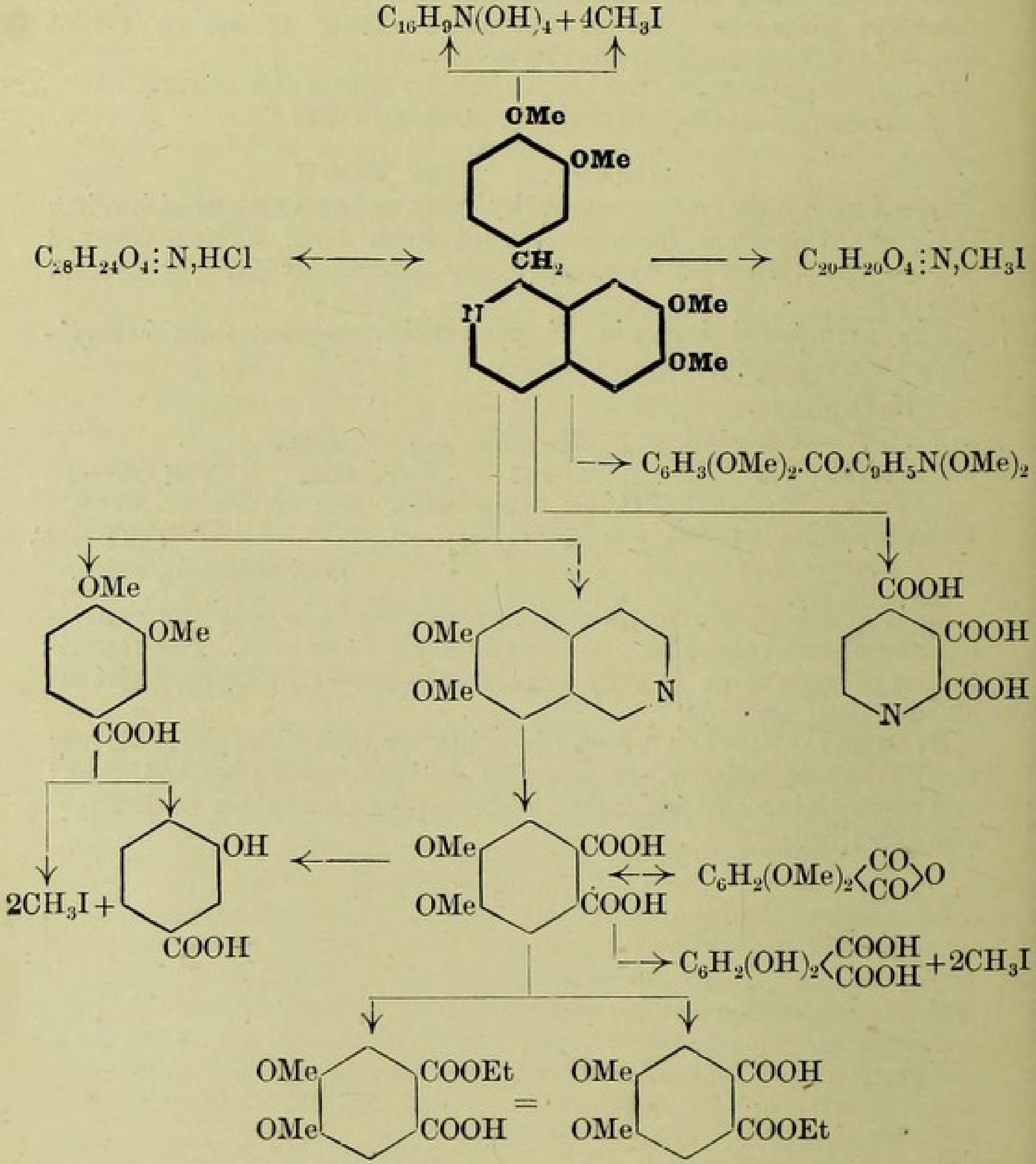


(Goldschmidt, 1888).

This is a typical example of the manner in which the constitutions of such complex compounds are determined. The constitution of narcotine is very similar, the molecule being built on an identical nucleus.

Synopsis.—Strychnine and brucine are quinoline derivatives; morphine and codeïne are probably derivatives of phenanthrene; and papaverine and narcotine are complex derivaties of benzyl-isoquinoline.

CONSTITUTION OF PAPAVERINE.



CHAPTER LXVII

THE THIOPHENE-PYRROL AND OTHER HETERONUCLEAL GROUPS

Thiophene.—Commercial benzene from coal-tar invariably gives a blue coloration when shaken with concentrated sulphuric acid containing a little isatin or phenanthraquinone, but pure benzene from benzoic acid does not do so; and commercial benzene ceases to give the colour after repeatedly shaking with small quantities of concentrated sulphuric acid. The formation of this blue colouring matter, indophenin, is due to the presence of a sulphur derivative, thiophene, C_4H_4S, which, as it is formed by passing coal-gas over red-hot pyrites is probably formed in this manner from the pyrites in its coal. Thiophene may be obtained in the pure state from its sulphonic acid, but is more readily prepared by dry-distilling a mixture of sodium succinate and phosphorus trisulphide.

Thiophene, C_4H_4S (V. Meyer, 1883), is a colourless liquid, which boils at 84°, and resembles benzene in a most remarkable manner. Not only is the liquid itself physically like benzene, but it forms a parallel series of derivatives which are scarcely distinguishable from the corresponding benzene derivatives except in composition, and are formed in precisely the same way.

Thus α-bromothiophene boils at 150°, bromobenzene at 155°. When boiled with methyl iodide and sodium it is converted into methyl-thiophene or thiotolene, a liquid resembling toluene, but boiling at 113°, instead of at 111°. This is oxidised by chromic acid mixture to α-thiophene-carboxylic acid, a substance resembling benzoic acid, and boiling at 260°, as against 250°.

The various substituting agents, however, act much more readily on thiophene than on benzene, and the sulphonic acid for instance is formed, even in the cold, with such energy that the thiophene must be diluted with benzene. Similarly in making nitro-thiophene, the vapour is best led into the acid. The dinitro-compound is coloured red by caustic alkali, and its presence may thus often be detected in meta-dinitro-benzene. Amidothiophene differs from aniline in that it does not form diazo-compounds.

On account of its similarity to benzene, thiophene is regarded as a ring compound, and this view is borne out by its synthesis from succinic acid—

$$\begin{matrix}CH_2.COOH\\ |\\ CH_2.COOH\end{matrix} \rightarrow \begin{matrix}CH=CH\\ |\\ CH=CH\end{matrix}>S.$$

An analogous selenophene has been made having very similar properties.

Furfurane.—When bran is distilled with dilute sulphuric acid, a colourless liquid passes over having all the properties of an aldehyde, and may be obtained in a pure state by means of its bisulphite compound.

Furfuraldehyde, $C_4H_3O.CHO$ (Fownes, 1845) (*furfur*=bran) is a colourless liquid of aromatic odour, boiling at 162°. It forms a crystalline oxime and phenyl-hydrazone, reduces silver, is reduced by sodium amalgam, and is converted by caustic alkalies into the corresponding alcohol and acid in the same way as benzaldehyde. The resemblance to the latter extends even to forming a green "malachite" dye with dimethylaniline, and a "cinnamic" acid with sodium acetate and acetic anhydride. Furfuraldehyde is distinguished from benzaldehyde however by forming an intense red colour with aniline.

Furfuraldehyde is formed quantitatively when xylose, arabinose and the other pentoses are distilled with hydrochloric acid, so that the amount of these carbohydrates in a mixture may be estimated by this means—

$$C_5H_{10}O_5=C_5H_4O_2+3H_2O.$$

The corresponding furfuryl alcohol, $C_4H_3O.CH_2OH$, formed, by the action of caustic soda on the aldehyde is a syrup which is coloured green by hydrochloric acid.

The acid obtained by oxidising the aldehyde with silver oxide, or, together with the alcohol, by the action of caustic alkali, is also obtained by the dry-distillation of mucic acid. It has been known for more than a century.

Pyromucic acid, $C_4H_3O.COOH$ (Scheele, 1780), is a crystalline substance which melts at 132°, and sublimes at about the same temperature. It forms metallic and alkylic salts, as well as a chloride, amide and nitrile. It is converted by bromine vapour however into a tetrabromide, $C_4H_3Br_4O.COOH$, and this is oxidised by chromic acid mixture to dibromo-succinic acid—

$$COOH.CHBr.CHBr.COOH.$$

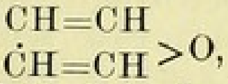
When barium pyromucate is distilled with soda-lime, it loses carbon dioxide in the normal manner, and is converted into furfurane, the mother substance of the group—

$$C_4H_3O.COOH=C_4H_4O+CO_2.$$

Furfurane or furane, C_4H_4O (Limpricht, 1873), occurs in the more volatile portions of pine-wood tar. It is a colourless volatile liquid which boils at 32°. Its odour is characteristic, and it is only sparingly soluble in water.

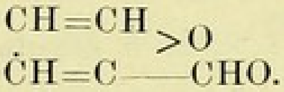
Hydrogen is not displaced from furfurane by sodium, so that it is neither an acid nor an alcohol, and it does not form an oxime or a hydrazone, so that it is not a ketone or aldehyde. The oxygen must therefore be combined in ethereal function.

From these various actions, and from the stability of the nucleus it must be assumed that furfurane is a ring compound analogous to thiophene, and having the constitution—



$$\begin{matrix}CH{=}CH\\ \dot{C}H{=}CH\end{matrix}{>}O,$$

and that in furfuraldehyde and its derivatives the active group is attached to the carbon atom next the oxygen—



$$\begin{matrix}CH{=}CH & \\ \dot{C}H{=}C & \!\!-\!\!-CHO.\end{matrix}{>}O$$

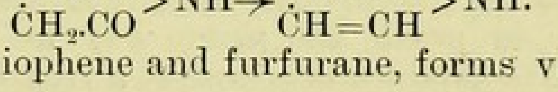
The furfurane compounds give a colour reaction resembling that of thiophene, a violet colour being formed when any member of the group is added to concentrated sulphuric acid, containing a little isatin or phenanthraquinone. Further, when a pine shaving moistened with concentrated hydrochloric acid is held in the vapour of any furfurane derivative, a green colour is developed.

Pyrrol.—The nitrogen analogue of thiophene and furfurane is known in pyrrol, C_4H_4NH, which can be isolated from bone-oil. The highly basic pyridines having been removed by shaking with acid, and the fatty nitriles hydrolysed by boiling with alkali, the pyrrol is separated from the 125° fraction by boiling with solid caustic potash, which converts it into a solid potassium derivative. The base is liberated from this by boiling with excess of water.

Pyrrol, C_4H_4NH (Runge, 1839), is a colourless liquid, which boils at 131°, and resembles chloroform in odour. It soon turns brown in air, and is resinified by concentrated acids. Like thiophene and furfurol, pyrrol forms a dark blue product, with isatin or anthraquinone and sulphuric acid; but it is especially distinguished by the fiery red colour (πυῤῥος) which it imparts to a pine shaving moistened with hydrochloric acid.

Pyrrol is but a feeble base, and dissolves only slowly in dilute acids, and although one of its hydrogen atoms is displaceable by metallic potassium or potash it is not affected by sodium. On warming the solution of pyrrol in dilute acids, an amorphous red colouring matter is precipitated, and ammonia is eliminated.

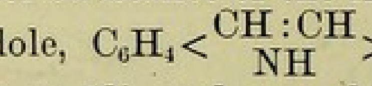
Pyrrol is formed in quantity when succinimide is heated with zinc dust, and its constitution follows from this and similar relations—



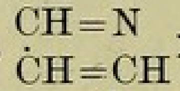
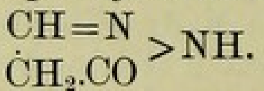
$$\begin{matrix}CH_2.CO\\ \dot{C}H_2.CO\end{matrix}{>}NH \rightarrow \begin{matrix}CH{=}CH\\ \dot{C}H{=}CH\end{matrix}{>}NH.$$

Pyrrol, like thiophene and furfurane, forms various substitution products.

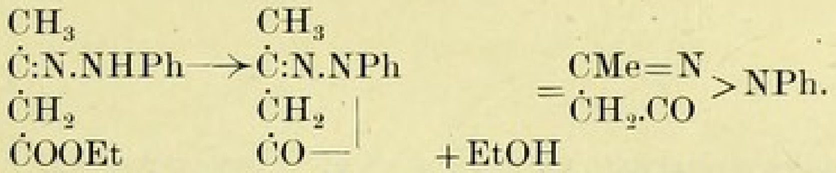
Derivatives and Analogues of the Thiophene-Pyrrol Group.—Like benzene and pyridine, the thiophene, furfurane and pyrrol rings may be linked in various combinations. Thus a thiophene derivative is known in which two rings are linked by common carbon atoms in the same way as in naphthalene. The most important of such compounds, however, are those in which the pyrrol ring is united with a benzene ring. The simplest product of this kind is indole, which is formed by distilling indigo or isatin with zinc dust, and is therefore the mother substance of the indigo group.

Indole,  $C_6H_4<\genfrac{}{}{0pt}{}{CH:CH}{NH}>$, is a crystalline substance, which melts at 52°, and resembles *a*-naphthylamine in odour. Like pyrrol, it imparts a red colour to a pine shaving moistened with concentrated hydrochloric acid and alcohol. It is only feebly basic, and is resinified by acids, but as a secondary amine it forms a nitroso-compound. *β*-Methyl-indole or skatole is a similar crystalline substance having a very pronounced fæcal odour; it actually occurs in small quantity in fæces.

Many compounds have been synthesised in recent times in which the methine groups of thiophene and allied rings are replaced by nitrogen. As far as the pyrrol ring is concerned, it may be said that any number of nitrogen atoms up to four may be introduced, and in any order. Such rings are formed as a rule by condensation of amido-compounds with aldehydes or ketones; but although their number is extremely large, as yet few of them are of other than theoretical interest. A prominent exception occurs in pyrazol, the di-nitrogen analogue of pyrrol.

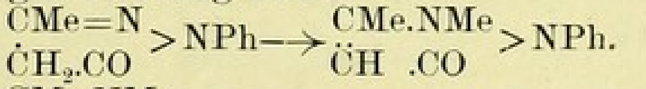
Pyrazol,  $\genfrac{}{}{0pt}{}{CH=N}{\dot{C}H=CH}>NH$, is a crystalline substance, which is formed by condensation of epichlorhydrin with hydrazine hydrate in presence of zinc chloride. It is feebly basic, and forms a silver compound analogous to potassium-pyrrol. Its interest lies in its relation to the well-known drug antipyrine, which is the phenyl-dimethyl-derivative of a ketonic derivative, pyrazolone,  $\genfrac{}{}{0pt}{}{CH=N}{\dot{C}H_2.CO}>NH$.

