V.—αω-Diacetyl-αω-diethylpentane.

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In the preceding paper we have described the preparation of a compound of the composition C₈H₁₄O, and have given an account of various experiments, from the results of which it seems to be proved that this substance is methyltetrahydrobenzene methyl ketone,

\[ \text{CH}_2<\text{CH}_2\text{CM}_{48}\text{CH}_2\text{CM}_{48}\text{CO} \cdot \text{CH}_3. \]

In order to distinguish between several of the theoretically possible formulae for this compound (compare p. 14), it became necessary to prepare a diketone of the formula R·CO·CHR1·[CH₄]ₓ·CHR·CO·R, and to study its behaviour under the same conditions as those employed in the preparation of the compound C₈H₁₄O from αω-diacetyl-pentane, COMe·[CH₄]ₓ·COMe.

A short account of these experiments will, we hope, not be without some interest.

When ethyl ethylacetoacetate (2 mols.) is treated with sodium ethoxide (2 mols.) and trimethylene bromide (1 mol.) in alcoholic solution, a moderately energetic reaction occurs on warming gently, and, after proceeding in the usual manner, a yellow oil is obtained.

The crude product, which consists of several compounds, contains about 40—45 per cent. of ethyl αω-diacetyl-αω-diethylpimelate, COOEt·CEt(COMe)·[CH₄]ₓ·CEt(COMe)·COOEt, produced by the combination of 1 mol. of trimethylene bromide with 2 mols. of ethyl sodioethylacetoacetate in accordance with the equation—

\[ 2\text{CH}_3\text{CO} \cdot \text{CNaEt} \cdot \text{COOEt} + \text{C}_3\text{H}_5\text{Br}_2 = \text{COOEt} \cdot \text{CEt} \cdot (\text{COMe}) \cdot [\text{CH}_4]_x \cdot \text{CEt} \cdot (\text{COMe}) \cdot \text{COOEt} + 2\text{NaBr}. \]

This ethereal salt is readily hydrolysed when boiled with alcoholic potash, the principal products being αω-diacetyl-αω-diethylpentane and ω-acetyl-αω-diethylcapric acid. The equations representing the decomposition are as follows:

\[ \text{COOEt} \cdot \text{CEt} \cdot (\text{COMe}) \cdot [\text{CH}_4]_x \cdot \text{CEt} \cdot (\text{COMe}) \cdot \text{COOEt} + 4\text{KOH} = \text{COMe} \cdot \text{CHEt} \cdot [\text{CH}_4]_x \cdot \text{CHEt} \cdot \text{COMe} + 2\text{K}_2\text{CO}_3 + 2\text{C}_2\text{H}_5\cdot\text{OH}, \]

and

\[ \text{COOEt} \cdot \text{CEt} \cdot (\text{COMe}) \cdot [\text{CH}_4]_x \cdot \text{CEt} \cdot (\text{COMe}) \cdot \text{COOEt} + 4\text{KOH} = \text{COMe} \cdot \text{CHEt} \cdot [\text{CH}_4]_x \cdot \text{CHEt} \cdot \text{COOK} + 2\text{C}_2\text{H}_5\cdot\text{OH} + \text{K}_2\text{CO}_3 + \text{CH}_3\cdot\text{COOK}. \]
It seems probable that, in addition to the two compounds referred to above, small quantities of \( \alpha\omega \)-diethylpimelic acid are also produced by the following reaction:

\[
\text{COOEt} \cdot \text{C} \text{Et(COME)} \cdot \text{[CH}_2\text{]}_2 \cdot \text{C} \text{Et(COME)} \cdot \text{COOEt} + 4\text{KOH} = \\
\text{COOK} \cdot \text{C} \text{Et(COME)} \cdot \text{[CH}_2\text{]}_2 \cdot \text{C} \text{Et(COME)} \cdot \text{COOK} + 2\text{C}_2\text{H}_5\cdot \text{OH} + 2\text{CH}_3\cdot \text{COOK}.
\]

