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# $XV.-ww_1$ -Diacetylbutane.

By T. RHYMER MARSHALL, D.Sc., and W. H. PERKIN, Jun., Ph.D.

This paper which is a continuation of the preceding one, contains a description of the preparation and properties of the following substances :—

$ww_1$ -Diacetylbutane		$CH_3 \cdot CO \cdot [CH_2]_4 \cdot CO \cdot CH_3.$
Methyldihydropentene-	l	$CH_3 \cdot C$ $C \cdot CO \cdot CH_3$
methyl ketone	ſ	$\dot{\mathbf{C}}\mathbf{H}_2 \cdot \mathbf{C}\mathbf{H}_2 \cdot \dot{\mathbf{C}}\mathbf{H}_2$
Methylpentamethylene-	1	$CH_3 \cdot CH - CH \cdot CH(OH) \cdot CH_3$
methyl carbinol	ſ	$\dot{\mathrm{CH}}_{2} \cdot \mathrm{CH}_{2} \cdot \dot{\mathrm{CH}}_{2}$

together with the iodide and acetate of this alcohol.

Methylethylpentamethyl-	$CH_3 \cdot CH - CH \cdot CH_2 \cdot CH_3$
ene	$\dot{\mathrm{CH}}_{2} \cdot \mathrm{CH}_{2} \cdot \dot{\mathrm{CH}}_{2}$
Methylethyldihydropen-	CH <sub>3</sub> ·C <u> </u>
tene methyl ketone $\int$	$C_2H_5 \cdot CH \cdot CH_2 \cdot CH_2$

and also of numerous other substances obtained as bye-products, in the preparation of the above compounds.

# $\omega \omega_1$ -Diacetylbutane, CH<sub>3</sub>·CO[CH<sub>2</sub>]<sub>4</sub>·CO·CH<sub>3</sub>.

Owing to the ease with which diacetylbutane is converted into methyldibydropentene methyl ketone, it has been found extremely difficult to prepare this substance in a pure state. The following method has, however, on two or three occasions been used with success.

Five grams of pure ethyl diacetyladipate (prepared from the ammonium compound, p. 219) were dissolved in a little methyl alcohol, mixed with a slight excess of a strong solution of pure potash in methyl alcohol, and heated to boiling on a water-bath for 15 minutes. The alcoholic solution was filtered from the precipitated potassium carbonate, the filtrate mixed with twice its volume of water, neutralized with dilute sulphuric acid, and the alcohol distilled off. The residue was extracted three times with ether, the ethereal solution washed with water, dried over anhydrous potassium carbonate, and evaporated. The resulting, almost colourless oil, after standing over sulphuric acid in a vacuum for some days in a cold place, deposited a quantity of flaky crystals, and in one case solidified almost entirely. These crystals were freed from oily impurities by spreading on a perous plate, and in this way a beautiful, colourless, flaky, crystalline mass was obtained, which on analysis gave the following numbers :---

0.1380 gram substance gave 0.1220 gram  $H_2O$  and 0.3410 gram CO<sub>2</sub>.

CH. CO	Theory.	O.CH.	Found.	
C	67.60 p	er cent.	67.39 per	cent.
н	9·86 <sup>^</sup>	"	9.82	"
0	22.54	,,	22.79	,,

Diacetylbutane is a colourless, crystalline substance which, when purified as above, melts at about 43-44°. It is readily soluble in almost all organic solvents, sparingly so in water. It combines readily with hydrogen sodium sulphate, with phenylhydrazine, and with hydroxylamine, forming well characterised derivatives, which were not prepared in any quantity, or analysed owing to the difficulty experienced in obtaining sufficient pure diacetylbutane.

