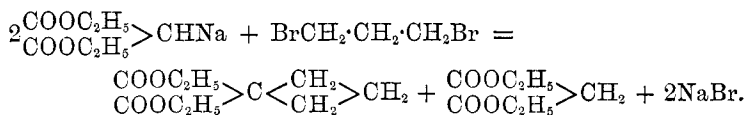


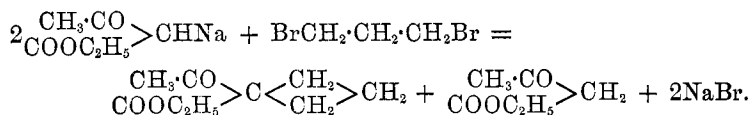
LXXIV.—*The Synthetical Formation of Closed Carbon-chains. Part II.*
(continued). *On the Action of Trimethylene Bromide on the Sodium Compounds of Ethylic Acetoacetate, Benzoylacetate, Paranitrobenzoylacetate and Acetonedicarboxylate.*

By W. H. PERKIN, Jun., Ph.D.

In a paper on "Tetramethylene-derivatives," which I brought before the notice of the Society a short time since (this vol., p. 1), I showed that when the sodium-derivative of ethylic malonate is digested with trimethylene bromide, ethylic tetramethylenedicarboxylate is formed thus:—

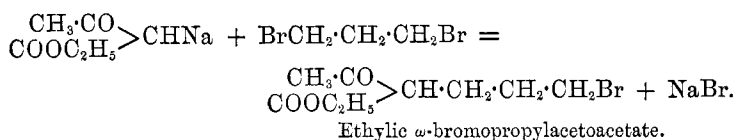


Whilst engaged on these experiments, it seemed probable that if ethylic acetoacetate or benzoylacetate were substituted for ethylic malonate, various tetramethylene-derivatives, of constitution similar to the above, might be obtained. Thus, in the case of ethylic acetoacetate, ethylic acetyltetramethylenecarboxylate should be formed:—

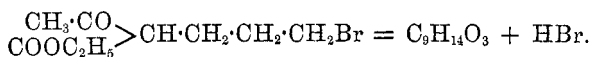


In a short account given of these experiments (*Ber.*, **16**, 1787), it was assumed that the products thus obtained were tetramethylene-derivatives. After careful study, however, it was found that these substances, from their decompositions and general reactions, must be quite differently constituted. The reaction between ethylic sodacetoacetate and trimethylene bromide evidently takes place in two distinct stages.

In the first place 1 mol. of trimethylene bromide reacts with 1 mol. of ethylic sodacetoacetate, forming ethylic ω -bromopropylacetoacetate, thus:—

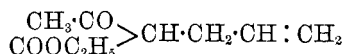


In the second phase of the reaction this intermediate product simply loses 1 mol. of hydrogen bromide, and is converted into the compound $C_9H_{14}O_3$,



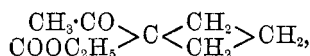
This change can take place in three different ways.

(1.) The bromine-atom can combine with the hydrogen-atom of the second CH_2 -group, producing a substance of the formula

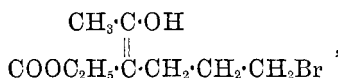


(ethylic allylacetoacetate).

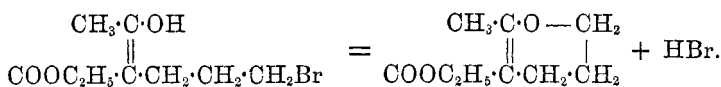
(2.) The bromine-atom can combine with the hydrogen-atom of the CH -group, in which case ethylic acetotetramethylenecarboxylate,



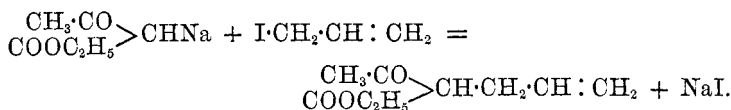
would be formed; or (3) ethylic ω -bromopropylacetoacetate is first transformed into its labile form,



and then hydrogen bromide is eliminated according to the equation—

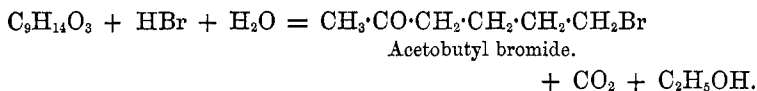


That the substance produced in this reaction is: (1) not ethylic allylacetoacetate, is easily proved by directly comparing it with the latter compound, which can easily be prepared synthetically by treating ethylic sodacetoacetate with allyl iodide,

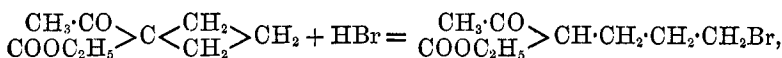


The greatest differences are found to exist between the two products, as will be shown in detail further on.

That the compound $C_9H_{14}O_3$ is not ethylic acetotetramethylenecarboxylate is easily shown in the following way. If this substance be mixed with a concentrated solution of hydrogen bromide, it dissolves, and on standing is decomposed into alcohol, carbonic anhydride, and acetobutyl bromide, thus:—

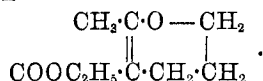


Now, if the substance $\text{C}_9\text{H}_{14}\text{O}_3$ be ethylic acetotetramethylenecarboxylate, this decomposition can only be explained on the assumption that the tetramethylene-ring is first split by the action of the hydrogen bromide thus :—



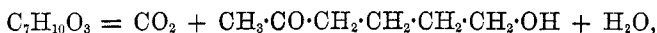
in which case ethylic *w*-bromopropylacetoacetate would first be formed, and then be further decomposed into alcohol, carbonic anhydride, and acetobutyl bromide.

It has, however, been shown (this vol., p. 6) that the tetramethylene-ring is not split even when submitted for weeks to the action of the most concentrated solution of hydrogen bromide, and it is therefore necessary to assume that the product of the action of trimethylene bromide on ethylic sodacetoacetate is not a tetramethylene-derivative, but has the constitution

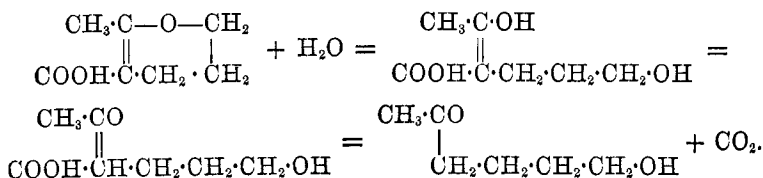


This is shown still more clearly from the following decompositions.

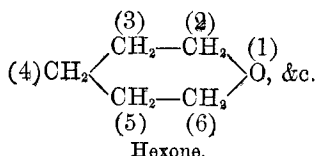
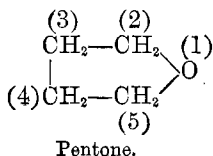
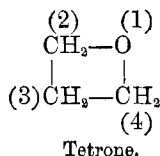
The ethereal salt, $\text{C}_9\text{H}_{14}\text{O}_3$, when submitted to hydrolysis, is easily transformed into the corresponding acid, $\text{C}_7\text{H}_{10}\text{O}_3$. If this acid be now boiled with water for a few minutes, it is quantitatively decomposed into acetobutyl alcohol and carbonic anhydride,



a reaction which cannot be accounted for on the assumption that the acid is a tetramethylene-derivative. If the acid, however, contain an oxygen carbon-chain, as represented above for its ethereal salt, this decomposition is very simply explained, as the acid is then simply a carboxylic acid of the anhydride of acetobutyl alcohol, and naturally is decomposed on boiling with water into this alcohol and carbonic anhydride. The reaction would then take place according to the following equations :—

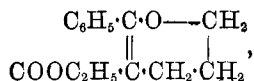


With regard to the nomenclature of these and other similarly constituted substances, I would suggest that the fully saturated oxygen carbon-rings, of which these substances are derivatives, should be named according to the following scheme:—



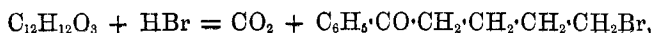
An acid of the formula $\text{CH}_3 \cdot \text{C} \cdot \text{O} - \text{CH}_3$ would therefore be
 $\text{COOH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}$
 methyldehydrohexonecarboxylic acid, [2 (2, 3), 3].

In continuing this research, experiments were next made on the action of trimethylene bromide on the sodium-derivative of ethylic benzoylacetate, and it was found that in this case also tetramethylene-derivatives were not formed. The principal product of the reaction, an ethereal salt of the formula $\text{C}_{14}\text{H}_{16}\text{O}_3$, evidently has the constitution—

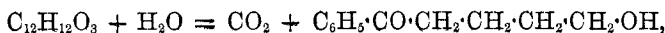


and is therefore ethylic phenyldehydrohexonecarboxylate, [2 (2, 3), 3].

Its formation is represented by an equation similar to that given above for the formation of ethylic methyldehydrohexonecarboxylate from trimethylene bromide and ethylic sodacetoacetate. This can be proved in exactly the same way as in the case of the ethylic methyldehydrohexonecarboxylate. If the ethereal salt, $\text{C}_{14}\text{H}_{16}\text{O}_3$, be submitted to hydrolysis, it is easily converted into the corresponding acid, $\text{C}_{12}\text{H}_{12}\text{O}_3$. This acid when treated with a concentrated solution of hydrogen bromide is decomposed into carbonic anhydride and benzoylbutyl bromide,

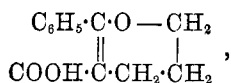


and when boiled with water it yields carbonic anhydride and benzoylbutyl alcohol,



reactions which are the counterpart of those which occur in the formation of acetobutyl alcohol and its bromide from methyldehydrohexonecarboxylic acid and its ethereal salt as described above. It is

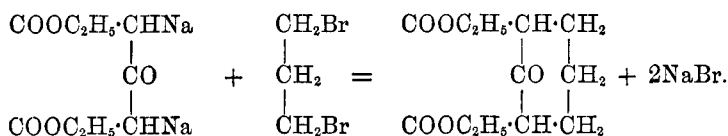
therefore evident that the acid, $C_{12}H_{12}O_3$, must be represented by the formula—



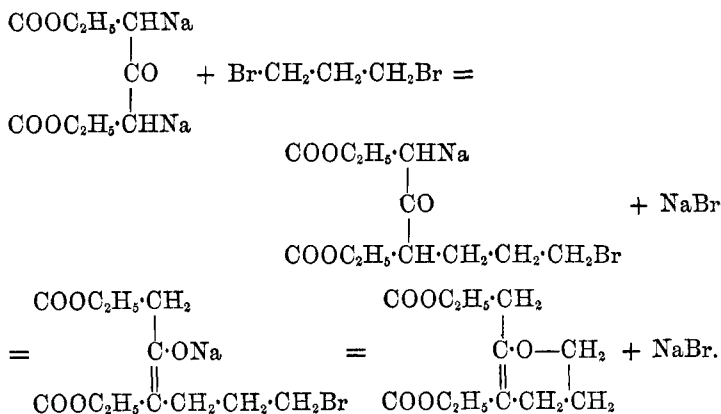
and be termed phenyldehydrohexonecarboxylic acid [2, (2, 3), 3].

As will be shown in the experimental part of this paper, results similar to these were also obtained when ethylic paranitrobenzoyl-acetate was substituted in the above reaction.