Antipyrine or phenyl-dimethyl-pyrazolone is manufactured synthetically by the successive action of phenyl-hydrazine and methyl iodide on ethyl acetoacetate. The ethereal salt condenses with the hydrazine, probably forming a hydrazone in the normal manner; but the imido-group of the latter at once interacts with the ethereal salt group at the other end of the chain, and an amido-compound is formed with elimination of alcohol, in much the same way as acetamide from ethyl acetate. The product is of course a ring compound, as the interacting groups are attached to the same chain—

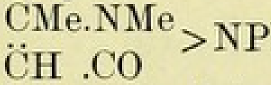


$$\begin{array}{l} CH_3 \\ \dot{C}:N.NHPh \\ \dot{C}H_2 \\ \dot{C}OOEt \end{array} \rightarrow \begin{array}{l} CH_3 \\ \dot{C}:N.NPh \\ \dot{C}H_2 \\ \dot{C}O \end{array} \begin{array}{c} \\ \\ \\ +EtOH \end{array} = \begin{array}{l} CMe{=}N \\ \dot{C}H_2.CO \end{array} > NPh.$$

On heating the crystalline phenyl-methyl-pyrazolone thus formed with methyl-iodide and methyl alcohol, at 100°, it is at once converted into antipyrine, the molecule at the same time undergoing slight rearrangement—



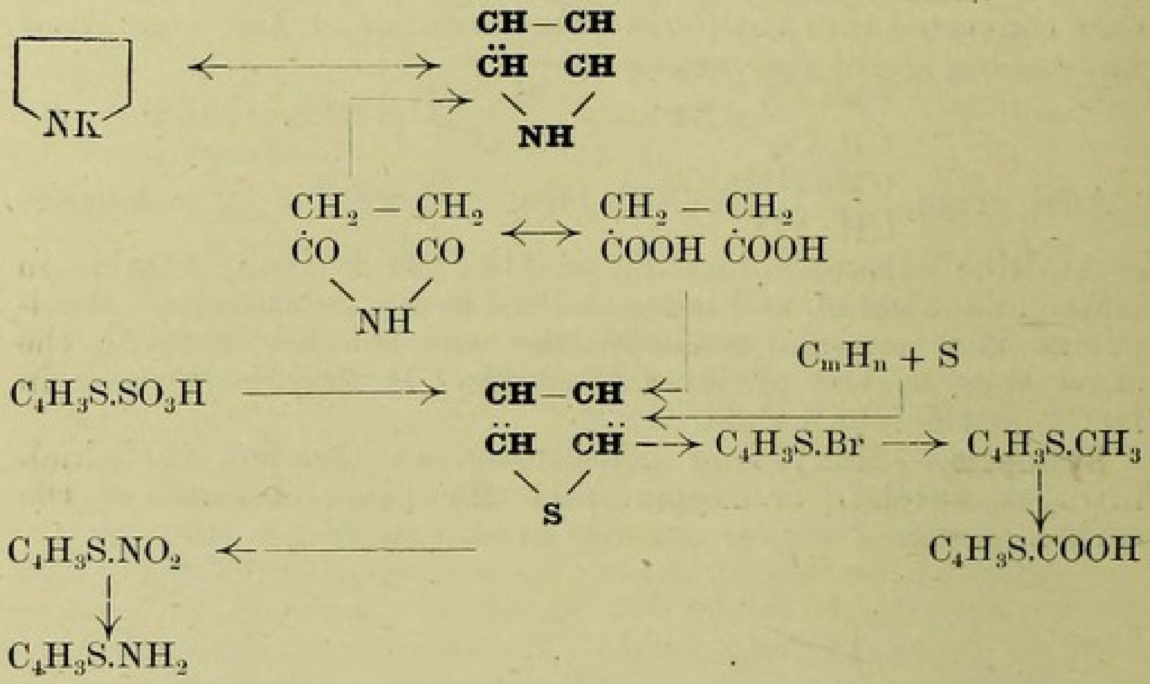
$$\begin{array}{l} CMe{=}N \\ \dot{C}H_2.CO \end{array} > NPh \longrightarrow \begin{array}{l} CMe.NMe \\ \ddot{C}H\ \ .CO \end{array} > NPh.$$

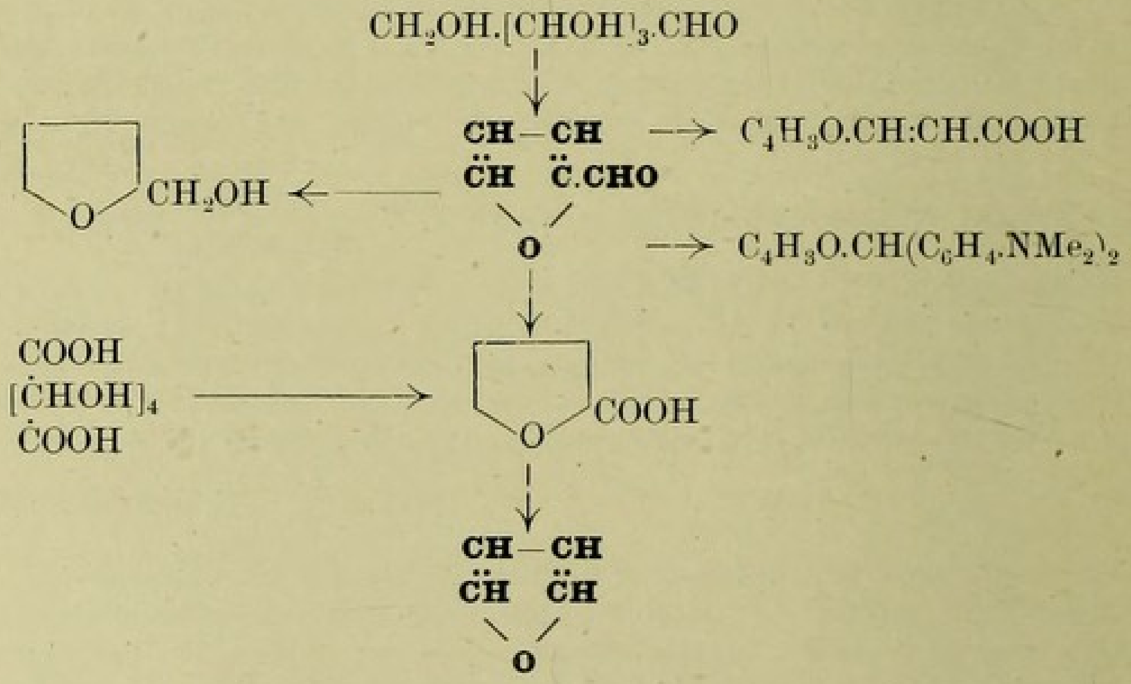


Antipyrine, $\begin{array}{l} CMe.NMe \\ \ddot{C}H\ \ .CO \end{array} > NPh$ (Knorr, 1883), is a colourless crystalline substance melting at 114°. It is freely soluble in water and alcohol, and is much used as an antipyretic. Antipyrine is a powerful monacid base, and behaves in much the same way as the pyridine alkaloids. It may be termed in fact an artificial alkaloid.

Synopsis.—Many ring compounds are known, in which nitrogen, sulphur, or oxygen take the place of some of the carbon atoms.

THIOPHENE, FURFURANE AND PYRROL.





APPENDIX I

LABORATORY NOTES[*]

PLAN OF WORK

Each chapter should be carefully studied before commencing work, and the necessary apparatus and materials collected. Progress will be slow at first, but speed will come with experience. Progress is much accelerated by writing out a careful account of each piece of work as soon as it is finished, comparing the results and yields actually obtained with the standard results. If an experiment fails, it saves time in the long run to repeat it.

It is recommended to work through the book in the order given, to the end of Part I. Parts II. and III. may then be taken concurrently. The experiments enclosed in square brackets are more complicated, and should be left until after the others. It is advisable to read ahead, and especially to note what materials are required, or the work may be delayed while the materials are being made or procured. When a preparation has to be kept some days before proceeding further, the early stages should be taken in advance, before the preceding experiments are completed.

LIST OF APPARATUS

Retort stand with three rings and adjustable clamp for condenser. Tripod and wire gauze. Sand bath. Tinplate saucepan, 5 inches diameter, for water bath. 8-oz. distilling flask. Ordinary flasks, 2-oz., 4-oz., 6-oz. Large wash bottle, fitted. Corks to fit flasks, test tubes, condenser, etc. Set of three cork-borers. Rat-tail file. Thermometer with paper scale to 250°. Bunsen burners and tubing. 100 c.c. graduated measuring cylinder. 30-inch Liebig's condenser, and $\frac{1}{8}$ inch indiarubber tubing. Rough balance (scales) and weights from 1 gram to 500 grams. Small chemical balance and weights from 1 milligram to 50 grams. Two porcelain crucibles and lids. Pipeclay triangle. Crucible tongs. Blowpipe. Platinum foil and wire. Test-tube stand. Twelve large and twelve small test tubes. Test-tube brush. Three beakers, 4-oz., 6-oz., 8-oz. Three funnels, 2-inch, 3-inch, 4-inch. Two packets of filters, 4-inch, 6-inch. Two thistle funnels. Three watch-glasses. One porous tile or plate. Glass tubing: soft, $\frac{1}{8}$ inch diameter; hard, $\frac{1}{2}$ inch diameter. Glass rods. Three-cornered file. Plain glass filter pump. Stout 500 c.c. bottle with neck $1\frac{1}{2}$ inch diameter, and cork to fit, to take funnel for pressure filtering. Pestle and mortar. Stoneware pneumatic trough and beehive shelf.

Students are recommended to work in couples. If working alone, some of the above apparatus will be required in duplicate.

PART I

CHAPTER I

Distilling Apparatus.—8-oz. distilling flask. Thermometer through ordinary cork, *top* of bulb just *below* side-tube. Flask on wire gauze on tripod or ring; no support necessary if cork to condenser tube fits well.

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[*] These notes should be taken in conjunction with the text.

Side tube of flask well into condenser. Condenser loosely into ordinary flask, which should rest on the bench and not on blocks, etc., or it may be overturned. Water into lower tubulure of condenser, and out of upper tubulure, just warm, not too fast—thin stream. Joints between condenser tube and jacket must be quite water-tight.

Distillation of Beer.—100 c.c. beer. Flask never more than two-thirds full. Heat with small flame, and steadily, otherwise bumping. If liquid persistently bumps, put in pieces of glass or platinum, first cooling. If it froths over, as it probably will do with beer, redistil distillate until clean liquid is obtained. Prove first part of distillate low b.-pt. and inflammable; freeze last part (pounded ice and salt, or cryst. sodium sulphate and conc. hydrochloric acid).

Boiling Point.—Thermometer stem is not in vapour, hence reading too low. For very accurate work add N (T−t) × 0.00015. [N=no. of degrees unimmersed, T=reading of thermometer, t=temperature of second thermometer half way between top of mercury and cork.] But better to use long-necked flask or short thermometer. Boiling point is temperature of vapour freely given off under standard pressure. Hence height of barometer must be noted. Take care thermometer is not superheated, *e.g.* by large flame. It should drip slowly with condensed liquid. Check graduation of thermometer once for all by distilling 100 c.c. of water through apparatus, and note correction for future use. Boiling points of liquids always determined in this way, *never* by placing bulb in liquid.

Specific Gravity.—Ordinary physical bottle method good enough for most purposes: 5 c.c. bulb blown on glass tube, indiarubber capped, drawn out in middle of neck, and marked lightly with file at narrow part. Weigh empty—w_1. Fill with dist. water with drawn-out pipette, immerse in water of known temperature (properly 4°, but temp. of water supply will do), and adjust to mark with pipette or filter paper. Dry outside and weigh—w^2. Weight of water=w_2-w_1. Repeat, and note these data once for all. Next thoroughly rinse with liquid, or best of all, dry flask by sucking air through it with pump, and warming. Fill with liquid, and adjust as before, at the same temperature. Replace stopper and weigh—w_3. Then weight of liquid=w_3-w_1, and sp.-gr. at t°=$(w_3-w_1) / (w_2-w_1)$.

Fractional Distillation.—Use small flame, and keep boiling steadily. Watch thermometer, and change receiver as mercury passes each temperature limit. *Do not alter or take away flame.* Measure fractions. Second fractionation: Clean out flask; and put in first fraction. When the first limit, 82°, is reached, some liquid still remains in the flask. Stop boiling and add second fraction to this. Resume distillation, but *do not change receiver.* Some liquid now comes over below 82°; collect *in same receiver.* When limit again reached, stop and add third fraction. Still a little passes over below 82°, and possibly a little on adding fourth and fifth fractions in same way. When distillate from fifth fraction reaches 82° do not stop boiling, but change receiver, and proceed exactly as in first fractionation. Measure fractions. Third fractionation: Same as second. Measure fractions, and take sp.-gr. of head and tail fractions. Note head fraction is inflammable. Keep it for testing (Chap. III.). Note tail fraction can be frozen.

Absolute Alcohol.—Boil 300 c.c. methylated spirit in reflux apparatus (p. 17) with 10 grams caustic soda for 1 hour. Flask heated on water bath, *i.e.* saucepan of boiling water (Fig. 1), preferably rather less in diameter than flask, so that latter is heated with steam. Then fit flask with wide bent tube leading to a condenser, and distil on w.-b. as long as anything passes over. There is no danger of cracking the flask if water is kept in the saucepan. Use as receiver large flask containing 140 grams fresh quicklime. See first that a lump heats with water, and falls to pieces. Spirit and lime should not more than half fill flask, or lime in swelling up will burst it. Fit with good cork, and after 24 hours distil again from w.-b., without pouring off from the lime, or transfering to second flask. Distil as from soda until no more passes over. B.-pt. given by thermometer through cork should be quite steady. Yield 80%. Take sp.-gr. of early and late sample; should be constant.

Chemical Tests of Purity.—Anhydrous copper sulphate by heating blue crystal in porcelain crucible until it crumbles. Should not be heated so strongly as to show brown oxide.

CHAPTER II

Hydrogen from Alcohol.—5 c.c. absolute alcohol in test tube with delivery tube. Clean sodium, size of pea. Collect gas, and prove by lightness and inflammability to be hydrogen.

Detection of Carbon and Hydrogen.—Burn absolute alcohol on watch glass beneath funnel connected through two flasks or test tubes with inverted wash bottle of water, or water pump. Prove moisture in first (keep cool) by copper sulphate, and carbon dioxide by lime water, in second.

[*Carbon and Hydrogen Combustion.*—Tube 90 cm. long, 1·5 cm. internal diam., hard glass; cut off cleanly at ends, widen and smooth in blowpipe; thoroughly clean and dry, and embed in asbestos in furnace trough, ends protruding about 5 cm. beyond end of trough. Singly-bored rubber corks at both ends, well dried and blackleaded to prevent sticking when hot. Drying apparatus depicted (Coram's) is convenient if much work to be done, but ordinary wash-bottles and U-tubes will serve. Concentrated potash, 1 in 5 (not soda, as carbonate less soluble), followed by conc. sulphuric acid, both tubes filled with small pumice. In combustion tube, starting from air end, (a) 10 cm. empty for boat, (b) 70 cm. with copper oxide, granulated, or better, made from wire—dried in crucible over flame, as it is hygroscopic, and is kept in position by loose plugs of asbestos at each end; (c) 10cm. empty. Sulphuric acid and pumice water-collecting tube as shown; whatever drying agent is used must be used throughout. Potash bulbs (Geissler's pattern) half filled with 1 in 5 solution, upper tube with pumice and sulphuric acid. U-tube of solid soda-lime, freshly dried in iron dish over small flame, may be substituted for potash, but the attached drying tube is small U-tube constricted at bottom to show rate of bubble passing through acid. Absorption apparatus protected from heat by large asbestos screen.

Begin with blank expt. in dry air stream, without boat. Heat copper oxide gradually, and when moisture has for some time ceased to appear at end of tube, place weighed absorption tubes in position, and continue heating and passing air until tubes cease to increase in weight. They must remain in balance case for half an hour before weighing, capped with short pieces of indiarubber tube stopped with short rounded pieces of glass rod.

When apparatus is thus clean and dry, make trial combustions of sugar candy, or of twice recrystallised oxalic acid, using about qties. indicated for alcohol. The copper oxide being red hot, the platinum (or porcelain) boat is weighed (and weighed again at finish, to prove no residue), filled with solid, weighed again, and pushed into empty space reserved, followed by a short roll of copper gauze, just fitting tube, to prevent backward passage of gases. Warm the boat with a single burner, with small flame, air passing at one bubble per 2 seconds, and as soon as rate increases turn off air. As carbon dioxide is absorbed, little gas escapes. Air then slightly increased, but rate through collecting absorption appts. must not exceed that indicated. Towards end of combustion, boat is heated to dull redness, and, if charred residue is left, oxygen is passed until this disappears. Finally air again for 15 minutes. In a series of combustions, the copper oxide need not be cooled, only the boat end of tube, and if two sets of collecting tubes are kept in use, the next combustion may be started forthwith.

Practice as above until concordant results are obtained.

In combustion of alcohol, make little bulb with long thin neck, of such size that the bulb will rest in the boat, and the neck project a little over the end. Weigh the bulb empty and quite dry, then introduce about the right amount of liquid by warming, and allowing neck to dip into liquid and cooling. Then fuse up end of neck and weigh. When combustion tube is in order, break off end of neck (any liquid in latter must be driven back into bulb), drop into boat with neck-end forwards, *quickly* push into combustion tube, and replace copper roll and cork. Heating must be exceedingly cautious, or vapour will come off too fast; hot tile over boat serves very well, At end of operation bulb must be quite empty. Avoid overheating boat, or glass may fuse.]

[*Vapour Density with Victor Meyer's Apparatus.*—Vapour of jacket liquid should not quite reach the cork. A few c.c. of mercury at bottom of displacement tube, or tube of substance, in falling, will break latter. Substance weighed in small stoppered tube supplied with apparatus. When expt. is finished and no more gas is displaced, remove cork of displacement vessel before stopping boiling, otherwise water will be forced back from pneumatic trough. Vapour pressure of water=9 mm. at 10°, 13 mm. at 15°, 17 mm. at 20°; for intermediate temperatures take as proportional. Clean and dry inner tube for each experiment.]

[*Molecular Weight by Cryoscopic Method.*—As stated, results good enough for most purposes can be obtained with an ordinary physical thermometer. In Beckmann's apparatus (which is that usually employed), thermometer is differential, very large bulb and very narrow bore, with reservoir at top also. Scale about 6° only, divided into $\frac{1}{100}$°, so that mercury must be passed into or withdrawn from reservoir, until column stands at about middle of scale at required temperature.]

