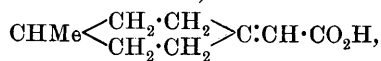


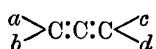
CIX.—*Experiments on the Synthesis of 1-Methylcyclohexylidene-4-acetic Acid,*



Part I.

By WILLIAM HENRY PERKIN, jun., and WILLIAM JACKSON POPE.

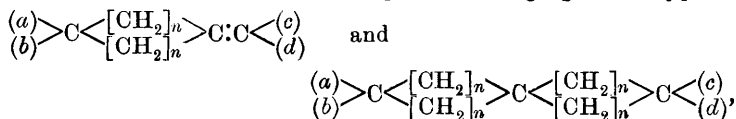
VAN'T HOFF has pointed out that the presence of an asymmetric atom is conceivably not the only cause from which optical activity can arise; a substance containing an asymmetric carbon atom exhibits optical activity in solution, because the presence of this peculiarity of constitution imparts an enantiomorphous configuration to the molecule. It is, however, possible to devise space formulæ which are enantiomorphous, but which contain no asymmetric atom; the substances thus represented would be expected to exhibit optical activity in solution. Thus van't Hoff notes (*The Arrangement of Atoms in Space*, 1898, 103) that allene derivatives of the type



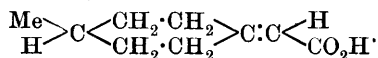
should exist in two enantiomorphously related, and hence optically active, forms.

Compounds which presumably possess enantiomorphous configurations, such as are described above, are already known, as, for instance, the symmetrical dimethylallene, $\text{CHMe} : \text{C} : \text{CHMe}$, but being synthetic products they naturally do not exhibit optical activity.

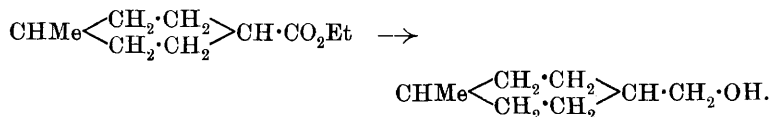
In order to obtain experimental information concerning the new kind of stereoisomerism thus indicated, we endeavoured, but without success, to prepare allene derivatives of the type mentioned, and of such constitutions that the ordinary methods of resolving externally compensated substances could be applied to them. We next turned our attention to the synthesis of compounds belonging to the types



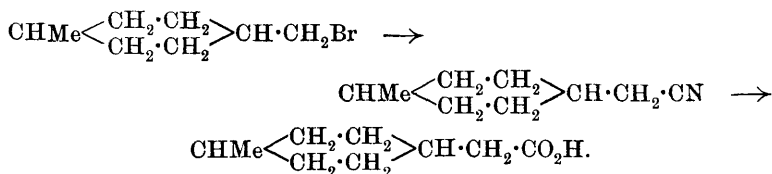
which contain symmetrical closed rings in the place of one or both of the double linkings in allene, and must therefore also exhibit enantiomorphism, and we selected for our purpose the synthesis of 1-methylcyclohexylidene-4-acetic acid,



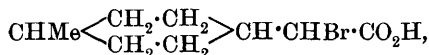
The starting point in this synthesis was 1-methylcyclohexylcarbinol, which was prepared in considerable quantities from ethyl 1-methylcyclohexane-4-carboxylate (Trans., 1905, 87, 644) by reduction with sodium and alcohol,



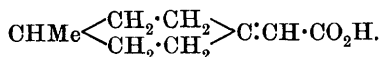
When this alcohol is heated with fuming hydrobromic acid, it yields 1-methylcyclohexylcarbinyl bromide, and this is converted by the action of potassium cyanide into the corresponding nitrile, which, on hydrolysis, yields 1-methylcyclohexyl-4-acetic acid:



The chloride of this acid behaves in the usual manner when it is heated with bromine, and the product is readily decomposed by formic acid with formation of *α*-bromo-1-methylcyclohexyl-4-acetic acid,

