

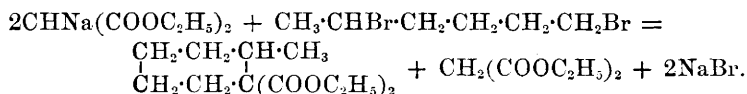
XIII.—*Synthesis of Pentamethylenecarboxylic acid, Hexamethylenecarboxylic acid (Hexahydrobenzoic acid), and Azelaic acid.*

By E. HAWORTH, B.Sc., and W. H. PERKIN, JUN., Ph.D., F.R.S.

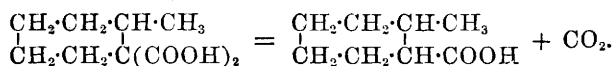
DURING the last few years, the behaviour of benzene derivatives on reduction has been the subject of much investigation, and Baeyer's classical researches in this field (*Annalen*, **245**, 103; **251**, 257; **269**, 145) have shown that, when subjected to the action of sodium amalgam, the phthalic acids yield a variety of interesting derivatives, the end product being in all cases the saturated hexahydro-acids formed by the complete reduction of the benzene ring. Although these acids contain a closed chain of six carbon atoms, they have none of the properties characteristic of benzene derivatives, but behave in almost all respects like saturated open chain acids of the fatty series.

Other hexahydrobenzene derivatives have also been obtained by the reduction of the corresponding benzene derivatives; but only in a very few instances have such compounds been synthetically prepared from substances belonging to the fatty series. One case of this kind, which has a special bearing on the present investigation, is the synthesis of 1:2-methylhexamethylenecarboxylic acid (hexahydro- α -toluic acid; Freer and Perkin, *Trans.*, 1888, **53**, 202), which was carried out in the following manner.

The sodium derivative of ethylic malonate was digested in alcoholic solution with methylpentamethylene dibromide, when reaction readily took place in accordance with the equation



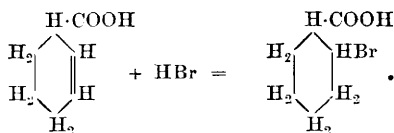
The ethylic methylhexamethylenedicarboxylate was converted by hydrolysis into the corresponding bibasic acid, which, when heated at 200°, was decomposed quantitatively into carbon dioxide and methylhexamethylenecarboxylic acid.



The action of reducing agents on α -toluic acid has not as yet been investigated; and, therefore, it has not been possible to compare the reduced benzene derivative with the synthetical acid; some time since, however, Aschan (*Annalen*, **271**, 231) succeeded in converting

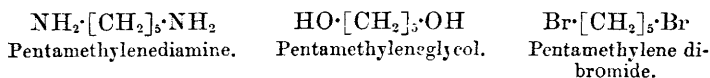
SYNTHESIS OF PENTAMETHYLENECARBOXYLIC ACID, ETC. 87

benzoic acid into hexahydrobenzoic acid, the method used being the following. In the first place, benzoic acid was reduced by excess of sodium amalgam in alkaline solution to Δ^2 -tetrahydrobenzoic acid; and, by treating this acid with hydrobromic acid, it was converted into β -(2)-bromhexahydrobenzoic acid.



Bromhexahydrobenzoic acid is readily reduced by sodium amalgam, yielding hexahydrobenzoic acid (hexamethylenecarboxylic acid). This important acid is very similar in its properties to the methylhexamethylenecarboxylic acid prepared synthetically by the method described above; and it appeared to us that it would be especially interesting to endeavour to obtain hexahydrobenzoic acid synthetically, as it would then be possible to compare the synthetical acid with the reduced benzene derivative.

For this purpose, pentamethylene dibromide, $\text{Br}[\text{CH}_2]_5\text{Br}$, was required, a substance which Gustavson and Demjanoff (*J. pr. Chem.*, **39**, 542) had already prepared from pentamethylenediamine by converting it into the corresponding glycol by the action of silver nitrite, and subsequently treating the glycol with hydrobromic acid.



Before commencing the study of the action of this dibromide on the sodium derivative of ethylic malonate, we wrote to Professor Gustavson, and in reply he informed us that Herr Demjanoff had already instituted experiments in this direction, but did not intend to proceed any further with them, and subsequently Herr Demjanoff not only agreed to allow us to continue this research, but he also very kindly gave us a detailed account of the results which he had obtained in his preliminary experiments.