[*Molecular Weight by Boiling Point Method.*—The vapour pressure of a liquid is lowered by the presence of an indifferent dissolved substance, and its boiling point therefore raised. The relation is indicated by the equation $M=KP/E$ (compare cryoscopic formula), where M=mol.-wt. of dissolved substance, P=no. of grams dissolved in 100 grams of solvent, E=elevation of b.-pt., and K=constant for solvent (5·2 for water, 25·3 for acetic acid, 26·7 for benzene); K is also equal to $T^2/50L$, where T is the absolute b.-pt. of the solvent, and L its latent heat of evaporation at its b.-pt. The thermometer bulb must be in the solution, and the vapour of the solvent must of course be returned by a reflux condenser or the concentration will be altered.

The solution usually bumps violently, and a short piece of platinum wire is therefore fused through the bottom of the flask. The sides of the flask must not be overheated. Beckmann's special apparatus is the most convenient.]

CHAPTER III

Sodium Ethoxide.—2 grams dry, bright sodium; 10 c.c. abs. alcohol. Heat drying tube in melted paraffin wax, dry coal gas with sulphuric acid. Tests: flame; copper oxide (carbon dioxide by lime water; water by copper sulphate). Keep in well-corked tube, as very hygroscopic.

Hydrolysis of Sodium Ethoxide.—Distil 10 c.c. from solution of 3 grams ethoxide in 30 c.c. water. Add stick of soda, cork (not too tightly) and leave. In a few hours layer of alcohol can be pipetted off; some burned, some tested by iodoform, aldehyde and ethyl acetate tests. Test also some methylated spirit and beer fraction.

Qualitative Tests for Alcohol.—Iodoform test very delicate. A drop of spirit in some water, make almost black with iodine in potassium iodide, add caustic soda cautiously until colour has almost disappeared, warm gently. Yellow crystalline ppt. or turbidity of iodoform (p. 116). Odour apparent, even if not enough to give turbidity. Aldehyde test fairly delicate. Warm liquid with two or three drops of potassium dichromate solution and a little dilute sulphuric acid. Chromate reduced to green chrome alum, and alcohol oxidised to aldehyde (p. 68), sweetish, pungent odour. Ethyl acetate test not very delicate. Mix liquid with few drops of acetic acid and twice its vol. of conc. sulphuric acid. Warm if necessary. Ethyl acetate formed (p. 34), fruity, pleasant odour. *Always make all three tests.*

Ethyl Bromide.—Flask, condenser and receiver quite dry. 6 grams red phosphorus and 50 c.c. abs. alcohol in flask, cooled with water. Pour through thistle funnel, drawn out at end to retain drop of liquid, not touching alcohol—very slowly, 14 c.c. bromine. A few drops only at a time, each time *thoroughly shaking*, allowing to become warm, and then cooling. *If these precautions are neglected, there will be an explosion.* Keep overnight if possible, well corked. Use small quantities of wash liquid, and 2 or 3 grams of calcium chloride. Pour off from latter before distilling. Avoid loss by volatilisation. Yield 25%. Note b.-pt. sp.-gr. No ppt. with silver nitrate until warmed with alcohol.

Qualitative Tests for Halogens. — (p. 15) Green-edged flame of ethyl bromide, green flame with copper oxide.

[*Estimation of Halogens.*—Stout combustion tube used, one end rounded, the other end, at short distance from end, *well thickened* and drawn out into wide-necked funnel. 2 Grams silver nitrate and 10 c.c. conc. nitric acid introduced through separate funnel without soiling upper part of tube; then substance, whether solid or liquid, in thin glass bulb, sealed as in carbon combustion. Bulb will adhere to wet sides of tube, and remain about half way down. The tube then carefully sealed, *with thick and well-annealed walls.* The bulb containing the substance is then broken by shaking briskly, and the tube placed in furnace. Heat applied gradually, first 100°, and so on, for an hour or so at each stage. The ends of the furnace must face brick or iron screen, to prevent damage should the tube explode. If much gas is expected it saves time to cool, and unseal after heating at 100°. To unseal, the tube is slid out of the oven tube and wound round with a cloth as it appears. Any drops of liquid at the narrow sealed end are then removed by cautiously holding near a hot tile, and the end then softened in a flame. The sealed end is held away from the operater, and the tube well wrapped up and held firmly. When the oxidation is complete the silver haloid lies at the bottom of the clear liquid. After unsealing the tube, the end is cut off just below the narrow part, and rinsed into the beaker into which the ppt. and liquid are transferred. The silver bromide, etc., is collected on a filter, and washed and transferred to a porclain crucible in the usual way. *It is not advised to attempt sealed tube work without supervision, as explosions happen in the most experienced hands.*]

Hydrolysis of Ethyl Bromide.—5 c.c. bromide with 5 grams caustic soda in 50 c.c. water. Ordinary flask without side-tube, as in Fig. 6. Narrow end of condenser downwards, and *projecting into neck at least an inch beyond cork.*

[*Ethyl Chloride.*—100 c.c. spirit, 40 grams zinc choride. Saturate cold. Gas from charges of 100 grams salt, warmed with mixture of 100 c.c. sulphuric acid and 20 c.c. water. Boil next day in paraffin bath, and pass in more gas if necessary. Condense chloride in U tube immersed in ice and salt. Yield 75%.]

CHAPTER IV

Ethyl Sodium Sulphate.—Pour 50 c.c. sulphuric acid carefully into 100 c.c. meth. spirit, shaking constantly. Heat in open flask on w.-b. Dilute to 500 c.c. and neutralise with whitening; earthenware pneumatic trough convenient. Filter at pump: large funnel into strong wide-necked bottle, which is connected through thick-walled rubber tube, or glass tube with very short rubber joints with suction pump attached to water tap (Fig. 9, p. 150).

Fair water-pressure necessary. Filter must fit well, and second small filter soaked in paraffin wax and pierced with pin-holes, placed first in funnel to strengthen it. Ppt. lime with washing soda solution, *taking care to avoid excess*; product should not effervesce with dilute acids. Drain crystals on porous (unglazed) tile or brick under bell-jar or inverted beaker. Very deliquescent. Yield 25%.

Qualitative Test for Sulphur.—As indicated (p. 21).

[*Estimation of Sulphur.*—As halogens, but without silver nitrate. Dilute well before precipitating. In this particular case the ethyl sulphates might be hydrolysed by boiling with dilute hydrochloric acid, and the sulphuric acid at once pptd.; or the solid sodium salt might be fused with sodium carbonate and nitre; but it is best to use the first process, which is applicable to all organic sulphur compounds.]

[*Estimation of Carbon and Hydrogen in Compounds containing Halogens or Sulphur.*—The copper oxide is replaced by fused and coarsely crushed lead chromate, and the substance mixed with five or six times its weight of the finely powdered chromate in a large iron boat, or simply in the tube. The chromate should not be heated at so high a temperature as the copper oxide. The halogens and sulphur are converted into the non-volatile lead chloride, etc., and sulphate.]

Hydrolysis of Ethyl Sodium Sulphate.—5 grams sulphate in 50 c.c. water with enough dilute sulphuric acid to make the whole distinctly acid. Boil in reflux apparatus half an hour, then distil. Iodoform, aldehyde and ethyl acetate tests to distillate. Evaporate residue for crystals of sodium hydrogen sulphate, which test.

Ether.—*Ether is very volatile, and its vapour very heavy and inflammable.* In working with it all flames should be kept away from the receiver, etc. In redistilling it use hot water, heated away from the apparatus. 20 c.c. spirit, and 20 c.c. sulphuric acid at 140° in distilling flask, thermometer bulb in liquid. When temperature rises run in gradually 80 c.c. more spirit from small inverted wash bottle with screw pinchcock ("feeding bottle" regulator) on tube attached to blowing tube. Spirit delivered beneath surface of boiling liquid. Yield 75%; b.-pt.; sp.-gr.; heaviness of vapour—pour into beaker on balance; inflammability; carbon dioxide left in beaker on burning vapour.

Ether from Ethyl Bromide.—2 c.c. ethyl bromide. 3 grams well dried sodium ethoxide. Warm in test tube. Note change of odour to that of ether. Prove white precipitate is sodium bromide.

CHAPTER V

Oxidation of Alcohol to Acetic Acid.—14 grams permanganate in 200 c.c. water, and 8 c.c. conc. sulphuric acid in litre flask with reflux condenser. 5 c.c. spirit and 50 c.c. water slowly poured down condenser. Action should be kept moderate. When finished boil for some time, and if colour of permanganate discharged, add more acid and permanganate solution. Then distil about three-fourths over. Note acidity to litmus and taste. Neutralise with washing soda, and evaporate as below. Apply qualitative tests.

Acetic Acid from Vinegar.—Distil vinegar. Note acidity of distillate. Neutralise with washing soda, and evaporate. Compare sodium salt with sodium acetate made from acetic acid as below. Apply qualitative tests.

Qualitative Tests for Acetic Acid (p. 29).—Distillable; acid reaction. Odour, with salts apparent on heating with dil. sulphuric acid. Ferric acetate, from ferric chloride (not containing free hydrochloric acid) and neutral acetate, red and soluble. Hydrolysed (colour discharged) by dil. hydrochloric acid. Hydrolysed to brown insol. basic salt by boiling with water, supernatant liquid becoming acid. Sodium acetate heated with dry white arsenic (very little of each) gives sickly offensive odour of cacodyl oxide (p. 234). Ethyl acetate: test as with alcohol.

Sodium Acetate.—100 c.c. ordinary B.P. acid exactly neutralised with washing soda and boiled down. When solution begins to bump, stir vigorously until solid. Then continue heating until mass again fuses, and pour on stone slab or bottom of retort stand. Note yield of sodium acetate (40% on weight of B.P. acid). Break up before quite cold, and keep in stoppered bottle.

Glacial Acetic Acid.—20 grams fused sodium acetate in small lumps, not powder. Distil from dry flask with 20 c.c. conc. sulphuric acid. Condenser and receiver quite dry. Redistil from clean dry flask with 2 grams powdered sodium acetate, quite dry. Note b.-pt., sp.-gr., and melting point. If acid will not freeze even in freezing mixture, add crystal of pure acid frozen from stock bottle, or shake and stir vigorously.

Melting Point.—Best determined on large quantity in test tube, with bulb and mercury column immersed. If substance pure, temperature is constant as long as solid and liquid, well stirred, are present together. If only bulb immersed, correction may be applied as in b.-pt. For small quantities, capillary tube method is the best. Ordinary quill tubing 3 in. long drawn to capillary at middle, and then fused into two tubes at middle of capillary. Narrow portion should just take an ordinary pin up to the head. Nearly fill capillary with powdered solid or liquid, fasten to thermometer stem with band cut from rubber tube, so that capillary rests against bulb, and open end against stem (Fig. 7). Freeze, and immerse bulb and capillary (not upper portion) in small beaker of some liquid, water in this case, at temperature below melting point of substance. Stir well, and gradually warm. If substance pure, opaque solid suddenly changes to transparent liquid on reaching melting point, and conversely liquid is as suddenly reconverted into the solid on cooling to freezing point. Melting and freezing points are then practically identical. If melting and freezing extend over several degrees, substance is impure.

Pure Acetic Acid.—Freeze 20 c.c. glacial acid in test tube in ice or sodium sulphate and hydrochloric acid, proceeding as directed until melting point ceases to rise. Determine b.-pt. and sp.-gr. of product. Note inflammability.

Molecular Weight by Silver Method.—Precipitate silver oxide with caustic soda from solution of 1 gram of silver nitrate. Wash free from alkali, and dry in a weighed porcelain crucible on a sand bath, *not above* 120°, till weight constant. Then heat to redness until weight again constant and silver in clean beads. Calculate molecular weight.

CHAPTER VI

Copper and Lead Acetates.—Make and crystallise (see copper formate chap. viii). Study hydrolysis of ferric salt.

Acetyl Chloride.—Mix 20 c.c. glacial acid and 10 c.c. phosphorus trichloride in flask, and pour into narrow cylinder. Whole of apparatus must be *perfectly dry*. Note b.-pt. Yield 75%. Keep in stoppered bottle.

Hydrolysis of Acetyl Chloride.—Note action of water and caustic soda, and test for acetic and hydrochloric acid in each case.

Acetic Anhydride.—5 c.c. chloride and 5 grams recently fused and powdered sodium acetate. Test with drop on glass rod, warmed with water and silver nitrate solution. No turbidity when pure. Note b.-pt. on redistillation. Best to redistil small quantities from test-tube with thermometer through cork and short right-angled tube to condenser. Hydrolysis in same way as with chloride.

Reduction of Acetyl Chloride.—5 c.c. chloride in loosely corked flask. Add, over a day or two, 4 grams sodium in 7 c.c. mercury. In making the sodium amalgam drop the sodium in small freshly cut pieces into warm dry mercury in a mortar, and press if necessary with a pestle. Action violent. The amalgam solidifies on cooling. Keep in a stoppered bottle. When reduction is finished pour off from the mercury, which can be used any number of times, and boil with excess of 1 in 10 caustic soda in a reflux apparatus before distilling.

CHAPTER VII

Preparation of Ethyl Acetate.—Boil 2 c.c. absolute alcohol with 2 c.c. glacial acetic acid in a test tube, and note odour. Hydrogen chloride method: gas as in ethyl chloride into mixture of 20 c.c. absolute alcohol and 20 c.c. glacial acetic acid. Brine and sodium carbonate solutions must be saturated. Calcium chloride as in ethyl bromide. Sodium acetate method: 50 grams acetate; 40 c.c. each meth. spirit and conc. sulphuric acid, all in distilling flask. Do not allow temperature to rise. Cork and keep at least 24 hours. Distil from w.-b. without further treatment. Note in each case b.-pt., sp.-gr., and yield: 80%.

Hydrolysis of Ethyl Acetate.—5 c.c. acetate; 5 grams caustic soda in 50 c.c. water. Prove alcohol and acetic acid.

Action of Acetyl Chloride and Oxide on Alcohol.—2 c.c. abs. alcohol; 2 c.c. chloride. Salt out. Same with oxide, but action less violent. Action best by alternately adding drop of the chloride or oxide and two or three drops of soda solution to the alcohol, shaking each time. Try also with amyl alcohol (fusel oil). Note pear odour.

CHAPTER VIII

Methyl Alcohol.—Dehydrate 100 c.c. commercial methyl alcohol in same way as ethyl alcohol. Note b.-pt., sp.-gr., imflammability, presence of carbon and hydrogen. Make sodium methoxide in same way as sodium ethoxide. Make methyl acetate from the alcohol, acetic acid and sulphuric acid in a test tube, and note odour. Make methyl sodium sulphate in exactly the same way as the ethyl salt, and with same quantities. Keep in stoppered bottle for chap. xi. Boil a little methyl alc. in test tube with acid permanganate and pass gas through lime water.

Formic Acid.—30 grams crystallised oxalic acid; 50 c.c. glycerol (glycerine); thermometer bulb *in mixture*. Test for carbon dioxide. At end of distillation (not above 135°) add 30 grams more oxalic acid, and so on for a third time. Note odour and acidity of product and conversion into carbon monoxide, by conc. sulphuric acid. Test as below. Mix distillates and redistil. Note yield 40 c.c. Convert 25 c.c. into barium formate: add barium carbonate to hot dilute solution until neutral, stirring well; boil and filter. Evaporate to crystallisation. Cover up for 24 hours; drain crystals carefully, and dry between filter paper. Evaporate mother liquor for second crop. Keep in a well corked tube. Convert 5 c.c. of acid into lead formate, using litharge in same way, and 5 c.c. into copper formate, using precipitated and washed copper oxide.

Qualitative Tests for Formates (p. 39).—Acid reaction. Odour, but on heating with conc. sulphuric acid carbon monoxide soon evolved (blue flame). Ferric formate same as ferric acetate. Formates reduce silver and mercuric chloride; acetates do not.

Butyric Acid.—Melt 25 grams butter slowly in beaker *under* hot sand bath. Pour off fat from water through hot dry filter, also under sand bath. Heat clear butter fat, with 60 c.c. meth. spirit and 10 grams caustic soda on w.-b. (gently) until clear yellow solution. Expel alcohol with water. (Odour and colour changes.) After distilling with sulphuric acid note acidity and rancid odour of distillate. Neutralise with sodium carbonate, add calcium chloride, and boil. Calcium butyrate precipitated. Collect while hot.

The Ethereal Salts.—Warm some calcium butyrate with a little absolute alcohol and conc. sulphuric acid, and note pineapple odour of ethyl butyrate. For amyl acetate see chap. viii.

CHAPTER IX

Saponification of Fat.—Boil 10 grams clarified suet; 10 grams caustic soda; 100 c.c. of water. Maintain level of liquid carefully, and boil vigorously. Purify and dry soap, and test detergent properties.

Fatty Acids.—5 grams soap; 50 c.c. water; excess dil. sulphuric acid. After washing, recrystallise from hot alcohol. Note faint acid reaction. Dissolve in hot caustic soda solution, avoiding excess. Add to portions of solution calcium chloride and magnesium sulphate, and note curdy precipitates as with hard water.