Experiments on the action of trimethylene bromide on ethylic acetonedicarboxylate, which were conducted with the kind permission of Professor H. v. Pechmann, were first initiated in the hope of obtaining hexamethylene-derivatives, thus:—



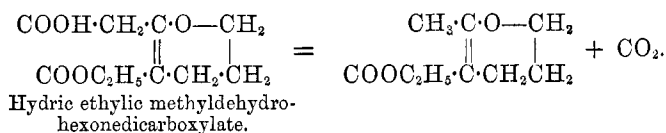
The further examination of the substances formed in this reaction has, however, shown that they are not hexamethylene-derivatives, but that in this case also hexone-derivatives result. It is most probable that this curious reaction takes place according to the following equation:—



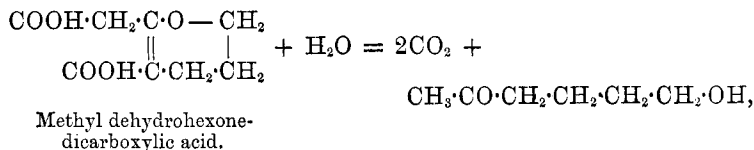
The product of this reaction is therefore ethylic methyldehydrohexonedicarboxylate, [2, (2, 3), ω , 3]. That this is the case is easily proved in the following way:—

Ethylic methyldehydrohexonedicarboxylate when submitted to hydrolysis, is first transformed into its acid ethylic salt, $C_{10}H_{14}O_5$. If

now this acid salt be distilled, it is decomposed into carbonic anhydride and ethylic methyldehydrohexonecarboxylate, which latter substance is identical with the compound obtained by the action of trimethylene bromide on ethylic sodacetoacetate. This interesting decomposition is clearly exhibited in the following equation:—



If this hydric ethylic methyldehydrohexonedicarboxylate is treated further with alkalis, it is converted into the dicarboxylic acid, $\text{C}_8\text{H}_{10}\text{O}_5$. This dicarboxylic acid when boiled with water is easily resolved into 2 molecules of carbonic anhydride and acetobutyl alcohol, thus:—



a reaction exactly similar to the formation of acetobutyl alcohol, and one molecule of carbonic anhydride from methyldehydrohexonemonocarboxylic acid described above.

In the early part of this introduction it was stated that the reaction between trimethylene bromide and the various sodium compounds employed could be also explained on the assumption that allyl-derivatives were formed, and this would also explain several of the reactions of these substances. It is therefore necessary to show that these compounds are not allyl-derivatives. This is easily done by comparing first of all their physical properties with those of the allyl compounds they might be supposed to be identical with, thus:—

Melting Points.

Methyldehydrohexonecarboxylic acid	119°	Allylacetoacetic acid	Unstable.
Phenyldehydrohexonecarboxylic acid	142—144°	Allylbenzoylacetic acid ...	$\left\{ \begin{array}{l} 122^\circ \\ 125^\circ \end{array} \right\} (?)$
Ethylic methyldehydrohexonecarboxylate	+ 9°	Ethylic allylacetoacetate ..	Oil.
Ethylic phenyldehydrohexonecarboxylate	59—60°	Ethylic allylbenzoylacetate.	Oil.
Ethylic paranitrophenyldehydrohexonecarboxylate ...	62—63	Ethylic allylparanitrobenzoylacetate	45—46°
Paranitrophenyldehydrohexonecarboxylic acid	172°	Allylparanitrobenzoylacetic acid	Unstable.

Boiling Points.

Ethylic methyldehydrohexonecarboxylate	226—227°	Ethylic allylacetoacetate ..	213—214°
Methyldehydrohexone	109°	Allylacetone	128—130
Phenyldehydrohexone	258—260°	Allylacetophenone	235—238

It is thus seen that these two series of substances differ most widely from each other, and cannot possibly be identical. The same differences become directly apparent on studying the chemical properties (see *Ber.*, 16, 1797).

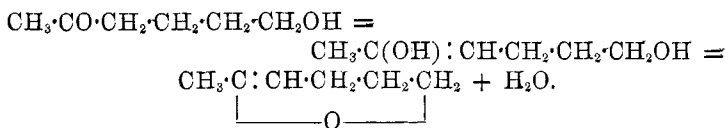
The careful study of the physical properties of these substances shows, however, that there are still several curious facts in connection with them which require explanation.

Thus whilst methyldehydrohexone (b. p. 109°) boils 20° *lower* than allylacetone (b. p. 128—130°), the ethereal salt of the carboxylic acid of methyldehydrohexone (ethylic methyldehydrohexonecarboxylate, b. p. 226—227°) boils 12° *higher* than the ethereal salt of the carboxylic acid of allylacetone (ethylic allylacetoacetate, b. p. 213—214°). The introduction of the same group, COOC_2H_5 , has in the one case raised the boiling point 117°, in the other case only 84°. Again, as methyldehydrohexone boils nearly 20° *lower* than allylacetone, phenyldehydrohexone should boil at a lower temperature than allylacetophenone, but it boils 20° *higher*. It is difficult to find an explanation for these discrepancies.

The study of the magnetic rotation of these substances has also given very curious results. The magnetic rotation of methyldehydrohexone is 6·074. Now, if ethylic methyldehydrohexonecarboxylate be really the ethereal salt of the carboxylic acid of methyldehydrohexone, it should have a magnetic rotation differing from that substance by the value of the group $\text{COOC}_2\text{H}_5-\text{H}$. The value of this group is easily calculated by subtracting from the magnetic rotation of ethylic malonate (7·410) the magnetic rotation of ethylic acetate (4·462), when $\text{COOC}_2\text{H}_5-\text{H} = 2·948$. Or a value still more suited to the case in point can be obtained by deducting the magnetic rotation of acetone (3·514) from that of ethylic acetoacetate (6·501) when $\text{COOC}_2\text{H}_5-\text{H} = 2·987$. In calculating the magnetic rotation of ethylic methyldehydrohexonecarboxylate we get methyldehydrohexone (6·074) + $\text{COOC}_2\text{H}_5-\text{H}$ (2·987) = 9·061 = calculated magnetic rotation of ethylic methyldehydrohexonecarboxylate. But the value actually found was 10·069, a difference of one whole number from the calculated; this is altogether unaccountable.

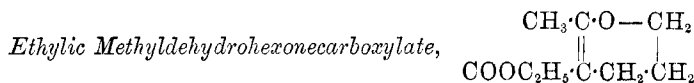
A further consideration which has perhaps some connection with this remarkable discrepancy is the following:—The magnetic rotation

of acetobutyl alcohol is 6.502, that of its anhydride, methyldehydrohexone, is 6.074. Therefore the loss of water involved in the formation of the anhydride has reduced the magnetic rotation by 0.428. But when acetobutyl alcohol is converted into its anhydride, it is supposed that the following changes take place:—



Now the diminution in magnetic rotation (0.428) can explain the dehydration which occurs, but it does not account at all for the fact that methyldehydrohexone is an unsaturated compound, in which case its magnetic rotation should be expected to be one whole number more, or about 7.074. The only theory which can be put forward at present to meet these difficulties is that methyldehydrohexone exists in two forms, namely, (α) magnetic rotation 7.074, as in ethylic methyldehydrohexonecarboxylate; and (β) magnetic rotation 6.074, as in the anhydride of acetobutyl alcohol. This would account for the high rotation of ethylic methyldehydrohexonecarboxylate which would be calculated thus: α -methyldehydrohexone (7.074) + $\text{COOC}_2\text{H}_5 - \text{H} = (2.987) = 10.061 = \text{calc. magnetic rotation}$. This agrees with the number actually found = 10.069. On distilling methyldehydrohexonecarboxylic acid, some remarkable change must take place, the α -methyldehydrohexone present in this acid being converted into the β -modification.

From these considerations it is evident that although the constitution of these various substances has been explained in a satisfactory way, from a chemical point of view, there are still several curious points of physical interest which are at present unexplained. It is hoped that further experiment will throw some light on, and afford a satisfactory explanation of these physical difficulties.



In the preparation of this substance the following method has been found to give the best results:—23 grams of sodium is dissolved in 250—270 grams of absolute alcohol. To this solution of sodic ethylate, when cold, a mixture of 130 grams of ethylic acetoacetate and 105 grams of trimethylene bromide is slowly added, the whole being well cooled during the operation. The clear solution formed is then heated to boiling on a water-bath in a flask connected with a

reflux condenser. In a short time the liquid becomes cloudy, owing to the separation of sodium bromide, and after about four hours' boiling, the reaction is usually at an end. In order to be sure of this, it is only necessary to mix a few drops of the solution with a little water, and test this with litmus-paper when, if the decomposition is finished, the product will show a neutral reaction. Sufficient water is now added to dissolve all the precipitated sodic bromide, and the mass is extracted about three times with ether. The ethereal solution is then well washed with water, dried over calcic chloride, and the ether distilled off. The residual slightly yellowish-coloured oil, which should weigh 140 to 150 grams, is then submitted to careful fractional distillation. The following fractions are obtained:—

100—170	=	8 grams.
170—200	=	36 ,,
200—240	=	80 ,,
Residue	=	6 ,,

The fraction 170—200 consists of regenerated ethylic acetoacetate, that boiling at 200—240° contains the ethylic methyldehydrohexonecarboxylate, and gives on further fractioning 45—50 grams boiling between 216—228°. This fraction is pure enough for ordinary purposes.

Pure ethylic methyldehydrohexonecarboxylate boils at 222—223° (720 mm.) and 225—226° (760 mm.).

* Analysis gave the following results:—

- I. 0.1519 gram substance gave 0.1142 gram H₂O and 0.3528 gram CO₂.
 II. 0.1808 gram substance gave 0.1333 gram H₂O and 0.4201 gram CO₂.

	Theory. C ₉ H ₁₄ O ₃ .	Found.	
		I.	II.
C.	63.53 per cent.	63.52	63.35 per cent.
H 	8.24 ,,	8.35	8.19 ,,
O 	28.33 ,,	28.13	28.46 ,

A vapour-density determination in aniline vapour by Hofman's method gave—

D.	6.21
Theory, C ₉ H ₁₄ O ₃	5.88

Ethylic methyldehydrohexonecarboxylate is a colourless oil having

* In the samples used for analysis, the slight trace of bromine which is almost invariably present in this ethereal salt when prepared as above, was first removed by treatment with zinc-dust and acetic acid.

a disagreeably penetrating, camphor-like smell. When cooled to 0° it solidifies to a white, crystalline mass which melts again at 9° . It is isomeric with ethylic allylacetoacetate which boils at $213-214^{\circ}$ (see p. 708). As this product of the reaction of trimethylene bromide on ethylic acetoacetate was thought to be of special interest, a very pure sample was carefully prepared and submitted to physical examination. The determinations of the specific gravity and magnetic rotation of this substance, which were performed by my father, gave the following results :—

I. Sp. gr. determinations

Preparation I.	Preparation II.
$d_{15^{\circ}}^{15^{\circ}} = 1.06457$	$d_{15^{\circ}}^{15^{\circ}} = 1.06840,$
$d_{25^{\circ}}^{25^{\circ}} = 1.05840$	$d_{20^{\circ}}^{20^{\circ}} = 1.06470,$
	$d_{25^{\circ}}^{25^{\circ}} = 1.06137.$

Magnetic Rotations. I.

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.0	1.1512	10.212
15.2	1.1473	10.178
15.2	1.1465	10.172
15.6	1.1472	10.180
15.8	1.1456	10.167
12.0	1.1561	10.240
12.0	1.1531	10.212
12.0	1.1517	10.200
14.1	1.1498	10.195

Magnetic Rotations. II.

<i>t.</i>	Sp. rotation.	Mol. rotation.
20.4	1.1419	10.130
18.8	1.1399	10.102
18.8	1.1424	10.125
18.8	1.1429	10.129
16.7	1.1443	10.127
16.7	1.1438	10.123
16.7	1.1444	10.128
18.1	1.1428	10.123

Dr. Gladstone has kindly determined the refraction equivalent of these preparations, together with that of the isomeric ethylic allyl-acetoacetate. He gave me the following account of his results:—

Preparation I.

	Temp.	μ_A .	μ_D .	μ_H .	Specific refraction.	Specific dispersion.	Refraction equivalent.
Ethylic methyldehydrohexonecarboxylate	13	1.4743	1.4818	1.5078	0.4446	0.0314	75.58
Ethylic allylacetoacetate.....	13.5	1.4356	1.4410	1.4598	0.4383	0.0210	74.51

"If we take Landolt's values for the three elements, $C_9H_{14}O_3$ should be 72.2. Now bodies belonging to the allyl series are about 2.0 above normal, which fairly accounts for the value of ethylic allylacetoacetate. The ethylic methyldehydrohexonecarboxylate is evidently of higher refraction and much higher dispersion, suggesting the presence of a still larger proportion of carbon in a highly refracting condition."

Preparation II.

<i>t.</i>	Sp. gr.	μ_A .	μ_D .	μ_H .	Observed.		Calculated.	
					Ref. eq. A.	Disp. eq. H-A.	Ref. eq. A.	Disp. eq. H-A.
24.5	1.0605	1.4697	1.4772	1.5033	75.29	5.39	72.2	3.26

"This agrees substantially with the previous specimen both in refraction and dispersion. The figures are very high, and I do not know how to interpret them."