The yield of pentamethylene dibromide obtained by Gustavson and Demjanoff (*J. pr. Chem.*, **39**, 542) was very small, only about 8 per cent. of the theoretical, and as we required considerable quantities of it, we, in the first place, made numerous experiments with the object of improving the method of preparation, but without success, so that ultimately we prepared our material by a method practically identical with that devised by Gustavson and Demjanoff. The preparation of the dibromide is exceedingly tedious: altogether 1500 grams of trimethylene bromide were used, the conversion of which into pentamethylene dibromide necessitated more than three months' steady

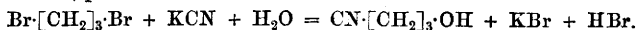
work, the ultimate amount of product obtained being only 90 grams.

The subsequent study of the action of this dibromide on the sodium compound of ethylic malonate yielded very remarkable results, which prove, as we believe, that the substance which was supposed to be comparatively pure pentamethylene dibromide is in reality a mixture of this substance and tetramethylene dibromide, $\text{Br} \cdot [\text{CH}_2]_4 \cdot \text{Br}$, the latter constituting, as it appears, as much as 70—75 per cent. of the whole. It is certainly very difficult to understand how tetramethylene dibromide can be thus produced from pentamethylenediamine; and it will hardly be possible to understand this remarkable method of formation, until a very careful examination of the action of silver nitrite on the hydrochloride of the diamine has been instituted, as the decomposition seems to be very complicated.*

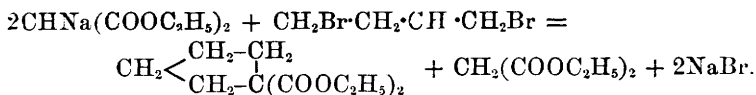
The reasons for assuming that the dibromide obtained by Gustavson and Demjanoff's method is a mixture, will be readily understood from the accompanying short sketch of the results obtained in investigating its action on the sodium derivative of ethylic malonate. In alcoholic solution, action takes place very readily on warming, with separation of sodium bromide and formation of an oily, ethereal salt, which, on distillation, yields, besides regenerated ethylic malonate, two principal fractions, 240—250° (760 mm.) and 270—275° (59 mm.). The fraction 240—250° contains traces of bromine, and, therefore, did not give good results on analysis; when hydrolysed by boiling with alcoholic potash, however, it yields a beautifully crystalline bibasic acid, which, on analysis, gave numbers agreeing sharply with those required by the formula $\text{C}_7\text{H}_{10}\text{O}_4$; this result was confirmed by the analysis of the silver salt, which has the composition $\text{C}_7\text{H}_8\text{Ag}_2\text{O}_4$.

This acid is, therefore, not hexamethylenedicarboxylic acid, the ethereal salt of which would have resulted from the action of pentamethylene dibromide on the sodium derivative of ethylic malonate; but it contains CH_2 less than this acid, and is, therefore, probably pentamethylenedicarboxylic acid, the ethereal salt of which would be produced in the following manner.

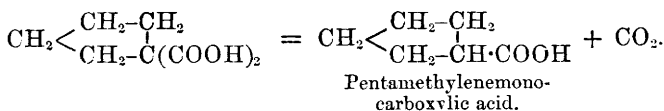
* While this paper was in the press, it occurred to me that this formation of tetramethylene dibromide might be explained as follows. When trimethylene dibromide reacts with potassium cyanide, it may be assumed that the decomposition, to some extent, proceeds thus,



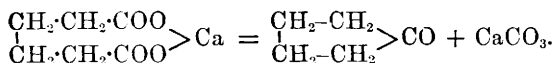
The cyanhydrin, thus produced, would then, on reduction, be converted into hydroxytetramethylethylamine, $\text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{OH}$, the hydrochloride of which, in contact with silver nitrite, would yield tetramethyleneglycol, $\text{OH} \cdot [\text{CH}_2]_4 \cdot \text{OH}$, tetramethylene dibromide being formed from this by the subsequent action of hydrogen bromide.—W. H. P., Jun.



