XXV.—*Action of Reducing Agents on $\alpha\alpha'$ -Diacetylpentane. Synthesis of Dimethyldihydroxyheptamethylene.*

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$\alpha\alpha'$ -Diacetylpentane, a diketone which has the constitution

as is proved by its method of preparation and properties (compare Trans., 1889, **55**, 330), behaves in a most remarkable manner both with dehydrating and with reducing agents.

When treated with concentrated sulphuric acid under suitable conditions, it is converted into a compound of the composition $\text{C}_9\text{H}_{14}\text{O}$, which, as has been previously shown (Trans., 1890, **57**, 13), is, doubtless, a methylacetyltetrahydrobenzene of the constitution

On reduction with sodium in moist ethereal solution, $\alpha\alpha'$ -diacetylpentane yields as principal product a colourless liquid of the composition $\text{C}_9\text{H}_{18}\text{O}_2$; the formation of this compound is represented by the equation

The method of preparation, properties, and some derivatives of this reduction product are described in the present paper, as are also various experiments which were made with the object of ascertaining its constitution; the results of these experiments seem to prove satisfactorily that the compound in question is a dimethyldihydroxyheptamethylene of the constitution

The formation of a heptamethylene derivative in this simple manner is an extremely interesting reaction, which may be regarded as analogous to the production of pinacone from acetone; the only difference between the two reactions is that in the formation of pinacone, combination takes place between two carbon atoms of two different acetone molecules, yielding an open-chain compound, whereas in the case of dimethyldihydroxyheptamethylene a closed-chain derivative is formed by the union of two carbon atoms of one and the same molecule of diacetyl-pentane.

The analogy between the two reactions is clearly shown with the aid of the following equations :—

Constitution of the Reduction Product of $\alpha\alpha'$ -Diacetyl-pentane.

In endeavouring to assign the correct constitutional formula to the reduction product of diacetyl-pentane, it is, in the first place, important to notice that the compound in question is formed by the addition of only two atoms of hydrogen to the diketone, a fact which is conclusively proved by the results of twelve analyses. Although many different samples have been analysed, the quantity of hydrogen found was never more than 11.75 per cent., usually about 11.5 per cent., results which agree very closely with those required for a compound of the composition $\text{C}_9\text{H}_{18}\text{O}_2$, which contains 11.39 per cent. of hydrogen.

A compound of the constitution $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2]_5\cdot\text{CHMe}\cdot\text{OH}$ which, it might be expected, would be produced by the reduction of the diketone, is evidently not formed in any appreciable quantity under the conditions employed in our experiments, as such a compound would contain 12.5 per cent. of hydrogen.

Now a compound of the composition $\text{C}_9\text{H}_{18}\text{O}_2$, obtained by reducing $\alpha\alpha'$ -diacetyl-pentane, $\text{COMe}\cdot[\text{CH}_2]_5\cdot\text{COMe}$, may, theoretically, have the constitution represented by one of the following formulæ :—

If its constitution be expressed by formula I, it would, in all probability, show the following behaviour :—

1. It would combine with hydroxylamine to form an oxime of the constitution $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot[\text{CH}_2]_5\cdot\text{CHMe}\cdot\text{OH}$, and with phenylhydrazine to form a hydrazone of the composition $\text{C}_9\text{H}_{18}\text{O}\cdot\text{N}_2\text{HPh}$.

2. It would be converted into a monacetyl-derivative of the constitution $\text{COMe}\cdot[\text{CH}_2]_5\cdot\text{CHMe}\cdot\text{OAc}$, on treatment with acetic anhydride.

3. When treated with hydrobromic acid, a monobromo-derivative of the constitution $\text{COMe}\cdot[\text{CH}_2]_5\cdot\text{CHMeBr}$ would be produced, whereas phosphorus pentabromide would convert it into a tribromide of the constitution $\text{CMeBr}_2\cdot[\text{CH}_2]_5\cdot\text{CHMeBr}$.

4. It would be easily reduced to a dihydric alcohol of the constitution $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2]_5\cdot\text{CHMe}\cdot\text{OH}$ by sodium amalgam, zinc-dust and hydrochloric acid, or some other suitable reducing agent.

