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SOME DERIVATIVES OF

UMBELLULONE

BY

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES

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LXIV.—*Some Derivatives of Umbellulone.*

By Frederic Herbert Lees.

In the preceding paper, it was shown that the new unsaturated ketone, umbellulone, $C_{10}H_{14}O$, as compared with the majority of ketones, behaves abnormally in its interactions with hydroxylamine and with semicarbazide, for not only does its carbonyl group undergo the usual transformation by reacting with one molecule of the respective

base, but, in each case, the elements of a second molecule of the latter become attached to the molecule of the ketone. The products, therefore, represent the interaction of one molecule of umbellulone with two molecules of hydroxylamine or semicarbazide.

A behaviour of this kind in respect to the interaction of hydroxylamine or semicarbazide with certain unsaturated ketones has been previously observed in many instances, particularly by Harries and his pupils (*Ber.*, 1899, 32, 1317), by Tiemann, and quite recently with regard to the action of semicarbazide, by Rupe and Schlochoff (compare this vol., p. 635).

It has been shown by these authors that the abnormal behaviour under consideration is common to those ketones which contain an ethylenic linking in an $\alpha\beta$-position with respect to the carbonyl group.

In the hope of ultimately elucidating the constitution of umbellulone, its behaviour towards a number of reagents is being studied, and some of the results obtained are recorded in this paper.

Umbellulone combines directly, in the cold, with only two atomic proportions of bromine, forming *umbellulone dibromide*, $C_{10}H_{14}OBr_2$; it would therefore seem to contain only one ethylenic linking. From its formula, $C_{10}H_{14}O$, and the foregoing considerations, umbellulone would appear to be an $\alpha\beta$-unsaturated cyclic ketone, containing two closed rings.

When umbellulone dibromide is slowly heated under diminished pressure, it rapidly becomes decomposed with evolution of hydrogen bromide. The product of this decomposition is an *unsaturated bromoketone*, having the formula $C_{10}H_{13}OBr$ (b. p. 140—145°/20 mm.); but, besides this, *dibromodihydroumbellulone*, $C_{10}H_{14}OBr_2$ (m. p. 119—119·5°) is also formed, the latter being probably the result of the subsequent combination of the unsaturated bromoketone with the elements of hydrogen bromide.

The unsaturated bromoketone, $C_{10}H_{13}OBr$, on reduction with zinc dust and acetic acid, becomes converted into a *saturated ketone*, $C_{10}H_{16}O$ (b. p. 214—217°).

When dibromodihydroumbellulone is reduced with zinc dust and acetic acid, it is only found possible to eliminate one bromine atom with the formation of *bromodihydroumbellulone*, $C_{10}H_{15}OBr$ (m. p. 58—59°). When the latter, however, is reduced by means of sodium and alcohol, *tetrahydroumbellulol*, $C_{10}H_{19}OH$, is produced (b. p. 207—208°/760 mm.).

Both dibromodihydroumbellulone and bromodihydroumbellulone behave as saturated substances, since they do not decolorise a solution of bromine in chloroform, even on boiling. In view of this fact, the formation of tetrahydroumbellulol, $C_{10}H_{20}O$, from bromodihydro-

umbellulone, $C_{10}H_{15}OBr$, can only be explained on the assumption that one of the two closed rings present in umbellulone, dibromodihydroumbellulone, and bromodihydroumbellulone becomes resolved by reduction in passing to the alcohol.

Umbellulone is readily oxidised by cold permanganate, yielding a *lactone*, $C_9H_{12}O_2$ (b. p. 217—221°), together with several acids which, on account of insufficiency of material, have not yet been investigated.

Experimental.

Action of Bromine on Umbellulone. Formation of Umbellulone Dibromide, $C_{10}H_{14}OBr_2$.