Under the influence of dehydrating agents, or by simply boiling with alcoholic potash, and apparently also on distillation, diacetylbutane undergoes internal condensation, yielding methyldihydropentene methyl ketone.

$$\begin{array}{c} \mathrm{CH}_3 \cdot \mathrm{CO} \cdot [\mathrm{CH}_2]_4 \cdot \mathrm{CO} \cdot \mathrm{CH}_3 = \mathrm{CH}_3 \cdot \mathrm{C} \underbrace{ \overset{}{\underset{\mathrm{CH}_2} \cdot \mathrm{CH}_2} }_{\mathrm{CH}_2 \cdot \mathrm{CH}_2} \mathrm{CO} \cdot \mathrm{CH}_3 + \mathrm{H}_2 \mathrm{O}. \end{array}$$

 $\begin{array}{c} \mathrm{CH}_3 \cdot \mathrm{C} \underbrace{\qquad} \mathrm{C} \cdot \mathrm{CO} \cdot \mathrm{CH}_3 \\ \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \end{array}$ Methyldihydropentene methyl ketone,

This substance is readily obtained by the action of strong boiling alcoholic potash on ethyl diacetyladipate. For this purpose it is not necessary to use pure ethyl diacetyladipate; the crude oil which is obtained on distilling the product of the action of ethylene bromide on ethyl sodioacetoacetate with steam, as described in the previous paper, answers equally well.

The quantities most conveniently employed are the following :----

Crude ethyl diacetyladipate, 50 grams.

Caustic potash, 50-55 grams (dissolved in the smallest quantity of boiling 80 per cent. alcohol).

The ethyl diacetyladipate is dissolved in an equal bulk of alcohol, heated to boiling on a water-bath, in a flask connected with a reflux apparatus, and one-third of the potash solution run in. After boiling vigorously for five minutes, another third of the potash solution is added, the mixture boiled for ten minutes, then the remaining potash solution added, and the alcohol at once distilled off. The dark-brown product is mixed with sufficient water to dissolve the potassium carbonate and other potash salts, extracted five times with ether, the ethereal solution washed with water, dried over anhydrous potassium carbonate, and evaporated. In this way a yellowish oil is obtained which should weigh 15 to 20 grams. On distillation, almost the whole of it passes over between 185 and 200° as a colourless oil, leaving only a very small dark residue in the retort, and on refractioning once or twice, the substance is readily obtained pure, and boiling constantly at 191° (760 mm.).

The numbers obtained on analysis agree with those required by the formula  $C_8H_{12}O$ .

0.1344 gram substance gave 0.1194 gram  $H_2O$  and 0.3804 gram  $CO_2$ .

	Theory.			
	C <sub>8</sub> H <sub>12</sub> Ö.		Found.	
C	77·42 pe	r cent.	77·19 per	cent.
н	9.68	37	9.87	"
0	12.90	,,	12.94	,,

Methyldihydropentene methyl ketone, which, by this method, may be obtained in a state of great purity with comparatively little labour, is a colourless, mobile oil, possessing a most powerful odour of peppermint.

A series of carefully conducted experiments have shown that it is identical with the compound obtained by the hydrolysis of the crude product of the distillation of ethyl diacetyladipate, as described in the foregoing paper (p. 231). Both these substances boil at the same temperature; they possess the same odour, have the same specific gravity, and give the same products on reduction.

As it was very important to be certain of the identity of the two substances, the oxime of the product obtained as above was prepared and compared with that previously obtained from the other compound,  $C_8H_{12}O$  (p. 232); 1 gram of the pure substance was dissolved in methyl alcohol, mixed with a dilute methyl alcoholic solution of 0.7 gram of hydroxylamine hydrochloride and 1.5 gram of potash, and the whole allowed to stand 24 hours. The resulting, colourless solution was mixed with an equal volume of water, boiled to expel the alcohol, cooled well, and acidified with dilute sulphurie acid. The crystalline precipitate thus obtained was collected, well washed with water, dried on a porous plate, and recrystallised from light petroleum. The beautifully crystalline substance thus obtained gave the following numbers on analysis :—

- I. 0.1733 gram substance gave 0.1490 gram  $H_2O$  and 0.4395 gram  $CO_2$ .
- II. 0.2677 gram substance gave 23.8 c.c. N;  $t = 14^{\circ}$ ; bar. = 744.

	Theory. C <sub>8</sub> H <sub>13</sub> NO.		Found.	
С	69 <sup>.</sup> 06 pe	er cent.	69·16 per	cent.
н	9.36	"	9.54	,,
N	10.07	"	10.30	,,

This oxime melts at 85°, is readily soluble in acids and alkalis, and agrees in all its properties with the substance already described in the last paper (p. 237).