**Action of Trimethylene Bromide on Ethyl Sodioethylacetoacetate.**

**Formation of Ethyl \( \alpha\omega \)-Diacetyl-\( \alpha\omega \)-diethylpimelate,**

\[
\text{COOEt} \cdot \text{C} \text{Et(COME)} \cdot \text{[CH}_2\text{]}_2 \cdot \text{C} \text{Et(COME)} \cdot \text{COOEt}.
\]

Ethyl diacetylidiethylpimelate is obtained, together with considerable quantities of compounds of lower boiling point, when ethyl sodioethylacetoacetate is treated with an alcoholic solution of trimethylene bromide.

Ethyl ethylacetoacetate (2 mols.) is added, in small quantities at a time, to a solution of sodium (1 mol.) in about 12 times its weight of alcohol, the temperature being kept below 25—30° by cooling under the tap from time to time; after adding the trimethylene bromide (1 mol.), the mixture is heated on the water-bath in a flask provided with a reflux condenser. As soon as the temperature rises to about 70—80°, an energetic reaction commences, sodium bromide separates from the solution, and the heat developed is sufficient to keep the alcohol in ebullition for several minutes. After heating for 2—3 hours to complete the reaction, the alcohol is evaporated, the residue mixed with water, and the precipitated oil extracted with ether. When the ethereal extract is evaporated, there remains a yellow oil, the quantity of which is about equal to that of the ethyl ethylacetoacetate employed.

The crude product is distilled with steam as quickly as possible, the distillation being continued as long as oily drops collect in the receiver. In this way the ethyl diacetylidiethylpimelate, which forms from 40 to 45 per cent. of the whole, is separated from the more volatile compounds. The dark yellow oil which remains in the flask is extracted with ether, the ethereal solution dried over calcium chloride and evaporated. That this process of separation is very efficient is shown by the following analysis, which was made with a portion of the residual oil after it had been kept over sulphuric acid under reduced pressure for about 24 hours.

0.1474 gram of substance gave 0.3430 gram of CO\(_2\) and 0.1220 gram of H\(_2\)O.
When the crude ethyl diacetyldiethylpimelate is distilled under reduced pressure (45-50 mm.), the thermometer rises rapidly to about 205°, then a little more slowly to 235°; almost the whole distils between 235° and 255°, a small quantity only passing over between 255° and 280°. The oil boiling at 235—255° was fractionated again under the same pressure, and the portion boiling constantly at 249—252° collected separately.

This fraction quickly solidifies to a mass of colourless crystals, and after having been spread on a porous plate to free it from traces of oily impurities, it melted at 42—43° with previous softening.

The analyses of the crystalline compound purified in this way gave the following results:

I. 0.2109 gram of substance gave 0.4937 gram of CO₂ and 0.1689 gram of H₂O.

II. 0.2500 gram of substance gave 0.5840 gram of CO₂ and 0.2016 gram of H₂O.

Ethyl diacetyldiethylpimelate separates from ether and alcohol in long, very slender needles melting at 44—45° with slight previous softening; it is very readily soluble both in ether and in alcohol, so that it cannot well be purified by crystallisation from these solvents. On adding water to a cold alcoholic solution, the ethereal salt is precipitated in an oily condition, but it almost immediately solidifies to a mass of ill-defined crystals. It is very readily soluble in benzene, light petroleum, xylene, chloroform, and most ordinary solvents, but it seems to be quite insoluble in cold water. Ferric chloride produces no coloration in alcoholic solutions. It is readily hydrolysed by warm alcoholic potash, the principal product being acetyldiethylcaproic acid. When treated with concentrated alcoholic potash in the cold, it is slowly decomposed; the solution contains small quantities of diacetyldiethylpentane, and the potassium salt of a thick, colourless acid, probably diacetyldiethylpimelic acid, which is mixed with some other acid richer in carbon.
By-products obtained in the preparation of Ethyl Diacetyladiethylpimelate.