CHAPTER X

Acetamide.—20 c.c. ethyl acetate, 20 c.c. strongest ammonia, sp.-gr. 0·880, in corked flask, till perfectly homogeneous (24–48 hours). Identify alcohol in early distillate (acidify and distil). Recrystallise acetamide until m.-pt. constant. Note b.-pt. and yield, 5 grams. From ammonium acetate: 20 c.c. glacial acid. Distil acetate from large test tube with wide bent tube.

Detection of Nitrogen (p. 49).—Heat a crystal of acetamide with soda-lime, and note ammonia. Heat with sodium in small bulb tube. Violent action. Break hot in a little water. Filter. Add few drops ferrous sulphate and ferric chloride warm. Acidify with dil. hydrochloric acid. Prussian blue.

[*Estimation of Nitrogen by Combustion or Absolute Method.*—Open tube. 90 cm. long, as in carbon combustion; carbon dioxide from continuous appts., well washed with water and dried roughly with calcium chloride. Starting from end at which gas enters; 5 cm. empty; 4 cm. short roll of copper gauze, 10 cm. powdered copper oxide, 16 cm. powdered substance, intimately mixed with 20 times its weight of finely powdered and sifted copper oxide; 40 cm. granulated or wire copper oxide; 10 cm. long roll of copper gauze, previously reduced by dipping red hot into a little methyl alcohol in a test tube, and dried at 120°; 5 cm. empty. Fill tube in slanting position through wide-necked funnel with neck cut off short. Gas collected in Schiff's nitrometer filled with conc. potash soln. (1 in 5), and finally measured over water. Carbon dioxide passed through cold tube until practically all absorbed, in nitrometer—traces of air always remain from marble, etc. The tube then heated, (1) main bulk of oxide and long roll; (2) short roll and adjacent oxide; and, finally, (3) very cautiously, mixture of substance and copper oxide. Stop when gas is again practically entirely absorbed.]

[*Estimation of Nitrogen by Sulphuric Acid Method* (*Kjeldahl*).—0·5 gram of substance heated in round bottomed flask on sand bath with 50 c.c. conc. sulphuric acid, just short of boiling point of latter, and when substance has dissolved, powdered permanganate is added in small quantites until liquid is permanently coloured green or purple. The nitrogen is thus converted into ammonium sulphate, and the carbon completely oxidised. The cooled solution is poured into 250 c.c. cold water, and made alkaline with 10% caustic soda soln. and gently distilled, the ammonia being received in standard acid (sulphuric or hydrochloric). The excess of unused acid is then titrated with the corresponding standard alkali.]

[*Estimation of Carbon and Hydrogen in Nitrogenous Substances.*—Use long roll of freshly reduced copper gauze as in nitrogen estimation, and proportionally shorter layer of copper oxide.]

Hydrolysis of Acetamide.—Boil 1 gram in open flask with 2 grams caustic soda in 20 c.c. water. Note ammonia. Distil with excess of dil. sulphuric acid and test distillate for acetate acid. Action of nitrous acid: 1 gram in 10 c.c. water and excess of dil. sulphuric acid. Soln. of 3 grams of nitrite in 10 c.c. water added until paper blued. Potassium-iodide-starch papers: rub 2 grams starch with 20 c.c. cold water, and boil; add 1 gram potassium iodide; dip in filter paper strips and dry in air. After nitrite prove nitrogen and distil for acetic acid.

Acetonitrile.—5 grams acetamide; crude from ammonium acetate will do. Redistil. Note b.-pt., yield 6 c.c., odour and colour of flame.

Hydrolysis of Acetonitrile.—2 c.c. nitrile with 5 grams caustic soda in 50 c.c. water. Prove ammonia and acetic acid.

Ethylamine.—2 c.c. nitrile in 50 c.c. water and 5 c.c. conc. hydrochloric acid. 5 grams zinc added by degrees. Next day add excess of strong caustic soda—10 grams in 50 c.c. water, and distil. End of condenser tube should dip under a little water in receiver. Note odour and alkalinity of distillate. Neutralise with dilute hydrochloric acid, evaporate to dryness, and warm evaporated residue with absol. alcohol on w.-b. Filter and evaporate filtrate. Heat crystals with soda-lime as in making ammonia, and note odour, alkalinity and inflammability of gas. Test for carbon dioxide in products of combustion. Dissolve remainder in dil. sulphuric acid, and add nitrite as with acetamide. Prove nitrogen and alcohol.

CHAPTER XI

Hydrocyanic Acid.—10 grams finely powdered potassium ferrocyanide; 40 c.c. water and 4 c.c. conc. sulphuric acid. Distil carefully, avoid bumping.

Qualitative Tests for Cyanides.—(Chapter xxxiv.)

Synthesis of Formic Acid.—4 grams potassium cyanide with 50 c.c. water; as directed. Prove formic acid and ammonia; latter comes off suddenly after half an hour or so.

Synthesis of Acetic Acid.—10 grams dry methyl sodium sulphate, and 5 grams dry *crystallised* potassium cyanide, finely powdered and intimately mixed. Distil from test tube connected with condenser. Note odour of distillate (cautiously). Shake with 5 c.c. dil. sulphuric acid. Filter and boil in reflux apparatus with 7 grams caustic soda in 50 c.c. water. Well acidify with dil. sulphuric acid before distillation. Boil with 2 grams mercuric sulphate, and redistil. Prove distillate acetic acid: reaction, odour and tests.

CHAPTER XIII

Preparation of Crude Aldehyde.—From alcohol: 35 c.c. meth. spirit, 120 c.c. water, 22 c.c. conc. sulphuric acid. Cool. 30 grams bichromate in small crystals, not powder. Thistle funnel. Cool, if necessary. Afterwards heat on w.-b., but not with flame. Use porous calcium chloride. As soon as two layers have formed, pour off the upper layer, and warm in reflux apparatus, with an equal bulk of porous chloride. Then at once distil from same flask with bent tube. Note odour and b.-pt. (very extended).

Qualitative Tests for Aldehyde.—Odour. Silver reduction. Reduces alkaline copper tartrate (p. 426). Rosaniline test; one drop of dye solution only, much sulphurous acid. Aldehyde resin.

Reduction of Acetic Acid to Aldehyde.—Chloride with sodium amalgam as before, but stop after an hour, and acidify and distil. Test distillate as above. Barium formate method: acetate from 50 c.c. B.P. acid in same way as formate. 5 grams formate: 8 grams acetate. Mix as described. Distil as with methyl cyanide, heating from behind. Tube should slope downwards to mouth. Collect distillate in a little water. Filter and test.

Oxidation of Aldehyde to Acetic Acid.—5 c.c. with permanganate precisely as with alcohol, but action more violent. Test for acetic acid.

Reduction of Aldehyde to Alcohol.—5 c.c. aldehyde in 50 c.c. water. 50 grams 4% sodium amalgam gradually added. Keep solution always distinctly acid with dil. sulphuric acid, or aldehyde resinified. Distil and test for alcohol when odour has disappeared.

Aldehyde-Ammonia and Pure Aldehyde.—Ammonia from ammonium chloride and lime, dried with quicklime. Aldehyde quite dry, and mixed with equal volume of dry ether; ether dried with calcium chloride and redistilled from w.-b. (hot water only, no flame). When ammonia passes freely from surface of liquid, drain and dry crystals. Pure dilute aldehyde from these by distln. with dil. sulphuric acid at low temperature. Note odour. Test as above. [Pure aldehyde, as described, must be condensed in U-tube, surrounded with ice and salt. Note b.-pt.]

[*Paraldehyde and Metaldehyde.*—From pure aldehyde in manner described. Metaldehyde also from crude aldehyde and calcium chloride—24 hours.]

Aldehyde Phenyl-hydrazone.—A few drops of crude aldehyde in water. Add solution of two drops phenyl-hydrazine in dilute acetic acid.

CHAPTER XIV

Acetone—50 grams barium acetate. Distil in 4 portions. Crude distillate shaken with twice volume of bisulphite soln. made by passing washed sulphur dioxide into dry washing soda crystals until they melt to a green liquid. Dry crystals, and then as described. Tests on dilute liquid. Hydrazone as aldehyde, but no resin or silver, and rosaniline very slight if pure.

Oxidation of Acetone.—5 c.c. acetone; 12 grams permanganate in (100 c.c. water +10 c.c. conc. sulphuric acid) gradually added. Prove carbon dioxide. Distil when permanganate is no longer decolourised, and test for acetic acid.

[*Zinc Methyl.*—Dry reflux apparatus with small U-tube at top with drop of mercury in bend. In flask, intimate mixture of 10 grams each, zinc dust and reduced copper. Add 15 c.c. methyl iodide and proceed as directed; dry carbon dioxide. Reduce copper by adding zinc dust to copper sulphate solution until decolourised. Precipitate boiled with dil. acetic acid to remove undissolved zinc, washed with water, and dried between filter paper, and finally at 100°. Zinc methyl must be received in tubes drawn out at neck (condenser end therefore also drawn out), and immediately afterwards sealed.]

Isopropyl Alcohol.—10 c.c. acetone with sodium amalgam and dilute sulphuric acid, as with aldehyde. Pour off mercury after a day or two. Repeated treatment with the amalgam required. When hydrogen at last comes off freely, pour off and distil, and dehydrate. Note b.-pt., action of sodium, action of acetyl chloride. Isopropyl acetate, fruity odour.

CHAPTER XV

[*Isobutyl and Amyl Alcohols.*--Fractionate crude fusel oil, if obtainable].

CHAPTER XVI

Methane.—5 grams fused sodium acetate and 6 grams soda-lime, finely powdered and intimately mixed. Heat in hard glass tube with delivery tube. Roll of filter paper in front to absorb moisture. Heat from back to front, tube inclined towards front. Note gas, colourless, insoluble, light; burns to carbon dioxide. Does not decolourise bromine water.

Ethane.—20 grams zinc. Small flask. Half fill with meth. spirit, and add 4 c.c. ethyl bromide, and one drop of dilute sulphuric acid to start action. Warm very gently; fill up flask with spirit and replace cork and delivery tube. Wash gas with caustic soda. Like methane, but not lighter than air. Same tests.

CHAPTER XVII

[*Purification of Light Paraffin Oil.*—Shake benzoline with acids as directed, and wash with water. Note ethereal odour. Fractionate roughly-dried product, and note boiling points.]

CHAPTER XVIII

Ethylene.—20 c.c. meth. spirit. To prepare sample of gas, 10 c.c. meth. spirit and 30 c.c. conc. acid at 180°, thermometer in liquid. Shake with caustic soda. Note odour, taste. Luminous flame. Instantly decolourises bromine water. From ethyl sodium sulphate: dry-distil 5 grams from test tube, collect, shake with soda, and test as above. From ethyl bromide: 5 c.c. bromide in test tube connected with 6 in. length of hard glass tube with 3 in. of soda-lime, packed with asbestos at each end. Red-hot with one burner. Boil bromide and collect gas. Wash and test as before. Test residual soda-lime for bromine.

Ethylene Bromide.—Ethylene from alcohol, as described above, running in further supply of equal volumes from tap funnel or through thistle funnel. Pass through two wash bottles each with 20 grams caustic soda in 100 c.c. water. 10 c.c. bromine. Purify as described. Note odour, b.-pt., m.-pt., and sp.-gr. Yield 90 %, *if no sulphur dioxide.*

CHAPTER XIX

Acetylene.—From 3 c.c. ethylene bromide and soda-lime in same way as ethylene. Odour; smoky flame; silver and copper compounds. Silver: 0.5 gram nitrate in 5 c.c. water, and ammonia until ppt. just redissolves. Use 2 c.c. Copper: 5 grams turnings and 5 grams copper oxide, boiled with 20 c.c. conc. hydrochloric acid until brown, syrupy solution. Pour off, and when cold add excess of ammonia. Keep in small stoppered bottle, containing copper turnings and full to stopper. Use 5 c.c. From Bunsen flame: strike back and test with small inverted beakers moistened with the metallic solutions. From calcium carbide: fragment under beaker at pneumatic trough, *quickly*, with tongs. Examine gas as before.

PART II

CHAPTER XX

Chloroform.—150 grams bleaching powder and 20 grams slaked lime made into a thin cream with 500 c.c. water; 30 c.c. meth. spirit added. If action does not set in, distil with steam at once. Chloroform rather soluble in water, hence add brine to distillate. Purify. Note odour, b.-pt. sp.-gr. yield (50 % theor.).

Hydrolysis of Chloroform. — 5 c.c.; 5 grams soda, 50 c.c. meth. spirit. When odour has disappeared distil off alcohol on w.-b. and save. Prove dry residue sodium chloride and formate.

Conversion of Chloroform into Cyanide.—Boil 5 c.c. in reflux appts. with 5 grams caustic soda, 50 c.c. meth. spirit, and 5 c.c. conc. ammonia. Distil off alcohol and evaporate to dryness. Test for cyanide.

Qualitative Tests for Chloroform (p. 115).—Volatility. Odour. Formation of chloride with soda (blank expt. should be made, as soda liable to contain chlorides). Reduces alkaline copper tartrate (p. 426) on boiling. Warm with alcoholic soda and a drop of aniline in test tube. Characteristic odour of phenyl isocyanide.

Iodoform.—4 c.c. meth. spirit to solution of 10 g. washing soda in 50 c.c. water. Warm to 70° and add iodine (about 5 grams) until slight brown colour. Then 1 drop caustic soda. Note odour, hexagonal crystals (under lens); m.-pt. by capil. method.

Hydrolysis of Iodoform.—Same as with chloroform, but on small qty. in test tube.

Conversion of Iodoform into Acetylene.—1 gram iodoform ground up intimately with ½ gram of zinc dust. Heat in test tube, but first expel air by dry carbon dioxide. Collect gas and note odour, smoky flame; apply metallic tests.

[*Trichloracetic Acid.*—10 grams chloral hydrate, 8 c.c. red nitric acid, sp.-gr. = 1·5. Note yield (50 %). Prove hydrolysis to chloroform and carbonate on 1 gram.]

[*Chloracetic Acid.* — 100 c.c. glacial acid; 10 grams flowers of sulphur. Note m.-pt.]

[*Chloral.*—100 c.c. *rectified* spirit. Note b.-pt. and convert into hydrate.]

Chloral Hydrate.—Hydrolyse 1 gram with cold soda. Filter from chloroform (which prove) and test for formate. Reduces ammoniacal silver quickly, and alkaline copper tartrate (p. 426). Gives rosaniline aldehyde reaction. Reduce ½ gram in water with sodium amalgam in same way as aldehyde. After two or three days, pour off and distil and test alcohol.

Qualitative Tests for Chloral (p. 118).—Volatile with steam. Odour. Hydrolysis. Rosaniline. Reduces ammoniacal silver and alkaline copper tartrate. Phenyl isocyanide as with chloroform. Gives reddish-brown ppt. with ammonium sulphide, especially on warming.

CHAPTER XXI

[*Glycollic Acid.*—A fair yield by boiling potassium chloracetate solution (acid exactly neutralised) in reflux apparatus for several hours. Potassium chloride separates first on concentration. Evaporate remaining soln. to dryness and extract acid with hot abs. alcohol. Note acid reaction of solution. Distil some crystals with conc. sulphuric acid. Note carbon monoxide and crystals of paraformaldehyde. Oxidise some with conc. nitric acid. Evap. to dryness and test for oxalic acid.]

[*Glycol.*—10 c.c. ethylene dibromide, 16 grams dry potassium carbonate, 150 c.c. water. Note sweet taste, b.-pt., and oxidation to oxalic acid.]

Oxalic Acid from Sugar.—20 grams cane sugar, 50 c.c. conc. nitric acid. Warm (very heavy fumes). Try two or three times if necessary. Recrystallise from small qts. of water until free from nitric acid. Note acid reaction, and loss of water at 100°. Test tube in beaker of boiling water, with dry air (calcium chloride tube) sucked through. Note sublimed crystals.

Qualitative Tests for Oxalates (p. 126).—Calcium salt (calcium chloride to neutral oxalate) insol. in water and boiling acetic acid. Heated gently on platinum foil leaves a residue of calcium carbonate, which effervesces with acids. With conc. sulphuric acid, carbon monoxide and dioxide. With warm acid permanganate, carbon dioxide evolved and permanganate decolourised.

Ammonium Oxalates.—Solution of 20 grams acid into two equal parts. First exactly neutralised with ammonia and evaporated to crystallisation—normal oxalate. Second again divided; first half neutralised and mixed with second half, and evaporated as before—acid oxalate. Note different shape of crystals and acidity to litmus.

Ethyl Oxalate.—40 grams cryst. oxalic acid dehydrated in a flask as above until no further loss of weight (11½ grams). Heat with 25 c.c. abs. alcohol as directed (thermometer in liquid) passing in vapour of 33 c.c. more as in steam distillation. Fractionate. Note b.-pt. and sp.-gr. Use the distilled alcohol for oxamide (below).