Twenty grams of umbellulone were dissolved in 100 c.c. of dry chloroform, and the solution cooled in a freezing mixture. A solution of 25 grams of dry bromine in 100 c.c. of dry chloroform was then run in, drop by drop; the bromine was instantaneously absorbed, and without any evolution of hydrogen bromide. When all the bromine had been added, the colour of the solution was red, and on this remaining permanent for some minutes, the slight excess of bromine was removed by shaking the liquid with a solution of sodium hydrogen sulphite. The nearly colourless liquid, after washing several times with water, was dried with calcium chloride, and the chloroform removed by allowing the liquid to boil under diminished pressure without the application of external heat. The resulting dibromide was a somewhat dark, heavy oil, the amount obtained being approximately equal to the combined weights of the umbellulone and bromine originally taken for its formation, thus showing that the process is one of addition and not of substitution. A portion was exposed in a vacuum desiccator over paraffin wax, and then analysed:

0·4554 gave 0·528 AgBr. Br = 49·3.

$C_{10}H_{14}OBr_2$ requires Br = 51·6 per cent.

Umbellulone dibromide is very unstable, readily losing hydrogen bromide even when kept at the ordinary temperature.

Action of Heat on Umbellulone Dibromide. Formation of an Unsaturated Bromoketone, $C_{10}H_{12}OBr$, *and Dibromodihydroumbellulone*, $C_{10}H_{14}OBr_2$.

A quantity of umbellulone dibromide was slowly heated in a distilling apparatus under 20 mm. pressure. An energetic evolution of hydrogen bromide commenced almost immediately, and a small amount of a colourless liquid passed over into the receiver while the temperature was

below 100°. The temperature gradually rose to 160°, when the evolution of hydrogen bromide ceased; in the meantime, a large fraction (*a*) had collected in the receiver (pressure = 20 mm.). The residual liquid was then rapidly distilled, and the last distillate, which passed over between 160° and 190°/20 mm., was collected separately from the first fraction, which distilled below 160°. A quantity of dark, resinous, undistillable residue remained in the distilling flask. The less volatile fraction, on cooling, became for the most part crystalline, and on diluting with an equal volume of light petroleum, a further amount of the crystalline substance separated. It was collected at the pump and washed with light petroleum. After the removal of the petroleum from the filtrate, the residual oil, together with the more volatile fraction (*a*), when fractionated under diminished pressure yielded a further quantity of the fraction (160—190°/20 mm.), which, on treatment with petroleum, afforded more of the crystalline substance, and also two other principal fractions, one of which distilled below 130°/80 mm., and the other at 140—145°/20 mm.

Fraction boiling below 130°/80 *mm.*—This was nearly insoluble in 70 per cent. alcohol, and consisted chiefly of a hydrocarbon; it was distilled repeatedly under the ordinary pressure, and finally twice over sodium, being thus obtained as a colourless, limpid liquid, which boiled at 175—177°, had the odour of cymene, and was evidently a hydrocarbon having the formula $C_{10}H_{14}$.*

0·1184 gave 0·3873 CO_2 and 0·1125 H_2O. C = 89·2; H = 10·6.
$C_{10}H_{14}$ requires C = 89·6; H = 10·4 per cent.

The Unsaturated Bromoketone, $C_{10}H_{13}OBr$.

Fraction 140—145°/20 *mm.*—This fraction was a heavy, light yellow oil, the vapour of which had a very irritating effect on the eyes. It contained bromine, and was unsaturated, since it instantaneously decolorised a solution of bromine in chloroform.

0·2134 gave 0·4090 CO_2 and 0·1168 H_2O. C = 52·3; H = 6·1.
0·1593 ,, 0·3029 CO_2 and 0·0875 H_2O. C = 51·9; H = 6·1.
$C_{10}H_{13}OBr$ requires C = 52·4; H = 5·7 per cent.

Action of Zinc Dust and Acetic Acid.—Fifteen grams of the unsaturated bromoketone were dissolved in 100 c.c. of glacial acetic acid,

* Sufficient of this hydrocarbon to admit of purification was only obtained by the employment of a large amount of the umbellulone fraction (b. p. 217—222°) (compare this vol., p. 634), afforded by direct fractional distillation of the essential oil of Californian laurel. The formation of a hydrocarbon, $C_{10}H_{14}$, would be explained on the assumption that there was associated with the umbellulone a small amount of a substance having the formula $C_{10}H_{16}O$.

and 50 grams of zinc dust introduced. A vigorous reduction took place, which was moderated by immersing the flask in cold water. When the reaction had become less energetic, the mixture was heated on the water-bath during 3 hours; the product was then ground up with water and the oil extracted with ether. The ethereal solution was washed successively with water, aqueous sodium carbonate, and water, dried over calcium chloride, and the ether removed. The residual yellow oil was fractionated under the ordinary pressure, when it nearly all passed over between 212° and 218°, but principally at 214—217°, as a nearly colourless liquid, which had an odour closely resembling that of pulegone. A portion of that which distilled at 214—217° was analysed:

0·1156 gave 0·3342 CO_2 and 0·1099 H_2O. C = 78·8; H = 10·6.
0·1234 „ 0·356 CO_2 „ 0·1174 H_2O. C = 78·7; H = 10·6
$C_{10}H_{16}O$ requires C = 79·0; H = 10·5 per cent.