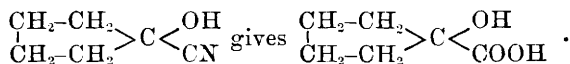
That the action actually takes place in this manner is proved by the following considerations. The bibasic acid of the formula $\text{C}_7\text{H}_{10}\text{O}_4$ does not decolorise potassium permanganate in dilute alkaline solution; it is, therefore, a saturated acid, and must contain a closed carbon chain; when heated above its melting point, it rapidly decomposes, carbon dioxide being evolved and an oily acid produced, which distils constantly at $214\text{--}215^\circ$. The analysis of this acid and its silver salt prove that it is a monobasic acid of the formula $\text{C}_6\text{H}_{10}\text{O}_2$, and its formation, on the assumption that the bibasic acid was pentamethylenedicarboxylic acid, may be represented thus



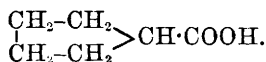
The properties of this monobasic acid coincide so exactly with those which could have been predicted for pentamethylenecarboxylic acid, that we had no hesitation in adopting this view of its constitution; curiously enough, however, while this research was in progress and nearing completion, Wislicenus and Gärtner (*Annalen*, **275**, 333), succeeded in preparing pentamethylenecarboxylic acid by a series of reactions which leave no doubt as to the constitution of their product. By the distillation of anhydrous calcium adipate, these chemists prepared, in the first place, the ketone of adipic acid (ketopentamethylene),



When this ketone is poured on to powdered potassium cyanide, and concentrated hydrochloric acid is added, the hydroxycyanide first produced is hydrolysed and converted into α -hydroxypentamethylene carboxylic acid.



This hydroxy-acid is readily reduced by heating with hydriodic acid and phosphorus in a sealed tube at $190\text{--}195^\circ$, and is thus converted into pentamethylenecarboxylic acid,



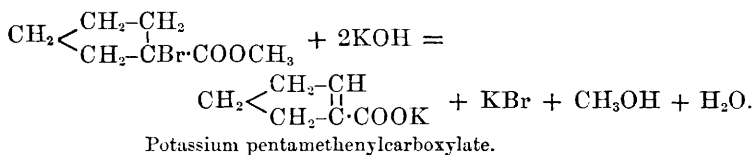
The same acid was also obtained by converting ketopentamethylene

into pentamethylenic alcohol by reduction; the alcohol, when treated with hydriodic acid, yields the corresponding iodide, which, when digested with potassium cyanide, is converted into pentamethylenic cyanide; from this, pentamethylenecarboxylic acid is obtained by hydrolysis.

At our request, Professor Wislicenus was kind enough to send us a small quantity of his acid in order to enable us to decide definitely as to its identity with our acid. We converted his specimen into the acid chloride, from which we prepared the anilide, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_5$, which crystallises from alcohol in a highly characteristic manner, and melts sharply at $159-160^\circ$. On repeating the experiment under precisely similar conditions, with our pentamethylenecarboxylic acid, we obtained an anilide which crystallised in the same characteristic manner, melted at $159-160^\circ$, and on careful comparison was found to be identical with the anilide of Wislicenus and Gärtner's acid.

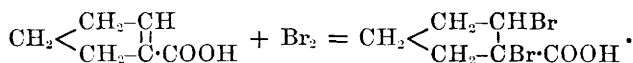
There can, therefore, be no doubt that the acid $C_6H_{10}O_2$ obtained by us in the manner described above is in reality pentamethylene-carboxylic acid.

During the course of this investigation the action of bromine in the presence of phosphorous on pentamethylenecarboxylic acid was studied, and in this way some very interesting results were obtained. If the product is poured into methyl alcohol, methylic α -bromopentamethylenecarboxylate, a colourless oil boiling at $122-125^\circ$ (60 mm.), is produced; and this, when treated with aqueous potash, yields Δ^1 -pentamethenylcarboxylic* acid.



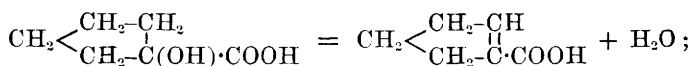
This acid melts at $119-121^\circ$, and in many of its properties shows a marked resemblance to benzoic acid, from which, however, it is sharply differentiated by its instability towards alkaline permanganate solution, which it instantaneously decolorises.

When subjected to the action of bromine vapour, pentamethenylcarboxylic acid is converted into a saturated dibromo-addition product, $C_6H_8Br_2O_2$; this is evidently dibromopentamethylenecarboxylic acid produced according to the equation



* This name is given to the acid in order to indicate its connection with the pentamethenyl derivatives described by Wislicenus and Gärtner (*Annalen*, **275**, 331).