Hydrolysis of Ethyl Oxalate.—As usual. 33 c.c. Prove alcohol and sodium oxalate.

Oxamide.—Ammonia to distilled alcohol from ethyl oxalate preparation. Also to 1 c.c. of pure ethyl oxalate. Wash ppt. and dry and filter.

Hydrolysis of Ethyl Oxalate.—In test tube. Prove ammonia and oxalate. Nitrous acid, as acetamide.

Oxalonitrile.—Heat ½ gram of oxamide with little phosphorus pentoxide in small bulb tube, and note pink flame of evolved gas.

CHAPTER XXII

Glycerol.—Saponify fat (ch. ix.) and distil lye with steam. Evap. distillate on w.-b. Test syrupy residue for glycerol, comparing with commercial sample.

Qualitative Tests for Glycerol (p. 129).—Syrupy; sweet. Residue on w.-b. Heated with excess of dry potassium hydrogen sulphate, turns brown and gives pungent acroleïn, which collected in water reduces silver, and resinifies with soda.

[*α-Dichlorhydrin.*—16 c.c. dry glycerol (heated in flask at 175°); 35 c.c. sulphur monochloride (from melted sulphur and dry chlorine—distils over—redistil—b.-pt. 139°). Reflux on w.-b. Note b.-pt. and chlorine flame.]

[*Hydrolysis of α-Dichlorhydrin.*—Boil 3 c.c. in reflux appts. with 5 grams caustic soda in 50 c.c. water. Steam distil glycerol and test. Test residue for chlorides.]

[*Glyceric Acid.*—30 c.c. glycerol and 38 c.c. water; 26 c.c. red nitric acid, sp. gr. 1·5. Note acidity of product.]

CHAPTER XXIII

Allyl Alcohol.—20 grams cryst. oxalic acid, 30 c.c. glycerol, ¼ gram ammonium chloride. Collect formic acid apart. A second quantity of oxalic acid to residue and again distil. Note b.-pt., sp.-gr., action of acetyl chloride (fragrant acetate) and bromine water. Oxidise a little to acrolein with chromic acid mixture.

Acroleïn.—5 grams glycerol. Distil from test tube with bent tube to condenser. Dissolve crude product in water and filter. Note odour, silver, rosaniline, resin and action of bromine water.

[*Acrylic Acid.*—From 10 c.c. acrolein as directed. Note acidity and action of bromine water.]

[*Oleïc Acid.*—Freeze stearin from olive oil, and saponify 10 c.c. oleïn with 10 grams litharge and 200 c.c. water in reflux apparatus (oil bath). When oil has disappeared, wash and dry soap (test soln. for glycerol), and powder and extract with ether. Filter. Separate oleïc acid as directed. Note action of bromine water.]

CHAPTER XXIV

[*Lactic Acid.*—100 grams loaf sugar, 0·5 gram tartaric acid, in 500 c.c. water. At same time leave 150 c.c. skim milk to turn sour and 4 grams of moistened cheese to putrefy in a warm place. After a week add these and 50 grams powdered zinc carbonate. Not above 30° or 35°.]

Solid Formulæ.—Cut out cardboard equilateral triangle, 2-inch sides. Bisect sides. Join up points of bisection. Score with penknife along sides of inner equilateral triangle thus formed, and fold up to tetrahedron. Fasten with sealing wax. Indicate groups by flag labels fastened to apices with pins. Try superposition and mirror relations.

CHAPTER XXV

[*Ethyl Acetoacetate.*—8 grams sodium, bright and clean; 80 c.c. *dry* ethyl acetate. 25 c.c. glacial acetic acid and same vol. water, or equivalent amount of B.P. acid. Yield 35 % on acetate not recovered.]

[*Distillation under Reduced Pressure.*—To stop bumping, bubbles of air slowly passed through liquid from drawn out jet just touching bottom of flask. Stream regulated by clamp at top (above thermometer, Fig. 9).]

[*Acetoacetic Synthesis of Butyric Acid.*—Ethyl iodide made in same way as bromide, but action quiet. Calc. quantities. 5 c.c. acetoacetate; calculated quants. of other materials. Recognise butyric acid by odour, b.-pt. and calcium salt.]

[*Ethyl Malonate.*—30 grams chloracetic acid, 60 c.c. water; powdered washing soda until neutral. 25 grams powdered pure crystallised cyanide. Boil together and evaporate on sand bath until viscid. Absol. alcohol 1 c.c. for every gram of powdered solid. Hydrogen chloride as with ethyl chloride. Heat on w.-b. 24 hours and saturate again. Note b.-pt. and yield (45 % theor.) Convert 5 c.c. into malonic acid. Note m.-pt. and decomposition into acetic acid, which identify.]

[*Malonic Acid Synthesis of Butyric Acid.*—On 10 c.c. of ethyl malonate. Calculated quants. Note b.-pt. and m.-pt. of ethyl derivatives, and identify butyric acid (yield 80 %).]

CHAPTER XXVI

[*Succinic Acid Synthesis.*—10 c.c. ethylene bromide, 17 grams pure crystallised cyanide, 100 c.c. abs. alcohol. After filtering potassium bromide from cold product, 10 grams caustic soda (yield 50%).]

Qualitative Tests for Succinic Acid (p. 157).—Calcium salt soluble, except in presence of alcohol and ammonia. Ferric salt red and gelatinous; no crystals with hydrochloric acid (see Beizzore acid). Acid melts on platinum foil, gives off suffocating fumes, and burns with clear flame.

CHAPTER XXVII

Tartaric Acid.—Prepare from 30 grams argol. Note m.-pt.

[*Racemic Acid.*—Heat 10 grams tartaric acid with 1 c.c. water in sealed tube. Recrystallise until m.-p. const.]

Qualitative Tests for Tartaric Acid (p. 165).—Chars on heating. Burnt sugar odour. Calcium salt (calcium chloride and neutral tartrate) appears in cold, but sol. in acetic acid and caustic soda. Reappears on boiling latter solution. Tartrate to copper sulphate prevents pptn. of oxide by caustic soda, simply dark blue solution. Tartrates reduce ammoniacal silver nitrate. (Distinction from citrate). Potassium hydrogen tartrate (potassium chloride and acetic acid) sparingly soluble, and appears on rubbing sides of tube.

Solid Formulæ of Tartaric Acids.—Fasten pairs of tetrahedra together with paper fasteners before sealing up. Ten tetrahedra wanted for complete set.

Qualitative Tests for Citric Acid (p. 169).—Calcium salt appears only on boiling. Citrates do not reduce silver. Potassium hydrogen citrate soluble.

[*Conversion of Citric Acid into Acetone.*—20 grams in conc. sulphuric acid (start with 20 c.c.) as indicated. Distil acetone-carboxylic acid, and prove carbon dioxide and acetone. Latter by b.-pt., bisulphite, and oxn. to carbon dioxide and acetic acid.]

CHAPTER XXVIII

Qualitative Tests for Cane Sugar (p. 173).—Non-volatile. Syrup or crystals on evapn. on w.-b. Chars with heat or conc. sulphuric acid; burnt sugar odour. Pale yellow with boiling caustic soda. No reduction of alkaline copper tartrate, unless soln. previously boiled with hydrochloric acid and neutralised. No osazone.

[*Estimation of Cane Sugar.*—Invert 100 c.c. soln., which should contain about $\frac{1}{20}$th of its weight of sugar, by heating it at 100° for 15 minutes with 5 c.c. conc. hydrochloric acid. Neutralise with sodium carbonate, make up to 500 c.c., and then as with glucose; 10 c.c. Fehling's soln. = 0·0475 gram cane sugar.]

Hydrolysis of Cane Sugar.—Half-gram sugar in 50 c.c. water and few drops of dil. hydrochloric acid. Heat on w.-b. for 15 minutes. Neutralise with sodium carbonate, and test with alkaline copper tartrate, as with glucose. Test original sugar soln. also.

[*Glucose.*—100 c.c. meth. spirit and 4 c.c. conc. hydrochloric acid at 45°. 35 grams powdered cane sugar. Yield 50%.]

Qualitative Tests for Glucose (p. 174).—Non-volatile. Sweet syrup on evapn. on w.-b. Not blackened by conc. sulphuric acid if pure. Dark brown product with boiling caustic soda. Reduces alkaline copper tartrate on warming (2 grams copper sulphate and 10 grams Rochelle salt in 25 c.c. water; when completely dissolved add solution of 3 grams caustic soda in 15 c.c. water). Reduces copper-acetic solution on boiling for 2 min. (see milk-sugar). Reduces bismuth hydroxide (bismuth nitrate and caustic soda). Crystalline osazone (chap. xxxi.).

[*Estimation of Glucose.*—Fehling's solution: Copper and alkaline tartrate solutions mixed just before use, as mixed solution does not keep well. Solution A: 17·32 grams recrystallised copper sulphate (exactly weighed) dissolved in 150 c.c. water, and cold solution made up to exactly 250 c.c. Solution B: 35 grams caustic soda and 90 grams recrystallised Rochelle salt dissolved in 150 c.c. water, and cold solution made up to exactly 250 c.c. To estimate sugar in solution, place 5 c.c. A, and 5 c.c. B in small flask, with 40 c.c. water and piece of glass to check bumping, and boil. Then run in sugar soln. from burette 2 c.c. at a time, until colour of supernatant liquid is just faintly yellow after ppt. has settled (sheet of white paper behind flask). 1 mol. glucose reduces 5 mols. copper sulphate, so that 10 c.c. of mixed soln. = 50 milligrams of glucose. This is therefore the quantity in the amount of solution required to decolourise the copper. If the strength of the sugar solution is less than $\frac{1}{2}$ gram or more than 1 gram per 100 c.c., results are only approximate, and estimation must be repeated on concentrated or diluted solution. If Fehling's solution old, prove by inverting 0·475 gram cane sugar as above, and making up to 100 c.c.; 10 c.c. of this should just decolourize 10 c.c. Fehling.]

[*Milk Sugar.*—Curdle 100 c.c. milk at 30° with a drop of hydrochloric acid. Evaporate filtered and neutralised whey to syrup, and cover up and leave to crystallise.]

Qualitative Tests for Milk Sugar (p. 175).—Gritty and only slightly sweet. Sparingly and only slowly soluble in cold water. Does not blacken when heated with conc. sulphuric acid. Does not colour with caustic soda. Reduces alkaline copper tartrate, but does not reduce copper-acetic solution on boiling for 2 minutes (1 gram copper acetate, 25 c.c. water, 20 drops B.P. acetic acid). Forms osazone characteristic crystals.

[*Estimation of Milk Sugar.*—As with glucose, but 10 c.c. Fehling = 0·067 gram lactose.]

Fermentation of Glucose.—10 grams glucose in 100 c.c. water, in a flask with delivery tube. Add a little yeast (teaspoonful), and keep at 30°. Note carbon dioxide, and when action is finished, distil and test for alcohol.

CHAPTER XXIX

Starch.—Separate starch from flour as indicated.

Qualitative Tests for Starch (p. 180).—Insoluble in cold, soluble in hot water; blue iodide, with iodine in potassium iodide. Decolourised by heat, colour returns on cooling; hydrolysis to glucose, which reduces copper.

[*Estimation of Starch.*—Heat 1 gram with 100 c.c. water and 10 drops conc. sulphuric acid in open flask on a w.-b. until drop of solution (cooled) ceases to give blue with iodine (30–60 min.). Then neutralise with soda and proceed as with glucose. 10 c.c. mixed Fehling = 0·0455 gram starch.]

Hydrolysis of Starch.—2 grams rubbed to cream with 10 c.c. water and made up to 200 c.c. Boil portion with few drops of dil. sulphuric acid for few minutes, and neutralise; test with copper and caustic soda tests.

Dextrin.—Moisten 5 grams starch with dil. sulphuric acid, and heat in test-tube in sulphuric acid bath at 200° for an hour. Brown product now soluble in water; reduces copper, and gives either red or no colour with iodine.

Cellulose.—Add excess of conc. ammonia to soln. of 2 grams copper sulphate in 20 c.c. water. Add filter paper to this as long as it disappears. Filter and add excess of dilute sulphuric acid.

Hydrolysis of Cellulose. Dissolve filter paper in 5 c.c. conc. sulphuric acid, and heat. When cold, pour into 6 c.c. water, and boil vigorously. Neutralise and test with copper.

Cellulose Nitrate.—As directed. Do not convert more than 1 gram of cotton, and destroy product.

CHAPTER XXX

[*Saccharic Acid.*—20 grams cane sugar, 30 c.c. nitric acid, 15 c.c. water.]

[*Mannitol and Sorbitol.*—Invert 10 grams cane sugar. Reduce with sodium amalgam in acid solution, as with aldehyde. Note copper reducing power eventually vanishes. Evap. to dryness on w.-b., separating sodium sulphate, and extract with strong spirit.]

[*Hexyl Iodide.*—Distil 20 grams commercial manna from oil bath with 100 c.c. distilled hydriodic acid b.-pt. 125° and 5 grams red phosphorus, Pour back and redistil several times. Purify as with ethyl iodide. Note b.-pt. Reduce to hexane with zinc and dil. hydrochloric acid. Wash dry and note b.-pt. and sp.-gr., and compare with benzoline hexane.]

CHAPTER XXXI

Glucosazone.—2 grams glucose in 15 c.c. water, mixed with solution of 2 grams phenyl-hydrazine in just sufficient dil. acetic acid. Both filtered. Heat in small flask in beaker of boiling water. Wash dry. Take m.-pt. by capillary tube method.

[*Synthesis of α-Acrose, etc.*—Add 5 c.c. bromine (about) very slowly to 5 c.c. freshly distilled acroleïn till just saturated. Keep ice-cold all the time. Mix product with ice-cold solution of 20 grams barium hydroxide in 100 c.c. water. Keep in cool place in loosely corked flask for a day or two. Then *exactly* ppt. barium with dilute sulphuric acid, and evaporate to syrup. Note hexose characters. Sweet. Reduces copper and silver, and forms a yellow osazone (mixture).]

CHAPTER XXXII

Urea from Urine.—100 c.c. fresh urine evaporated to one-sixth on w.-b. Cool syrup thoroughly and add 16 c.c. of conc. nitric acid, keeping cool. Pour off mother liquor from nitrate, and drain on plate or loose asbestos plug in funnel. Wash with 5 c.c. conc. nitric acid. Barium carbonate as cream with water. Take m.-pt. Apply tests.

Synthesis of Urea from Cyanide.—9 grams ordinary potassium cyanide *thoroughly* fused with 15 grams red lead in iron spoon or dish. Powder and boil with 30 c.c. water; filter; add 10 grams ammonium sulphate, and evaporate on w.-b. Extract hot with meth. spirit. Take m.-pt. Apply tests.

Hydrolysis of Urea.—1 gram boiled with very strong caustic soda soln.—2 grams in 4 c.c. Prove ammonia and carbonate. Nitrous acid as with acetamide—1 gram. Prove nitrogen and carbon dioxide—one-third of evolved gas soluble in caustic soda. Hypobromite: Fill test tube with ordinary caustic soda soln. to which bromine has been added—keeping cold—until deep yellow colour. Invert in basin of caustic soda. Introduce $\frac{1}{2}$ gram dry urea crystals, and compare volume of nitrogen with theoretical.

Condensation of Urea.—Heat $\frac{1}{2}$ gram at 200° in dry test tube in sulphuric acid bath. Dissolve in dil. caustic soda and add very dilute copper sulphate—violet biuret colour. Dissolve 1 gram urea in dil. hydrochloric acid, evap. to dryness on w.-b. Heat as directed, and convert half residue into barium salt—very little ammonia and barium chloride. Heat other half strongly in dry test tube, and note pungent odour of cyanic acid.

Qualitative Tests for Urea (p. 196). Non-volatile. Cryst. residue on evapn., especially from alcohol. Nitrate. Ammonia with *concentrated* soda only. Hypobromite. Cyanurate.

[*Estimation of Urea in Urine.*—Hypobromite process is the best. 150–250 c.c. flask containing 10 c.c. caustic soda in which bromine has been dissolved, *without rise of temperature*—colour should be bright yellow, not red from excess of bromine. 5 c.c. urine in small test tube which can be passed down neck of flask without spilling urine. Flask then corked and placed in beaker of water, and connected by glass tube through cork and rubber tube to clip burette, nearly filled with water and inverted in cylinder of water. Burette raised or lowered until level of water same inside and outside, and reading noted. Clip then opened, and urine slowly poured into hypobromite by tilting flask. Clip left open until generating flask has returned to original temperature, then burette raised until water again level, and reading taken. Difference between two readings = no. of c.c. of nitrogen. 37·1 c.c. of moist nitrogen at 18° and 760 mm. = 0·1 gram urea, or no. of c.c. × 2·7 = no. of milligrams of urea in sample. In Allen's modification 2½ times weight of potassium cyanate is added to urea, to prevent, by mass action, reconversion of urea into ammonium cyanate, and the bromine, dissolved in potassium bromide solution, is added to the mixture of the urea-cyanate solution with caustic soda.]