5. When heated with concentrated hydriodic acid and amorphous phosphorus at a high temperature, it would be converted into a hydrocarbon of the paraffin series having the constitution

The behaviour of the reduction product with each of the reagents just enumerated was carefully examined, in most cases the experiments being repeated several times under varied conditions; the results were, however, completely at variance with those which, in all probability, would have been obtained had the reduction product been a ketone alcohol; its constitution cannot, therefore, be represented by formula I.

On the other hand, the chemical behaviour of the reduction product is exactly what might be expected, assuming that it is a dihydroxy-compound of the constitution expressed by formula II; this will be evident from a consideration of the following facts:—

1. It does not combine with hydroxylamine or with phenylhydrazine.

2. It yields a diacetyl-derivative of the composition $\text{C}_{13}\text{H}_{22}\text{O}_4$ with acetic anhydride.

3. Phosphorus pentabromide converts it into a dibromide of the composition $\text{C}_9\text{H}_{16}\text{Br}_2$; this substance seems also to be formed with difficulty on prolonged heating with concentrated hydrobromic acid.

4. It is not acted on by such reducing agents as zinc and hydrochloric acid in alcoholic solution, sodium amalgam, sodium and alcohol.

5. On reduction with hydriodic acid and amorphous phosphorus, it is converted into a hydrocarbon of the composition C_9H_{18} .

These facts are, we believe, amply sufficient to warrant the conclusion that the reduction product of $\alpha\alpha'$ -diacetylpentane is a dimethyldihydroxyheptamethylene of the constitution

The derivatives of this compound, which are referred to above, and described in the experimental part of the paper, have, therefore, the constitutions represented by the following formulæ:—

Dimethyldihydroxyheptamethylene diacetate,

Dimethyldibromoheptamethylene,

Dimethylheptamethylene,

The compounds obtained in the course of this investigation are, we believe, the first and only derivatives of the 7-carbon ring—heptamethylene—which have yet been prepared, and the constitution of which has been proved with any degree of certainty.

Markownikoff has, however, lately published an interesting paper on some compounds obtained from suberone (*Compt. rend.*, **110**, 466—468), which, including suberone itself, he considers to be derivatives of heptamethylene; and by reducing suberonyl alcohol with hydriodic acid, he obtained a hydrocarbon of the composition C_7H_{14} , which he supposes to be heptamethylene.

It appears to us that the results obtained by Markownikoff can be equally well explained on the assumption that suberone is a methylketohexamethylene, a dimethylketopentamethylene, or some other ketopolymethylene derivative, and that as yet no evidence has been brought forward to warrant the conclusion that suberone is a heptamethylene derivative.

Dimethyldihydroxyheptamethylene (dimethylheptamethylene glycol) and small quantities of a condensation product of high molecular weight are obtained by the reduction of $\alpha\alpha'$ -diacetyl-pentane in the following manner:—A solution of the pure diketone in 5 to 6 times its volume of pure ether is poured into a large bottle which contains

about 150 c.c. of concentrated soda, and is provided with a reflux condenser. Sodium is then added in small portions at a time, any considerable rise of temperature being avoided by immersing the bottle in cold water. When the reduction has proceeded for some time, the metal becomes covered with a thick layer of a colourless sodium derivative of the glycol, and in some cases a considerable quantity of this compound is deposited on the sides of the vessel, but on agitating the alkaline liquid, it gradually passes into solution. The addition of sodium is continued until 6 to 8 times the quantity theoretically necessary for complete reduction, that is, 4 atoms of sodium to 1 mol. of the diketone, has been employed.

The ethereal solution is then separated, the alkaline liquid extracted once or twice with ether, the combined ethereal solutions very carefully dried over anhydrous potassium carbonate, filtered, and evaporated, when there remains a yellowish oil, the weight of which is about the same as that of the diketone employed. The crude product is submitted to fractional distillation under reduced pressure, say, 180 mm.; the thermometer quickly rises to 195° ; almost the whole of the product passing over between 195° and 205° , the temperature then rises rapidly to about 300° , when a thick, yellowish oil collects in the receiver. The quantity of this compound of high boiling point is only about 3—6 per cent. of the crude reduction product; it will be referred to again hereafter.