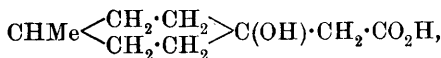


which crystallises well and melts at 78°. When the ester of the acid is digested with diethylaniline, hydrogen bromide is eliminated, and an unsaturated ester is formed, and this, on hydrolysis, yields an acid which crystallises from formic acid in glistening plates, softens at 63°, and melts at 70°. The analysis of this acid gave results agreeing with the formula $\text{C}_9\text{H}_{14}\text{O}_2$, and this formula was confirmed by the analysis of the ester and other derivatives. Since the alkaline solution of the acid instantly decolorised permanganate, there seemed to be no other alternative than to conclude that it had been produced normally, and was, in fact, 1-methylcyclohexylidene-4-acetic acid,



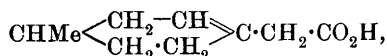
While these experiments were in progress, W. Markwald and R. Meth (*Ber.*, 1906, 39, 1171) published an account of an investigation which they had made with the same object as we had in view, namely, that of synthesising 1-methylcyclohexylidene-4-acetic acid and then resolving it into its active modifications. Their method of synthesising this acid was, however, quite different from ours, and was as follows: 4-Methylcyclohexanone was treated with ethyl bromoacetate and magnesium and the product hydrolysed, when the two

stereoisomeric modifications of 4-hydroxy-1-methylcyclohexyl-4-acetic acid,

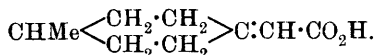


were obtained, both of which are decomposed by boiling dilute sulphuric acid with elimination of water and formation of an unsaturated acid, $\text{C}_9\text{H}_{14}\text{O}_2$, which melts at 41° .

A glance at the formula of the hydroxy-acid shows at once that the elimination of water may take place in two directions, and that the resulting unsaturated acid may be either 1-methyl- Δ^3 -cyclohexene-4-acetic acid,



or 1-methylcyclohexylidene-4-acetic acid,



Markwald and Meth are of opinion that their unsaturated acid is to be regarded as having the latter constitution, but we, on the other hand, consider it probable that it contains the double linking in the ring, and is, in fact, 1-methyl- Δ^3 -cyclohexene-4-acetic acid.

In reply to this criticism, Markwald and Meth (*Ber.*, 1906, 39, 2404) have published further evidence in support of their view, and Wallach (*Annalen*, 1907, 313, 311) has also investigated the subject, and is of opinion that the acid of melting point 41° is 1-methylcyclohexylidene-4-acetic acid. It is unfortunate that we have not yet been able to prepare our unsaturated acid free from small quantities of 1-methylcyclohexyl-4-acetic acid. The ester of this latter acid is apparently produced in small quantities as the result of a secondary reaction during the elimination of hydrogen bromide from ethyl α -bromo-1-methylcyclohexyl-4-acetate by means of diethylaniline, and its presence was first discovered during a series of experiments on the oxidation of the unsaturated acid by means of ozone.

It follows from this that the melting point which we have given for our unsaturated acid can only be approximately correct, and must therefore be accepted with reserve. On the other hand, the results of a long and interesting series of experiments which are in progress seem to show that, in spite of all the evidence to the contrary, the unsaturated acid of melting point 41° , prepared by Markwald and Meth, is not 1-methylcyclohexylidene-4-acetic acid.

The experimental investigation of this matter has proved to be most complex and difficult, and, as the investigation may not be completed for a considerable time, we have thought it best to publish now the details of those experiments of which a brief account was given in our preliminary communication (*Proc.*, 1906, 22, 107).



The process used in the preparation of this carbinol is similar to that employed by Bouveault and Blanc (*Compt. rend.*, 1903, 136, 1676; 137, 60) in their experiments on the conversion of cyclohexanecarboxylic ester into cyclohexylcarbinol. Sodium (30 grams), in pieces about the size of a marble, is placed in a 2-litre flask, connected with a long condenser, and heated in an oil-bath at 80°.