In spite of the close agreement in magnetic rotation of these two preparations, it was thought, for reasons which are explained in the introduction (p. 708), that these numbers must still be considerably too high, and that the substance prepared in this way was not pure enough for physical measurements.

A very pure sample of ethylic methyldehydrohexonecarboxylate was therefore prepared from the silver salt of the acid by means of

ethyl iodide. In doing this 50 grams of ethylic methyldehydrohexonecarboxylate (b. p. 224—228°) were hydrolysed by boiling for four hours on a water-bath with 40 grams of pure potash dissolved in pure methyl alcohol. The alcohol was then distilled off, first on a water-bath and then over a naked flame, and the resulting nearly colourless solution carefully acidified in the cold with very dilute sulphuric acid (1 : 6). In this way, the methyldehydrohexonecarboxylic acid was thrown down as a beautifully white, crystalline precipitate, which after collecting, well washing with water, and drying on a porous plate, was obtained as a colourless, crystalline powder, melting at 118—119°. This was dissolved in dilute ammonia, the solution carefully neutralised with nitric acid, and precipitated with nitrate of silver. The silver salt after washing and drying over sulphuric acid in a vacuum was mixed with an excess of ethyl iodide, dissolved in ten times its volume of pure dry ether, and boiled for four hours on a water-bath. The precipitated iodide of silver was filtered off from the ethereal solution, and washed two or three times with pure ether. The filtrate was then shaken with a little sodic carbonate solution, dried over potassic carbonate, and the ether distilled off, when an almost colourless oil remained, which on twice refractioning boiled constantly at 226·5—227° (760 mm.), and gave the following result on analysis:—

0·1663 gram substance gave 0·1238 gram H₂O, and 0·3864 gram CO₂.

	Theory.	Found.
C	63·53 per cent.	63·37 per cent.
H	8·24 ,,	8·27 ,,
O	28·33 ,,	28·36 ,,

The determination of the magnetic rotation of this preparation gave the following results:—

$$\begin{array}{ll}
 \text{Sp. gr.} & d_{9^{\circ}}^{9^{\circ}} = 1\cdot0744 \qquad d_{20^{\circ}}^{20^{\circ}} = 1\cdot0660, \\
 & d_{15^{\circ}}^{15^{\circ}} = 1\cdot0696 \qquad d_{25^{\circ}}^{25^{\circ}} = 1\cdot0626.
 \end{array}$$

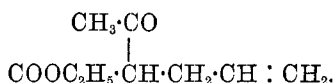
Magnetic Rotation.

<i>t.</i>	Sp. rotation.	Mol. rotation.
24·0	1·1314	10·050
24·0	1·1349	10·082
23·5	1·1349	10·080
23·5	1·1334	10·065
23·7	1·1336	10·069

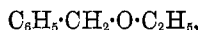
The number 10·069 (which agrees fairly well with that obtained by the other measurements) is probably the true magnetic rotation of ethylic methyldehydrohexonecarboxylate.

Ethylic methyldehydrohexonecarboxylate does not combine with phenylhydrazine. In order to prove this, 4 grams of the pure ethereal salt were mixed with 3 grams of phenylhydrazine and gently heated on a water-bath for half-an-hour. The product, which was a comparatively limpid mass, was distilled in steam until no more oil* came over, and the distillate extracted several times with ether. The ethereal solution after drying over calcic chloride and distilling off the ether deposited 3 grams of a slightly yellowish oil, which on distilling proved to be unchanged ethylic methyldehydrohexonecarboxylate.

When the experiments on the action of trimethylene bromide on ethylic sodacetoacetate were first instituted, it was very important to show that ethylic methyldehydrohexonecarboxylate did not contain a hydrogen-atom displaceable by sodium, *i.e.*, that it was not a mono-substituted ethylic acetoacetate such as ethylic allylacetoacetate,



This was determined by treating 10 grams of the pure ethereal salt with 1·4 grams of sodium (as sodic ethylate) and 7·5 grams of benzyl chloride. After heating on a water-bath for some hours, the product was found to consist of a mixture of benzyl ethyl ether,



and unchanged ethylic methyldehydrohexonecarboxylate.

A few experiments were also made on the action of phosphorous pentachloride on ethylic methyldehydrohexonecarboxylate.

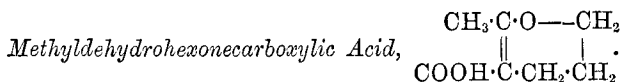
35 grams of the pure ethereal salt was mixed with 70 grams of chloroform and then 45 grams of phosphorous pentachloride slowly added. After each addition of the pentachloride, vigorous reaction set in, which had to be moderated by careful cooling. Towards the end the whole was warmed gently, mixed with water to decompose the phosphorous oxychloride and unchanged pentachloride, extracted with ether, and the ethereal solution washed with dilute sodic carbonate. On distilling off the ether and chloroform, a colourless oil remained behind, which after repeated fractioning under reduced pressure (200 mm.) boiled constantly at 212—215°.

Two chlorine determinations gave the following results, agreeing with the formula $\text{C}_9\text{H}_{13}\text{O}_2\text{Cl}$:—

* Only traces of phenylhydrazine were carried over during the operation.

I.	0.2883	gram substance	gave	0.2103	gram AgCl.
II.	0.3681	„	„	0.2745	„
Found.	I.		18.05	
	II.		18.45	
Theory.	C ₉ H ₁₃ O ₃ Cl		18.83	

As this substance has not been further examined, no idea can be formed as to its constitution.



This acid is easily obtained from its ethylic salt by hydrolysis with alcoholic potash. The fraction boiling between 215° and 230° is mixed with a fairly concentrated solution of alcoholic potash (containing twice the theoretical quantity of KOH) and boiled on a water-bath for six hours. The alcohol is then distilled off, the residue dissolved in a little water, gently evaporated on a water-bath to get rid of the last traces of alcohol, well cooled, and acidified with dilute sulphuric acid. In this way methyldehydrohexonecarboxylic acid is precipitated as a beautifully white, crystalline mass, which after collecting, well washing with cold water, and drying on a porous plate, is nearly pure.

To obtain the pure acid, this product is dissolved in a little boiling benzene or light petroleum (b. p. 70—90°), from which solution it crystallises on cooling in beautiful, colourless needles.

Analyses.

I.	0.1964	gram substance	gave	0.1254	gram H ₂ O	and	0.4252	gram CO ₂ .
II.	0.1803	gram substance	gave	0.1154	gram H ₂ O	and	0.3894	gram CO ₂ .
III.	0.2191	gram substance	gave	0.1462	gram H ₂ O	and	0.4768	gram CO ₂ .

	Theory.	Found.		
	C ₇ H ₁₀ O ₃ .	I.	II.	III.
C	59.15 per cent.	59.05	58.90	59.35
H	7.05 „	7.09	7.11	7.41
O	33.80 „	33.86	33.99	33.24

Methyldehydrohexonecarboxylic acid melts at 119°, but decomposes at a somewhat higher temperature into carbonic anhydride and methyldehydrohexone, as will be described later on. If, however, a small quantity of the acid is rapidly heated in a test-tube, it distils

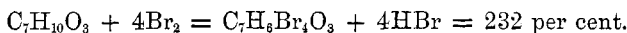
almost without decomposition, and solidifies on the cooler portions of the tube in beautiful, leaf-like crystals. It is easily soluble in hot benzene, light petroleum, alcohol, chloroform and ether, but more sparingly so in these solvents in the cold. When mixed with hot water, it dissolves readily, and the solution, if rapidly cooled, deposits the greater part of the acid in beautiful, colourless needles. On boiling with water, methyldehydrohexonecarboxylic acid is rapidly decomposed into carbonic anhydride and acetobutyl alcohol (see p. 718). In alkaline solutions this acid is very stable, and can be boiled for hours with strong potash without any apparent decomposition.

When heated at 200° with strong aqueous ammonia, it is split up into carbonic anhydride, acetobutyl alcohol, and a volatile base, which from its odour and reactions would appear to be a derivative of pyridine.

I have not further examined this base, but from its method of preparation it is probable that it is closely related to the interesting base obtained by Lipp (*Ber.*, **18**, 3282) by treating ethylic α -bromo-propylacetoacetate, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5$, with alcoholic ammonia.

Methyldehydrohexonecarboxylic acid dissolves easily in concentrated aqueous solution of hydrogen bromide (sp. gr. 1.83), and if the solution be quickly extracted with ether, a brominated acid is obtained, which, however, is very unstable and cannot be obtained in a pure state; but if the acid solution be allowed to stand at ordinary temperatures, carbonic anhydride is slowly evolved, and if after some hours water be added, a heavy oil is precipitated; this, after extracting with ether, seemed to be nearly pure acetobutyl bromide, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ (see p. 721).

When exposed to the vapour of bromine, methyldehydrohexonecarboxylic acid appears in the first case to form an unstable additive product. By the further action of the bromine, substitution takes place with evolution of hydrogen bromide. 2.036 grams of acid, after standing in an atmosphere of bromine for two days had taken up 4.767 grams of bromine = 234 per cent. calculated for the equation



The product of this reaction was a thick, uninviting syrup, which could not be obtained in a crystalline form, and therefore was not analysed.

Salts of Methyldehydrohexonecarboxylic Acid.

Ammonium Salt.—To prepare this salt the pure acid is dissolved

in a slight excess of ammonia, and the solution allowed to evaporate to dryness over sulphuric acid in a vacuum. It is a white, crystalline solid, very easily soluble in water.

Silver Salt, $C_7H_9O_3Ag$.—If silver nitrate is added to a neutral solution of ammonium methyldehydrohexonecarboxylate, a white, crystalline precipitate of the silver salt is thrown down. This, after collecting, well washing with water, and drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

- I. 0.2997 gram substance gave 0.1010 gram H_2O , 0.3705 gram CO_2 , and 0.1299 gram Ag.
 II. 0.4668 gram substance gave 0.2027 gram Ag.

	Theory. $C_7H_9O_3Ag$.	Found.		per cent.
		I.	II.	
C.	33.73	33.64	—	
H	3.62	3.74	—	
Ag	43.37	43.24	43.41	
O	19.27	19.28	—	

This silver salt dissolves fairly easily in boiling water, and crystallises on cooling in beautiful, leafy tufts. It is very stable, and is only very slowly decomposed on boiling with water or exposing to light.

Copper Salt.—Copper methyldehydrohexonecarboxylate is precipitated on the addition of cupric sulphate to the neutral solution of the ammonium salt as a light-green, amorphous precipitate almost insoluble in water. It was collected, well washed with water, and dried over sulphuric acid in a vacuum.

Analyses.

- I. 0.3337 gram substance gave 0.0720 gram CuO .
 II. 0.4020 ,, ,, 0.0870 ,,

	Found.		Theory. $(C_7H_9O_3)_2Cu + H_2O$.
	I.	II.	
Cu	17.22	17.28 p. c.	17.42 p. c.

This copper salt, therefore, appears to contain 1 mol. H_2O . Unfortunately this could not be determined by a direct experiment, as the salt when heated begins to decompose at 90—100°.

Action of Water on Methyldehydrohexonecarboxylic Acid. Formation of Acetobutyl Alcohol, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$.

When recrystallising methyl dehydrohexonecarboxylic acid from hot water, it was noticed that if the boiling was carried on for any

length of time carbonic anhydride was evolved, and on cooling no crystals separated out. As the decomposition of the acid, which evidently takes place here, might throw some light on its constitution, it was carefully studied. 20 grams of the pure acid was boiled with 70 grams of distilled water in a vessel, provided with a reversed condenser, the end of which was connected with a flask containing baryta-water. The acid slowly dissolved with evolution of a considerable quantity of gas, which on passing through the baryta-water instantly caused the precipitation of baric carbonate. After boiling for about half an hour no more gas was given off, and the reaction was complete. The solution now contains acetobutyl alcohol, which is extracted in the following way.