The portion passing over between 195° and 205° consists of slightly impure dimethyldihydroxyheptamethylene, from which the pure compound can be easily obtained by submitting it to repeated fractional distillation under reduced pressure.

Analyses of various preparations of the pure compound gave the following results:—

- I. 0.2016 gram substance gave 0.5062 gram CO_2 and 0.2098 gram H_2O .
- II. 0.1852 gram substance gave 0.4624 gram CO_2 and 0.1923 gram H_2O .
- III. 0.2112 gram substance gave 0.5266 gram CO_2 and 0.2178 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{18}\text{O}_2$.	Found.		
		I.	II.	III.
C	68.36 p. c.	68.5	68.1	68.0 p. c.
H	11.39 „	11.6	11.5	11.5 „
O	20.25 „	20.9	20.4	20.5 „

Dimethyldihydroxyheptamethylene is a moderately thick, colourless oil, with a sharp, burning taste, and a characteristic smell re-

calling that of thyme; it is specifically lighter than water, and is volatile with steam and alcohol vapour. It boils at 201° under a pressure of 180 mm., at $203\text{--}205^{\circ}$ under a pressure of 186 mm., and at $180\text{--}185^{\circ}$ under a pressure of 100 mm., the thermometer being entirely in the vapour in all three cases; when cooled below 0° , it becomes very thick, but shows no signs of crystallising even when kept below 0° for some time.

It is miscible with alcohol, ether, chloroform, glacial acetic acid, &c., in all proportions, but is only sparingly soluble in cold water, from which it separates again on warming or on adding sodium carbonate; it is insoluble in soda. It dissolves in concentrated sulphuric acid with development of heat, and it is also soluble in concentrated hydrobromic acid, although it quickly separates from the solution again, having been partially converted into an insoluble bromide. It does not combine with sodium hydrogen sulphite, hydroxylamine, or phenylhydrazine, but it is readily acted on by boiling acetic anhydride, yielding a diacetyl-derivative, and by phosphorus pentabromide, which converts it into an oily dibromide.

It is a curious fact that a mixture composed of about 94 per cent. of dimethyldihydroxyheptamethylene, and about 6 per cent. of water, has approximately the same boiling point as the anhydrous glycol, and is not separated into its constituents on fractional distillation under reduced pressure. This fact was brought under our notice at an early stage of the investigation in the following manner:—The ethereal solution of the crude reduction product of diacetyl-pentane, having been treated for a short time with anhydrous calcium chloride, was evaporated, the residue submitted to fractional distillation under a pressure of 150 mm., and the portion passing over between $197\text{--}199^{\circ}$ collected separately.

Two analyses of this liquid gave the following results:—

- I. 0.1760 gram substance gave 0.4161 gram CO_2 and 0.1854 gram H_2O .
 II. 0.1432 gram substance gave 0.3386 gram CO_2 and 0.1528 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{18}\text{O}_2 + 6 \text{ p. c. } \text{H}_2\text{O}$.	Found.	
		I.	II.
C	64.3 per cent.	64.5	64.5 per cent.
H	11.4 ..	11.7	11.7 ..
O	24.3 ..	23.8	23.8 ..

This fraction (b. p. $197\text{--}199^{\circ}$; 150 mm.) was distilled again under a pressure of 100 mm., the portion passing over between 182° and 186° collected separately, and analysed:—

0·1640 gram substance gave 0·3850 gram CO_2 and 0·1737 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{18}\text{O}_2 + 6 \text{ p. c. of } \text{H}_2\text{O}$.	Found.
C	64·3 per cent.	64·6 per cent.
H	11·4 ,,	11·7 ,,
O	24·3 ,,	23·7 ,,

Water is, doubtless, the impurity to which the low percentage of carbon found is due, because when anhydrous potassium carbonate is employed for drying the ethereal solution, other conditions remaining the same, the glycol is easily obtained in a pure condition; the experiments show, moreover, that the water cannot be eliminated by fractional distillation, just as is the case with other mixtures of like nature.

Sodium Derivative of Dimethyldihydroxyheptamethylene.