As the yield of methyldihydropentene methyl ketone was far from that which should have been obtained theoretically, it was thought that interesting results might be obtained by examining the solution of the potassium salts from which the above ketone had been extracted.

The dark-brown solution was evaporated till free from alcohol. acidified with dilute sulphuric acid, and extracted several times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a dark-brown, acid-smelling oil, which, even after long standing over sulphuric acid in a vacuum, showed no signs of crystallising. In order to purify this crude product, it was dissolved in a slight excess of baryta-water, the solution heated to boiling, and treated with carbon dioxide until the excess of baryta had been removed. On filtering, the solution was found to be much less coloured, whilst the barium carbonate precipitated was distinctly brownish, showing that a considerable quantity of impurity had been removed. The boiling solution of the barium salt was acidified with dilute hydrochloric acid, well agitated, filtered from a small quantity of resinous matter, and after cooling, repeatedly extracted with ether. On drying the ethereal solution over calcium chloride and evaporating, a dark-yellow oil was obtained, which, after standing for some days over sulphuric acid in a vacuum, deposited These were separated from the oily mother liquor as crystals. completely as possible by spreading on a porous plate, and then further purified by recrystallisation from water.

The colourless crystals thus obtained gave the following results on analysis :---

- I. 0.2146 gram substance gave 0.1240 gram  $\rm H_2O$  and 0.4490 gram  $\rm CO_2$
- 11. 0·1594 gram substance gave 0·0903 gram  $\rm H_2O$  and 0·3323 gram  $\rm CO_2.$

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CH <sub>3</sub> ·C C·COOH	Found.	
$COOH \cdot CH \cdot CH_2 \cdot CH_2$	í. 11.	
С 56.47 р. с.	56.96 56.86 р. с	•
H 5·88 <sup>-</sup> ,,	6.26 $6.29$ ,	
O 37.65 "	36.78 36.85 ,,	

This acid melts at 188°, and is evidently identical with the substance obtained by the hydrolysis of the oil  $C_{11}H_{16}O_3$ , as described in the last paper. The formation of this acid by the hydrolysis of ethyl diacetyladipate would be represented by the following equation :—

$$\begin{array}{c} CH_{3} \cdot CO \\ COOC_{2}H_{5} \end{array} > CH \cdot CH_{2} \cdot CH_{2} \cdot CH < \begin{array}{c} CO \cdot CH_{3} \\ COOC_{2}H_{5} \end{array} + 3KOH = \\ CH_{3} \cdot C \underbrace{\qquad} CH_{3} \cdot C \underbrace{\qquad} C \cdot COOK \\ COOK \cdot CH \cdot CH_{2} \cdot CH_{2} \end{array} + CH_{3} \cdot COOK + H_{2}O + 2C_{2}H_{5} \cdot OH. \end{array}$$

Action of Reducing Agents on Methyldihydropentene Methyl Ketone. Formation of Methylpentamethylene Methyl Carbinol, CH<sub>3</sub>·CH — CH·CH(OH)·CH<sub>3</sub> CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>

The products obtained in the reduction of methyldihydropentene methyl ketone vary remarkably with the nature of the reducing agents employed; thus, whereas on treatment with sodium in ethereal solution methylpentamethylene methyl carbinol results, when sodium amalgam is employed, scarcely a trace of this substance is formed. In preparing methylpentamethylene methyl carbinol, 20 grams of the ketone was dissolved in 100 grams of ether, the solution floated on about 50 c.c. of water, and about three times the calculated quantity of sodium very gradually added, and if necessary small quantities of water, from time to time, the flask being carefully cooled by a stream of running water. As soon as all the sodium has been added, the ethereal solution was separated, washed with water, dried over potassium carbonate, evaporated, and the resulting, thick, colourless submitted to fractional distillation under reduced pressure oil (55 mm.). In this way the oil was readily separated into two principal fractions,  $120-150^{\circ}$  and  $230-260^{\circ}$ . On repeatedly refractioning the lower fraction at ordinary pressures, pure methylpentamethylene methyl carbinol was readily obtained as a colourless oil, boiling constantly at 180°.