The colourless liquid, after filtering, is treated with anhydrous potassic carbonate until thoroughly saturated, and allowed to stand for a short time, the greater part of the acetobutyl alcohol has then separated as a thick oily layer on the surface of the liquid. This is extracted ten times with ether, the ethereal solution dried over potassic carbonate, filtered, and the ether distilled off. The residue, which consists of almost pure acetobutyl alcohol, on rapid distillation passes over between $226-227^{\circ}$, almost without decomposition. On analysis the following results were obtained:—

- I. 0.1974 gram substance gave 0.1834 gram H_2O and 0.4497 gram CO_2 .
 II. 0.1711 gram substance gave 0.1480 gram H_2O and 0.4042 gram CO_2 .

	Theory.	Found.	
		I.	II.
$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$.			
C	62.07 per cent.	62.12	62.21 per cent.
H	10.34 „	10.33	10.09 „
O	27.59 „	27.55	27.70 „

Acetobutyl alcohol is a thick, colourless oil, which distils at $226-227^{\circ}$ (760 mm.), with the formation of traces of an anhydride, probably methyldehydrohexone. It mixes with water in all proportions, forming a solution of burning but slightly sweet taste. It does not reduce Fehling's solution, or an ammoniacal solution of silver oxide in the cold. On warming with these reagents, a very slow reduction takes place in the case of the Fehling's solution, but the silver solution is, on the contrary, very quickly reduced, a bright mirror being formed on the sides of the vessel containing it.

Phenylhydrazine hydrochloride, dissolved in a solution of sodic acetate, produces at first a turbidity only on the addition to an aqueous solution of acetobutyl alcohol; in a short time, however, the

phenylhydrazine compound separates out in large, yellow, oily drops. Several attempts were made with the object of obtaining this interesting substance in a crystalline condition suitable for analysis, but without success.

When mixed with concentrated nitric acid, acetobutyl alcohol is not attacked in the cold; on warming gently, a dark pink coloration is first formed, and on further heating oxidation rapidly sets in, torrents of red fumes being evolved.

An aqueous solution of acetobutyl alcohol, if treated with iodine and potash, gives quantities of iodoform.

Acetobutyl alcohol has been subjected to physical examination by my father, with the following results:—

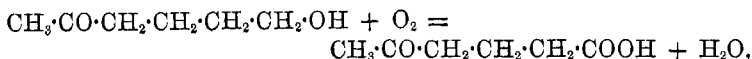
$$\begin{aligned}\text{Sp. gr.} \quad d_{4^{\circ}}^{4^{\circ}} &= 0.99771, \\ d_{15^{\circ}}^{15^{\circ}} &= 0.98947, \\ d_{25^{\circ}}^{25^{\circ}} &= 0.98270.\end{aligned}$$

Magnetic Rotations.

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.5	0.99101	6.492
19.5	0.9972	6.515
17.5	0.9969	6.504
17.5	0.9960	6.498
18.5	0.9953	6.502

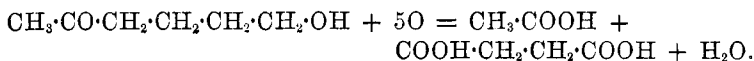
From its method of preparation, and the numbers obtained as its magnetic rotation, there can scarcely be a doubt that the acetobutyl alcohol described above really has the constitution assigned to it, but as it was most important in explaining the constitution of these methyldehydrohexone-derivatives to be perfectly certain on this point, it was thought that some additional evidence of its constitution was necessary.

If acetobutyl alcohol were oxidised with chromic acid, the first product which should result would be acetobutyric acid, thus:—



and on further oxidation with an excess of the oxidising agent, acetic

and succinic acids should be formed, according to Popoff's rule (*Annalen*, **161**, 285)—



Acetobutyric acid has been prepared by Wolff (*Annalen*, **216**, 129), who describes it as a thick, oily liquid, boiling at 274—275°.

On oxidising acetobutyl alcohol with the calculated quantity of chromic acid and sulphuric acid, I obtained an oily acid which possessed all the properties of acetobutyric acid. As, however, without working with large quantities of acetobutyl alcohol it would have been difficult to prove definitely the identity of the two acids, it was thought more satisfactory to examine the end products of the oxidation of this alcohol. To this purpose 4 grams of pure acetobutyl alcohol was dissolved in 20 grams of water, and then slowly mixed with a slight excess of a solution of potassic dichromate in dilute sulphuric acid. As soon as the oxidation, which set in at once, was complete, the product was submitted to distillation in steam until the condensed water showed neutral reaction. The distillate was then digested with a slight excess of baric carbonate, filtered, and the filtrate evaporated to dryness, when a considerable quantity of a white residue remained. On the addition of silver nitrate to a clear solution of this salt in water, a beautiful, crystalline salt was thrown down, which possessed all the properties of acetate of silver. It was filtered off, washed with water, dried over sulphuric acid in a vacuum, and analysed, with the following result:—

0·4657 gram substance gave 0·3010 gram Ag.

	Theory. CH ₃ ·COOAg.	Found.
Ag	64·66	64·64 per cent.

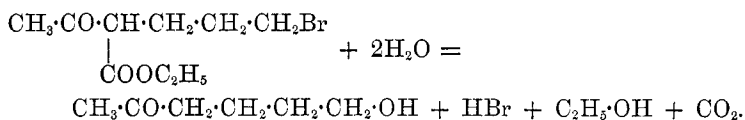
Acetic acid was therefore one of the products of the oxidation of acetobutyl alcohol.

The residue remaining in the retort, after distilling off the acetic acid, was made slightly alkaline by the addition of caustic potash, well boiled until all the chromium had been precipitated, the precipitate filtered off and washed. The filtrate was then rendered slightly acid with dilute sulphuric acid, evaporated to dryness on a water-bath, and the finely powdered residue extracted several times with hot alcohol. The alcoholic solution was evaporated, the dry residue again extracted with alcohol and evaporated, when a white, crystalline substance was obtained, showing all the properties of succinic acid. After once recrystallising from water, colourless crystals were obtained, melting at 180—182° (succinic acid 180°). The solution in water gave, on

the addition of ferric chloride, the characteristic, brown-red precipitate. In order to prove that this acid really was succinic acid, it was heated in a small retort for some time to its boiling point, and then distilled. After reheating and redistilling, a colourless mass of succinic anhydride was obtained, melting at 118—119°. This was further characterised by conversion into succinylfluorescein by heating with resorcinol.

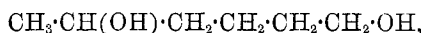
The end products of the oxidation of acetobutyl alcohol are therefore acetic acid and succinic acid, a proof that this substance has the formula $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$.

Under the name acetobutyl alcohol, a substance has already been described by Lipp (*Ber.*, 18, 3280), who prepared it by boiling ethylic ω -bromopropylacetoacetate with dilute hydrochloric acid—



Lipp describes it as a fairly mobile oil, smelling of camphor and boiling at 154—155° (718 mm.), whereas the acetobutyl alcohol obtained by me was a thick, almost odourless oil, boiling at 226—227°, or as much as 70° higher than Lipp's substance.

As acetobutyl alcohol undoubtedly should be formed by the reaction used by Lipp, it is probable that he has made some slip in describing this substance. This is the more likely from the fact that the reduction product of this alcohol, hexylene glycol,



as prepared by Lipp, has approximately the same boiling point as that obtained by me from my acetobutyl alcohol.

In order to render more complete these experiments on the decomposition of methyldehydrohexonecarboxylic acid, by boiling with water, some quantitative determinations of the amount of carbonic anhydride produced during the reaction have been made. A weighed quantity of pure acid was boiled with water in a Würtz flask connected with a reflux condenser, and the carbonic anhydride evolved, after passing through a drying-bottle containing sulphuric acid, collected in a Geissler's potash-bulb. At the end of the operation the carbonic anhydride still left in the apparatus was swept out by means of a current of air, free from carbonic anhydride, and the potash-bulbs, after standing for some time, weighed. Two experiments were made with the following results:—

- I. 3.1042 grams substance gave 0.9441 gram CO₂.
 II. 2.7940 " " 0.8500 "

	Theory.	Found.	
		I.	II.
CO ₂	30.98	30.44	30.43 per cent.

The amount of acetobutyl alcohol formed, as determined by saturating with carbonate of potash and repeatedly extracting with ether, was found in the two experiments to be about 4.2 grams, whereas the calculated amount is 4.81 grams.

It is therefore seen that the decomposition of the acid into acetobutyl alcohol and carbonic anhydride on boiling with water is a quantitative one.

δ-Hexyleneglycol, CH₃·CH(OH)·CH₂·CH₂·CH₂·CH₂·OH.

δ-Hexyleneglycol was first prepared by Lipp (*Ber.*, 18, 3282), who obtained it by reducing his acetobutyl alcohol with sodium amalgam. As this substance, and more especially its dibromide, were of great value for the further development of these researches on the synthetic formation of closed carbon-chains, I have repeated Lipp's experiments with my acetobutyl alcohol. 10 grams of the pure alcohol were dissolved in a little water and treated with 50 grams of 3 per cent. sodium amalgam, as described by Lipp. As soon as the reduction was finished, the product was saturated with carbonic anhydride, and extracted several times with ether. After drying over potassic carbonate and distilling off the ether, a thick oil remained, which on twice refractioning boiled fairly constantly at 228—233°, and gave the following results on analysis:—

0.1527 gram substance gave 0.1649 gram H₂O and 0.3411 gram CO₂.

	Theory.	Found.
	C ₆ H ₁₄ O ₂ .	
C	61.01 per cent.	60.92 per cent.
H	11.86 ,,	11.98 ,,
O	27.13 ,,	27.10 ,,

This substance agrees in all its properties with the *δ*-hexyleneglycol described by Lipp.

δ-Hexylene Dibromide, CH₃·CHBr·CH₂·CH₂·CH₂·CH₂Br.

This substance is easily prepared in the following way:—Pure *δ*-hexyleneglycol is dissolved in an excess of fuming hydrobromic acid, and the mixture heated in a sealed tube at 120° for two

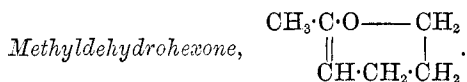
hours. The contents of the tube are then cooled to 0° , resaturated with hydrogen bromide, and again heated in a sealed tube as before at 120° for two hours. The product, which consists of two layers, is extracted with ether, dried over calcic chloride, and rapidly fractioned under 100 mm. pressure. It is then easily obtained pure, boiling at $153\text{--}154^{\circ}$ (100 mm.).

Analysis.

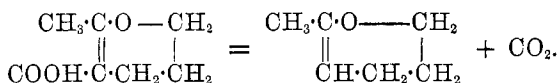
0.2390 gram substance gave 0.3654 gram AgBr.

	Theory. $\text{C}_6\text{H}_{12}\text{Br}_2$.	Found.
Br.	65.58 per cent.	65.34 per cent.

δ -Hexylene bromide is a heavy, colourless liquid, which, on standing for any length of time, undergoes slight decomposition, at the same time turning slightly dark-coloured. A detailed description of this interesting substance is reserved for a future paper.



If pure methyldehydrohexonecarboxylic acid is gently heated in a small retort to a temperature of $140\text{--}150^{\circ}$ decomposition sets in,* carbonic anhydride is evolved, and a colourless oil distils over which consists of nearly pure methyldehydrohexone. This reaction takes place according to the following equation:—



As a considerable quantity of methyldehydrohexone was required for physical measurements and other experiments, as much as 30 grams of the pure acid were operated on. This amount on slow distillation gave 19.8 grams of oil (theory 20.7 grams), which on carefully fractioning nearly all passed over between $109\text{--}110^{\circ}$ as a colourless, limpid liquid, which on analysis gave the following results:—

- I. 0.2246 gram substance gave 0.2091 gram H_2O and 0.6015 gram CO_2 .
- II. 0.1557 gram substance gave 0.1466 gram H_2O and 0.4186 gram CO_2 .
- III. 0.1731 gram substance gave 0.1594 gram H_2O and 0.4640 gram CO_2 .

* This acid begins to give off carbonic anhydride at $128\text{--}130^{\circ}$, the decomposition being very rapid at $145\text{--}150^{\circ}$.