This compound frequently separates from the ethereal solution in the preparation of dimethyldihydroxyheptamethylene in the manner described above. In order to determine its composition, some of the substance adhering to the sides of the bottle, and out of contact with the aqueous alkali, was picked out, quickly washed with ether on a porous plate, and then kept for some days in a desiccator.

The analyses of three different samples obtained in this way, and quickly weighed from stoppered bottles, gave the following results:—

I.	0·3362 gram substance gave 0·1156 gram Na_2SO_4 .
II.	0·2932 ,, ,, 0·1022 ,,
III.	0·3254 ,, ,, 0·1112 ,,

	Calculated for $\text{C}_9\text{H}_{17}\text{O}_2\text{Na} + \text{H}_2\text{O}$.	Found.		
Na.....	11·5 per cent.	I.	II.	III.
		11·1	11·3	11·1 per cent.

These analyses show that the compound is a mono-sodium derivative of the glycol, containing, very probably, 1 mol. of water. In spite of the hygroscopic nature of the substance, there is no reason to suppose that this view of its composition is incorrect, since ethyl sodacetate and other compounds of like nature have been proved to contain water of crystallisation.

The sodium derivative of the glycol is a colourless, semi-crystalline, deliquescent compound which gradually decomposes on exposure to the air or when heated at about 50 – 60° in the air; it melts below 100° , and is quickly decomposed by cold water, but rather slowly by very concentrated soda.

It is, perhaps, unnecessary to remark that the formation of a mono- instead of a di-sodium derivative, under the conditions described above, cannot be regarded as evidence against the view that the reduction product is a dihydroxyheptamethylene derivative.

Constitution of Dimethyldihydroxyheptamethylene.

In accordance with the views put forward in the introduction, the reduction product of diacetyl-pentane may, theoretically, have the constitution represented by one of two formulæ (p. 215); in one case it would be an open-chain ketone-alcohol, in the other a closed-chain dihydric alcohol. It was necessary, therefore, in the first place, to investigate its behaviour with phenylhydrazine and with hydroxylamine; the following experiments were made for this purpose.

Behaviour of the Reduction Product with Phenylhydrazine.—A small quantity (3 grams) of the crude reduction product was heated at about 100° for three hours in sealed tubes with phenylhydrazine hydrochloride (4.8 grams) and sodium acetate (4.5 grams) in dilute alcoholic solution. The clear solution was then diluted with a large volume of water, the precipitated oil extracted with ether, the ethereal extract washed with very dilute hydrochloric acid, dried over calcium chloride, and evaporated. The yellowish, oily product weighed 2.8 grams, and showed all the properties of the original reduction product; a qualitative examination showed that it contained a trace of nitrogen, but the quantity was so small that it was quite evident that the formation of a hydrazone had not taken place.

Behaviour of the Reduction Product with Hydroxylamine.—Two experiments were made under different conditions, in order to try and prepare an oxime of the reduction product of diacetyl-pentane, but both were unsuccessful. In the first, the crude reduction product (4 grams) was treated with hydroxylamine hydrochloride (4 grams) and potassium carbonate (3 grams) in dilute alcoholic solution for three days at the ordinary temperature. After evaporating most of the alcohol on the water-bath, the residue was extracted with ether, the solution dried over calcium chloride, and evaporated, when there remained a light-yellow oil (3.8 grams); this oil contained a trace of nitrogen, but was insoluble in alkalis, and possessed all the properties of the original reduction product.

In the second experiment, the pure compound (3 grams) was treated with hydroxylamine hydrochloride (1.4 grams) and potash (5 grams) in dilute methyl alcoholic solution according to Auwers' method. After keeping the mixture for two days at the ordinary temperature, the alcohol was evaporated, the oil extracted with ether, the ethereal solution washed with very dilute hydrochloric acid, dried

over calcium chloride, and evaporated. There remained a yellowish oil (2.4 grams) which did not contain a trace of nitrogen, and which showed all the properties of the original compound.