By treating hydroxypentamethylenecarboxylic acid with hydriodic acid and phosphorus at 150°, Wislicenus and Gärtner (*loc. cit.*, p. 337) also obtained, in almost quantitative yield, an acid $C_6H_8O_2$, which melted at 120°, and was readily volatile with steam. There is no doubt that this acid is identical with pentamethylenecarboxylic acid, and its formation is readily understood, if it be assumed that the hydriodic acid of the strength employed acted simply as a dehydrating agent, thus,



the above mentioned chemists, indeed, discuss this possibility, but consider it very improbable that the reaction proceeds in this way without, however, giving any cogent reasons against this assumption; they are, moreover, unable to suggest any formula, other than the above, which corresponds with the properties of the acid.

The next step was to determine whether by the action of the mixed bromides on the sodium derivative of ethylic malonate any hexamethylene derivative had been formed. In order to decide this point, the various mother liquors of the pentamethylenedicarboxylic acid were evaporated to dryness and the residue was distilled. The colourless oily distillate, after treatment with permanganate to remove unsaturated compounds, was very carefully fractionated, and in this way rather more than 3 grams of a colourless acid, boiling at 231—233°, was obtained. It solidified in a freezing mixture, and on analysis gave numbers agreeing with the formula $C_7H_{12}O_2$, a result which was confirmed by the analysis of the silver salt, $C_7H_{11}AgO_2$.

That this acid is hexahydrobenzoic acid (hexamethylenecarboxylic acid), $CH_2 < \begin{array}{c} CH_2-CH_2 \\ CH_2-CH_2 \end{array} > CH \cdot COOH$, may be said to be clearly proved by the following facts:—

1. It has the same boiling point as Aschan's hexahydrobenzoic acid.
2. It is a saturated acid, since its solution in dilute sodium carbonate does not decolorise potassium permanganate.
3. The mixed dibromides from pentamethylenediamine undoubtedly contain considerable quantities of pentamethylene dibromide, as is proved by the synthesis of azelaic acid (see below), for the production of which the presence of this dibromide is necessary: as, therefore, this dibromide is present, it would be most remarkable if by its action on the sodium derivative of ethylic malonate, some ethylic hexamethylenedicarboxylate were not produced; and the latter, on hydrolysis and subsequent decomposition by heat, must yield hexahydrobenzoic acid (compare Freer and Perkin, *Trans.*, 1888, 53, 206).

The formation of hexahydrobenzoic acid by this reaction is further confirmed by Demjanoff, who (as he states in the description of his experiments which he kindly sent us) obtained an ethereal salt boiling at 244—255°, which, on hydrolysis, yielded a bibasic acid melting and decomposing at 145—160°; on analysis, it gave numbers agreeing with the formula of hexamethylenedicarboxylic acid, $C_8H_{10}(COOH)_2$.

Found, C = 55.6; H = 7.2. Theory, C = 55.8; H = 7.

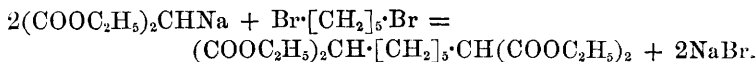
This bibasic acid, on distillation, yielded an oily monobasic acid, the calcium salt of which contained water of crystallisation, and, after drying, gave numbers agreeing with the formula $(C_6H_{11}O_2)_2Ca$:

Found, Ca = 13.6 per cent. Theory, 13.6 per cent.

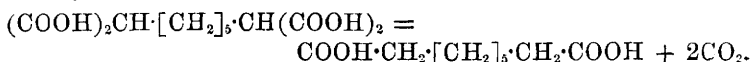
According to Aschan, the calcium salt of hexahydrobenzoic acid has the formula $(C_6H_{11}O_2)_2Ca + 4H_2O$. There can be no doubt that the latter was hexahydrobenzoic acid, and its synthesis from pentamethylene dibromide was, therefore, first accomplished by Demjanoff.

Synthesis of Azelaic acid.

When the product of the action of the mixed dibromides on the sodium derivative of ethylic malonate is fractionated, the temperature rises rapidly after the fraction 240—250°, which has just been described, has passed over, and if the distillation be continued under reduced pressure, a quantity of a thick oil is obtained, boiling at 270—275° (50 mm.). This oil, which constitutes about 25 per cent. of the product, is ethylic heptanetetracarboxylate, formed by the action of 1 mol. of pentamethylene dibromide on 2 mols. of ethylic sodiomalonate.