## Analyses.

I. 0.1231 gram substance gave 0.1412 gram  $\rm H_2O$  and 0.3389 gram  $\rm CO_2$ 

II. 0.1631 gram substance gave 0.1814 gram H<sub>2</sub>O and 0.4487 gram CO<sub>2</sub>.

CH. CH-	Theory. ——CH·CH(OH)·CH <sub>2</sub>	Fo	und.
ČH <sub>2</sub> C	$H_2 \cdot CH_2$	í.	II.
C	75 <sup>.</sup> 00 p. c.	75.08	75.03 р. с
н	$12.50^{-},$	12.74	12·35 ,
0	12.50 "	12.18	12.62 ,,

Methylpentamethylene methyl carbinol is a colourless, moderately mobile oil, having a strong odour of menthol. It is readily soluble in organic solvents, and also slightly soluble in water.

Methylpentamethylene methyl carbinol yields an acetate when treated with acetic anhydride (p. 249), and an iodide when digested with hydriodic acid (p. 249).

In order to demonstrate the existence of a closed chain in methyl dihydropentene methyl ketone, it was important to show clearly that this substance on reduction is only capable of taking up at the most 4 atoms of hydrogen. As methylpentamethylene methyl carbinol was possibly only an intermediate product of the reduction of the ketone, experiments were made with the view of reducing this alcohol still further.

Five grams of the pure alcohol were mixed with 200 grams of absolute alcohol, heated to boiling on a water-bath, in a flask connected with a reflux apparatus, and then 20 grams of sodium thrown in as rapidly as possible. The product was mixed with water, the alcohol distilled off, and the residue extracted with ether. The resulting oil, on distillation under reduced pressure (80 mm.), distilled at 119-120°, and on subsequent fractioning under ordinary pressure at 178-181°, and gave the following numbers on analysis :--

0.1294 gram substance gave 0.1443 gram H<sub>2</sub>O and 0.3532 gram  $CO_2$ .

	Theory.		Found	
с	75.00  per	cent.	74.44 per	cent.
Н	12.50	**	12.39	,,
0	12.50	59	13.17	,,

This result tends to show that methylpentamethylene methyl carbinol is a fully saturated substance, not capable of combining further with hydrogen, a fact which is proved conclusively by the results of the experiments on the action of hydriodic acid on the iodide of this alcohol.

In reducing methyldihydropentene methyl ketone in a moist ethereal solution with sodium, a considerable quantity of a very thick oil is obtained, which boils at about  $230-260^{\circ}$  (55 mm.). As it was thought that the examination of this substance might lead to interesting results, it was most carefully fractioned several times under a pressure of 50 mm., after which the greater part boiled at  $250-255^{\circ}$  (50 mm.).

Two separate preparations, both boiling at the same temperature, gave the following results on analysis :---

- I. 0.2572 gram substance gave 0.2615 gram  $H_2O$  and 0.7230 gram  $CO_2$ .
- II. 0.1568 gram substance gave 0.1574 gram  $H_2O$  and 0.4410 gram  $CO_2$ .

		$\mathbf{Fo}$	und.
	Theory.		<u>۸</u>
	$C_{16}H_{28}O_2$ .	I.	11.
C	76 <sup>.</sup> 19 р. с.	76.88	76 <sup>.</sup> 65 р. с.
н	11·11 ,,	11.29	11.15 "
0	12·70 "	11.83	12·20 "

A determination of its molecular weight by Raoult's method, using acetic acid as a solvent, gave the following results :----

Weight of substance	1.2890
" acetic acid	50·17
Melting point of acetic acid	15·74°
,, mixture	15.33
Depression of m. p	0.41

Molecular weight,  $C_{16}H_{28}O_2$ , 252. Found, 244.

This substance, which appears to have the formula  $C_{16}H_{28}O_2$ , is a colourless, transparent syrup, so thick that a test-tube half full of the syrup may be inverted for some time without the substance falling out. It has a decided odour of menthol, distils at the ordinary pressure with slight decomposition, and under reduced pressure (50 mm.) at 250-255°, without the slightest decomposition. From its mode of formation and general properties, it appears probable that this substance has the formula—

 $\begin{array}{c} \mathrm{CH}_3 \cdot \mathrm{C} \underbrace{\qquad} \\ \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 & \mathrm{CH}_2 & \mathrm{CH}_2 & \mathrm{CH}_3 & \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 & \mathrm{CH}_2 & \mathrm{CH}_3 & \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \\ \end{array}$ 

being a condensation-product derived from 1 mol. of ethyldihydropentene methyl ketone, and 1 mol. of methylpentamethylene methyl ketone.