	Theory. C ₈ H ₁₆ O.	Found.		
		I.	II.	III.
C	73·47 p. c.	73·04	73·32	73·10 p. c.
H	10·20 „	10·34	10·46	10·23 „
O	16·33 „	16·62	16·22	16·67 „

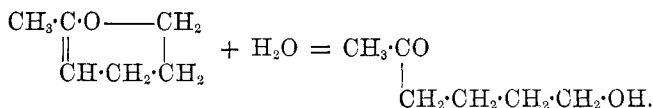
Methyldehydrohexone is a colourless, mobile, ethereal-smelling liquid which boils constantly at 109—109·5°. In preparing it, it is very important to start from pure acid. If crude methyldehydrohexonecarboxylic acid is used, peculiar condensation-products of high boiling point are formed in large quantity; they have not been further examined. Their formation appears to be due to the presence of a trace of sulphuric acid, which is difficult to completely wash out of the crude acid.

Methyldehydrohexone being the anhydride of acetobutyl alcohol, a careful study of its behaviour towards water seemed interesting. 5 c.c. of the pure substance when shaken with an equal volume of water did not appear to dissolve at all, but on standing for 24 hours the volume of the upper layer (that is of the methyldehydrohexone) had diminished to 3·6 c.c. and in another 24 hours to 2·4 c.c. After standing for about four days, the upper layer had entirely disappeared, a clear solution being formed. This on saturation with potassic carbonate deposited a quantity of a colourless oil, which on extracting with ether, drying over potassic carbonate, and fractioning, boiled almost constantly at 226—228°, and was evidently pure acetobutyl alcohol. The analysis gave the following results:—

0·1317 gram substance gave 0·1233 gram H₂O and 0·3004 gram CO₂.

	Theory. CH ₃ ·CO·CH ₂ ·CH ₂ ·CH ₂ ·CH ₂ ·OH.	Found.
C	62·07 per cent.	62·20 per cent.
H	10·34 „	10·40 „
O	27·59 „	27·40 „

The formation of acetobutyl alcohol from methyldehydrohexone by the action of water takes place according to the following equation:—



This transformation takes place much more rapidly when methyldehydrohexone is warmed with water, and is then usually finished in a few hours.

The magnetic rotation of methyldehydrohexone has been determined by my father with the following results:—

Specimen I, b. p. 109—109·5°.

$$\begin{aligned}\text{Sp. gr.} \quad d_{4^{\circ}}^{4^{\circ}} &= 0\cdot92272, \\ d_{15^{\circ}}^{15^{\circ}} &= 0\cdot91278, \\ d_{25^{\circ}}^{25^{\circ}} &= 0\cdot90502.\end{aligned}$$

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·5	1·0123	6·051
17·5	1·0156	6·071
18·0	1·0126	6·056
18·0	1·0121	6·052
17·7	1·0131	6·057

This specimen was then carefully refractioned and found to boil at the same temperature. It was again remeasured with the following results:—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot91225.$$

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·5	1·0115	6·072
22·5	1·0130	6·076
22·5	1·0122	6·074

Action of Hydrogen Bromide on Ethylic Methyldehydrohexonecarboxylate.

Formation of Acetobutyl Bromide, CH₃·CO·CH₂·CH₂·CH₂·CH₂Br.

Ethylic methyldehydrohexonecarboxylate dissolves readily in a strong solution of hydrogen bromide, producing a colourless liquid which, however, on standing soon turns brown, with evolution of carbonic anhydride. In studying the product of this reaction, the pure ethereal salt was mixed with two or three times its volume of hydrobromic acid (sp. gr. 1·83), and then allowed to stand until the evolution of carbonic anhydride had ceased, which was the case after

about two days. On the addition of water, the dark, brownish-coloured product deposited a heavy oil which was taken up in ether and well washed first with water and then with a dilute solution of sodic carbonate. After drying over calcic chloride and distilling off the ether, the residue was purified by rapid distillation. In this way a colourless oil was obtained which boiled constantly at 214—215°, and gave the following numbers on analysis:—

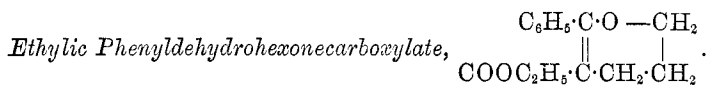
I.	0.1453	gram substance	gave	0.1509	gram AgBr.
II.	0.2498	„	„	0.2538	„

		Theory.		Found.	
		C ₆ H ₁₁ OBr.		I.	II.
Br	44.69	p. c.	44.22	43.20 p. c.

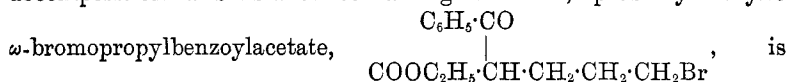
Acetobutyl bromide is a colourless oil having a penetrating and disagreeable camphor-like odour. On standing in the air it gives off a small quantity of hydrogen bromide and gradually becomes darkly coloured. When boiled with water or dilute hydrochloric acid it seems to be slowly converted into acetobutyl alcohol.

It is probably identical with the substance obtained by Lipp (*Ber.*, 18, 3282) by distilling his acetobutyl alcohol with hydrogen bromide solution.

Action of Trimethylene Bromide on Ethylic Benzoylacetate.



This substance, a short description of which appeared some time ago (*Ber.*, 16, 1790), is prepared in the following way:—A solution of 2.5 grams of sodium in 30 grams of absolute alcohol, after well cooling, is mixed with 20 grams of pure ethylic benzoylacetate and then heated to gentle boiling on a water-bath with 21 grams of trimethylene bromide. The reaction sets in almost immediately, and is usually finished in two or three hours, as is shown by the liquid becoming perfectly neutral to test-paper. At this stage of the decomposition a substance containing bromine, probably ethylic



present, which by the further action of sodic ethylate is transformed into ethylic phenyldehydrohexonecarboxylate. To effect this transformation, the product is well cooled, mixed with a second quantity of sodic ethylate (containing, as before, 2.5 grams of sodium), and

heated again on a water-bath until the product, on testing, shows neutral reaction. This is usually the case in about five or six hours. The brownish-coloured mass, after cooling, is filtered from the precipitated sodium bromide, the precipitate well washed with absolute alcohol, and the filtrate distilled on a water-bath until nearly all the alcohol has been removed. The residue is then mixed with water, and the oil which separates extracted two or three times with ether. The ethereal solution after washing, drying over calcic chloride, and evaporating, leaves a dark-coloured oil behind which, after standing for some days over sulphuric acid in a vacuum, deposits a quantity of long crystals. These are separated from the mother-liquor by filtering with the aid of a vacuum pump and washing with small quantities of ether. The resulting almost colourless mass is dissolved in as small a quantity of warm ether as possible, and the solution allowed to evaporate slowly at the ordinary temperature, when the new substance separates in long, colourless prisms which, after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

- I. 0.1866 gram substance gave 0.4929 gram CO_2 and 0.1197 gram H_2O .
 II. 0.1973 gram substance gave 0.5214 gram CO_2 and 0.1240 gram H_2O .

	Theory. $\text{C}_{14}\text{H}_{16}\text{O}_3$.	Found.	
		I.	II.
C	72.41 p. c.	72.04	72.07 p. c.
H	6.89 „	7.13	6.98 „
O	20.69 „	20.83	20.95 „

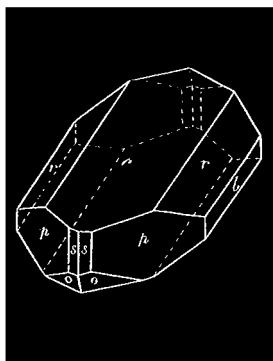
Ethylc phenyldehydrohexonecarboxylate melts at $59-60^\circ$ and distils at a high temperature almost without decomposition. It is readily soluble in most of the usual solvents, and can be obtained by the slow evaporation of its solutions in ether, bisulphide of carbon, and light petroleum in magnificent, colourless, prisms. Professor Haushofer was kind enough to measure some crystals which were grown in a saturated ethereal solution of the substance. He gave me the following description of the results of his experiments:—

Ethylic Phenyldehydrohexonecarboxylate.

Crystalline system. Monoclinic.

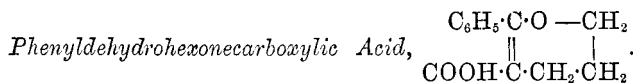
$$a : b : c = 1.0017 : 1 : 0.5914.$$

$$\beta = 68^\circ 34'.$$



Moderately large but incompletely developed crystals of the combination $OP(c)$, $\infty P(p)$, $R\infty(r)$, $\infty R\infty(b)$, $R\frac{1}{2}(o)$, $\infty R\frac{1}{2}(s)$. The faces s and o are generally very small; c and r generally run into one another, the angle between them becoming rounded.

	Measured.	Calculated.
$c : p =$	$*105^\circ 30'$	— —
$p : p =$	$*94 \quad 0$	— — front
$c : r =$	$*151 \quad 10$	— —
$r : r =$	$122 \quad 30$	$122^\circ \quad 20'$ top
$r : r =$	$57 \quad 46$	$57 \quad 40$ side
$s : s =$	$130 \quad 0$	$130 \quad 0$
$o : o =$	$132 \quad 1$	$132 \quad 4$
$r : p =$	$124 \quad 13$	$124 \quad 16$



To obtain this acid, 5 grams of ethylic phenyldehydrohexonecarboxylate is boiled with a fairly concentrated solution of alcoholic potash (containing 2 grams of KOH) for about four hours on a water-bath. After distilling off the alcohol, a little water is added, the almost colourless solution gently evaporated until the last trace of alcohol has been driven off, and then filtered. On acidifying the filtrate with dilute sulphuric acid, the new acid is precipitated as a white, crystal-

line mass. This is collected, well washed with water, dried on a porous plate, and recrystallised from ether. It is thus obtained in beautiful, colourless prisms which, after drying over sulphuric acid in a vacuum, gave the following numbers:—

0.1914 gram substance gave 0.4930 gram CO_2 and 0.1041 gram H_2O .

	Theory. $\text{C}_{12}\text{H}_{12}\text{O}_2$.	Found.
C	70.59 per cent.	70.25 per cent.
H	5.88 „	6.04 „
O	23.53 „	23.71 „

Phenyldehydrohexonecarboxylic acid melts at about $142\text{--}144^\circ$ with evolution of carbonic anhydride. It is easily soluble in alcohol, chloroform, benzene, carbon bisulphide, ether, and light petroleum, almost insoluble in cold water. When in a very finely-divided state it dissolves, however, to a considerable extent in boiling water, and crystallises out again on cooling in fine, colourless needles. The most beautiful crystals are obtained when a concentrated ethereal solution of the acid is allowed to evaporate at ordinary temperatures.

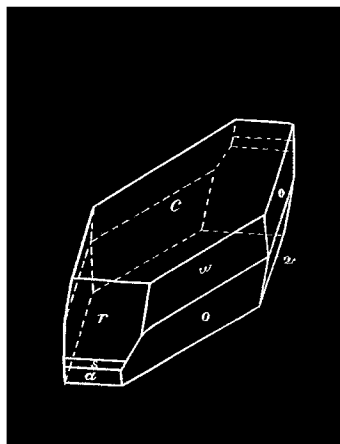
Professor Haushofer, who was kind enough to examine some of these, gave the following description of them:—

Phenyldehydrohexonecarboxylic Acid.

Crystalline System. Monoclinic.

$$a : b : c = 2.6379 : 1 : 3.3984.$$

$$\beta = 74^\circ 44'.$$



Beautifully lustrous, well-developed crystals of the combination $0P(c)$, $-P(w)$, $P(o)$, $-P\infty(r)$ $-2P\infty(s)$ $\infty P\infty(a)$. In many crystals the face s is missing, whilst on others it completely disappears into a ; neither of these faces admit of accurate measurement as they are, as a rule, flawed and rounded; c also shows many flaws.

	Measured.	Calculated.
$c : w =$	$*110^{\circ} 54'$	— —
$c : o =$	$*100 40$	— —
$o : o =$	$*46 28$	— —
$w : w =$	$58 10$	$58^{\circ} 16'$
$c : r =$	$137 1$	$137 8$
$w : r =$	$119 5$	$119 8$
$r : a =$	$148 15$	$148 8$
$c : a =$	105 approx.	$105 16$
$o : w =$	$138 40$	$138 50$
$w : o =$	$148 27$	$148 26$
$o : a =$	$106 50$	$106 44$
$c : s =$	124 approx.	$124 2$

The plane of the optical axis is the plane of symmetry, $\infty P\infty$. The polarisation figure of one axis is visible on the face c (in the obtuse angle β).

Salts of Phenyldehydrohexonecarboxylic Acid.