Behaviour of the Reduction Product with Reducing Agents.—Although the above experiments had shown pretty conclusively that the reduction product does not contain a carbonyl group, it seemed advisable to obtain further experimental proof that such is in reality the case by investigating its behaviour with reducing agents in the manner described below:—

Exp. 1.—The pure reduction product (about 20 grams) was dissolved in alcohol, and zinc-dust and hydrochloric acid added to the boiling solution in small portions at a time, the operation taking about three hours; the solution was then diluted with water, the precipitated oil extracted with ether, and again submitted to the same treatment with zinc-dust and hydrochloric acid. Finally, the product was fractionated, and the portion passing over between 205° and 215° (210 mm.), which formed about 70 per cent. of the whole, collected separately and analysed; the percentage of hydrogen was found to be 11.6, proving that in this case also reduction had not taken place.

Exp. 2.—The original reduction product was dissolved in dilute alcohol, and a large quantity of sodium amalgam added to the boiling solution, in small portions at a time. The product, isolated in the usual manner, was fractionated under a pressure of about 280 mm., and the portion boiling at 200—210° collected for analysis. It was found to contain 11.57 per cent. of hydrogen, and to possess all the properties of the original compound.

Exp. 3.—The pure compound (16 grams) was dissolved in alcohol (100 grams), and sodium added in small portions at a time, the process being continued until a large excess (26 grams) of the metal had been employed, dilute alcohol being added from time to time whenever the reaction began to slacken. The alcohol was then evaporated as completely as possible, the residue diluted with water, the precipitated oil extracted with ether, dried, and fractionated under reduced pressure. Two analyses, made with different portions of the product, gave 11.72 and 11.76 per cent. of hydrogen respectively, proving conclusively that reduction had not taken place, since the addition of 2 atoms of hydrogen to the original reduction product would increase the percentage of hydrogen from 11.4 to 12.5 per cent.

Up to this stage of the investigation, it had been proved that the reduction product of diacetylpentane cannot be a ketone-alcohol of the constitution represented by formula I (p. 215); the following experiments show that it is a dihydric alcohol of the composition $C_9H_{18}O_2$.

When the reduction product is treated with phosphorus pentabromide under suitable conditions, it is converted into a dibromide of the composition $\text{C}_9\text{H}_{16}\text{Br}_2$, which has, doubtless, the constitution assigned to it above. Before describing the preparation and properties of this dibromide, it will be as well, perhaps, to give a short account of the behaviour of the reduction product with hydrobromic acid.

A considerable quantity of the pure compound was heated at $100-115^\circ$ in sealed tubes for about two hours with five times its volume of concentrated hydrobromic acid; on opening the tubes, it was found that the contents had separated into two layers, the upper one consisting of a dark-coloured oil. This oil was extracted from the diluted and partially neutralised solution by means of ether, the ethereal extract washed, dried, and evaporated, and the residue distilled under reduced pressure (about 140 mm.). The whole passed over between 160° and 220° , but no constant boiling point could be observed; the portion boiling at $160-200^\circ$ was collected and analysed, and found to contain only 39 per cent. of bromine. As a compound of the composition $\text{C}_9\text{H}_{17}\text{BrO}$ contains 36.1, and a compound of the composition $\text{C}_9\text{H}_{16}\text{Br}_2$ 56.3 per cent. of bromine, it would seem that the liquid analysed consisted principally of the monobromide. In order to try and convert it into the dibromide, the whole of the distilled product was again heated at about 120° for several hours with a large excess of concentrated hydrobromic acid. The dark reddish-brown, heavy oil, obtained in this way, was distilled under a pressure of about 70 mm., and the portion boiling at $160-167^\circ$ collected separately; the analysis of this fraction gave the following result:—

0.1758 gram substance gave 0.2047 gram AgBr .

Calculated for			
	$\text{C}_9\text{H}_{17}\text{BrO}$.	$\text{C}_9\text{H}_{16}\text{Br}_2$.	Found.
Br	36.1 p. c.	56.3 p. c.	49.5 p. c.

These experiments show that the reduction product is partially converted into a dibromide by concentrated hydrobromic acid, a fact which is of considerable importance as a proof that it is a dihydric alcohol; as, however, the change is only incomplete even after prolonged heating with the acid, a more suitable method had to be employed for the preparation of the dibromide.