It was thus shown that the action of zinc dust and acetic acid on the unsaturated bromoketone, $C_{10}H_{13}OBr$, is to form a ketone having the formula $C_{10}H_{16}O$. This new ketone was shown to be saturated, since it did not decolorise a very dilute solution of bromine in chloroform even after some time.

The *semicarbazone*, when prepared in the ordinary way, was first obtained as a viscid oil, which, however, soon became crystalline. It was drained on a porous plate, and then crystallised several times from dilute methyl alcohol, from which it separated in fine, white needles melting at 171—172°.

0·051 gave 0·0118 CO_2 and 0·043 H_2O. C = 63·1; H = 9·4.
$C_{10}H_{19}ON_3$ requires C = 63·1; H = 9·1 per cent.

The semicarbazone is soluble in dilute sulphuric acid (25 per cent.), and on warming the solution it is decomposed, regenerating the pure ketone.

Dibromodihydroumbellulone, $C_{10}H_{14}OBr_2$.

The crystalline substance which was separated from the less volatile fraction (160—190°/20 mm.), obtained as a product of the action of heat on umbellulone dibromide (p. 642), after washing with petroleum, melted at 118°; when recrystallised from warm, light petroleum (b. p. 40—50°), it formed beautiful, white, glistening leaflets melting at 119—119·5° without decomposition:

0·123 gave 0·1754 CO_2 and 0·0525 H_2O. C = 38·9; H = 4·7.
0·1909 „ 0·2744 CO_2 „ 0·0785 H_2O. C = 39·2; H = 4·6
0·3489 „ 0·4225 AgBr. Br = 51·5.
$C_{10}H_{14}OBr_2$ requires C = 38·7; H = 4·5; Br = 51·6 per cent.

A solution containing 0·5232 gram in 25 c.c. of chloroform gave $\alpha_D + 0°8'$ in a 1 dm. tube, whence $[\alpha]_D + 6·4°$.

Dibromodihydroumbellulone can also be conveniently recrystallised from hot ethyl alcohol; it separates from the solution on cooling in glistening, prismatic needles. It is a saturated substance, since its solution in chloroform containing bromine can be boiled without the colour of the latter becoming discharged. It is also very stable towards boiling nitric acid, for its bromine is not eliminated on boiling with this reagent in the presence of silver nitrate. It does not interact with hydroxylamine even in boiling alcoholic solution.

Bromodihydroumbellulone, $C_{10}H_{15}OBr$.

Twenty grams of dibromodihydroumbellulone were dissolved in 100 c.c. of glacial acetic acid, and 40 grams of zinc dust added. The mixture was heated on a water-bath during five hours, and then ground up with more glacial acetic acid. The insoluble mixture of zinc salts was then removed by filtration at the pump, and the bromo-derivative precipitated from the filtrate by the addition of water. The crystalline precipitate, when washed, and dried on a porous plate, weighed 13 grams, and then melted at 58—59°. It was recrystallised from dilute methyl alcohol, from which it separated in well-defined, transparent, prismatic needles melting at 58—59°.

0·2042 gave 0·3885 CO_2 and 0·1181 H_2O. C = 51·9; H = 6·4.
0·2046 „ 0·3912 CO_2 „ 0·1224 H_2O. C = 52·1; H = 6·6.
$C_{10}H_{15}OBr$ requires C = 51·9; H = 6·5 per cent.

A solution containing 0·4163 gram in 25 c.c. of chloroform gave $\alpha_D - 1°10'$ in a 1 dm. tube, whence $[\alpha]_D - 70·1°$.