The crude product of the action of trimethylene bromide on ethyl sodioethylacetoacetate contains, as has been stated above, a considerable proportion (55—60 per cent.) of an oil which can be separated from the ethyl diacetyladiethylpimelate by distilling with steam; when the distillate is extracted with ether, and the extract dried over calcium chloride and evaporated, a yellowish, mobile oil with a pleasant ethereal odour is obtained. This oil is probably a mixture of unchanged ethyl ethylacetoacetate and ethyl ethylallylacetoacetate; the last-named compound would probably be produced by the interaction of the trimethylene bromide and ethyl sodioethylacetoacetate according to the equations—

\[
\text{CH}_3\text{CO}\cdot\text{CETNa}\cdot\text{COOEt} + \text{C}_3\text{H}_5\text{Br}_2 = \\
\text{CH}_3\text{CO}\cdot\text{CET}(\text{COOEt})\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \text{ and} \\
\text{CH}_3\text{CO}\cdot\text{CET}(\text{COOEt})\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{CH}_3\text{CO}\cdot\text{CETNa}\cdot\text{COOEt} = \\
\text{CH}_3\text{CO}\cdot\text{CET}(\text{COOEt})\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 + \text{CH}_3\text{CO}\cdot\text{CET} \cdot \text{COOEt} + \text{NaBr}.
\]

It was repeatedly submitted to fractional distillation under the ordinary pressure in order to try and isolate the ethyl ethylallylacetoacetate, but the attempt was unsuccessful. Various fractions were analysed, but in all cases the results agreed with those required by a mixture of ethyl ethylacetoacetate and ethyl ethylallylacetoacetate, the analyses giving from 64·4 to 65·3 per cent. of carbon and about 9·1 per cent. of hydrogen instead of 66·7 per cent. of carbon and 9·0 per cent. of hydrogen as required by ethyl ethylallylacetoacetate.

\(\alpha\omega\)-Diacetyl-\(\alpha\omega\)-diethylpentane, \(\text{CH}_3\text{CO}\cdot\text{CET}[\text{CH}_2]_3\text{CET} \cdot \text{CO}\cdot\text{CH}_3\)

Diacetyladiethylpentane is best prepared by treating ethyl diacetyldiethylpimelate with alcoholic potash as described in the preparation of diacetylpentane.

The ethereal salt is dissolved in a small quantity of alcohol, and the solution heated to boiling in a flask provided with a reflux condenser; about one-third of a hot, moderately concentrated, alcoholic solution of potash (4 mols.) is then added, and the mixture is boiled again. As soon as no further separation of potassium carbonate occurs, another third of the potash solution is poured in and the mixture is heated again for about 10 minutes; the remainder of the alcoholic potash is then added and the alcohol is immediately evaporated. The alkaline residue is mixed with water, the precipitated diketone
extracted with ether, the ethereal solution dried over potassium carbonate and evaporated. The yellowish-brown, mobile oil which is thus obtained consists of impure diacetyldiethylpentane; the quantity of the crude product is only 11—12 grams from 50 grams of the ethereal salt, the small yield being due to the formation of large quantities of acid decomposition-products.

As the crude diketone showed no signs of crystallisation even when cooled below 0°, it was submitted to fractional distillation under a pressure of 110 mm. The thermometer rose rapidly to about 160°, and about 10 per cent. of the whole distilled below 206°; the thermometer then remained very constant at 207—208°, about 50 per cent. passing over between 200° and 210°, and the remainder at a slightly higher temperature.

The fraction 200—210° was distilled again under the same pressure and the portion boiling at 207—208° collected separately. This liquid on analysis gave the following results:—

0·1690 gram of substance gave 0·4533 gram of CO₂ and 0·1751 gram of H₂O.