CHAPTER XXXIII

Uric Acid.—Saturate 100 c.c. urine with ammonium chloride (about 30 grams required), add a few drops of ammonia, and after 15 minutes filter. Pierce filter, wash ppt. into test tube with little water, dissolve in very little boiling caustic soda, cool, and filter. Acidify filtrate with dil. hydrochloric acid. Uric acid slowly pptd.; collect, wash, and apply murexide test.

Qualitative Tests for Uric Acid (p. 200).—Insol. water and dil. acids; sol. alkalies. Murexide test.

[*Estimation of Uric Acid in Urine.*—Ppt. as ammonium urate, and titrate with dil. permanganate. 100 c.c. urine, saturated with finely powdered ammonium chloride as above, stirring vigorously. Add few drops of ammonia, still stirring, and after 15 minutes transfer to filter and wash with sat. soln. of ammonium sulphate, until no chlorides. Rinse ppt. of acid ammonium urate off filter with hot water, dilute to 100 c.c. with cold water, and add 20 c.c. conc. sulphuric acid, and stir, thus raising temperature to about 60°. Then quickly run in permanganate (N/20 = 1·578 grams per litre) until pink tint ceases to vanish *instantly* on shaking. Further decolourisation may occur on standing, but this is to be disregarded. 1 c.c. permanganate = 0·00375 gram uric acid.]

[*Alloxan.*—5 grams uric acid (twice pptd. from conc. sulphuric acid), 10 c.c. conc. nitric acid + 5 c.c. water (= nitric acid sp.-gr. = 1·3). Proceed as directed.]

[*Parabanic Acid.*—From 5 grams alloxan as directed.]

Urea (and Allantoïn) from Uric Acid.—On 5 grams as directed. Test urea.

CHAPTER XXXIV

Potassium Ferrocyanide.—Boil 5 grams potassium cyanide with 3·5 grams cryst. ferrous sulphate and 50 c.c. water, filter and crystallise. Test ferrocyanide. Add bromine to hot soln. of 3 grams of ferrocyanide until ferric chloride ceases to give blue ppt. with sample. Crystallise and test ferricyanide. Heat 2 grams powdered ferrocyanide to redness in test tube. Break up, powder, and boil with water. Evap. filtered solution and test for cyanides.

Qualitative Tests for Cyanides (p. 205).—Ferrocyanides; ferric salts, dark blue; ferrous salts, light blue. Carbon monoxide with warm conc. sulphuric, hydrocyanic acid with dil. sulphuric acid. Copper salts, chocolate.

Insol. ferrocyanides decomposed by caustic soda. Ferricyanides: brown colour with ferric, dark blue with ferrous. Simple cyanides: mercuric cyanide must be decomposed by metallic zinc. Prussian blue test: Add ferrous sulphate, ferric chloride, caustic soda, and warm, then excess of dilute hydrochloric acid. Thiocyanate test: Evap. hydrocyanic acid to dryness with yellow ammonium sulphide, *without overheating*; ferric chloride gives red ferric thiocyanate. Silver test: Silver cyanide, like silver chloride, insol. in nitric acid, sol. in ammonia, but sol. in excess of cyanide. Last three tests best with watch-glass inverted over small beaker containing cyanide, and warm dilute hydrochloric acid. Watch-glass smeared with caustic soda, ammonium sulphide or silver nitrate; leave 3 minutes.

[*Estimation of Hydrocyanic Acid.*—Potassium or hydrogen cyanide dissolved in, or diluted if necessary with, water, and rendered just *faintly* alkaline by the addition of dilute nitric acid (to highly alkaline potassium salt) or caustic soda, and *kept in this state throughout operation* (solution coloured with litmus). Silver solution (4·25 grams per 250 c.c.$=AgNO_3/10$ per litre) *quickly* run in until *slight* permanent ppt. of AgCN. KCN thus converted into double cyanide AgCN, KCN. 1 c.c. silver=0·0054 grams hydrogen cyanide ($=2HCN/10$).]

Mercuric Cyanide and Cyanogen.—9 grams dry powdered mercuric sulphate stirred into hot solution of 6 grams cryst. potassium ferrocyanide in 40 c.c. water. Boil gently, filter hot. Mercuric cyanide separates at once. Recrystallise from water, filtering. Dry on filter paper. Salt does not give tests for mercury or cyanides until decomposed with zinc. Cyanogen: Heat dry crystals in small test tube, note inflammable gas, pink flame. Cyanogen is intensely poisonous.

Ethyl Isocyanate.—Heat a little ethyl sodium sulphate with potassium cyanate in dry test tube. Note pungent unpleasant odour of isocyanate. Methyl isocyanide already incidentally formed in synthesis of acetic acid.

Ammonium Thiocyanate.—20 c.c. conc. ammonia, 20 c.c. meth. spirit, 3 c.c. carbon bisulphide. Proceed as directed. Evaporate residue to dryness on w.-b., extract with hot spirit, crystallise and test.

Mustard Oil (see Aniline).—From methylamine or ethylamine and carbon bisulphide (1 drop), warmed with ferric chloride.

CHAPTER XXXV

Methylamine.—5 grams acetamide mixed with 4½ c.c. bromine, and 5 grams in 50 c.c. caustic soda in 50 c.c. water added till yellow product. Run this through thistle funnel into distilling flask containing 12 grams caustic soda in 36 c.c. water at 70°—not above. Condenser to dip under little water in receiver. Then proceed as in chapter x. for methylamine hydrochloride crystals.

CHAPTER XXXVI

Glycosine.—From 5 grams hippuric acid and 10 c.c. conc. hydrochloric acid as directed. Suspend lead glycosine in water and evaporate filtered solution on w.-b. Note m.-pt. and methylamine with soda-lime (odour and inflammability). Nitrogen with nitrous acid, as with ethylamine. Dissolve some freshly ppt. copper oxide in solution of ½ gram, and evap. filtered solution for copper amido-acetate. [From 10 grams chloracetic acid and 12 grams ammonium carbonate as directed. Compare with hippuric acid product.]

CHAPTER XXXVII

[*Ethyl Nitrate.*—Dangerous.]

Ethyl Nitrite.—Warm a little alcohol with copper turnings and a few drops conc. nitric acid in a test tube, and note odour.

[*Nitro-methane.*—Calculated quantities.]

[*Mercuric Fulminate.*—3 grams mercury, 18 c.c. conc. nitric acid, 9 c.c. water. Add 20 c.c. meth. spirit, then 20 c.c. more. Dry and detonate portion of fulminate. Convert rest into hydroxylamine hydrochloride.]

CHAPTER XXXVIII

[*Estimation of Phosphorus.*—As with sulphur. Phosphoric acid converted into magnesium pyrophosphate in usual manner.]

Cacodyl.—In very small quant. by heating dry sodium acetate ($\frac{1}{2}$ centigram), with equal bulk white arsenic. Vapour poisonous and produces nausea.

Zinc Ethyl.—(See chap. xiv.).

Mercaptan.—9 grams ethyl sodium sulphate; 3 grams caustic soda Form mercury compound.

PART III

CHAPTER XXXIX

[*Benzene from Commercial Product.*—Fractionate 50 c.c. "50%" benzene from w.-b. Neglect residue boiling above 100°. Re-fractionate until fraction 79–81° obtained. Then freeze until m.-pt. constant. Take sp.-gr. (Benzene vapour, like ether *very heavy and inflammable.*)]

✓ *Bromobenzene.*—14 c.c. benzene (const. m.-pt.), 10 c.c. bromine, $\frac{1}{2}$ gram iron filings. (Pass hydrogen bromide into 20 c.c. water and keep for chap. xlvii.; large bulb pipette just dipping under surface of water prevents passage backwards after air is expelled). In steam distillation ordinary flask may be substituted for distilling flask; tilt to keep spray from condenser. Wash with caustic soda before drying. Note b.-pt., sp.-gr., and halogen flame. Yield 70%.

✓ *Nitrobenzene.*—20 c.c. nitric, 20 c.c. sulphuric acid, 20 c.c. benzene. Product into beaker of cold water. Note b.-pt. and sp.-gr. Yield 80%.

Sodium Benzene-Sulphonate.—40 c.c. benzene, 80 c.c. conc. acid or same qty. fuming acid. Sodium salt as in chap. iv.; or by brine method (60 grams salt in minimum qty. of water; not so certain). Test for sulphur. Yield 70%.

Benzene-Sulphonic Chloride.—10 grams sulphonate, 15 grams pentachloride, 50 c.c. water. Distil off ether on w.-b., and chloride from test-tube over gauze. Note b.-pt. and odour. Prove sulphur. Hydrolyse two or three drops, and prove chlorine. Yield 60%.

Benzene-Sulphonamide.—Use remainder of sulphonic chloride; 10 grams carbonate per c.c. Recrystallise until m.-pt. sharp. Prove sulphur and nitrogen. Hydrolyse with caustic soda in test-tube, and prove ammonia. Yield 80%.

CHAPTER XL

✓ *Aniline.*—20 c.c. nitrobenzene, 120 c.c. conc. hydrochloric acid, 40 grams tin, 50 grams caustic soda powder in 200 c.c. water added until product grayish and fairly limpid. Steam distil from large flask. Collect yellow drops, dry with solid caustic soda, and pour off and distil from gauze. Shake water with $\frac{1}{10}$th its vol. of ether, and 5 grams caustic soda; separate. Repeat once. Dry mixed ethereal extracts with stick of soda, pour off, and distil off ether from w.-b. (*no flame*) and save; then aniline from test tube over gauze. Note b.-pt. of both portions. Test. Yield 80%.

✓ *Qualitative Tests for Aniline* (p. 247).—Odour (alkali if necessary). Pure liquid pptd. by dil. hydrochloric acid. Isocyanide. Mustard oil. Nitrogen and phenol with nitrite. Violet with bleaching soln. Blue with bichromate and conc. sulphuric acid.

✓ *Acetanilide.*—10 c.c. aniline; 10 c.c. glacial acid; four hours at least. Distil as with acetamide; anilide passes over above 280°. Recryst. from hot water (filter hot) until m.-pt. const. Yield 90%.

Hydrolysis of Acetanilide.—Boil 2 grams with 2 grams caustic soda and 20 c.c. water. Steam distil aniline and test. Distil residue with dil. sulphuric acid and prove acetic acid.

CHAPTER XLI

Phenol from Benzene-Sulphonate.—8 grams sulphonate, 40 grams caustic *potash*, 4 c.c. water. Stir well with thick iron wire. Thermometer bulb must be protected with silver cap, or else placed in sand under dish. Distil phenol from test tube after removing ether. Note b.-pt. Test. Yield 50%.

Phenol from Aniline.—10 grams aniline to 10 c.c. conc. sulphuric acid in ✓ 90 c.c. water. 10 grams sodium nitrite in 40 c.c. water until paper blue (chap. x.). Prove nitrogen. Note b.-pt. and test. Yield 85%.

Qualitative Tests for Phenol (p. 251).—Odour. Tribromophenol, and reconversion into phenol. Blue with ~~bleaching~~ solution. Liebermann's blue; ✓✗ about ½ gram sodium nitrite in 5 c.c. conc. sulphuric acid; two or three drops of phenol soln. to this. Picric acid: warm with little conc. nitric-sulphuric acid, pour cool into water; yellow, darkened by alkali, purple with cyanide. Ferric C

CHAPTER XLII

[*Diazobenzene Nitrate.*—10 c.c. aniline in cold mixture of 8 c.c. conc. nitric acid and 15 c.c. water. Drain cryst. mass and wash with small qties. of cold water until only slightly acid. (Trioxide from 25 grams white arsenic, lumps, not powder, and 25 c.c. conc. nitric acid; warmed on w.-b.; gas through empty bottle to deposit acid spray.) *Keep aniline paste ice-cold.* Diazo crystals may not appear at once; keep in ice, and wait two hours before trying again (stir occasionally). Decompose with water (note nitrophenol on steam dist.); alcohol; hydrochloric acid; potassium iodide; and bromine for perbromide. Explode a little.]

Bromobenzene from Aniline by Diazo-Reaction.—5 c.c. aniline in hydrobromic acid from bromobenzene prepn., diluted to 60 c.c. Cool in ice, and add nitrite soln. as with phenol. Then add gradually moist pptd. copper from 10 grams zinc dust and 40 grams copper sulphate. (See chap. xiv. zinc methyl note). When reaction over, steam dist. and dry. Compare product with bromination product. B.-pt.; sp.-gr. Yield 75%.

Elimination of Amido-Group from Aniline.—5 c.c. aniline in mixture of 15 c.c. conc. hydrochloric acid and 32 c.c. water; ice-cold. Diazotise cryst. ✓✗ magma with nitrite as before, and add 40 c.c. ice-cold 25% caustic soda powder soln., keeping cold. Pour this product *gradually* through condenser into reflux appts. containing at ordinary temperature soln. of 23 grams stannus chloride in 55 c.c. water to which about 25% caustic soda soln. has been added until ppt. has practically redissolved. When evolution of nitrogen ceases, steam distil, dry and redistil. Note odour, b.-pt. and m.-pt. of benzene. Yield 80%.

Phenyl-hydrazine.—Ice-cold paste of 14 c.c. aniline and 135 c.c. conc. ✓✗ hydrochloric acid diazotised with 20% nitrite (tests on *dilute* samples), and ice-cold soln. of 65 grams stannous chloride in 60 c.c. conc. hydrochloric acid added. Keep cold, wait half an hour before filtering. Note b.-pt. Yield 80%. Convert some into glucosazone and benzene (below).

Reducing Action of Phenyl-hydrazine.—Boil two or three drops with ✓✗ alkaline copper tartrate. Note nitrogen and red oxide.

Reduction of Phenyl-hydrazine to Benzene.—Run soln. of 4 grams hydrazine in 9 c.c. B.P. acetic acid and 25 c.c. water, into copper sulphate soln. (20 grams in 60 c.c.) boiling in reflux appts. Note evolution of nitrogen (prove), and distil off benzene with steam. Yield 70%. Identify by odour and conversion into nitrobenzene (odour).

CHAPTER XLIII

Conversion of Benzoic Acid into Benzene.—Dry distil intimately ground mixture of 5 grams benzoic acid, 5 grams soda lime, and 5 grams fine iron filings from test tube, heating from front backwards. Identify benzene by nitration. Yield 50%.

Benzonitrile from Aniline.—Diazotise 10 c.c. aniline as in elimination of amido-group, and pour slowly, with vigorous shaking, down condenser of reflux appts. containing cuprous soln. at ordinary temp. Cuprous soln. made by adding (*in good draught—poisonous cyanogen* evolved in large qties.) hot soln. of copper sulphate soln. (26 grams in 100 c.c. water) to potassium cyanide soln. (60 grams ordinary fused cyanide in 52 c.c. water), until initial white ppt. has just redissolved. When all diazo soln. added, heat on w.-b. until no more nitrogen, and distil with steam. No need to dry, as wanted for next expt. Note odour. Yield 60%.

Benzoic Acid from Benzonitrile.—Make up steam distillate to 100 c.c. with water, and boil in reflux appts. with 10 grams caustic soda. When no more ammonia, acidify with hydrochloric acid, and purify and sublime pptd. benzoic acid. Yield 80%. Take m.-pt. by capillary tube method. Test. Compare with stock acid.

Qualitative Tests for Benzoic Acid (p. 260).—Ferric chloride in neutral soln. buff pulverulent ppt. After pressing dissolves in a few drops warm conc. hydrochloric acid, which deposits paste of acid on cooling. Recrystd. from very little hot water forms plates. Odour of acid. Smoky flame. Benzene with soda-lime, which identify by conversion into nitrobenzene.

Benzoyl Chloride.—5 grams acid, 10 grams powdered pentachloride (good draught). Distil from test tube, with water out of condenser. Redistil and note b.-pt. and odour. Try action of cold and hot water on two or three drops, and then add caustic soda and prove benzoate and chloride. Yield 50%.

Benzoating Alcohol.—Convert half benzoyl chloride into ethyl benzoate as with mannitol (p. 262); equal vol. alcohol; make very slightly alkaline each time, and shake well.

Benzamide.—Rest of chloride with powdered ammonium carbonate (2 grams per c.c.) Shake cold product with cold water to remove excess carbonate; recryst. boiling water. Take m.-p.t. Yield 50%. Hydrolyse with caustic soda and prove ammonia and benzoate.

Benzoic Acid from Hippuric Acid.—Gently boil 3 grams hippuric acid in test tube with 10 c.c. conc. hydrochloric acid for five minutes. Cool. Wash and sublime benzoic acid, and prove by m.-pt. and test.