For this purpose, a small quantity of the pure reduction product

is dissolved in a large volume of anhydrous chloroform, and a fair excess of the theoretical quantity of phosphorus pentabromide gradually added; evolution of hydrogen bromide quickly commences, and, after keeping for some time at the ordinary temperature, the reaction is at an end. The solution is decanted from the unchanged pentabromide, poured into cold water, and as soon as the decomposition of the phosphorus oxybromide is complete, the chloroform solution of the dibromide is separated, washed with dilute sodium carbonate and water consecutively, dried over calcium chloride, and the chloroform evaporated on the water-bath, when dimethyldibromoheptamethylene remains as a thick yellowish oil.

A bromine determination, made with a portion of the product which had been kept for 24 hours over sulphuric acid and paraffin, gave the following result:—

0.1036 gram substance gave 0.1370 gram AgBr.

	Calculated for $C_9H_{16}Br_2$.	Found.
Br	56.3 per cent.	54.8 per cent.

Dimethyldibromoheptamethylene is a thick, almost colourless oil with a sweetish, rather unpleasant smell; it is specifically heavier than, and insoluble in, water, but miscible with most ordinary organic solvents in all proportions. It seems to undergo slight decomposition when it is kept over sulphuric acid under reduced pressure.

When the glycol obtained from diacetylpentane is heated with hydriodic acid of sp. gr. 1.96, it seems to be almost completely converted into the moniodide, $C_9H_{17}OI$; the diiodide, $C_9H_{16}I_2$, if produced at all, is only formed in very small quantities.

The moniodide was prepared in the following manner:—The pure glycol was mixed with a considerable quantity of hydriodic acid of sp. gr. 1.96, and the mixture heated on the water-bath in a flask provided with a reflux condenser, first at a moderately low temperature, and then for about two hours at 100° . A portion of the contents of the flask was then distilled off, because it was thought that the diiodide would probably be more volatile than the moniodide, and if any of the former had been produced, it would collect in the receiver, leaving the moniodide behind. The small quantity of oil in the acid distillate was extracted with ether, the solution washed with dilute sodium carbonate and water, consecutively, dried over calcium

chloride, and evaporated. The colourless oil obtained in this way was kept over sulphuric acid under reduced pressure for about 12 hours, and then an iodine determination carried out with the following result:—

0.1735 gram substance gave 0.1622 gram AgI.

	Calculated for $C_9H_{17}IO$.	Found.
I	47.29 per cent.	50.49 per cent.

The compound obtained by distillation as described above evidently consists principally of the moniodide, but contains a little of the diiodide; the former can be isolated in a pure condition from the residue in the flask by extracting with ether, and evaporating the washed and dried solution.

A portion of the oil (which remained in the flask) was kept under reduced pressure, and analysed with the following result:—

0.1661 gram substance gave 0.1455 gram AgI.

	Calculated for $C_9H_{17}IO$.	Found.
I	47.29 per cent.	47.06 per cent.

Dimethylhydroxyiodoheptamethylene is a colourless, mobile oil with a pleasant sweetish smell; it is readily soluble in ether, alcohol, and most ordinary organic solvents, but insoluble in water. It gradually decomposes, and turns brown on keeping, but it seems to boil without decomposition when heated in small quantities under the ordinary pressure.

When the reduction product of diacetylpentane is treated with acetic anhydride under suitable conditions, it is completely converted into a diacetyl derivative of the composition $C_9H_{16}(OAc)_2$; the formation of this diacetyl derivative is one of the strongest proofs that the compound described above as dimethyldihydroxyheptamethylene contains two hydroxy-groups.

In preparing the diacetyl derivative, the pure glycol is dissolved in excess of acetic anhydride, and the mixture boiled for about $2\frac{1}{2}$ hours in a flask provided with a reflux condenser; the acetic anhydride is then partially distilled off under the ordinary pressure, and the residue submitted to fractional distillation under a pressure of 65 mm. The thermometer rises rapidly to about 180° , a small quantity only passing over below 190° ; the thermometer then remains

fairly constant, and between 192° and 207° about 70 per cent. of the whole passes over, the thermometer finally rising to about 215° .