1-Methylcyclohexane-4-carboxylic ester (30 grams), dissolved in alcohol (150 c.c.), is then added in a thin stream down the condenser, the decomposition being allowed to proceed as vigorously as possible.

When the action slackens, the temperature of the oil-bath is raised to 130°, and small quantities of alcohol added until the sodium has dissolved. The product is diluted with water (3 vols.) and extracted three times with ether, the ethereal solution is washed several times with water, dried over anhydrous sodium sulphate, evaporated, and the residual oil purified by distillation under ordinary pressure. During the first distillation almost the whole quantity passes over at 190—200°, very little oil of higher boiling point remaining in the flask, and, on repeating the operation, the substance boils constantly at 197—198° (768 mm.) :

0.1726 gave 0.4734 CO₂ and 0.1886 H₂O. C = 74.8; H = 12.2.

0.1382 „ 0.3790 CO₂ „ 0.1539 H₂O. C = 74.8; H = 12.4.

C₈H₁₆O requires C = 75.0; H = 12.4 per cent.

1-Methylcyclohexyl-4-carbinol has an odour of isoamyl alcohol and at the same time of peppermint. The yield of alcohol obtained by the above process is 20—25 grams from 60 grams of 1-methylcyclohexane-4-carboxylic ester, and the alkaline solution, from which the alcohol has been extracted with ether, yields on concentration and precipitation with hydrochloric acid the unchanged 1-methylcyclohexane-4-carboxylic acid, which is collected and used in a subsequent operation.

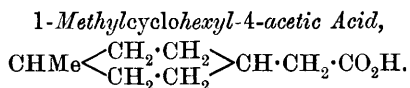
1-Methylcyclohexyl-4-carbinyl Bromide.—1-Methylcyclohexyl-4-carbinol dissolves in twice its volume of a solution of hydrogen bromide in glacial acetic acid (saturated at 0°) with very little rise of temperature, and if heated for two hours at 100° and then for one hour at 120° the liquid separates into two layers.

The whole is diluted with water, extracted with ether, the ethereal solution well washed with water, dried, and evaporated. The residual bromide distils at 135—137° under 150 mm. pressure, the yield being almost quantitative :

0.5274 gave 0.5136 AgBr. Br = 41.5.

C₈H₁₅Br requires Br = 41.8 per cent.

1-Methylcyclohexyl-4-carbinyl bromide is a very stable substance, which may be distilled in small quantities under the ordinary pressure with only slight decomposition. It has a pungent and rather aromatic odour, which somewhat resembles that of trimethylene bromide.



Three methods have been employed in the preparation of this acid.

Method I. The Hydrolysis of 1-Methylcyclohexyl-4-carbinyl Cyanide.—This process was found to be very laborious on account of the fact that 1-methylcyclohexyl-4-carbinyl bromide is not readily converted into the cyanide by treatment with potassium cyanide.

After a long series of comparative experiments, carried out under very varied conditions, the following process, which still leaves much to be desired, seemed to yield the best results. The bromide (10 grams) is heated in a sealed tube with pure potassium cyanide (Kahlbaum, 10 grams) and 70 per cent. alcohol (30 c.c.) for two hours at 120°, the tube is then allowed to cool, well shaken, and heated at 150° for three hours. The product, which smells of ammonia and, owing to the separation of azulmic acid, is very dark coloured, is diluted with water, extracted with ether, the ethereal solution washed with water until free from alcohol, and evaporated.