Qualitative Tests for Hippuric Acid (p. 263).—Ferric chloride in neutral soln. brown flocculent ppt. Crystals as with benzoic acid long needles. With soda lime, benzene (which identify) *and ammonia.* For last, use *well-washed* ferric chloride ppt.

[*Acetophenone.*—Dry distil 20 grams barium benzoate and 10 grams acetate, mixed as in reduction of acetic acid, ch. xiii. Avoid overheating benzoate in drying it. Fractionate product to sept. benzone, and note b.-pt. Shake a little with phenyl-hydrazine acetate and note hydrazone. Oxidise some acetophenone with permanganate, as with acetone, and note carbon dioxide and benzoic acid.]

CHAPTER XLIV

Benzaldehyde from Benzoic Acid.—Dry distil 5 grams barium benzoate mixed with 2 grams barium formate, as in reduction of acetic acid, chap. xiii. Note silver and rosaniline reactions, and hydrazone—2 or 3 drops distillate, same qty. phenyl-hydrazine dissolved in dil. acetic acid.

Oxidation of Benzaldehyde to Benzoic Acid.—Boil 3 c.c. commercial aldehyde with 10 grams bichromate, 5 c.c. conc. sulphuric acid and 50 c.c. water. Cool, filter off benzoic acid, drain, dissolve in dil. caustic soda, filter. Re-dissolve in soda, and reppt. until colourless. Sublime and test.

Condensation of Benzaldehyde with Acetone.—2 c.c. benzaldehyde, 4 c.c. acetone, 10 drops ordinary caustic soda soln. diluted with 50 c.c. water. Warm together in beaker of boiling water for an hour; crystallise cold, and recrystallise from hot water. Note m.-pt., 112°.

CHAPTER XLV

[*Oxidation of Toluene to Benzoic Acid.*—5 c.c. toluene, 18 grams bichromate, 15 c.c. conc. sulphuric acid, 100 c.c. water. Several hours' boiling. Prove carbon dioxide and benzoic acid.]

[*Synthesis of Toluene from Bromobenzene.*—7 grams *clean* sodium *gently* boiled with 50 c.c. ether in reflux appts. on w.-b. (good condensation) until no more hydrogen. Then cool, and add ice-cold and *dry* mixture of 10 c.c. bromobenzene, 10 c.c. ethyl bromide; finally 1 c.c. *dry* ethyl acetate. Allow reaction to take place quietly, not boiling. Keep 24 hours. Distil off ether on w.-b., and then toluene over gauze. Note b.-pt. Prove sodium bromide.]

Benzyl Bromide.—20 c.c. toluene, 10 c.c. bromine. Boil till no more hydrobromic acid evolved. Collect gas as with bromobenzene. Pour product into cold water; wash oil with dilute caustic soda until colourless; dry and fractionate (173°).

Oxidation of Benzyl Bromide to Benzoic Acid.—Boil half product in reflux apparatus with 50 c.c. dil. nitric acid, until dissolved, and prove benzoic and hydrobromic acids.

[*Benzyl Chloride.*—In sunlight or bright daylight until proper increase of weight.]

[*Oxidation of Benzyl Chloride to Benzaldehyde.*—Twice weight of lead nitrate dissolved in 10 times weight of water. Slow stream of washed carbon dioxide.]

[*Benzyl Alcohol and Benzoic Acid from Benzaldehyde.*—5 c.c. aldehyde; 5 grams caustic soda in 4 c.c. water; shake vigorously. Ether off on w.-b., and benzoic acid from aqueous soln. with hydrochloric acid.

Alkylic Hydroxyl in Benzyl Alcohol.—Shake 1 c.c. with 1 c.c. benzoic chloride, and a few drops of caustic soda. Note aromatic odour of ethereal salt.

CHAPTER XLVII

Meta-dinitrobenzene.—As with nitrobenzene, but red nitric acid, sp.-gr. = 1·5, and add benzene to acid mixture drop by drop, allowing to heat. Finally, 1 hour on w.-b. Wash water and recryst. alcohol until const. m.-pt.

Metanitraniline and Metanitrophenol.—10 grams dinitro.; 35 c.c. meth. spirit; 6 c.c. conc. ammonia. *Washed* sulphuretted hydrogen until 6 grams increase of weight. Note m.-pt. Convert portion into metanitrophenol in same way as aniline into phenol, and note nitrogen. M.-pt. of nitrophenol.

Ortho- and Para-Nitracetanilides.—10 grams powdered anilide, 25 c.c. red nitric acid, sp.-gr. = 1·5; shake with portions of 4 c.c. cold chloroform 5 times, filtering through small filter or asbestos each time. Recryst. and note colour and m.-pts.

Ortho- and Para-Nitraniline.—Conc. acid until dissolved. Note colours and m.-pts.

Ortho- and Para-Nitrophenol.—10 grams phenol; 15 c.c. conc. nitric acid + 30 c.c. water. Note m.-pts. and properties. Make sodium salts with washing soda (note carbon dioxide) and recrystallise. Note colours.

Picric Acid.—10 grams phenol + 7 c.c. conc. sulphuric acid; solution diluted with 20 c.c. water and slowly added to 30 c.c. conc. nitric acid diluted with 10 c.c. water. Shake well. Heat on w.-b. till yellowish. Note m.-pt. (Capillary tube.) Make sodium salt (with washing soda). Note carbon dioxide. Note purple with cyanide.

[*Metaphenylene-Diamine.*—20 grams dinitro.; 60 grams reduced iron; 3 c.c. glacial acetic; 60 c.c. water.]

[*Paramido-dimethylaniline.*—5 grams methyl orange in hot water; add soln. of stannous chloride in conc. hydrochloric acid till colour discharged.

Cool and stir; sulphanilic acid separates; nearly neutralise silver with washing soda, add excess caustic soda and extract with ether.]

CHAPTER XLIX

[*Resorcinol.*—Heat 10 grams sodium benzene sulphonate with 20 c.c. fuming sulphuric acid in reflux apparatus on sand-bath for 2 hours. Isolate sodium disulphonate (+ unchanged monosulphonate) by calcium carbonate method. Fuse the mixed mono- and di-sulphonate with potash as in phenol prepn., and sept. phenol and resorcinol by fract. distn. Note m.-pt. and colour with ferric chloride.]

[*Quinol.*—Use crude black quinone product as before ether extraction. Yield 25%.]

Quinone.—10 c.c. aniline, 50 c.c. conc. sulphuric acid, 250 c.c. water, ice-cooled; add 12 grams powdered bichromate in minimum qty. of water. Keep overnight at ordinary temp. Next day cool again, and add 24 grams bichromate in min. qty. water. After 3 hours, extract; 3 extractions. Distil off ether on w.-b.; residue with steam. Yield 30%. Note m.-pt., colour, volatility, odour.

[*Phloroglucinol.*—5 grams resorcinol, 25 grams caustic soda, 3 c.c. water. Yield 60%. Note m.-pt. and ferric chloride colour.]

Pyrogallol.—Heat gallic acid to its m.-pt. in test tube. Note carbon dioxide and sublimed pyrogallol. M.-pt. of latter, and colour with iron salts. Absorption of oxygen from air by its soln. in caustic alkali.

CHAPTER L

Salicylic Acid.—Dissolve 5 grams caustic soda in 7 c.c. water in iron dish; add 10 grams phenol; heat gently and stir vigorously until powder obtained—not cake. Place in dist. flask, and pass *washed and dried* carbon dioxide raising temperature gradually from 100° to 200°—4 hours. Yield 50%. Note m.-pt. and tests.

Qualitative Tests for Salicylic Acid (p. 303).—Violet with ferric chloride, in neutral soln. not changed by acetic acid. Flocculent tribromo-cpd. Intimate mixture with lime gives phenol (odour: picric acid).

Qualitative Tests for Gallic Acid (p. 306).—Blue-black with ferric or ferroso-ferric salts. No ppt. with gelatine. Rufigallic acid—moisten solid with conc. sulphuric acid on watch-glass, warm till red, turn into cold water.

Qualitative Tests for Tannin (p. 306).—Blue-black with iron salts. Ppt. with *cold, fresh* gelatine solution. (Soak fragment of gelatine in cold water until it swells, then warm with a little water.) Rufigallic acid, as with gallic acid.

CHAPTER LI

Toluene-sulphonic Acid.—Mixed *o*- and *p*-compounds in same way as with benzene, but more easily.

Cresols.—Mixed *o*- and *p*-cpds. as with phenol. Note colours and b.-pts.

Nitrotoluenes and Toluidines.—Mixed *o*- and *p*-cpds. in same way as nitrobenzene and aniline. Note b.-pts. Separate bases with sulphuric acid.

CHAPTER LII

Paratoluic Acid from Paratoluidine.—Precisely as with benzoic acid from aniline. Note m.-pt. and reactions (same as benzoic acid).

[*Paraxylene.*—Distil 10 grams camphor with 10 grams zinc chloride. Warm product with conc. hydrochloric acid; wash with alkali and water; dry and fractionate.]

Phthalic Acid and Anhydride.—6 grams naphthalene and 11 grams potassium chlorate (separately powdered), mixed and added slowly (draught cupboard) to 40 c.c. conc. hydrochloric acid. Washed chloride placed in reflux appts., and 80 c.c. conc. nitric acid *slowly* added (draught cupboard). Boil down in draught cupboard. Note m.-pt. anhydride. Soda until just alkaline (after boiling). Note m.-pt. of acid and conversion into anhydride.

Phthalic Acid to Benzene.—1 gram mixed with 10 grams powdered lime and 2 grams iron filings. Prove benzene by nitration.

[*Oxidation of Paraxylene to Paratoluic Acid.*—Boil 5 c.c. with 30 c.c. dil. nitric acid (1 : 4) until dissolved. Wash and dry product. Note sublimes without melting.]

Oxidation of Paratoluic to Terephthalic Acid.—3 grams acid, 2 grams caustic soda, 240 c.c. water; add to boiling soln. slowly 11 grams permanganate in 440 c.c. water, until supernatant liquid shows *permanent* pink colour. Wash and dry terephthalic acid, noting insolubility. Sublime.

CHAPTER LIII

Mesitylene.—50 c.c acetone, 65 c.c. conc. sulphuric acid, diluted with 30 c.c. water, 100 grams clean sand. Separate and purify mesitylenic and uvitic acids, and note m.-pts. Toluene and xylene from them by distn. with slaked lime.

CHAPTER LIV

Cinnamic Acid.—Boil 10 c.c. benzaldehyde, 28 c.c. acetic anhydride—both freshly distilled—with 5 grams recently fused and powdered sodium acetate in a flask with air-condenser, 6 hours without intermission. Mix the molten product with water, and steam distil. Animal charcoal, 5 grams powdered. Yield 30%. Note m.-pt. and action of bromine and alkalies. Yellow ppt. with ferric chloride.

Styrene from Cinnamic Acid.—Distil 5 grams cinnamic acid with 10 grams lime. Redistil distillate with steam. Dry and note b.-pt. and action of bromine. Take m.-pt. of dibromide.

Aniline from Indigo.—Distil 2 grams indigo from test tube with 4 grams caustic soda and 4 c.c. water. Prove aniline.

CHAPTER LV

Pinene.—Distil some ordinary spirit of turpentine with steam. Saturate some with dry hydrogen chloride gas. Shake some with permanganate soln.

[*Carvacrol and Cymene.*—Distil 24 grams camphor with 5 grams iodine, and fractionate distillate. Note b.-pt. Distil product with phosphorus pentasulphide (red phosphorus warmed with sulphur in dish; theor. qties.). Oxidise cymene with dil. nitric acid, and identify terephthalic acid.]

[*Dehydration of Camphor.*=Distil 10 grams with same wt. pentoxide. Redistil distillate, and note b.-pt. and characters.]

[*Camphoric Acid.*—20 grams camphor; 100 c.c. conc. nitric acid.]

CHAPTER LVI

[*Diphenyl.*—Benzene dropped from tap-funnel (15–25 drops per minute) into turned-up end of long iron gas pipe, filled with pumice in combustion furnace; dull red heat. Yield 50% on benzene unrecovered. Fractionate with air condenser and note m.-pt.]

Benzoïn.—10 grams benzaldehyde; 1 gram potassium cyanide in 30 c.c. meth. spirit; 20 c.c. water, heated in reflux appts. on w.-b. for an hour. Recryst. from alcohol, and note m.-pt.

Benzil.—5 grams of benzoïn; 10 c.c. conc. nitric acid. Reflux appts. Note m.-pt. and violet with alcoholic potash.

CHAPTER LVII

Rosaniline.—Boil 1 c.c. commercial aniline with 1 gram mercuric chloride and 10 c.c. water. Note colour.

Mordants.—Soak cotton rag in rosaniline soln., drain and dry. Note colour washed out by soap. Dip rag in dilute tannin soln.; wring; dip in dil. tartar emetic soln.; wring; finally in rosaniline. Note colour now fast to soap. Repeat with picric acid and aluminium acetate (alum soln. to lead acetate soln. until all lead pptd.; use clear filtrate).

Colour Base and Leuco-Base.—All following on few milligrams only. Decolourise rosaniline soln. with conc. hydrochloric acid, and restore colour with water. Ppt. white colour base with caustic soda, and redissolve in acid. Reduce dye with zinc dust and dil. hydrochloric acid. Add excess of caustic soda, and extract leuco-base with ether. Distil off ether on w.-b. and warm residue with few drops of conc. sulphuric acid; pour into water, and note dye.

[*Triphenylmethane.*—60 c.c. benzene; 8 c.c. chloroform, both perfectly dry, in reflux appts.; 2 grams fresh, dry aluminium chloride added 6 times. Yield 40%. Note m.-pt. (Aluminium chloride from 5 grams aluminium foil previously boiled with 5 c.c. absolute alcohol and dried at 100° in dry air-stream; heated to dull redness in stream of hydrogen chloride dried with conc. sulphuric acid. Expel air before heating, or explosion from hydrogen. Use chloride *at once*; old specimens are of no use.).]

[*Pararosaniline from Triphenylmethane.*—2 grams. Not too much nitric acid or zinc dust; when excess of latter, hydrogen freely evolved.]

CHAPTER LIX

[*Methylene Blue.*—$\frac{1}{4}$ gram paramido-dimethylaniline in 20 c.c. water and enough dilute sulphuric acid. Keep this solution as test. Add 2 or 3 drops and 2 or 3 drops of hydrochloric acid to solution containing trace of soluble sulphide; then ferric chloride—blue colour.]

[*Leuco-Malachite-Green.*— 9 grams fused and powdered zinc chloride, 20 c.c. dimethylaniline, 9 c.c. benzaldehyde. After removal of excess of the aniline, cryst. leuco-base from alcohol.]

[*Malachite Green.*—4 grams leuco-base, 200 c.c. of water, 4 c.c. conc. hydrochloric acid, 5 c.c. B.P. acetic acid. Stir in slowly *washed* lead peroxide, just pptd. by adding excess of bleaching soln. to soln. of 5 grams lead acetate. Add sodium sulphate soln. (6 grams in 30 c.c.) until no more ppt.; filter off lead sulphate and chloride. Salt out with sat. soln. of 5 grams zinc chloride until a drop of product no longer *stains* filter paper.]

[*Phenol-Phthaleïn.*—5 grams phthalic anhydride, 7 grams phenol, 10 c.c. conc. sulphuric acid. 2 hours boil with dil. hydrochloric acid (5 c.c., 90 c.c. water) before soda; filter and wash; dissolve phthaleïn in caustic soda (extract with more soda as long as soln. coloured). Finally ppt. with dil. hydrochloric acid.]

CHAPTER LX

Naphthalene.—Distil 10 grams commercial naphthalene, 5 grams caustic soda, 100 c.c. water with steam. Dry hydrocarbon and sublime, as with benzoic acid.

Nitronaphthalene.—10 grams naphthalene, 50 c.c. glacial acetic, 10 c.c. conc. nitric acid. Recryst. washed product from alcohol. Note m.-pt.

Naphthalene-β-Sulphonic Acid.—20 grams powdered naphthalene, 14 c.c. conc. sulphuric acid in flask for 4 hours at 180°. Pour into 500 c.c. water, filter off unchanged naphthalene, and then as with ethyl sodium sulphate. Yield 80% on unrecovered hydrocarbon.

α-Naphthylamine.—5 grams nitro-cpd., 2 grams iron filings, 10 c.c. B.P. acetic acid. Then as with aniline (hydroxide ppt. does not redissolve). Compare with aniline.

β-Naphthol.—5 grams sodium sulphonate, 15 grams caustic soda, 1 c.c. water. Temperature 200° for an hour, and finally 300° for a few minutes. Cold melt dissolved in 500 c.c. hot water, and naphthol pptd. from filtered soln. with dil. hydrochloric acid. Recryst. hot water. Yield 60%. Note m.-pt. Compare with phenol tests.