<table>
<thead>
<tr>
<th>Calculated for</th>
<th>Found.</th>
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<tbody>
<tr>
<td>C₃H₂₄O₂</td>
<td>73·59 per cent.</td>
</tr>
<tr>
<td>H</td>
<td>11·32 &quot;</td>
</tr>
<tr>
<td>O</td>
<td>15·09 &quot;</td>
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</tbody>
</table>

Diacetyldiethylpentane is a colourless, moderately mobile oil with a slight, rather pleasant, aromatic odour similar to that of diacetyl-pentane. It boils at 207—208° (110 mm.), and shows no signs of crystallising. It is insoluble or only very sparingly soluble in water, but miscible with alcohol, ether, and other ordinary solvents in all proportions. It does not combine with sodium hydrogen sulphite even when left for a long time in contact with a concentrated aqueous solution of the salt. It dissolves in cold concentrated sulphuric acid with a yellowish-brown coloration, but it undergoes no change even after two days' time, as is proved by the experiments described below.

aw-Diacetyl-aw-diethylpentanedioxime,
NOH:CMc3CHEt-[CH₂]₃CHEt-CMe:NOH.

Diacetyldiethylpentane combines readily with hydroxylamine in alkaline solution, yielding the dioxime.

The diketone (about 1 gram) is dissolved in alcohol, treated with an alcoholic solution of hydroxylamine hydrochloride (1·5 gram) and potash (5 grams), and the mixture kept at the ordinary temperature for 24 hours; the alcohol is then partially evaporated on the water-
bath, the residue mixed with water and treated with a slight excess of dilute hydrochloric acid. The oil which is precipitated is extracted with ether, and after drying the extract over calcium chloride, the ether is evaporated. The dioxime remains in the form of a thick, yellowish oil which soon solidifies to a mass of crystals. After removing oily impurities by spreading the crystals on a porous plate, a nitrogen determination was made with the following result:—

0·1184 gram of substance gave 12 c.c. of nitrogen measured at 12° and 755 mm. pressure.

<table>
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<th>Calculated for</th>
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<tbody>
<tr>
<td>C_{12}H_{26}N_{2}O_{2}</td>
<td>N .......... 11·6 per cent. 11·9 per cent.</td>
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</table>

Diacetyldiethylpentanedioxide separates from a mixture of benzene and light petroleum in colourless, microscopic crystals melting at 110—111°. It is readily soluble in alcohol, ether, acetic acid, benzene, and other ordinary solvents, but only very sparingly in cold light petroleum; on adding light petroleum to the benzene solution, the dioxime is precipitated in a crystalline condition. It dissolves freely in alkalis and in moderately concentrated mineral acids.

**Behaviour of Diacetyldiethylpentane with Concentrated Sulphuric Acid.**

The chief object in view in preparing diacetyldiethylpentane was to study its behaviour with sulphuric acid. It has been shown in the previous paper that diacetylpentane dissolves in cold concentrated sulphuric acid, and is thereby converted into a compound C_{5}H_{10}O; the various theoretically possible formulae for this compound have been already discussed, and it has been shown that its constitution is probably that of an orthomethyltetrahydrobenzene methyl ketone. One of the chief arguments in support of this view is the fact that diacetyldiethylpentane does not yield an analogous product under the same conditions, and is, in fact, unchanged by concentrated sulphuric acid.

About 8 grams of crude diacetyldiethylpentane was dissolved in about 60 grams of concentrated sulphuric acid; a slight development of heat was observed and the solution gradually turned brown. After keeping for about 24 hours, the solution was poured into a large volume of cold water and the precipitated oil extracted with ether. A yellowish-brown oil remained when the ether was evaporated, and the weight of this product was about 6·5 grams. The crude oil was submitted to fractional distillation under the ordinary pressure; the thermometer rose rapidly to 230°, and only a small quantity distilled between 230° and 240°, the greater portion passing over at 245—255°.
KIPPING AND PERKIN: αω-DIACETYL-αω-DIETHYLPENTANE. 35

This fraction was collected separately, and analysed without any further purification. The following results were obtained:

\[
0.2228 \text{ gram of substance gave } 0.5863 \text{ gram of } \text{CO}_2 \text{ and } 0.2239 \text{ gram of } \text{H}_2\text{O}.
\]