On hydrolysis with alcoholic potash, this ethereal salt yields an oily tetrabasic acid, which, when heated at 200°, is readily decomposed into carbon dioxide and a dark brown, crystalline acid. The latter crystallises from water in glistening plates, melts at 107°, and is in all respects identical with azelaic acid, as was clearly proved by a direct comparison with a sample of the latter obtained by the oxidation of Chinese wax. The synthesis of azelaic acid has not been accomplished previously, and its formation by the action of heat on heptanetetracarboxylic acid is readily understood with the aid of the following equation.



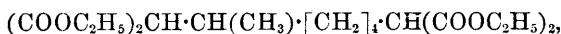
No trace of any other acid, suberic acid for example, was formed

in this reaction. It is very remarkable that tetramethylene dibromide and pentamethylene dibromide should differ so markedly in their behaviour towards ethylic sodiomalonate: that is, that pentamethylene dibromide should yield, besides ethylic hexamethylenedicarboxylate, also ethylic heptanetetracarboxylate, but that tetramethylene dibromide under precisely similar conditions should be quantitatively converted into ethylic pentamethylenedicarboxylate, without a trace of ethylic hexanetetracarboxylate,

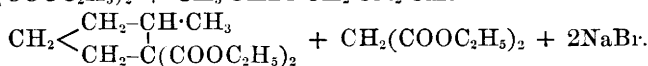
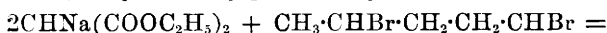


being formed.

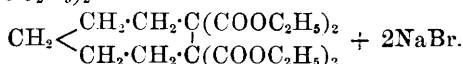
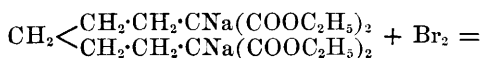
In connection with this point, it is interesting to note that methylpentamethylene dibromide, $\text{CH}_3\cdot\text{CHBr}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Br}$, and methyltetramethylene dibromide, $\text{CH}_3\cdot\text{CHBr}\cdot[\text{CH}_2]_2\cdot\text{CH}_2\text{Br}$, behave in a precisely similar manner when heated with ethylic sodiomalonate; the former (Freer and Perkin, *Trans.*, 1888, **53**, 202, 215) yielding ethylic methylhexamethylenedicarboxylate and considerable quantities of ethylic iso-octanetetracarboxylate,*



whereas in the case of the latter (Colman and Perkin, *Trans.*, 1888, **53**, 185) ethylic methylpentamethylenedicarboxylate alone is formed.



As we were in possession of several grams of ethylic heptanetetracarboxylate, we studied the action of bromine on the disodium derivative of this ethereal salt, in order to determine whether it were possible in this way to accomplish a synthesis of a 7-carbon ring.



The product, on hydrolysis, gave an oily acid, which decomposed at 200°, carbon dioxide being evolved; the oily residue, after a time, deposited crystals of azelaic acid; unfortunately we were not able to isolate any other crystalline substance from the mother liquor of these crystals.

Experiments on the action of bromine on the disodium derivative of ethylic iso-octanetetracarboxylate which were instituted some time since by Freer and one of us (*loc. cit.*) gave a similar negative result. As, however, it has been shown (Kipping and Perkin, *Trans.*, 1891, **59**, 214—229; Wislicenus and Meyer, *Annalen*, **275**, 356—366)

* Previously erroneously called ethylic isoeptanetetracarboxylate.

that a 7-carbon ring is capable of existence, it is very probable that if these experiments were repeated under different conditions a more satisfactory result would be attained.

The results of this research prove conclusively that the dibromide produced from the product of the action of silver nitrite on the hydrochloride of pentamethylenediamine contains, besides pentamethylene dibromide as its chief constituent, tetramethylene dibromide. It is, therefore, possible that the hydrocarbon obtained by Gustavson and Demjanoff (*Ber.*, **24**, 4002) by the action of sodium on these mixed dibromides, and which boiled at 35° , was not pure pentamethylene as these chemists supposed, but a mixture of this hydrocarbon with tetramethylene.

Wislicenus and Hentzschel (*Annalen*, **275**, 327) prepared a hydrocarbon, which is probably pentamethylene, by reducing an alcoholic solution of pentamethylenic iodide, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{CH}_2-\text{CHI} \end{smallmatrix}$, with zinc and hydrochloric acid; it boiled at $50.25-50.75^\circ$, or about 15° higher than Gustavson and Demjanoff's product.