The residue, which has a pungent odour of a cyanide and consists of 1-methylcyclohexyl-4-carbinyl cyanide and a considerable quantity of regenerated 1-methylcyclohexyl-4-carbinol, is mixed with an equal volume of acetic-hydrobromic acid (saturated at 0°) and heated in a sealed tube at 120° for two hours. The product contains crystals of ammonium bromide, and is diluted with water, extracted with ether, the ethereal solution washed several times with water in order to remove as much acetic acid as possible, and then extracted with dilute potassium hydroxide. After drying over calcium chloride, the ethereal solution yields, on evaporation, methylcyclohexylcarbinyl bromide, which is distilled and used in a subsequent operation. The potassium hydroxide solution is again extracted with ether, heated on the water-bath until free from ether, cooled with ice, and acidified, when about 1.5—2 grams of a yellow, crystalline acid separates.

This is collected, washed well, dissolved in sodium carbonate, the solution digested with animal charcoal, filtered and acidified, and the colourless, crystalline acid purified by recrystallisation from formic acid, from which it separates in satiny plates which melt at 73—74°.

Method II. The Action of Magnesium and Carbon Dioxide on 1-Methylcyclohexyl-4-carbinyl Bromide.—Magnesium (8 grams) is

suspended in ether and rendered active by treatment with a little methyl iodide; the ether is then decanted and replaced by an ethereal solution of methylcyclohexylcarbonyl bromide (30 grams), when a rather vigorous action takes place, which, however, soon slackens. After heating for one hour on the water-bath, carefully-dried carbon dioxide is passed for two hours, the whole decomposed by dilute hydrochloric acid, and extracted with ether.

The ethereal extract is shaken with dilute potassium hydroxide, and the alkaline solution, after heating on the water-bath until free from ether, cooled and acidified, when a pale yellow, crystalline precipitate (3 grams) is obtained, which, after crystallisation from formic acid, melts at 73—74°. As the amount of acid obtained in this way was so small, another experiment was made, using magnesium which has been rendered active by heating with iodine under the conditions recommended by Baeyer (*Ber.*, 1905, **38**, 2759), but the yield was not much better.

The disadvantage in the use of magnesium lies in the fact that excess has to be employed, and, when the product is subsequently treated with hydrochloric acid, a good deal of the unchanged bromide becomes reduced and thus very valuable material is lost. It was for this reason that this method was abandoned.

Method III. The Reduction of β -Bromo-1-methylcyclohexyl-4-acetic Acid (p. 1082).*—This method, which is probably the most satisfactory for the preparation of methylcyclohexylacetic acid, is carried out in the following way. β -Bromomethylcyclohexylacetic acid is dissolved in cold alcohol, mixed with acetic acid and a few drops of hydrochloric acid, magnesium turnings are then added, and the whole well agitated, care being taken that the temperature does not rise above 35°. As soon as the magnesium has dissolved, the product is distilled in steam, and the distillate, which contains besides methylcyclohexylacetic acid considerable quantities of methylcyclohexylideneacetic acid (m. p. 41° of Markwald and Meth, p. 1077), is then neutralised with sodium carbonate and oxidised with potassium permanganate (1 per cent.) until the pink colour remains. The filtrate and washings of the manganese precipitate are evaporated to a small bulk and acidified, when a colourless acid separates which, after crystallisation from formic acid, melts at 73° and consists of pure methylcyclohexylacetic acid. The acid prepared by each of the above methods was analysed with the following results:

* Wallach (*Annalen*, 1907, **353**, 313) has lately prepared 1-methylcyclohexyl-4-acetic-acid from ethyl β -hydroxy-1-methylcyclohexyl-4-acetate by treatment with acetic-hydrobromic acid and subsequent reduction with zinc dust. The melting point (63—65°) which he gives is, however, too low.

- I. 0.1442 gave 0.3674 CO₂ and 0.1332 H₂O. C = 69.4 ; H = 10.3.
 II. 0.1589 ,, 0.4031 CO₂ ,, 0.1471 H₂O. C = 69.1 ; H = 10.3.
 III. 0.1115 ,, 0.2826 CO₂ ,, 0.1032 H₂O. C = 69.1 ; H = 10.3.
 C₉H₁₆O₂ requires C = 69.2 ; H = 10.3 per cent.