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<tr>
<td>(\text{C}<em>{13}\text{H}</em>{22}\text{O}_2)</td>
<td>(\text{C}<em>{13}\text{H}</em>{24}\text{O}_2)</td>
</tr>
<tr>
<td>C</td>
<td>80.4</td>
</tr>
<tr>
<td>H</td>
<td>11.3</td>
</tr>
<tr>
<td>O</td>
<td>11.3</td>
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This analysis shows that the fraction boiling at 245—255° consisted of impure diacetyldiethylpentane, and proves conclusively the absence of any compound richer in carbon. Since this fraction formed about 60 per cent. of the crude product, and most of the remainder boiled at a temperature above 255°, the experiment would show that the formation of a compound \(\text{C}_{13}\text{H}_{24}\text{O}\) does not take place under these conditions.

In order to prove beyond doubt that such is really the case, the experiment was repeated in the following manner:—10 grams of almost pure diacetyldiethylpentane was dissolved in 300 grams of cold concentrated sulphuric acid and the solution kept for two days at the ordinary temperature; there was only a slight evolution of sulphurous anhydride, but the solution gradually darkened in colour. It was poured into a large volume of cold water, the oil extracted with ether, the extract dried over potassium carbonate and evaporated; the residual oil weighed about 8.8 grams. When the oil was distilled under the ordinary pressure, the thermometer rose at once to 215°, and the whole passed over between 215—270°, the greater portion boiling at about 250°. The fraction 215—270°, that is to say, the whole of the crude product, was distilled again under the ordinary pressure, and the portions passing over at 215—225° and 225—235° were collected separately. These two fractions were analysed with the following results:

I. Fraction boiling at 215—225°: 0.1568 gram of substance gave 0.1441 gram of \(\text{CO}_2\) and 0.1617 gram of \(\text{H}_2\text{O}\).
II. Fraction boiling at 225—235°: 0.1654 gram of substance gave 0.4371 gram of \(\text{CO}_2\) and 0.1733 gram of \(\text{H}_2\text{O}\).
These analyses show that both fractions consisted of impure diacetylidiethylpentane, the purer of the two being naturally that of higher boiling point, as it approaches more closely that of the pure diketone. Now, since, if any dehydrating action had occurred, the resulting compound must have been contained in these two lowest boiling portions of the crude oil, it is clear that no compound of the composition \( \text{C}_{13}\text{H}_{23}\text{O} \) had been formed.

This experiment, therefore, confirms the previous results and proves conclusively that diacetylidiethylpentane is not converted into a compound of the composition \( \text{C}_{13}\text{H}_{23}\text{O} \) under conditions which, in the case of diacetylpentane, result in the formation of a compound of the composition \( \text{C}_9\text{H}_{18}\text{O} \); this difference in behaviour can be explained only by assuming that the latter has the constitution of an ortho-methyltetrahydrobenzene methyl ketone, a view which is fully borne out by other experiments.

\( w\text{-Acetyl}-w\text{-diethylcaproic Acid, CH}_3\text{CO}\cdot\text{CHET} \cdot [\text{CH}_2]_2 \cdot \text{CHET} \cdot \text{COOH}. \)

The alkaline mother-liquors from which the diacetylidiethylpentane has been extracted with ether contain the potassium salts of acetyl-diethylcaproic acid, acetic acid, and probably also diethylpimelic acid; these compounds having been produced by the hydrolysis of ethyl diacetylidiethylpimelate in accordance with the equations given on pp. 29 and 30. On acidifying with dilute sulphuric acid, a thick, yellowish oil is precipitated; the solution is shaken three or four times with ether, the ethereal extract dried over calcium chloride, and the ether evaporated. As the thick, sour-smelling oil which remained showed no signs of crystallising even when cooled below 0°, it was submitted to fractional distillation under reduced pressure (110 mm.). The acetic acid which passed over at the commencement of the distillation was readily identified by its odour and by converting it into ethyl acetate; the thermometer then rose rapidly to 200°, a small quantity only distilled below 240°, and the whole of the remainder passed over between 240° and 280°. The portion boiling at 240—280° was fractionated again under a pressure of 90 mm., and a fairly large quantity, boiling at 253—255°, collected separately.