The boiling point of pentamethylene may be calculated in various ways, as for example, by subtracting the difference between the boiling points of heptamethylene ($98-101^\circ$) and of hexamethylene (80°) from that of the latter the calculated boiling point being thus about 50° , a value agreeing with that found by Wislicenus and Hentzschel. It is, however, remarkable that the unsaturated hydrocarbon pentamethenylene, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2-\text{CH} \\ || \\ \text{CH}_2-\text{CH} \end{smallmatrix}$, prepared by Wislicenus and Gärtner, which should boil higher than pentamethylene, was found to boil at 45° .

Action of Silver Nitrite on Pentamethylenediamine Hydrochloride.

Gustavson and Demjanoff (*J. pr. Chem.*, ii, **39**, 542), who first studied this decomposition, obtained as a result a substance boiling at 162° under a pressure of 30 mm., which they concluded was pentamethylene glycol, $\text{C}_5\text{H}_{10}(\text{OH})_2$; by heating this with fuming hydrobromic acid in sealed tubes at 100° , they prepared a dibromide boiling at $204-206^\circ$, which, on analysis, gave numbers agreeing with the formula $\text{C}_5\text{H}_{10}\text{Br}_2$.

The yield of the glycol and bromide was, however, but small, 17 grams of the latter being obtained from 80 grams of pentamethylenediamine, whereas, according to theory, the yield should have been 180 grams. As it seemed likely that in the course of our experiments we should require considerable quantities of this dibromide, we made in the first place, numerous experiments with the object of improving

the yield, using silver nitrite, sodium nitrite, free nitrous acid, &c., under a great variety of conditions, but the results were unsatisfactory. Ultimately, we found it best either to follow the method of Gustavson and Demjanoff exactly, or, in any case, to introduce only very slight modifications. The method of procedure finally adopted was the following:—To a fairly strong solution of pentamethylenediamine hydrochloride rather more silver nitrite was added than the amount required by theory. The nitrite was made into a thin paste with water and added little by little to the solution of the hydrochloride, the mixture being kept well cooled during the addition; care is necessary in performing this operation, as, owing to the evolution of nitrogen, the mixture froths very much, especially if the solution be too concentrated. Next day the mixture was heated on the water bath in a reflux apparatus for one hour; the precipitated silver chloride was then filtered off, washed with a little water, and the combined liquors concentrated by distillation in a flask connected with a fractionating column so as to prevent the glycol being carried over with the steam. In this operation, a small quantity of oil of very unpleasant odour passed over with the water, but was not obtained in quantity sufficient for further examination.

The residual liquid, after the bulk of the water had passed over, was made into a thick paste with anhydrous potassium carbonate, and the glycol which separated as an oil was removed by extracting six times with ether. On distilling off the ether, a considerable quantity of a brown oil remained, which was alkaline and smelt of ammonia. This was mixed with 10 times its volume of fuming hydrobromic acid (saturated at 0°), which at once acted on it, producing a hissing sound and dense, white fumes, a considerable amount of heat being generated. The mixture was heated on the water bath in a flask attached to a reflux condenser for about two hours, then resaturated with hydrogen bromide, sealed up in tubes, and heated in boiling water for four hours.

When cold, the contents of the tubes were poured into water, the heavy oily product extracted with ether, the ethereal solution washed with water and sodium carbonate solution, and dried over calcium chloride. On distilling off the ether, a dark brown liquid remained which had the odour characteristic of the higher dibromides in the fatty series. The bromine determination was made by Carius' method.

0.2398 gave 0.3925 AgBr. $\text{Br} = 69.63$.

$\text{C}_5\text{H}_{10}\text{Br}_2$ requires $\text{Br} = 69.56$ per cent.

This result agrees closely with that obtained by Gustavson and Demjanoff, the mean of their analyses giving $\text{Br} = 70.1$ per cent. In spite of the close agreement of the analytical numbers with

those required by the formula $\text{Br}[\text{CH}_2]_5\text{Br}$, the result of our subsequent experiments with this bromide proves that it is not by any means pure pentamethylene dibromide, but contains only approximately 25 per cent. of the latter, the remainder being tetramethylene dibromide, $\text{Br}[\text{CH}_2]_4\text{Br}$; a mixture of this kind contains 72.89 per cent. of bromine.

As it is quite usual for a dibromide such as this, owing to slight decomposition and consequent loss of hydrogen bromide, to give numbers from 1 to 2 per cent. below the theoretical, it is not surprising that the numbers found in the present case are also inaccurate.

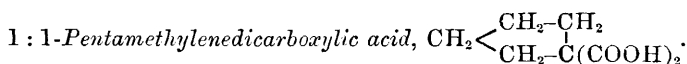
Action of the Mixed Tetramethylene and Pentamethylene Dibromides on the Sodium Derivative of Ethylic Malonate.