1-Methylcyclohexyl-4-acetic acid melts at 73—74°, and is readily soluble in most organic solvents, but almost insoluble in cold water.

It separates from dilute formic acid in colourless, glistening plates with a satiny lustre.

The silver salt, C₉H₁₅O₂Ag, obtained by adding silver nitrate to a slightly alkaline solution of the ammonium salt, is a white, caseous precipitate, which rapidly becomes crystalline. It was well washed and dried over sulphuric acid :

- 0.2665 gave 0.4000 CO₂ and 0.1363 H₂O. C = 41.3 ; H = 5.7.
 0.3738 ,, 0.1546 Ag. Ag = 41.3.

C₉H₁₅O₂Ag requires C = 41.1 ; H = 5.7 ; Ag = 41.1 per cent.

α-Bromo-1-methylcyclohexyl-4-acetic Acid. — The bromination of methylcyclohexylacetic acid was carried out under the following conditions. The acid (3.5 grams) was mixed with phosphorus pentachloride (5 grams) in a tube, and, when the formation of the acid chloride was complete, bromine (4 grams) was added, the tube sealed, and heated in boiling water for ten hours. The product, which was only slightly coloured, was mixed with three volumes of formic acid (sp. gr. 1.22) and heated for about an hour on the water-bath, when it was noticed that the liquid had separated into two layers. Since no crystallisation* took place after standing for twenty-four hours, the bromo-acid was precipitated by adding water, the gum which separated was kneaded with cold water until it had solidified, and, after washing well and draining on porous porcelain, the substance was finally crystallised from formic acid :

- 0.1938 gave 0.3285 CO₂ and 0.1115 H₂O. C = 46.2 ; H = 6.4.
 0.2651 ,, 0.2114 AgBr. Br = 34.0.

C₉H₁₅BrO₂ requires C = 46.0 ; H = 6.4 ; Br = 34.0 per cent.

α-Bromo-1-methylcyclohexyl-4-acetic Acid melts at 78°, is readily soluble in hot formic acid, and the solution clouds on cooling, but if stirred vigorously the bromo-acid separates in glistening leaflets.

Ethyl α-bromo-1-methylcyclohexyl-4-acetate was prepared in two different ways. In the first place the bromo-acid chloride, obtained as described above, was poured into alcohol, and, after remaining for twenty-four hours, the alcoholic solution was diluted with water, the

* If, however, a crystal is available and is added at this stage, the bromo-acid rapidly crystallises and, after filtering and washing with a little cold formic acid, is almost pure.

heavy oil extracted with ether, the ethereal extract washed with water and dilute sodium carbonate, dried, and evaporated.

The viscid, unpleasant smelling bromo-ester was placed over sulphuric acid in an evacuated desiccator until free from ether.

Subsequently, the bromo-ester was prepared by leaving the solution of the pure bromo-acid in 10 per cent. alcoholic sulphuric acid for three days. The product was diluted with water, the heavy oil extracted with ether, the ethereal solution was washed with sodium carbonate, dried, and evaporated. After remaining for two days over sulphuric acid in an evacuated desiccator, the viscid, almost colourless oil yielded the following result on analysis :

0.2642 gave 0.1851 AgBr. Br = 29.8.

$C_{11}H_{19}O_2Br$ requires Br = 30.4 per cent.

β-Bromo-1-methylcyclohexyl-4-acetic Acid.—This substance was prepared by two different methods, namely, by the action of fuming hydrobromic acid on *β-hydroxymethylcyclohexylacetic acid* (p. 1077), and on *methylcyclohexylideneacetic acid* (m. p. 41° of Markwald and Meth, p. 1077).

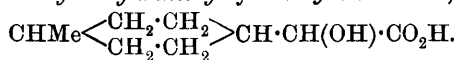
The hydroxy-acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and in a few minutes the solution clouds and crystals begin to form. After adding water, the crystalline precipitate is collected, left in contact with porous porcelain until quite dry, and crystallised, first from formic acid, and then from light petroleum (b. p. 50—60°). From this latter solvent, the substance separates in magnificent, glistening prisms melting at 87° :

0.2120 gave 0.1691 AgBr. Br = 33.9.