The fraction boiling at 192 — 207° was fractionated again under the same pressure, and the portion boiling constantly at 199 — 202° collected separately.

The analysis of this fraction gave results which agreed well with those required by a diacetyl derivative of dimethyldihydroxyheptamethylene.

0.1555 gram substance gave 0.3681 gram CO_2 and 0.1323 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{16}(\text{OAc})_2$.	Found.
C	64.5 per cent.	64.67 per cent.
H	9.1 "	9.45 "
O	26.4 "	25.88 "

As, however, a monacetyl-derivative of the composition $\text{COMe}[\text{CH}_2]_5\text{CHMe}\cdot\text{OAc}$ would have approximately the same composition (C = 66.0 per cent., H = 10.0 per cent., O = 24 per cent.), elementary analysis alone is not sufficient to prove beyond doubt that the compound is really a diacetyl derivative. As this point was of the utmost importance in deciding between the two possible formulae for the reduction product, the quantity of acetic acid given on hydrolysis was determined. Three estimations of this kind were made; in each case, a weighed quantity of the pure compound was boiled with excess of standard potash, and the excess of alkali determined by titration with standard sulphuric acid, phenolphthalein being used as indicator.

The following results were obtained:—

- I. 1.169 gram substance was boiled for $1\frac{1}{2}$ hours with 150 c.c. of potash (1 c.c. = 0.00597 gram of $\text{C}_2\text{H}_4\text{O}_2$), and the cold solution titrated with sulphuric acid of the same strength; 56.4 c.c. of acid were required, showing that 93.6 c.c. of potash had been neutralised.
- II. 0.8638 gram substance was boiled for two hours with 100 c.c. of potash, and the solution titrated with sulphuric acid; 44.3 c.c. of acid were required.
- III. 0.5676 gram substance was boiled for an hour with 100 c.c. of potash, and the cold solution titrated; 54.7 c.c. of sulphuric acid were required.

	Calculated for $\text{C}_9\text{H}_{16}(\text{OAc})_2$.	Found.		
		I.	II.	III.
$\text{C}_2\text{H}_4\text{O}_2$	49.58 p. c.	47.8	48.4	47.6 p. c.

These results show conclusively that the compound in question is a diacetyl derivative, and, consequently, the presence of two hydroxy-groups in the original reduction product may be considered as proved.

Dimethylheptamethylene diacetate is a colourless, mobile liquid possessing a sweet, rather pleasant smell, and boiling at $199-202^\circ$ under a pressure of 65 mm. It seems to be insoluble in cold water, but is readily soluble in alcohol, ether, acetic anhydride, and other organic solvents. It is readily hydrolysed even by very dilute aqueous potash, as is shown by the quantitative experiments referred to above.

One of the most important facts that can be adduced in favour of the closed-chain formula for the reduction product of diacetyl-pentane is that, when treated with hydriodic acid and amorphous phosphorus at a high temperature, it is converted into a hydrocarbon of the molecular formula C_9H_{18} , which, from its method of formation must be a saturated compound. This hydrocarbon, dimethylheptamethylene, is obtained in the following way:—The pure glycol is first heated for about two hours at 100° in a flask provided with a reflux condenser, with excess of concentrated hydriodic acid, in order to convert it into the moniodide described above; this product is isolated in the usual manner, and then heated in sealed tubes at $230-260^\circ$ for 8 to 10 hours with a large excess of hydriodic acid of sp. gr. 1.96, and a little amorphous phosphorus, about 4 grams only of the crude iodide being placed in each tube. When the tubes were opened, the hydrocarbon, which formed a lighter-coloured layer on the surface of the acid, was separated with the aid of a funnel, washed well with sodium carbonate, dried over potassium carbonate, and distilled. The thermometer rose at once to about 145° , and between 145° and 160° almost three-quarters of the crude product passed over; the liquid which then remained in the flask boiled at a very much higher temperature, and was not examined further, owing to its small quantity. The fraction boiling at $145-160^\circ$ was then distilled two or three times over potassium, and finally a sample of the liquid boiling constantly at $153-154^\circ$ was collected separately for analysis.