8 grams of sodium were dissolved in 100 grams of absolute alcohol, the solution well cooled, and a mixture of 40 grams of the bromide and 56 grams of ethylic malonate added. At ordinary temperatures, no change appears to take place except on long standing, but, on gently warming, the action soon begins, sodium bromide separates, and the liquid boils vigorously for some time; as soon as the reaction becomes sluggish, the mixture is heated on the water bath in a reflux apparatus for about two hours, allowed to cool, poured into twice its volume of water, and then extracted with ether four times. The ethereal solution is well washed with water to free it from alcohol, dried over calcium chloride, and the ether distilled off. Two experiments were made in this way, the total amount of bromide used being 90 grams.

The products from both these experiments were mixed and fractionated under reduced pressure (50 mm.), and in this way separated into three fractions boiling (1) between 130° and 145° ; (2) between 155° and 180° ; and (3) between 180° and 275° .

A small portion of fraction 2, which boiled at $162\text{--}165^\circ$ under a pressure of 30 mm., was collected for analysis, but it did not give satisfactory numbers, owing to the fact that it contained traces of bromine.

The two fractions $130\text{--}180^\circ$ were then mixed, and distilled under ordinary pressure, when they were separated into two parts, the one boiling below 210° and consisting almost entirely of ethylic malonate, the other a thick oil boiling at $210\text{--}250^\circ$. The further purification of fraction 3 boiling at $180\text{--}285^\circ$ (50 mm.) will be described later (p. 104).



The fractions of the products of the action of the mixed bromides on ethylic sodiomalonate boiling at $200\text{--}210^\circ$ and $210\text{--}250^\circ$ cannot

be readily purified by fractional distillation, owing to the fact that the oil contains bromine which cannot readily be removed, and the presence of which renders the results of analysis valueless; for this reason, the oils were directly submitted to hydrolysis and the resulting acids further examined.

Fraction 200—210°, consisting principally of ethylic malonate, and weighing 37 grams, was mixed with a strong solution of 40 grams of pure caustic potash in methylic alcohol, and heated in a reflux apparatus for two hours. The alkaline solution was then diluted with water, evaporated on a water bath till free from alcohol, and the residue cooled, acidified with dilute sulphuric acid, and extracted five times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a small quantity of crude pentamethylenedicarboxylic acid, the malonic acid remaining almost entirely in the aqueous solution. This was subsequently worked up with the principal quantity obtained from the fraction 210—250°.

During the hydrolysis of the fraction 210—250°, weighing 55 grams, with 40 grams of potash dissolved in methylic alcohol, a considerable quantity of a crystalline potassium salt separated. The whole dissolved readily in water, and on evaporating, acidifying, and extracting with ether, as described above, 42 grams of a brown, oily acid was obtained, which, on standing over sulphuric acid in a vacuum, deposited crystals, and gradually became semi-solid. This crude product was spread on biscuit ware, and when the brownish, oily mother liquor had been entirely absorbed, the colourless, crystalline mass which remained was recrystallised several times from water. It then formed colourless prisms, which, on analysis, gave results agreeing with the formula of pentamethylenedicarboxylic acid, $C_5H_8(COOH)_2$.

0.1570 gave 0.3060 CO_2 and 0.0910 H_2O . $C = 53.16$; $H = 6.44$.

0.1281 „ 0.2493 „ „ 0.0752 „ $C = 53.08$; $H = 6.53$.

$C_5H_8(COOH)_2$ requires $C = 53.16$; $H = 6.33$ per cent.

1:1-Pentamethylenedicarboxylic acid is readily soluble in hot, but comparatively sparingly in cold, water. It crystallises from water in colourless prisms, which, when heated in a capillary tube, melt at about 184—185°, undergoing decomposition into carbon dioxide and pentamethylenemonocarboxylic acid; this decomposition also takes place to some extent when the aqueous solution of the acid is evaporated, as the solution acquires a strong odour of the monocarboxylic acid. It is readily soluble in alcohol and ether, sparingly in benzene, and almost insoluble in light petroleum. The solution of this acid in sodium carbonate does not decolorise potassium permanganate, even on long standing, showing that the acid is saturated.