Oxidation of Naphthalene to Phthalic Acid.—(See chap. lii.)

CHAPTER LXI

Anthraquinone.—8 grams anthracene in 16 c.c. glacial acid; 12 grams chromium trioxide in 18 c.c. acid gradually added. Sublime. Note colour and m.-pt.

Conversion of Anthraquinone into Benzoic Acid.—Fuse 3 grams in iron spoon at 200° with 3 grams caustic soda and 1 c.c. water. Dissolve melt in water and ppt. benzoic acid with dil. hydrochloric acid. Collect, wash, dry, and sublime; identify by m.-pt. and tests.

[*Sodium Anthraquinone-Sulphonate.*—4 grams anthraquinone, 10 c.c. fuming sulphuric acid; heat until nearly all dissolved. Dilute, filter, neutralise hot with sodium carbonate; sodium salt cryst. on cooling.]

[*Alizarin.*—2 grams sulphonate, 7 grams caustic soda, $\frac{1}{2}$ gram potassium chlorate, 10 c.c. water. Heat in sealed tube (one-third full) for day and night at 165–175°. Extract alizarin with boiling water and ppt. dye with dilute acid. Wash, dry, and sublime. Note m.-pt., colour, solubility in caustic alkalies, and pptn. from these solns. by metallic salts. Note colours of lakes.]

CHAPTER LXII

Azoxybenzene.—4 grams sodium, 20 c.c. dry alcohol; 5 c.c. nitrobenzene. Note m.-pt. Yield 50%. Distil some with fine iron filings and compare azobenzene with that prepared by following method.

Azobenzene.—Boil 10 grams caustic soda, 50 c.c. meth. spirit until nearly dissolved (reflux appts.); then add at ordinary temp. 10 c.c. nitrobenzene. After 2 hours add 6 grams zinc dust and boil for 3 hours. Dist. off alcohol, extract residue with hot water, wash with dil. hydrochloric acid to remove zinc cpds. Finally wash with water and extract with boiling alcohol. Yield 70%. Purify, and note m.-pt. and red. vapour.

Amido-Azobenzene.—5 grams aniline hydrochloride, dissolved in 20 c.c. aniline at 35°; add 2·5 grams sodium nitrite in minimum qty. water (3 or 4 c.c.). Keep at 35–40° for $1\frac{1}{2}$ hours. Next day stir in 14 c.c. conc. hydrochloric acid; strain and press; dissolve liquid in excess of dilute acid, filter; add excess of caustic soda; collect and crystallise residue.

[*Triamido-Azobenzene.*—A few drops of a dilute soln. of metaphenylene-diamine salt to soln. contg. trace of nitrite. Can be used for the colorimetric estimation of nitrites in water.]

[*Methyl Orange.*—Make sulphanilic acid: 10 c.c. aniline heated for 5 hours at 20° with 20 c.c. conc. sulphuric acid. Crystallise repeatedly from hot water. Use 12 grams acid in 200 c.c. water; neutralise with washing soda. Calculated qties. for diazo, etc. Note red with acids, colourless with alkalies.]

CHAPTER LXIII

Quinoline.—10 c.c. nitrobenzene, 20 c.c. aniline, 50 c.c. glycerol; mix and cautiously stir in 30 c.c. conc. sulphuric acid. Yield 40%. Note b.-pt., odour. Make hydrochloride and crystallise.

Quinolinic Acid.—5 c.c. quinoline in good sized flask (reflux) with 5 grams permanganate in 100 c.c. water. Boil until purple colour (of clear liquid) disappears. Then add gradually through condenser, still boiling, 5 grams permanganate in 100 c.c. water, until purple colour permanent. Filter off manganese dioxide, slightly acidify with dil. sulphuric acid, decolourise excess of permanganate with drop of sulphite solution, and shake out with ether. Note m.-pt.

Pyridine from Quinolinic Acid.—Distil 1 gram quinolinic acid with 3 grams powdered soda-lime, as with benzoic acid. Collect distillate in water. Note odour, solubility and basicity.

CHAPTER LXIV

[*Collidine.*—20 c.c. ethyl acetoacetate and 6 grams *fresh* aldehyde ammonia. Yield 70% at each stage.]

CHAPTER LXV

Quinoline from Cinchonine.—Distil 5 grams cinchonine from test tube with 7 grams crushed caustic soda and 4 c.c. water. Sand bath, at as low a temperature as possible. Redistil quinoline with steam, and compare with synthetic product.

Qualitative Tests for Alkaloids in General (p. 397).—Phosphomolybdate (2 grams phosphomolydbic acid, 25 c.c. water, and just enough caustic soda to dissolve to clear colourless soln.); iodine in potassium iodide (2 grams iodine, 2 grams potassium iodide, 50 c.c. water; potassium mercuriodide (1 gram mercuric chloride, 2 grams potassium iodide, 25 c.c. water). Most alkaloids bitter. Soluble in acids, and mostly repptd. by ammonia.

[*Estimation of Total Alkaloids in Cinchona Bark.*—(The alkaloids are set free with lime, extracted with alcohol, converted into sulphates, purified, again set free with caustic soda, extracted with chloroform, and weighed after evaporating solvent.) 20 grams finely powdered cinchona bark, weighed after drying at 100°, thoroughly mixed to cream with 5 grams quicklime and 50 c.c. water, and dried to solid below 80°. The mass, which should be brown and homogeneous, is powdered and boiled in reflux appts. with 200 c.c. dehydrated meth. spirit, cooled and filtered, residue boiled again with 100 c.c., and finally washed twice with 50 c.c. spirit. Filtrates and washings, which contain the alkaloids set free by the lime, are mixed, and *slightly* acidified with dil. sulphuric acid, and the calcium sulphate thus pptd. is filtered off and washed with a little alcohol. The alcohol is then distilled off on w.-b., and the residual soln. of alkaloid sulphates filtered (the solid residue washed with a little acidified—sulphuric—water) and concentrated on w.-b. to about 50 c.c. It is then made strongly alkaline with caustic soda, and the alkaloids thus set free extracted by shaking with chloroform, first with 40 c.c. and then three times with 25 c.c. The chloroform is distilled on w.-b. from the mixed extracts, and the residual alkaloids (+water) evaporated to dryness on w.-b., and dried at 100° until weight constant. Good bark contains 5 to 6% of alkaloids, about half of which is quinine or cinchonidine].

Qualitative Tests for Quinine (p. 397).—Fluorescence with *dilute* sulphuric acid in *dilute* soln. Very bitter. Pptd. by ammonia. Chlorine tests.

Qualitative Tests for Cinchonine (p. 397).—Sol. in acids, pptd. by ammonia. Ferrocyanide from conc. soln. only.

CHAPTER LXVI

Extraction of Alkaloids from Organic Mixture.—Acid ether (tartaric) to remove fat, etc., then alkaline ether-chloroform (sodium carbonate) to extract alkaloid. Evaporate ether-chloroform soln. and test residue.

Qualitative Tests for Strychnine (p. 400).—Sol. acids, pptd. by ammonia. Bichromate crystal through cold conc. sulphuric acid soln., violet. Very bitter.

Qualitative Tests for Brucine (p. 400).—Sol. acids, pptd. by ammonia. Very bitter. Red with nitric acid, *changed to violet* by stannous chloride.

Qualitative Tests for Morphine (p. 401).—Sol. in acids. Blue with ferric chloride (faint; masked by meconic acid). Iodine with iodic acid, chloroform purple. Small crystal of ammonium molybdate to soln. of dry alkaloid in conc. sulphuric acid (cooled), fine blue colour.

[*Estimation of Morphine in Opium.*—(The morphine is dissolved in lime-water, pptd. by ammonium chloride, impurities and extractive matter are dissolved out with alcohol, and the alkaloid pptd. in crystalline form from the aqueous soln. by ether). A mixture of 10 grams powdered opium (dried at 100°) with 5 grams slaked lime is thoroughly mixed with 100 c.c. water in a mortar, and after some minutes filtered. (The meconic and resin acids are thus pptd.) The lime-water soln. of the alkaloid is well mixed, and 52 c.c. of it (=5 grams of opium, allowing for the bulk of the latter) is mixed with 6 c.c. dehydrated meth. spirit and 30 c.c. ether in a stoppered vessel and well shaken. 3 grams ammonium chloride next added (ammonia and calcium chloride thus formed), the shaking continued at intervals for half an hour. Nearly all the morphine is thrown down by the ether in crystals in 2 hours, the whole in 12 hours, the impurities remaining in solution in the upper layer of alcohol-ether. The upper layer is pipetted off and passed through a small tared filter, the aqueous residue shaken with 15 c.c. more ether, and the latter again pipetted off, and the crystals on the filter washed twice with 5 c.c. of ether. The filter is now allowed to dry in the air, at the ordinary temperature, and the aqueous layer with the morphine crystals transferred to it, the vessel being rinsed on to the filter with 15 c.c. water in small successive portions. The filter is drained and folded up, and dried, first by pressure between filter papers, and finally gradually heated to 100° until its weight is constant.]

CHAPTER LXVII

[*Thiophene.*—10 c.c. coml. benzene, 10 c.c. conc. sulphuric acid, containing a small crystal of phenanthraquinone (which make). Note blue.]

Dinitrothiophene.— Make a little meta-dinitrobenzene from "50%" benzene, and note red colour with alkali.

Furfuraldehyde.—Distil 5 grams chopped straw with 5 c.c. conc. hydrochloric acid and 100 c.c. water. Note colour of distillate with aniline.

APPENDIX II

QUALITATIVE ANALYSIS

The following scheme will be found useful in determining the nature of artificial mixtures of the organic compounds specified below with inorganic acids, bases, etc. (The tests for the individual compounds are given in Appendix I.).

LIST OF SUBSTANCES

I. ACIDS.—(*Precipitable by calcium chloride; precipitable or coloured by ferric chloride; precipitable by mineral acids*) :—

- i. *Calcium salts precipitable:* **oxalates** (p. 423), *white, immediate;* **tartrates** (p. 425), *white, on rubbing;* **citrates** (p. 425), *white, on boiling with ammonia.*
- ii. *Ferric salts coloured, and precipitable in cold:* **benzoates** (p. 432), *buff, pulverulent;* **hippurates** (p. 432), *brown, flocculent;* **succinates** (p. 425), *red, gelatinous.* [Tartrates also precipitated from very concentrated solutions, and cyanides from slightly alkaline solutions.]
- iii. *Ferric salts coloured and precipitable on boiling:* **acetates** (p. 416), *red solution, brown precipitate;* **formates** (p. 418), *same.*
- iv. *Ferric salts coloured and imperfectly precipitable:* **gallates** (p. 434), *black;* **tannates** (p. 434), *black;* **ferrocyanides** (p. 428), *dark blue.*
- v. *Ferric salts or compounds coloured and soluble:* **thiocyanates** (p. 429), *red;* **ferricyanides** (p. 428), *greenish-brown;* **salicylates** (p. 434), *violet;* **phenates** (p. 431), *violet.*
- vi. *Convertible into compound precipitable by ferric chloride:* **Simple cyanides** (p. 428).
- vii. *Insoluble in acids:* **uric acid** (p. 428); benzoic and succinic acids; phenol (*oil from concentrated solution*).

II. ALKALOIDS AND AMINES.—(*Precipitable by sodium carbonate or caustic soda*) :—

- i. *Solid precipitate:* **strychnine** (p. 438); **quinine** (p. 438); **morphine** (p. 438).
- ii. *Oil* (*from concentrated solution*): **aniline** (p. 431).

III. AMIDE.—*Soluble in water; hydrolysable by concentrated caustic soda;* **urea.**

IV. CARBOHYDRATES. — (*Precipitable only by special agents; non-volatile* :—

- i. *Soluble in cold water:* **cane-sugar** (p. 425), *readily;* **milk-sugar** (p. 426), *with difficulty;* **glucose** (p. 425), *readily.*
- ii. *Soluble only in hot water:* **starch** (p. 426).

V. ALCOHOLS AND DERIVATIVES.—(*Distillable alone, or with alkalies or acids; and precipitable only by special agents*) :—

- i. *Stable to alkalies:* **alcohol** (p. 414), *readily volatile;* **glycerol** (p. 424), *difficultly volatile;* [acetic and formic acids].
- ii. *Decomposed by alkalies:* **chloral** (p. 423), *immediately;* **chloroform** (p. 422), *with conc. alcoholic alkali;* [hydrocyanic acid].

PROCEDURE

A. Preliminary Examination of a Solution.—

i. Note colour,[1] odour [2] (especially on warming); reaction to litmus.

ii. Evaporate some to dryness on water bath, and note whether no residue,[3] syrupy residue,[4] or solid residue. Examine solid residue by B.

iii. Distil some from test tube with cork and bent tube leading to bottom of second test tube cooled in beaker of water; note odour and reaction of distillate, and test by A–i and C, and specially.[5]

iv. If solution acid, distil with slight excess of caustic soda, and examine distillate by A–i and C.

v. If solution alkaline, distil with slight excess of dilute sulphuric acid, and examine distillate by A–i and C.

B. Preliminary Examination of Solid.

i. Heat a little in bulb-tube, and note odour,[6] melting,[7] partial or complete volatilisation,[8] blackening.[9]

ii. If residue remains in bulb-tube, heat on fragment of porcelain and examine carbon-free residue (if any) for metals.[10]

iii. Boil substance with water. If entirely soluble, proceed to A–i–iii–iv and C; if partially soluble (evaporate few drops, filtered, on watch-glass at 100°), filter and boil residue with small quantities of water as long as anything is dissolved. Examine solution by A–i–iii–iv and C.

iv. Heat solid, or insoluble and soluble portions separately, to redness on fragment of porcelain. If metallic residue, boil portion with sodium carbonate, and filter (see C–i), and examine solution by A–i–iii–iv and C. Precipitate may contain alkaloids; shake with a little cold water and ether-chloroform, latter dissolves alkaloids.

v. If no residue on ignition, and solid insoluble,[11] dissolve in dilute sulphuric acid or caustic soda.

C. Examination of Solution.

i. If acid, neutralise; add solid sodium carbonate, a little at a time, as long as there is violent effervescence, then add more of the acid

---

[1] Iron and copper salts coloured; organic solutions often turn brown from oxidation.

[2] The following have characteristic odours:—Alcohol, chloral, chloroform, aniline, phenol, tannin; acetic, formic, hydrocyanic and benzoic acids, and certain of their salts.

[3] The following are completely volatile at 100°:—Free acetic, formic and hydrocyanic acids; water, alcohol, chloral, and chloroform.

[4] The following are syrupy:—Glycerol; free phenol; sugars (milk sugar may crystallise quickly); free tartaric and citric acids (crystallise only slowly).

[5] The following are easily volatilised:—Alcohol, chloral, chloroform, and free acetic, formic and hydrocyanic acids; the following with difficulty: glycerol, free benzoic and succinic acids; aniline (from alkaline solution), phenol (from acid solution).

[6] Burnt feather odour=uric acid, alkaloids (nitrogen); burnt sugar=sugars, tartrates; aromatic=benzenoid acids; suffocating=succinates, citrates.

[7] Sugars, urea, and many acids and salts melt easily.

[8] Completely or partially volatile, see Notes 3 and 5.

[9] Blackening=carbohydrates, tartrates, etc.

[10] Solid residue on ignition contains all metals except mercury and arsenic, and possibly antimony; examine for these specially.

[11] Probably uric acid or free alkaloid.

solution until the whole is distinctly acid; then neutralise with ammonia. Precipitate contains metals (except antimony and, perhaps, lead); and iron and copper in presence of hydroxy-compounds; these must be eliminated with sulphuretted hydrogen or ammonium sulphide); and alkaloids (B-iv).

ii. If alkaline, neutralise with dilute hydrochloric acid, and note odour. If precipitate, see I–vii.

iii. To portion of filtered, neutralised solution add ferric chloride; if precipitate, filter off, and examine for acids, I–ii–iv; boil filtrate, and if further precipitate, filter off and examine for acids, I–iii; if filtrate still coloured, examine for acids, I–iv–v.

iv. To fresh portion add ammonium chloride, ammonia (slightly alkaline only) and plenty of calcium chloride (half volume); note whether precipitate immediately, or on rubbing, or only on boiling with ammonia (I-i). Ammonia may precipitate alkaloids (II–i, B–iv).

v. Examine for alkaloids, first by general tests, and then if present by special tests; aniline always specially, after ether-chloroform extraction.

vi. Examine for urea, sugars, and starch.

vii. Examine for cyanides (beaker tests); mercuric cyanide must be decomposed with metallic zinc.

viii. Examine for uric acid.

D. Examination of Mixture.

If two organic substances are present, the second is found in the same way, bearing in mind that its reactions may be obscured or modified by the presence of the first. Volatile and non-volatile substances are readily separated by distillation; precipitable and non-precipitable by filtration.

NAME INDEX

SUBJECT-MATTER INDEX

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