Bromodihydroumbellulone is readily soluble in cold ethyl and methyl alcohols, ethyl acetate, benzene, chloroform, and petroleum. When it is melted and warmed somewhat, its vapour has an odour resembling that of α-bromocamphor. It is a saturated substance, since its solution in chloroform containing bromine can be boiled without decolorising the latter. Like the dibromo-derivative, bromo-dihydroumbellulone does not interact with hydroxylamine.

Tetrahydroumbellulol, $C_{10}H_{19}\cdot OH$.

Thirteen grams of bromodihydroumbellulone were dissolved in 150 c.c. of ethyl alcohol, and 10 grams of sodium gradually introduced in small pieces. The solution was not cooled, but was allowed to boil vigorously. When all the sodium had dissolved, the liquid was cooled and diluted with water in order to precipitate the oil, which was then

taken up with ether, the ethereal solution washed with water, dried with calcium chloride, and the ether removed. The residual oil was first distilled under 60 mm. pressure, when it nearly all passed over between 125° and 130°; when finally fractionated under the ordinary pressure, the oil passed over for the most part at 205—209°, but boiled most constantly at 207—208° (corr.)/760 mm.; it was thus obtained as a colourless liquid, which had a camphoraceous odour resembling that of borneol.

0·1317 gave 0·3696 CO_2 and 0·1521 H_2O. C = 76·5; H = 12·8.
0·1305 ,, 0·3672 CO_2 ,, 0·1512 H_2O. C = 76·7; H = 12·9.
$C_{10}H_{20}O$ requires C = 76·9; H = 12·8 per cent.
Sp. gr. = 0·9071 at 15°/15°. $[\alpha]_D - 6·6°$.

Oxidation of Umbellulone with Potassium Permanganate. Formation of a Lactone, $C_9H_{12}O_2$.

Thirty grams of umbellulone were mixed with 500 c.c. of water and the mixture cooled by introducing a few pieces of ice. A 3 per cent. solution of potassium permanganate was then added, with vigorous shaking, so long as the colour of the latter was discharged. It was found that, working in this way, 80 grams of potassium permanganate, which is the equivalent of 4 atomic proportions of oxygen, were required. The liquid, after the removal of the manganese dioxide precipitate, was evaporated to a small volume, acidified with the calculated amount of sulphuric acid, and distilled in steam. The distillate contained a very small amount of an insoluble oil, which had a pleasant, lactonic odour. The cooled acid residue was then saturated with ammonium sulphate, whereupon a quantity of viscid oil separated; this was taken up with ether, the ethereal solution washed once with water, dried with calcium chloride, and the ether removed. The residual viscid oil was then fractionated under 20 mm. pressure. With the exception of a small fraction which passed over below 170°/20 mm., the whole distilled between 170° and 220° as a light yellow oil. It was found to be only partly soluble in sodium carbonate solution. Consequently, the whole of the fraction 170—220° was shaken with cold aqueous sodium carbonate and the undissolved portion then taken up with ether. The ethereal solution, after shaking several times with sodium carbonate solution, was washed with water, dried with potassium carbonate, and the ether removed. The residual oil, when fractionally distilled under the ordinary pressure, was ultimately obtained as a nearly colourless liquid boiling at 217—221° and having a pleasant, sweetish, lactonic odour.

0·1269 gave 0·3284 CO_2 and 0·0926 H_2O. C = 70·6; H = 8·1.
$C_9H_{12}O_2$ requires C = 71·1; H = 7·9 per cent.

This substance was evidently a lactone, and this conclusion was confirmed by converting it into the barium salt of the corresponding hydroxy-acid. For this purpose, the pure lactone was digested with a concentrated solution of barium hydroxide until all the oil had disappeared. The excess of barium was then removed by means of carbon dioxide. The filtered solution was then evaporated, and finally left in a vacuum desiccator over sulphuric acid. The barium salt was thus obtained as a hard, white cake, which was powdered, dried at 110°, and then analysed.

0·2118 gave 0·1033 $BaSO_4$ instead of 0·1039, which is the calculated amount for $(C_9H_{13}O_3)_2Ba$.

The barium salt is extremely soluble in cold water, and on the addition of silver nitrate to the solution, the silver salt is not precipitated.

The author particularly wishes to reserve the further study of umbellulone and its derivatives.

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