Phenyldehydrohexonecarboxylic acid dissolves easily in alkalis, alkaline carbonates, and ammonia. Its solution in a slight excess of ammonia was allowed to stand for some hours over sulphuric acid in a vacuum until quite neutral, and then the following salts prepared by precipitation with various reagents.

The *silver salt* is thrown down on the addition of nitrate of silver as a white, crystalline precipitate which, after collecting, well washing with water, and drying over sulphuric acid in a vacuum, was analysed with the following result:—

0.2735 gram substance gave 0.0952 gram silver.

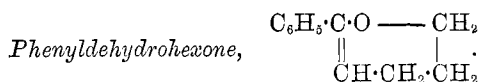
	Theory. $C_{12}H_{11}O_2Ag$.	Found.
Ag.....	34.73 per cent.	34.81 per cent.

This silver salt dissolves, though not easily, in boiling water, and separates out again on cooling in beautiful, colourless needles.

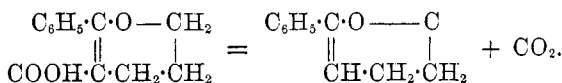
The *copper salt* is obtained as a light-green precipitate on adding a solution of cupric sulphate to the ammonium salt.

The *lead salt* is a white precipitate insoluble in water; *calcic* and

baric chlorides give no precipitate when added to a solution of the ammonium salt.



When phenyldehydrohexonecarboxylic acid is heated a few degrees above its melting point, rapid decomposition into carbonic anhydride and phenyldehydrohexone takes place thus:—



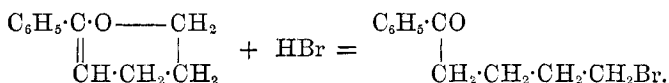
In order to examine the products of this reaction, the pure acid was heated in a small Wurtz flask in a metal bath at about 200° until the evolution of carbonic anhydride had ceased, and the resulting oil fractionated. On the first distillation, the whole passed over between 235—255°, and on refractioning once or twice the pure substance was obtained as a colourless oil boiling constantly at 249—251° (720 mm.).

Analyses.

- I. 0.1712 gram substance gave 0.1166 gram H₂O and 0.5164 gram CO₂.
 II. 0.1645 gram substance gave 0.1138 gram H₂O and 0.4952 gram CO₂.

	Theory. C ₁₁ H ₁₂ O.	Found.	
		I.	II.
C	82.50 p. c.	82.27	82.10 p. c.
H	7.50 „	7.56	7.69 „
O	10.00 „	10.17	10.21 „

Phenyldehydrohexone is a thick, colourless, aromatic-smelling oil, which boils almost without decomposition at 249—251°. After long standing it polymerises and becomes quite gelatinous. It does not appear to combine with phenylhydrazine. It is insoluble in cold water, but on long boiling a part seems to dissolve, probably being converted into benzoylbutyl alcohol. When dissolved in concentrated aqueous hydrogen bromide, phenyldehydrohexone is converted quantitatively into benzoylbutyl bromide, thus:—



Action of Hydrogen Bromide on Phenyldehydrohexonecarboxylic Acid and Phenyldehydrohexone.

Formation of Benzoylbutyl Bromide, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Br$.

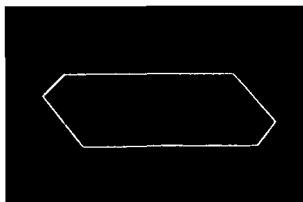
Phenyldehydrohexonecarboxylic acid dissolves easily in concentrated aqueous hydrogen bromide (sp. gr. 1.83) with evolution of heat. If the solution be allowed to stand, much carbonic anhydride is evolved, and in about one hour the whole solidifies to a mass of crystals of benzoylbutyl bromide. These are filtered off on a vacuum-pump, washed with a small quantity of water, and dried on a porous tile over sulphuric acid in a vacuum. They are then further purified by recrystallisation from petroleum ether (b. p. 45—70°).

Analyses.

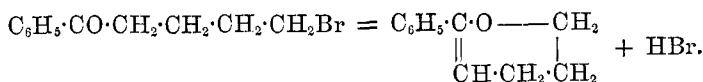
- I. 0.1683 gram substance gave 0.0828 gram H_2O , and 0.3360 gram CO_2 .
 II. 0.2928 gram substance gave 0.2288 gram $AgBr$.

Theory.		Found.		
$C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Br$.				
		I.	II.	
C	54.77 p. c.	54.45	—	p. c.
H	5.39 „	5.47	—	„
Br	33.19 „	—	33.25	„
O	6.64 „	—	—	„

Benzoylbutyl bromide melts at 61°. It is easily soluble in alcohol, benzene, chloroform, carbon bisulphide, ether, and light petroleum, almost insoluble in water. It crystallises from dilute alcohol in glistening plates, which have very much the appearance of benzoic acid. From light petroleum it crystallises in six-sided plates, which have the form



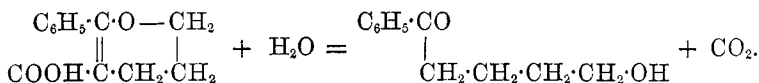
When warmed with alcoholic potash benzoylbutyl bromide is transformed into phenyldehydrohexone.



Benzoylbutyl bromide is most easily prepared from phenyldehydrohexone. If this substance is dissolved in twice its volume of highly concentrated aqueous hydrogen bromide and then cooled, the whole solidifies to a mass of crystals of benzoylbutyl bromide, which when treated as described above are easily obtained pure.

Action of Water on Phenyldehydrohexonecarboxylic Acid.

When boiled with water for any length of time, phenyldehydrohexonecarboxylic acid is split up into benzoylbutyl alcohol and water, thus :—



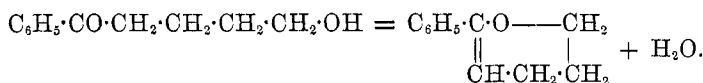
It is necessary to have the acid in as finely divided a state as possible, in order that it may dissolve in the water, and this is easily brought about by dissolving it in dilute ammonia and then carefully reprecipitating with dilute sulphuric acid. The fine powder thus obtained is collected, washed with water, and well agitated with boiling water until it completely dissolves. On boiling this solution in a reflux apparatus decomposition sets in, and carbonic anhydride is rapidly evolved, the reaction being generally finished in about six or eight hours. The resulting clear solution on the addition of anhydrous potassic carbonate, yields the benzoylbutyl alcohol in oily drops; it is extracted four or five times with ether, and dried over potassic carbonate. On evaporating this ethereal solution, a colourless oil is obtained which in a short time solidifies to a crystalline cake. This, after drying rapidly on a porous plate over sulphuric acid in a vacuum, was analysed with the following result :—

0·1134 gram substance gave 0·3010 gram CO_2 and 0·0798 gram H_2O .

	Theory.	Found.
$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$.		
C	74·27 per cent.	74·51 per cent.
H	7·86 „	7·80 „
O	17·97 „	17·69 „

If this alcohol is left for a few hours over sulphuric acid in a vacuum, the crystals gradually disappear and give place to a colourless oil. The small quantity of crystals at my disposal had thus in four days completely liquefied, and therefore I was not able to take a melting point or examine the properties. I hope, however, to be able to fill up these details at a later date. The change which takes place

here is simply elimination of water and formation of the anhydride, phenyldehydrohexone, thus:—



An analysis of the substance obtained after the benzoylbutyl alcohol had stood over sulphuric acid for seven days, gave the following numbers:—

0.1574 gram substance gave 0.1071 gram H_2O and 0.4701 gram CO_2 .

	Theory. $\text{C}_{11}\text{H}_{12}\text{O}$.	Found.
C	82.50 per cent.	82.07 per cent.
H	7.50 „	7.56 „
O	10.00 „	10.37 „

This substance is identical with the phenyldehydrohexone obtained by the dry distillation of phenyldehydrohexonecarboxylic acid, as described previously (p. 731). When dissolved in concentrated aqueous hydrogen bromide it combines with it to form benzoylbutyl bromide, which from its melting point and other properties was found to be identical with that obtained previously (p. 732).

It is curious that acetobutyl alcohol and benzoylbutyl alcohol should differ so remarkably in stability, the former even on distillation being only to a very slight extent converted into its anhydride, whereas the latter suffers this change completely at the ordinary temperature.

On the Action of Trimethylene Bromide on the Sodium-derivative of Ethylic Paranitrobenzoylacetate.

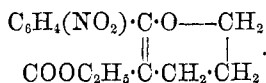
If the sodium compound of ethylic paranitrobenzoylacetate is treated with trimethylene bromide, the paranitro-derivative of ethylic phenyldehydrohexonecarboxylate is formed, the reaction taking place in a way precisely similar to that which has already been described in the last section. The only difference being that ethylic paranitrobenzoylacetate is substituted for ethylic benzoylacetate.

As ethylic paranitrobenzoylacetate, and more especially its sodium-derivative (Trans., 1886, 440), are such beautifully crystalline substances, it seemed that in this case it would be more easy to follow the mechanism of the reaction with trimethylene bromide; this was found to be the case.

Before describing these experiments I should like to thank Dr.

Gustav Bellenot for the valuable help he rendered me in carrying them out.

Ethylic Paranitrophenyldehydrohexonecarboxylate,



In order to obtain this compound 10 grams of the pure sodium compound of ethylic paranitrobenzoylacetate (*ibid.*, 448), 8 grams of trimethylene bromide, and 30 grams of absolute alcohol were heated at 100° in a sealed tube for three or four hours, after which time a quantity of sodium bromide had separated out and the mixture had become neutral. 0.9 gram of sodium dissolved in the least possible quantity of absolute alcohol was then added, the tube resealed, and once more heated at 100° for four hours. The tube was then opened, and the alcohol distilled off. On adding water to the remainder, the product of the reaction separates as a thick, brownish oil, which was extracted several times with ether. After drying over calcic chloride and distilling off the ether, a dark-brown liquid remains behind, the greater part of which solidifies on standing over sulphuric acid in a vacuum. The crystals were spread on a porous plate in order to free them roughly from mother-liquor, and afterwards dissolved in a little warm ether. An equal volume of light petroleum was then added and the mixture allowed to evaporate slowly at ordinary temperatures. Magnificent, lustrous, yellow crystals were thus obtained which on analysis gave the following results:—

I. 0.2664 gram substance gave 0.1300 gram H₂O and 0.5889 gram CO₂.

Ia. 0.1703 gram substance gave 8.2 c.c. N. *t* = 15°; bar. = 720 mm.

	Theory. C ₁₄ H ₁₅ NO ₅ .	Found.
C	60.64 per cent.	60.29 per cent.
H	5.41 „	5.42 „
N	5.05 „	5.24 „
O	28.90 „	29.05 „

Ethylic paranitrophenyldehydrohexonecarboxylate melts at 62—63°. It is easily soluble in ether, benzene, and alcohol, sparingly so in light petroleum, insoluble in water.

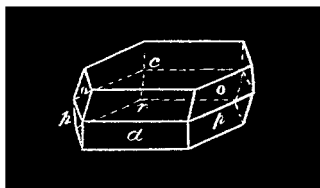
Professor Haushofer has kindly examined this beautiful substance crystallographically, and given me the following account of his experiments:—

Ethylic Paranitrophenyldehydrohexonecarboxylate.

Crystalline system. Monoclinic.

$$a : b : c = 2.3530 : 1 : 1.8530.$$

$$\beta = 80^\circ 42'.$$

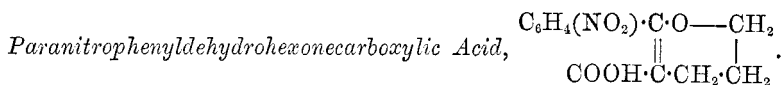


Small tabular crystals of the combination,

$$\begin{aligned} 0P &= (001) = c \\ \infty P &= (110) = p \\ \infty P \infty &= (100) = a \\ -P \infty &= (101) = r \\ -P &= (111) = o \end{aligned}$$

Generally the basal plane predominates, elongated in the direction of the axis b . The face c is usually flawed or slightly curved. The faces o and p are incompletely developed. The plane of the optical axis is the plane of symmetry; one axis is approximately normal to the face c .