# Reduction of Methyldihydropentene Methyl Ketone by Sodium Amalgam.

During the first experiments on the reduction of this ketone, several attempts were made to obtain the unsaturated alcohol  $CH_3 \cdot C \equiv CH(OH) \cdot CH_3$  by the action of sodium amalgam on CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>

dilute alcoholic solutions of the substance.

The pure ketone was dissolved in 50 per cent. alcohol, and treated with a large excess of  $1\frac{1}{2}$  per cent. sodium amalgam, the oil which soon separates out being kept in solution by the addition of further quantities of alcohol. The product of the reaction was a very thick oil, which on fractioning under a pressure of 25 mm. separated into two principal fractions, 220-225° and 250-260°, scarcely a trace of any low boiling substance being obtained.

Fraction 250-260° (25 mm.), which was a very thick, slightly brownish oil, gave on analysis the following numbers :---

0.1800 gram substance gave 0.1703 gram H<sub>2</sub>O and 0.5086 gram CO<sub>2</sub>.

	Theory.			
	C <sub>16</sub> H <sub>26</sub> Ŭ <sub>2</sub> .		Found.	
C	76·80 p	er cent.	<b>7</b> 7·05 per	cent.
н	10.40	"	10.51	,,
0	12.80	;,	12.44	,,

A determination of its molecular weight by Raoult's method gave the following results :---

Weight of substance	9 <b></b>	1.2797	gram.
" acetic aci	d	49.14	,,
Melting point of ace	tic acid	$15.76^{\circ}$	
" mi	xture	$15.34^{\circ}$	
Depression of melti	ng point	$0.42^{\circ}$	

Molecular weight of C<sub>16</sub>H<sub>26</sub>O<sub>2</sub>, 250. Found, 242.

This substance is evidently the pinacone of methyldihydropentene methyl ketone, and its constitution must therefore be represented by the formula-

$$\begin{array}{c} \mathrm{CH}_3 \cdot \mathrm{C} \underbrace{\longrightarrow}_{l} \mathrm{C} \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \\ \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 & \mathrm{H}_3 \mathrm{C} & \mathrm{CH}_3 & \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \end{array}$$

The fraction 220-225° (25 mm.) obtained in the reduction of methyldihydropentene methyl ketone with sodium amalgam gave on analysis numbers agreeing approximately with the formula  $C_{16}H_{24}O$ (i.e.,  $C_{16}H_{26}O_2 - H_2O$ ), and it is, therefore, probably an anhydride of the above pinacone. As we had only a very small quantity of this

substance at our disposal, no further experiments were made with it. It is a very thick, slightly brownish oil, having a faint odour of peppermint.

In preparing this substance, the pure alcohol was boiled with twice the calculated quantity of acetic anhydride on a reflux apparatus for two hours, the acetic acid and excess of anhydride distilled off, and the residual oil distilled under reduced pressure.

The fraction boiling at  $145-150^{\circ}$  (130 mm.), gave on analysis the following numbers:—

0.1531 gram substance gave 0.1459 gram  $H_2O$  and 0.3960 gram  $CO_2$ .

	Theory.			
	$C_{10}H_{18}O_2$ .		Found.	
C	70.58 per	cent.	$70.54  { m per}$	cent.
Н	10.60	,,	10.29	,,
0	18.82	,,	18.87	,,

This acetate is an agreeably smelling and strongly refracting liquid, which appears to distil under the ordinary pressure without decomposition. In order to more clearly prove its constitution, it was hydrolysed by boiling with excess of standard potash solution for six hours, and the amount of acetate formed determined by estimating the amount of unused alkali present in the solution by means of standard sulphuric acid. It was thus found that 1.349 gram substance on hydrolysis neutralised 79.5 c.c. of standard potash solution, 1 c.c. of which was equal to 0.00597 gram of CH<sub>3</sub>·COOH. This corresponds to 35.1 per cent. of CH<sub>3</sub>·COOH, whereas theory requires 35.3 per cent.