The analysis of this fraction (b. p. 253—255°) showed that it consisted of acetylidiethylcaproic acid:

0·1420 gram of substance gave 0·3490 gram of CO₂ and 0·1305 gram of H₂O.

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<thead>
<tr>
<th>Calculated for</th>
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<tbody>
<tr>
<td>( \text{C}<em>{12}\text{H}</em>{22}\text{O}_3 )</td>
<td>( \text{C} ) 67·28 per cent. 67·03 per cent.</td>
</tr>
<tr>
<td></td>
<td>( \text{H} ) 10·28 ,, 10·21 ,,</td>
</tr>
<tr>
<td></td>
<td>( \text{O} ) 22·43 ,, 22·76 ,,</td>
</tr>
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</table>
Acetyldiethylcaproic acid is a thick, colourless liquid having an odour very like that of pyruvic acid; it becomes semi-solid when cooled strongly, but it has not yet been obtained in a crystalline condition. It is insoluble, or only very sparingly soluble, in water, but miscible with alcohol, ether, benzene, and other ordinary solvents in all proportions.

The silver salt, \( \text{CH}_2\text{CO}\cdot\text{CHEt}\cdot\text{(CH}_2)_3\text{CHEtCOOAg} \), was prepared by dissolving a portion of the fraction boiling at 253—255° in ammonia, and fractionally precipitating the neutral solution with silver nitrate. It is a colourless, seemingly amorphous compound, and rather sparingly soluble in hot water; it seems to be stable in the light.

A silver determination, made with a portion of the second fraction of the salt, gave the following result:—

\[
\begin{array}{ll}
0.4714 \text{ gram of substance gave } 0.1605 \text{ gram of silver.} \\
\end{array}
\]

Calculated for 
\( \text{C}_{15}\text{H}_{23}\text{O}_3\text{Ag} \)  Found. 
\begin{align*}
\text{Ag} & \quad 33.64 \text{ per cent.} & \quad 34.03 \text{ per cent.} \\
\end{align*}

The first fraction gave a somewhat larger percentage of silver probably owing to the presence of small quantities of diethylpimelic acid.

In neutral aqueous solutions of the ammonium salt, lead acetate and mercuric chloride produce a colourless precipitate; ferric chloride, a buff-coloured precipitate; and copper sulphate, a dark-green precipitate.

The calcium salt and the barium salt are readily soluble in water.

\( \omega\)-Acetyldiethylcaproic Acid Oxime,
\[
\text{NOH}\cdot\text{CMe}\cdot\text{CHEt}\cdot[\text{CH}_2]_3\text{CHEtCOOH}. 
\]

Acetyldiethylcaproic acid oxime can be obtained by treating the acid with hydroxylamine hydrochloride and excess of potash in dilute alcoholic solution; after keeping for about 24 hours, the alcohol is evaporated on the water-bath, the residue dissolved in water, the solution slightly acidified with hydrochloric acid, and extracted with ether. The crude product is a thick, yellowish oil, but it slowly solidifies to a mass of crystals; the crystalline substance, after having been spread on a porous plate and washed with a little light petroleum, melted at 102—103°.

A nitrogen determination gave the following result:—

\[
0.0961 \text{ gram of substance gave } 5.05 \text{ c.c. of nitrogen measured at } 14^\circ \text{ and } 745 \text{ mm. pressure.} 
\]
Acetyldiethylcaproic acid oxime crystallises from a mixture of benzene and light petroleum in colourless, microscopic plates; it is readily soluble in alcohol and benzene, but only sparingly in light petroleum, and, seemingly, insoluble in water; it dissolves freely in alcalis and in concentrated hydrochloric acid.

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