	Measured.	Calculated.
$p : c = (110)(001)$	*93° 40'	— —
$a : p = (100)(110)$	*113 18	— —
$p : p = (110)(\bar{1}\bar{1}0)$	— —	46° 36'
$c : o = (001)(111)$	*119 34	— —
$c : a = (001)(100)$	99 17	99 18
$c : r = (001)(101)$	145 21	145 25
$r : o = (101)(111)$	126 36	126 50



To prepare this acid, the pure ethylic salt was mixed with a tolerably concentrated solution of alcoholic potash and allowed to stand for several hours, by which means it is easily and completely hydrolysed. Sufficient water to effect solution is added to this potassic salt, the whole, if necessary, filtered, and the filtrate acidified with dilute sulphuric acid, when the new acid is precipitated in the form of

yellow flakes, which are best extracted with ether. After drying over calcic chloride and filtering, the ether is evaporated, the crude acid thus being left behind as a yellow crust, which after several times recrystallising from benzene is obtained in the form of thick, colourless needles. These on analysis gave numbers which agree well with the formula $C_{12}H_{11}NO_5$.

0.2265 gram substance gave 0.0869 gram H_2O and 0.4788 gram CO_2 .

0.2467 gram substance gave 13.5 c.c. N. $t = 12^\circ$; bar. = 718 mm.

	Theory.	Found.
C	57.83 per cent.	57.64 per cent.
H	4.41 „	4.26 „
N	5.62 „	5.61 „
O	32.14 „	32.49 „

Paranitrophenyldehydrohexonecarboxylic acid when crystallised from benzene melts at 172° . It is easily soluble in benzene, ether, alcohol, and light petroleum, but crystallises best from benzene. The crystalline acid is almost insoluble in water. If, however, it is carefully precipitated from its solution in dilute ammonia by the addition of dilute acids, a seemingly amorphous precipitate is obtained which dissolves to a considerable extent in boiling water, and crystallises on cooling in long, colourless, glistening needles, which fuse at 183° . It will be seen that the melting point given here is 10° higher than that given for the same substance crystallised from benzene.

Phenyldehydrohexonecarboxylic acid has, as I have already shown, the same peculiarity, the thick prisms of this substance obtained from ether fusing at $142-144^\circ$, whereas the needles obtained from water melt at $149-150^\circ$.

Paranitrophenyldehydrohexonecarboxylic acid when heated above 200° is split up into carbonic anhydride and a neutral substance, which, however, has not been further examined.

The *salts* of paranitrophenyldehydrohexonecarboxylic acid are very stable. A solution of the ammonium salt is easily obtained by dissolving the free acid in a slight excess of ammonia, and then allowing the liquid to stand over sulphuric acid in a vacuum until it reacts quite neutral.

If nitrate of silver be added to this solution, a slightly yellow, amorphous *silver* salt is thrown down. This after collecting, well washing with water, and drying first in a vacuum and then at 100° , gave the following analytical results:—

0.1990 gram substance gave 0.0601 gram Ag.

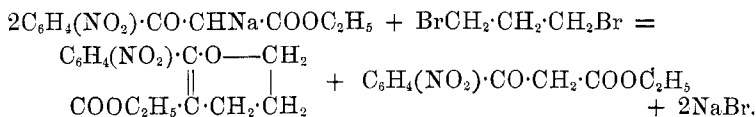
	Theory.	Found.
	$C_{12}H_{10}NO_5Ag$.	
Ag	30·34 per cent.	30·20 per cent.

This silver salt dissolves in hot water, and crystallises out on cooling in light yellow needles.

On adding a solution of acetate of copper to the ammonium salt, the *copper* salt is precipitated as a light-green, flocculent precipitate.

The *lead* salt is a white, amorphous precipitate almost insoluble in water.

The main object in conducting these experiments with ethylic paranitrobenzoylacetate was to prove that when the sodium-derivatives of this and analogously constituted substances are treated with dibromides such as ethylene and trimethylene bromides, the reaction really takes place between two molecules of the sodium compound and one of the bromide. Thus in the case of trimethylene bromide the reaction is :



The experiment was carried out in the following way :—

An intimate mixture of 5 grams of the pure sodium-derivative of ethylic paranitrobenzoylacetate, 4 grams of trimethylene bromide, and about 10 grams of alcohol were heated in a sealed tube at 100° until the reaction was complete (about six to eight hours). The product after gently warming on a water-bath to free it from alcohol, was treated with water and several times extracted with ether. The ethereal solution was carefully dried over calcic chloride and distilled, when a brownish-coloured, thick oil remained behind, a trace of which dissolved in alcohol and treated with ferric chloride gave a deep brownish-red coloration, showing the presence of considerable quantities of ethylic paranitrobenzoylacetate. To the solution of this oil in pure alcohol, 0·5 gram of sodium dissolved in alcohol was added. In this way, a dark-brown solution was formed, from which, on the addition of an equal volume of pure ether, a yellowish-brown sodium compound was slowly precipitated. After standing for 24 hours this was collected, washed with a mixture of ether and alcohol, and analysed with the following result :—

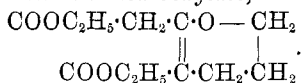
	Theory.	Found.
	$C_6H_4(NO_2) \cdot CO \cdot CHNa \cdot COOC_2H_5$.	
Na	8·88 per cent.	9·24 per cent.

This substance was therefore the sodium-derivative of ethylic paranitrobenzoylacetate. The amount obtained in this way weighed

upwards of 2 grams, whereas the yield calculated for the above equation should be 2.5 grams. The filtrate from this sodium compound was now mixed with more ether, the ethereal solution well washed with water, dried over calcic chloride, and distilled, when a brownish oil was obtained, which, after long standing over sulphuric acid in a vacuum, almost entirely solidified. The crystals, after spreading on a porous plate and recrystallising from ether and light petroleum, were easily purified, and then showed all the properties of ethylic paranitrophenyldehydrohexonocarboxylate. From this result it is seen that the formation of this substance takes place according to the equation given above.

Action of Trimethylene Bromide on the Disodium-derivative of Ethylic Acetonedicarboxylate.

Ethylic Methyldehydrohexonedicarboxylate,



In studying this reaction, a mixture of 200 grams of ethylic acetonedicarboxylate and 205 grams of trimethylene bromide was slowly added to a cold solution of 46 grams of sodium dissolved in 500 grams of absolute alcohol, care being taken to cool the mass well during the mixing, as otherwise a violent reaction, difficult to control, is apt to set in. On warming the resulting clear solution on a water-bath, sodium bromide soon begins to separate out, and after boiling for 10 hours in a reflux apparatus, the reaction may be considered as being at an end. Water is now added, and the oily product of the reaction separated from the aqueous solution by extraction with ether. The ethereal solution is next evaporated, and the almost colourless oil thus obtained, submitted to distillation in a rapid current of steam until no more oil passes over with the water. In this way the product was easily separated into two nearly equal parts, each of which weighed about 90 grams. The ethylic methyldehydrohexonedicarboxylate which remains behind in the retort is extracted with ether, the ethereal solution washed with a little dilute sodic carbonate, and dried over calcic chloride. After distilling off the ether, an almost colourless oil is obtained, which is purified by fractioning under reduced pressure (150 mm.). At the first distillation nearly the whole passed over between 225—250°, leaving a small residue in the retort, and on repeatedly fractioning the distillate, an oil was at last obtained, which boiled constantly at 238—240° (150 mm.). The analysis of this fraction gave the following results:—

0.2172 gram substance gave 0.1497 gram H_2O and 0.4730 gram CO_2 .

	Theory. $C_{12}H_{18}O_5$.	Found.
C	59.50 per cent.	59.40 per cent.
H	7.44 „	7.65 „
O	33.06 „	32.95 „

Ethylc methyldehydrohexonedicarboxylate is a thick, colourless oil, having a disagreeable smell somewhat resembling that of ethylc methyldehydrohexonemonocarboxylate. This oil, when dissolved in alcohol gives, on the addition of a drop of ferric chloride, a beautiful violet coloration; this is, however, probably due to traces of ethylc acetonedicarboxylate, which appear always to be present in samples of ethylc methyldehydrohexonedicarboxylate prepared by the above reaction.

When mixed with alcoholic potash, a yellow solution is formed, and on heating hydrolysis rapidly sets in.

It now seemed interesting to examine the oil which distilled over with the steam during the purification of the crude product of the action of trimethylene bromide on ethylc acetonedicarboxylate, as described above. For this purpose, the aqueous distillate was extracted with ether, the ethereal solution dried over calcic chloride, filtered, the ether distilled off, and the resulting colourless oil fractioned. It was thus easily separated into two principal fractions, $170-200^\circ$ and $200-235^\circ$, of which the latter was the larger. This fraction, $200-235^\circ$, yielded by repeated fractioning a beautiful, colourless oil, which boiled constantly at $223-224^\circ$ (720 mm.), and on analysis proved to be ethylc methyldehydrohexonocarboxylate.

0.2081 gram substance gave 0.1572 gram H_2O and 0.4800 gram CO_2 .

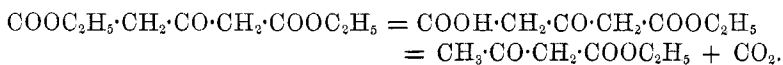
	Theory. $C_9H_{14}O_3$.	Found.
C	63.53 per cent.	62.91 per cent.
H	8.23 „	8.39 „
O	28.23 „	28.70 „

In order to characterise this substance it was subjected to hydrolysis, and the free acid obtained recrystallised from benzene. It then melted at 119° , and showed all the properties of methyldehydrohexonocarboxylic acid. An analysis of the silver salt gave the following numbers:—

0.2805 gram substance gave 0.1209 gram of silver = 43.10 per cent.; theory $C_7H_5O_3Ag$ = 43.38 per cent.

Ethylic methyldehydrohexonocarboxylate is probably produced from the dicarboxylate by partial hydrolysis and elimination of carbonic anhydride, as described below.

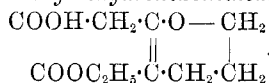
The fraction 170—200° of the original oil, on repeated distillation, was found to boil for the most part between 175—185°, and to consist of nearly pure ethylic acetoacetate. It was not thought necessary to analyse this, its reactions being so well known that identification is a matter of ease. It is evidently formed from ethylic acetonedicarboxylate by partial hydrolysis and elimination of carbonic anhydride, thus:—



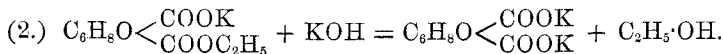
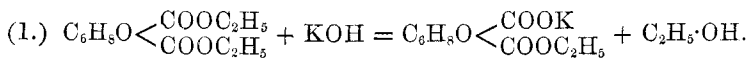
a reaction which always takes place when ethylic acetonedicarboxylate is treated with alkalis.

Hydrolysis of Ethylic Methyldehydrohexonedicarboxylate.

(1.) *Hydric Ethylic Methyldehydrohexonedicarboxylate,*



The hydrolysis of ethylic methyldehydrohexonedicarboxylate takes place in two stages. In the first place an acid ethereal salt of the formula given above is formed, which then by the further action of alkalis is finally converted into the dicarboxylic acid :



In preparing the hydric ethylic salt, pure ethylic methyldehydrohexonedicarboxylate is mixed with a large excess of a fairly concentrated solution of alcoholic potash, and allowed to stand at the ordinary temperature, until a sample taken out dissolves completely in H₂O (10 to 14 hours). In order to isolate the new compound, dilute sulphuric acid (1 acid to 5 H₂O) is added in excess, care being taken to keep the liquid cool during the operation. The product is then extracted five or six times with ether, the ethereal solution washed until free from alcohol, dried over calcic chloride, and the ether distilled off at as low a temperature as possible. A thick oil is thus obtained, which, after standing for some days over sulphuric acid in a vacuum, almost completely solidifies to a mass of crystals. These

are roughly separated from oily impurities by spreading out on a porous plate, then washed with a little pure ether, and finally completely dissolved in this solvent. If this solution is allowed to evaporate slowly at ordinary temperatures, the acid ethylic salt separates out in magnificent, colourless, transparent crystals, which after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

- I. 0.2060 gram substance gave 0.1240 gram H_2O and 0.4208 gram CO_2 .
 II. 0.1870 gram substance gave 0.1155 gram H_2O and 0.3805 gram CO_2 .