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Methylpentamethylene methyl carbinol is readily attacked by boiling hydrochloric, hydrobromic, and hydriodic acids, with formation of heavy oils, consisting no doubt of the corresponding chloride, bromide, and iodide of the alcohol. Of these the latter only has been prepared in quantity and examined. It is best obtained by boiling the alcohol with an excess of hydriodic acid of sp. gr. 1.96 for about half an hour on a reflux apparatus. The product is mixed with twice

its volume of water, extracted several times with ether, the ethereal solution washed well with water and dilute sodium carbonate solution, dried over anhydrous potassium carbonate, and evaporated, the resulting oil, after removing free iodine by shaking with mercury, being purified by fractionation under reduced pressure (90 mm.). A considerable portion of the substance distilled between 155 and 160° (90 mm.), and gave on analysis the following numbers:—

0.2543 gram substance heated with nitric acid and nitrate of silver at 180° for four hours gave 0.2460 gram AgI.

	Theory.	
	$C_8H_{15}I.$	Found.
I	53.21 per cent.	52.26 per cent.

This iodide is a colourless, heavy oil, having an odour strongly resembling that of hexyl iodide. When distilled, even under reduced pressure, it undergoes slight decomposition, with formation of products of high boiling point; it is better for most purposes, therefore, to use the crude oil, without fractioning.

Methylethylpentamethylene (1.2),  $\begin{array}{c} \mathrm{CH}_{3} \cdot \mathrm{CH}_{----} - \mathrm{CH} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{3} \\ \overset{1}{\mathrm{CH}}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \end{array}$ 

In preparing this interesting substance, methyl- $\alpha$ -iodethylpentamethylene was heated in sealed tubes with excess of the strongest hydriodic acid and a little amorphous phosphorus at 240—250° for 12 hours. The contents of several tubes, each of which had contained about 5 grams of the iodide, were transferred to a separating funnel, allowed to stand for some hours, and the dark-coloured aqueous liquid separated as completely as possible from the layer of hydrocarbon which floated on the surface. The residual, limpid oil, after drying over potassium carbonate and distilling, passed over completely between 120 and 130°, and after repeated distillation over sodium and lastly over potassium the pure substance was obtained boiling constantly at 124°. The analysis gave the following numbers :—

I. 0.1313 gram substance gave 0.1708 gram  $H_2O$  and 0.4136 gram  $CO_2$ .

II. 0.1100 gram substance gave 0.1435 gram  $H_2O$  and 0.3465 gram  $CO_2$ .

		Fo	und.
	Theory.		~ <u> </u>
	$C_8H_{16}$ .	İ.	II.
C	85·71 p. c.	85.91	85 <sup>.</sup> 71 p. c.
$\mathbf{H}\ldots\ldots$	14.29 ,,	14.45	14·30 ,,

A determination of the vapour-density of this substance, by Victor Meyer's method, in aniline vapour gave the following results:----

0.042 gram substance displaced 8.5 c.c. of air;  $t = 13^{\circ}$  C.; bar. = 755 mm.

Molecular weight calculated, 118. Found, 112.

Methylethylpentamethylene is only with difficulty attacked by bromine; on boiling the two substances together, slight action takes place with evolution of hydrogen bromide. On shaking the hydrocarbon with fuming hydrobromic acid (sp. gr. 1.85) even for days, no appreciable action could be detected. When boiled with nitric acid (sp. gr. 1.16), oxidation rapidly sets in, and in the course of a few hours the oily layer of hydrocarbon entirely disappears and a colourless solution is obtained from which no definite substance could be extracted.

$$\begin{array}{c} \text{ Ethylmethyldihydropentene Methyl Ketone,} & \begin{array}{c} \text{CH}_3 \cdot \text{C} = & \text{C} \cdot \text{CO} \cdot \text{CH}_3 \\ \text{C}_2 \text{H}_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \end{array}$$

In order to get some further proof of the constitution of methyldihydropentene methyl ketone, several experiments were made with the object of preparing diethyldiacetylbutane,

$$CH_3 \cdot CO \cdot CH(C_2H_5) \cdot CH_2 \cdot CH_2 \cdot CH(C_2H_5) \cdot CO \cdot CH_3,$$

and studying its behaviour towards dehydrating agents.