The results obtained were the following:—

0.1300 gram substance gave 0.4072 gram CO_2 and 0.1717 gram H_2O .

	Calculated for C_9H_{18} .	Found.
C	85.7 per cent.	85.42 per cent.
H	14.3 ,,	14.67 ,,

A vapour density determination carried out in Hofmann's apparatus, and employing aniline as the heating vapour, gave the following result:—

0·0782 gram substance gave 68 c.c. of vapour. Barometer = 748 mm. Difference of level 490 mm. Temperature of vapour 184°, and of air 11°.

	Calculated for C_9H_{18} .	Found.
V.D.	63	61·2

Two elementary analyses of a sample of the hydrocarbon from another preparation gave the following results:—

I. 0·1271 gram substance gave 0·3965 gram CO_2 and 0·1702 gram H_2O .

II. 0·1192 gram substance gave 0·3727 gram CO_2 and 0·1588 gram H_2O .

	Calculated for C_9H_{18} .	Found.	
		I.	II.
C	85·7 p. c.	85·08	85·14 p. c.
H	14·3 „	14·88	14·83 „

Dimethylheptamethylene is a colourless mobile, strongly refractive liquid with an odour very like that of light petroleum; it boils at 153° under the ordinary atmospheric pressure. It is insoluble in water, and in concentrated hydriodic acid, but is miscible with organic solvents in all proportions. It seems to be a very stable substance, but owing to the small quantity at our disposal, we have not been able to investigate its properties as completely as would be desirable. It is not acted on by concentrated hydriodic acid; when treated with concentrated nitric acid, a reaction soon sets in, heat is developed, and dense brown fumes are evolved, but the reaction soon slackens, and heat must be applied before complete solution ensues; as far as our experiments went, no compounds other than acids of low molecular weight are formed by the oxidation of the hydrocarbon in this way.

Condensation Product of Dimethyldihydroxyheptamethylene.

It has been mentioned above that in the preparation of dimethyldihydroxyheptamethylene there is formed in small quantities a liquid of considerably higher boiling point, which seemed to be a condensation product of the glycol. In order to investigate the nature of this compound, the residues obtained in several operations were united, and the liquid submitted to fractional distillation under a

pressure of about 200 mm.; at first, a small quantity of dimethyldi-hydroxyheptamethylene passed over, and then the thermometer rose rapidly to about 300°, the remainder boiling almost constantly at 305—310°.

This high boiling liquid gave the following result on analysis :—

0·2011 gram substance gave 0·4143 gram CO_2 , and 0·2082 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{34}\text{O}_3$.	Found.
C	72·48 per cent.	72·6 per cent.
H	11·41 „	11·4 „
O	16·11 „	16·0 „

A molecular weight determination by Raoult's method in glacial acetic acid solution gave the following data :—

0·9116 gram substance dissolved in 43·1 grams acetic acid lowered the melting point 0·271, as a mean of two closely agreeing observations.

	Calculated for $\text{C}_{18}\text{H}_{34}\text{O}_3$.	Found.
M. W.	298	305

This result shows that the compound in question has been formed by the condensation of two molecules of diacetyl-pentane, or its reduction product; the analysis given above agrees very well with the formula $\text{C}_{18}\text{H}_{34}\text{O}_3$, but not so well with the formula $\text{C}_{18}\text{H}_{32}\text{O}_3$, which would require 72·9 per cent. of carbon and 10·8 per cent. of hydrogen. Considering, also, that a large excess of sodium was invariably employed in the reduction of diacetyl-pentane, and that the only other product is the glycol $\text{C}_9\text{H}_{18}\text{O}_2$, it seems almost certain that the condensation product is formed from the glycol, and not from the ketone, according to the equation

just as diethylene glycol is formed from two molecules of ethylene glycol with elimination of one molecule of water.

The condensation product of the heptamethylene derivative has no well-defined properties; it is an almost colourless, very thick oil, boils at about 305—310° (200 mm. pressure), and shows no signs of crystallising even when kept for months at the ordinary temperature, or for some hours in a freezing mixture. It is insoluble in water, but the ordinary organic solvents dissolve it in large quantities.

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