$C_9H_{15}O_2Br$ requires Br = 34.0 per cent.

In the second experiment, *methylcyclohexylideneacetic acid* was finely powdered and stirred with fuming hydrobromic acid (saturated at 0°), when it partly dissolved, and was then converted into an oil, which soon solidified. The product was diluted with water, the precipitate collected, dried on porous porcelain, and then crystallised from light petroleum. The substance separated in glistening prisms, melted at 87°, and was identical with the bromo-acid obtained by the first process. This bromo-derivative has already been prepared by this latter method by Wallach (*Annalen*, 1907, 353, 312).

α-Hydroxy-1-methylcyclohexylacetic Acid,



This acid is produced when the corresponding bromo-acid (p. 1081) is boiled with sodium carbonate or dilute potassium hydroxide for about half an hour. The alkaline solution is extracted with ether to remove

a trace of neutral oil, acidified, and again extracted four or five times. The ethereal solution is dried and evaporated to a small bulk, when the hydroxy-acid soon separates in colourless, glistening plates. After recrystallisation from ether, the following results were obtained on analysis :

0·1840 gave 0·4202 CO₂ and 0·1508 H₂O. C = 62·3 ; H = 9·1.

0·1825 „ 0·4204 CO₂ „ 0·1510 H₂O. C = 62·8 ; H = 9·2.

C₉H₁₆O₃ requires C = 62·8 ; H = 9·3 per cent.

α-Hydroxy-1-methylcyclohexyl-4-acetic acid melts at 148°, and is sparingly soluble in cold water, but dissolves somewhat readily on boiling and separates, when the solution is allowed to cool slowly, in striated plates often aggregated in the form of stars. The solution in dilute sodium carbonate is stable to permanganate.

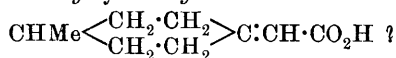
When the powdered acid is stirred with concentrated sulphuric acid, carbon monoxide soon begins to be disengaged, and the evolution is rapid if the mixture is warmed at 40°. If, as soon as the decomposition has ceased, the brown solution is diluted with water, a pleasant smelling oil separates, which is probably the corresponding aldehyde (compare Wallach, *Annalen*, 1906, **347**, 346). At 60—70°, the hydroxy-acid is rapidly decomposed by sulphuric acid, sulphur dioxide is produced, and the solution becomes very dark coloured.

The *silver* salt, C₉H₁₅O₃Ag, was obtained as a chalky precipitate when silver nitrate was added to a warm slightly alkaline solution of the ammonium salt. For analysis, the substance was dried first over sulphuric acid and then in the water-oven :

0·3771 gave 0·1460 Ag. Ag = 38·7.

C₉H₁₅O₃Ag requires Ag = 38·7 per cent.

The ethereal mother liquors from the crystallisation of the hydroxy-acid (see above) were evaporated, when a viscid oil remained which soon crystallised. After remaining in contact with porous porcelain for a couple of days, the residue was dissolved in hot water, digested with animal charcoal, and the colourless solution concentrated, when, on cooling, a large quantity of the same hydroxy-acid of melting point 148° separated. It was to be expected that during the bromination of 1-methylcyclohexyl-4-acetic acid and subsequent conversion of the bromo- into the hydroxy-acid, two stereoisomeric modifications would result, and therefore the mother liquors of the two acids were very carefully investigated, but in neither case could any evidence of the existence of a second modification be obtained.

1-Methylcyclohexylidene-4-acetic Acid,

In our first attempts to prepare this acid, a series of experiments were made with the object of eliminating hydrogen bromide from α -bromo-1-methylcyclohexyl-4-acetic acid by means of alcoholic potash, diethylaniline, &c., but without success. In the case of diethylaniline, for example, a considerable quantity of a viscid, neutral oil was formed, which had an odour resembling that of oenanthol. When, however, the ester of the bromo-acid was heated with diethylaniline, the reaction appeared to proceed normally.