A short time since, Dr. Kipping and one of us (this vol., p. 29 et seq.) prepared diethyldiacetylpentane by treating ethylic ethylacetoacetate with sodium ethylate and trimethylene bromide, and hydrolysing the resulting ethylic diethyldiacetylpimelate, thus :---

$$2 \frac{CH_{3} \cdot CO}{COOC_{2}H_{5}} > CNa \cdot C_{2}H_{5} + C_{3}H_{6}Br_{2} = \frac{CH_{3} \cdot CO}{COOC_{2}H_{5}} > C(C_{2}H_{5}) \cdot [CH_{2}]_{3} \cdot C(C_{2}H_{5}) < \frac{CO \cdot CH_{3}}{COOC_{2}H_{5}} + 2NaBr.$$
  
kthyl diethyldiacetylpimelate.

In endeavouring to prepare diethyldiacetylbutane by substituting ethylene bromide for trimethylene bromide in the above equation, we obtained only a trace of substance of high boiling, which might have been diethyl diacetyladipate, the principal product of the reaction being ethyl butyrate.

We then experimented on the action of ethyl iodide on the disodium compound of ethyl diacetyladipate in the hope of thus obtaining ethylic diethyldiacetyladipate, according to the equation

A mixture of 60 grams of crude ethyl diacetyladipate and 60 grams of ethyl iodide were slowly added, with careful cooling, to a solution of sodium ethylate, prepared by dissolving 9.7 grams of sodium in 100 grams of absolute alcohol. The whole was transferred to a soda-water bottle and heated on a water-bath for 12 hours. The alcohol was then distilled off, sufficient water added to dissolve the inorganic salts, and the product extracted four times with ether. The ethereal solution was washed with water, the ether distilled off, and the residual oil at once hydrolysed by boiling with alcoholic potash, the same quantities and the same method of procedure being employed as in the case of ethyl diacetyladipate itself. As soon as hydrolysis was complete the alcohol was distilled off, water added, and the oil which separated repeatedly extracted with ether. The ethereal solution, after washing with water, drying over anhydrous potassium carbonate, and evaporating, deposited a considerable quantity of a brownish oil which, on distillation, all passed over between 200° and 270°. This, on repeated fractionation, separated into two fractions, 210-215° and 250-255°, the latter, however, being very small.

Fraction 210-215° gave the following results on analysis:---

0.1199 gram of substance gave 0.1149 gram  $\rm H_2O$  and 0.3375 gram  $\rm CO_2.$ 

	Theory.		Found	
C	78.94 per	cent.	78.74 per	cent.
н	10.53	,,	10.57	,,
0	10.53	"	10.69	,,

This substance is evidently ethylmethydihydropentene methyl ketone, formed from ethylic ethyldiacetyladipate according to the equation-

# ACTION OF CHROMIUM OXYCHLORIDE ON NITROBENZENE. 253

In order to corroborate this, the substance was converted into its oxime. 4 grams of the oil were dissolved in a little methyl alcohol, and mixed with 4 grams of hydroxylamine hydrochloride dissolved in a small quantity of water, and 10 grams of pure potash dissolved in methyl alcohol. After 24 hours, the alcohol was evaporated by gently warming the solution on a water-bath, the residue mixed with water, rendered faintly acid by the addition of a few drops of hydrochloric acid, and repeatedly extracted with pure ether. The ethereal solution, after well washing with water, drying over calcium chloride, and evaporating, deposited the oxime as an oil which showed no signs of crystallisation on standing for 24 hours over sulphuric acid in a vacuum. The analysis gave the following numbers :—

0.1286 gram substance gave 9.4 c.c. N; bar. = 740 m.;  $t = 13^{\circ}$ .

	' Theory.	
	$C_{10}H_{17}NO.$	Found.
N	8.38 per cent.	8.40 per cent.

The fraction  $250-255^{\circ}$  appeared to consist of impure diethyldiacetylbutane, but the quantity obtained was so small that it was found impossible to obtain it in a pure state. With hydroxylamine it gave a solid dioxime.

We hope to be able to prepare this interesting substance by some other reaction, and to study its behaviour with dehydrating agents with a view of proving the formula given in this and the previous paper for methyldihydropentene methyl ketone.

Heriot Watt College, Edinburgh.