	Theory. $\text{C}_6\text{H}_5\text{O} \begin{cases} \text{COOH} \\ \text{COOC}_2\text{H}_5 \end{cases}$	Found.	
		I.	II.
C	56.07 per cent.	55.71	55.49
H	6.55 „	6.69	6.86
O	37.38 „	37.60	37.65

It melts at 114° , is easily soluble in alcohol and ether, and sparingly so in hot water. If the hot aqueous solution be allowed to cool slowly the substance crystallises out in beautiful, colourless, four-sided needles. The alcoholic solution gives no coloration with ferric chloride, and it is for this reason that it appeared to me likely that the beautiful coloration produced in solutions of the diethylic salt by ferric chloride was caused by the presence of traces of ethylic acetone-dicarboxylate. The best solvent to crystallise the acid ethylic salt from is pure ether. In this way most magnificent crystals can be obtained. Professor Haushofer was kind enough to measure these, and gave me the following account of his experiments.

Hydric Ethylic Methyldehydrohexonedicarboxylate.

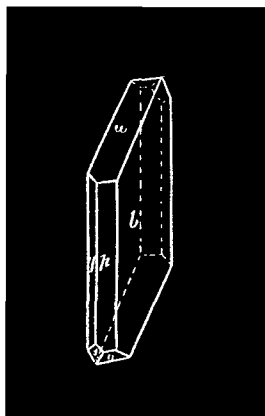
Crystalline system. Triclinic.

$$a : b : c = 0.7741 : 1 : 0.3371.$$

$$\alpha = 89^\circ 40'$$

$$\beta = 98^\circ 18'$$

$$\gamma = 89^\circ 50'$$



Colourless, lustrous crystals of the combination---

$$\infty P_{\infty} = (010) = b$$

$$P^i = (111) = w$$

$$\infty P_i = (110) = p$$

$$P_i = (11\bar{1}) = o$$

$$\infty_i P = (1\bar{1}0) = q$$

$$P_{\frac{1}{3}} = (3\bar{1}\bar{1}) = s$$

Development tabular to the face b . The face q was only observed on a single crystal, it was very small, but sharply developed. The faces b are frequently rounded, and sometimes deviate some degrees from the parallel. Cleavage moderately distinct, parallel to w .

	Measured.		Calculated.	
$w : b = (111)(010) =$	$*105^{\circ}$	27'	—	—
$w : p = (111)(110) =$	$*123$	19	—	—
$p : o = (110)(11\bar{1}) =$	$*113$	56	—	—
$p : q = (110)(1\bar{1}0) =$	$*104$	48	—	—
$p : b = (110)(010) =$	$*127$	19	—	—
$o : b = (11\bar{1})(010) =$	108	33	108°	37'
$q : o = (1\bar{1}0)(11\bar{1}) =$	90	20	91	3
$q : w = (1\bar{1}0)(111) =$	102	26	102	48
$s : p = (3\bar{1}\bar{1})(110) =$	117	40	117	44
$s : o = (3\bar{1}\bar{1})(11\bar{1}) =$	134	42	135	17
$s : b = (3\bar{1}\bar{1})(010) =$	77	58	78	0
$s : q = (3\bar{1}\bar{1})(1\bar{1}0) =$	135	49	135	46

The results of the measurements of the angles do not absolutely exclude the possibility of the crystals belonging to the monoclinic system, whilst the smallness and brittleness of the crystals prevented

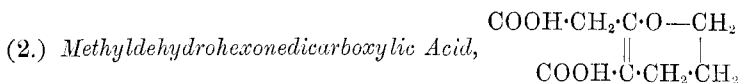
the optical properties being sufficiently determined to decide the crystalline system with certainty; the direction of the only cleavage plane, however, leaves scarcely any doubt as to the crystals belonging to the triclinic system.

This acid ethylic salt dissolves easily in alkalis, and gives well characterised salts, of which the *silver* salt has been carefully prepared and examined. This salt is thrown down on adding nitrate of silver to a neutral solution of the ammonium salt as a white, curdy precipitate sparingly soluble in water. It was collected, well washed with water, and dried over sulphuric acid in a vacuum.

Analysis.

0.2330 gram substance gave 0.0870 gram H_2O , 0.3168 gram CO_2 , and 0.0786 gram Ag.

	Theory.		Found.
	$C_6H_5O \begin{smallmatrix} \text{COOAg} \\ \text{COOC}_2H_5 \end{smallmatrix}$		
C	37.38 per cent.		37.09 per cent.
H	4.05 "		4.14 "
Ag	33.64 "		33.73 "
O	24.92 "		25.04 "



This acid may be obtained by the hydrolysis of the acid ethylic salt, but it was usually prepared directly from ethylic methyldehydrohexonedicarboxylate. The pure ethylic salt is mixed with an excess of alcoholic potash and heated to boiling for three or four hours on a water-bath. The slightly brownish-coloured solution is then diluted with twice its volume of water, and evaporated in an open dish on a water-bath until all the alcohol has been expelled. After filtering and acidifying with dilute sulphuric acid, the solution is allowed to stand 24 hours in a cool place, at the end of which time it is usually found that a crystalline crust, consisting of the nearly pure dicarboxylic acid, has separated on the bottom of the vessel containing the liquid. This is collected, washed with a little water, and dried on a porous plate (A). The mother-liquors are then extracted four or five times with ether, the ethereal solution washed, dried over calcic chloride, and the ether distilled off. A further quantity of impure dicarboxylic acid is thus obtained, usually as a thick oil, which, however, after standing for some days over sulphuric acid in a vacuum, deposits a quantity of crystals. These are roughly separated from impurities by spreading out on a porous plate, then

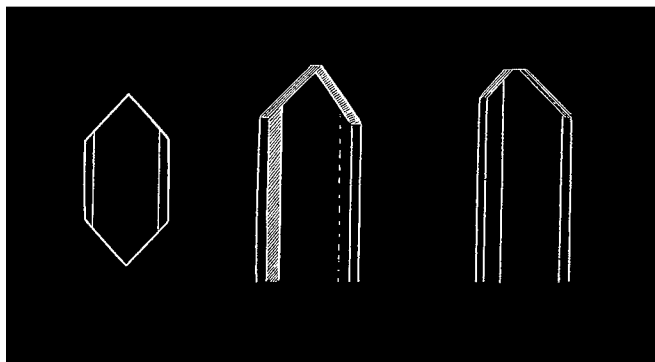
washed with a little ether, and mixed with the crop (A) first obtained. The whole is now dissolved in a little hot water, and the solution filtered. On standing, the dicarboxylic acid soon begins to crystallise out in colourless plates, which after collecting, washing with water, and drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

- I. 0·1489 gram substance gave 0·0756 gram H_2O and 0·2819 gram CO_2 .
 II. 0·1757 gram substance gave 0·0889 gram H_2O and 0·3306 gram CO_2 .

Theory.		Found.	
$\text{C}_6\text{H}_8\text{O} \begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$		I.	II.
C	51·61 per cent.	51·63	51·32 per cent.
H	5·38 „	5·64	5·67 „
O	43·01 „	42·73	43·01 „

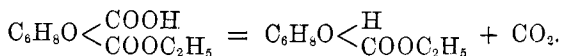
Methyldehydrohexonedicarboxylic acid melts at about $185-190^\circ$ with decomposition, evolution of carbonic anhydride, and formation of a curiously reddish-coloured liquid. This red coloration appears to be always produced when the pure acid is heated above its melting point, and is very characteristic. When heated in a test-tube the acid gives off carbonic anhydride, and an oil is formed which has in a marked degree the peculiar odour of methyldehydrohexone.

Methyldehydrohexonedicarboxylic acid is easily soluble in hot water and hot alcohol, but sparingly soluble in ethyl acetate, ether, and benzene. It crystallises from water in beautiful, colourless plates, which under the influence of polarised light show a fine play of colours. The forms of the crystals are generally the following:—



Formation of Ethylic Methyldehydrohexonecarboxylate from Hydric Ethylic Methyldehydrohexonedicarboxylate.

Hydric ethylic methyldehydrohexonedicarboxylate when heated is easily decomposed with evolution of carbonic anhydride and formation of ethylic methyldehydrohexonecarboxylate, thus:—



In carrying out this decomposition, the pure acid ethylic salt is transferred to a Wurtz flask and gradually heated in a metal-bath to 200° until the evolution of carbonic anhydride ceases. The resulting oil when fractioned, distils constantly between 223° and 225° , and is pure ethylic methyldehydrohexonecarboxylate.

Analysis.

0.1519 gram of substance gave 0.1135 gram H_2O and 0.3526 gram CO_2 .

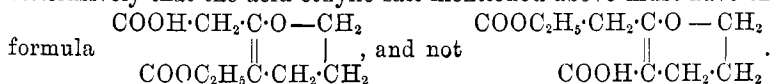
	Theory. $\text{C}_9\text{H}_{11}\text{O}_3$.	Found.
C	63.53 per cent.	63.26 per cent.
H	8.24 ,,	8.22 ,,
O	28.23 ,,	28.52 ,,

As it was important to be sure of the identity of this ethereal salt, it was converted into the corresponding acid by hydrolysis with alcoholic potash (as described under the heading "Methyldehydrohexonecarboxylic Acid," p. 715). The acid obtained after recrystallisation from benzene melted at 119 — 120° , and gave the following numbers on analysis:—

0.1764 gram substance gave 0.1132 gram H_2O and 0.3810 gram CO_2 .

	Theory. $\text{C}_7\text{H}_{10}\text{O}_3$.	Found.
C	59.15 per cent.	58.90 per cent.
H	7.04 ,,	7.12 ,,
O	33.80 ,,	33.98 ,,

The formation of ethylic methyldehydrohexonecarboxylate from hydric ethylic methyldehydrohexonedicarboxylate not only shows the close relation existing between these two substances, but also proves conclusively that the acid ethylic salt mentioned above must have the



In the latter case on elimination of carbonic anhydride an ethereal salt of the formula

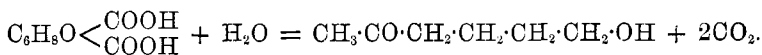
$$\text{COOC}_2\text{H}_5\cdot\text{CH}_2\cdot\text{C}\cdot\text{O}\text{---}\text{CH}_2$$

$\begin{array}{c} \parallel \\ \text{CH}\cdot\text{CH}_2\cdot\text{CH}_2 \end{array}$

should be obtained; this would be isomeric, and not identical, with ethylic methyldehydrohexonocarboxylate.

Action of Water on Methyldehydrohexonedicarboxylic Acid.

In the introduction it was mentioned that methyldehydrohexonedicarboxylic acid when boiled with water was decomposed into acetobutyl alcohol and two molecules of carbonic anhydride, thus:—



About 5 grams of the pure acid was dissolved in a small quantity of hot water and the solution then heated to boiling in a flask connected with a reversed condenser until the evolution of carbonic anhydride had ceased. The resulting liquid was saturated with anhydrous potassic carbonate, the oil thus precipitated extracted about ten times with pure ether, the ethereal solution dried over potassic carbonate, filtered, and the ether distilled off. In this way a colourless syrup was obtained, which, after standing for some time over sulphuric acid in a vacuum to free it from traces of ether, gave the following approximate numbers on analysis:—

0.1314 gram substance gave 0.1206 gram H_2O and 0.3041 gram CO_2 .

	Theory.	
$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}.$		Found.
C	62.07 per cent.	63.11 per cent.
H	10.34 „	10.19 „
O	27.59 „	26.70 „

Owing to the small amount of material at my disposal it was not possible to purify this ketone alcohol by fractional distillation, but a qualitative comparison of the substance obtained as above with a specimen prepared from methyldehydrohexonemonocarboxylic acid (p. 715) showed conclusively that the two were identical. In order to be sure that the reaction really took place according to the equation just given, a determination was made of the amount of carbonic anhydride evolved when a definite amount of the acid was decomposed by boiling with water, with the following results:—

2.4811 gram substance gave 1.1432 gram CO_2 . Theory for $2\text{CO}_2 = 47.32$ per cent. Found 46.07 per cent.

The amount of acetobutyl alcohol formed was not determined.

The principal part of this research was carried out in Professor A. v. Baeyer's laboratory in Munich. Through the kindness of Professors Roscoe and Dixon, I was subsequently enabled to fill in some of the details at the Owens College, Manchester.