Ethyl α -bromomethylcyclohexyl acetate (25 grams) was digested for three hours with freshly-distilled diethylaniline (70 grams), care being taken that both substances were quite dry. The dark brown liquid was dissolved in ether and extracted with hydrochloric acid until quite free from diethylaniline, the ethereal solution was filtered from a little tarry matter, dried, and the ether evaporated. The residual oil was then distilled under reduced pressure, when almost the whole quantity passed over at 156—158° (100 mm.). Two different preparations gave the following analytical results :

0·2085 gave 0·5513 CO₂ and 0·1956 H₂O. C = 72·1 ; H = 10·4.

0·1664 „ 0·4416 CO₂ „ 0·1542 H₂O. C = 72·3 ; H = 10·3.

C₁₁H₁₈O₂ requires C = 72·5 ; H = 9·9 per cent.

Ethyl 1-methylcyclohexylidene-4-acetate is a colourless oil, which appears to distil under ordinary conditions without decomposition, and possesses in a marked degree the unpleasant odour characteristic of unsaturated esters. The free acid was obtained by digesting the ester (15 grams) with methyl-alcoholic potash (8 grams KOH), when hydrolysis took place rapidly, and, after a few minutes, water was added and the solution evaporated until quite free from methyl alcohol. The alkaline liquid was cooled with ice and acidified with hydrochloric acid, when a crystalline acid separated, which was collected and twice crystallised from formic acid (D = 1·22) :

0·1619 gave 0·4142 CO₂ and 0·1380 H₂O. C = 69·8 ; H = 9·4.

0·1134 „ 0·2903 CO₂ „ 0·0955 H₂O. C = 69·8 ; H = 9·3.

C₉H₁₄O₂ requires C = 70·1 ; H = 9·1 per cent.

Obtained and purified in this way, *methylcyclohexylidene-4-acetic acid* softens at about 63°, and melts at about 70° ; it is readily soluble in warm formic acid, from which it separates as a satiny, crystalline mass, somewhat resembling benzoic acid. It dissolves readily in benzene or light petroleum, but is almost insoluble in cold water. If,

however, the acid is boiled with a large volume of a water, the filtered solution deposits a voluminous, crystalline mass, which mats together like cotton wool. The solution of the acid in sodium carbonate decolorises permanganate rapidly, even at 0° .

During the course of this investigation, a considerable quantity (about 20 grams) of the above acid was prepared, but, in spite of repeated recrystallisation from various solvents, the melting point was always unsatisfactory. In order to obtain further evidence of the constitution of this acid, 10 grams were oxidised in dilute alkaline solution by ozone, and, as soon as the ozone passed freely, the solution was diluted, acidified, and placed in the ice-chest. After a few days, a small quantity of a crystalline acid had separated, which, after crystallisation from formic acid, melted at 73° , and was found to consist of 1-methylcyclohexyl-4-acetic acid :

0.1240 gave 0.3122 CO_2 and 0.1174 H_2O . $\text{C} = 68.7$; $\text{H} = 10.5$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C} = 69.2$; $\text{H} = 10.2$ per cent.

The quantity of this acid obtained was nearly half a gram, and it is therefore obvious that reduction must have taken place to some extent, probably during the elimination of hydrogen bromide from ethyl bromomethylcyclohexylacetate by diethylaniline. In spite of the analytical data, the methylcyclohexylideneacetic acid described above is evidently not a pure substance, and the melting point given must therefore be considered as quite unreliable.

The principal product of the oxidation of this acid by ozone is a syrup readily soluble in water, and from which, so far, it has not been found possible to isolate anything crystalline.

The authors wish to thank Messrs. G. B. Stones and W. N. Haworth for valuable assistance in carrying out the above experiments.

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