Silver Salt of 1:1-Pentamethylenedicarboxylic acid.—This was ob-

tained as a white, amorphous precipitate, on adding silver nitrate to a neutral solution of the ammonium salt of the acid; it is very sparingly soluble in water. After being well washed, it was dried over sulphuric acid in a vacuum and analysed.

0.2893 gave 0.2418 CO₂, 0.0551 H₂O and 0.1668 Ag. C = 22.79;

H = 2.11; Ag = 57.66.

0.3157 gave 0.1816 Ag. Ag = 57.52.

C₅H₈(COOAg)₂ requires C = 22.58; H = 2.15; Ag = 58.06 per cent.

Pentamethylenemonocarboxylic acid, $\text{CH}_2 < \begin{array}{l} \text{CH}_2-\text{CH}_2 \\ | \\ \text{CH}_2-\text{CH}\cdot\text{COOH} \end{array}$

When pure pentamethylenedicarboxylic acid is heated in a distilling flask, carbon dioxide is evolved, and an oil consisting of pure pentamethylenemonocarboxylic acid distils over constantly at 214–215°.

As the quantity of pure dicarboxylic acid at our disposal was small, we extracted, with ether, the biscuit ware containing the crude oily dicarboxylic acid (p. 97), evaporated the ethereal solution, and decomposed the brownish residue, by heating it at 200° until no more carbon dioxide was evolved. On distilling the residual oily acid, the whole (20 grams) passed over between 210° and 230° as a very unpleasant-smelling oily liquid which did not solidify when cooled in a freezing mixture. This acid is a mixture of pentamethylenedicarboxylic and hexamethylenedicarboxylic acids, the former being present in by far the larger quantity. The acids are, however, contaminated with some impurity which causes the alkaline solution to decolorise permanganate solution in the cold.

In order to remove this impurity, the mixed acids were dissolved in dilute sodium carbonate solution, cooled below 0°, and permanganate solution (1 per cent.) added until the pink colour was permanent. The excess of permanganate was then removed by adding a few drops of alcohol, the product filtered, and the filtrate evaporated to a small bulk. The acids were then liberated by adding dilute sulphuric acid, extracted with pure ether, and the ethereal solution, dried over calcium chloride, was evaporated. The residual oil (17 grams), submitted to very careful and repeated fractional distillation, gave about 9 grams of oil boiling constantly at 214–215° (the higher fraction is mentioned later), which, on analysis, gave results agreeing with the formula of pentamethylenemonocarboxylic acid.

0.1998 gave 0.4612 CO₂ and 0.1585 H₂O. C = 62.95; H = 8.80.

C₅H₈COOH requires C = 63.16; H = 8.77 per cent.

The silver salt, C₆H₉O₂Ag, obtained by adding silver nitrate to a neutral solution of the ammonium salt, as a voluminous, white, amor-

phous precipitate, was well washed with water, dried over sulphuric acid in a vacuum, and analysed.

0.1496 gave 0.1778 CO₂, 0.0582 H₂O, and 0.0730 Ag. C = 32.41; H = 4.32; Ag = 48.79.

0.1872 gave 0.0908 Ag. Ag = 48.5.

C₅H₉COOAg requires C = 32.58; H = 4.07; Ag = 48.86 per cent.

The relative density, magnetic rotation, and refractive power determinations were carried out by Dr. W. H. Perkin, sen., who obtained the following results.

Pentamethylenemonocarboxylic acid.

The density determinations gave—

$d\ 4^{\circ}/4^{\circ}$	1.0540.	$d\ 15^{\circ}/15^{\circ}$	1.0452.
$d\ 10^{\circ}/10^{\circ}$	1.0489.	$d\ 20^{\circ}/20^{\circ}$	1.0416.
$d\ 25^{\circ}/25^{\circ}$	1.0385.		

The refractive power determinations gave—

$t.$	$\mu_A.$	$\mu_C.$	$\mu_D.$	$\mu_F.$	$\mu_G.$
17.7°	1.44759	1.45040	1.45280	1.45858	1.46314
	$\frac{\mu-1}{d}p.$				
	48.966	49.273	49.536	50.168	50.668

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
18.5°	0.9633	5.851
18.5	0.9708	5.896
18.5	0.9738	5.914
18.5	0.9669	5.873
18.5	0.9753	5.924
Average 18.5	0.9700	5.891

As in the case of all the saturated closed carbon chain carboxylic acids which have so far been examined, the magnetic rotation is very low.

Pentamethylenecarboxylic Chloride, C₅H₉COCl.

This was prepared by heating the pure monocarboxylic acid (2 grams) with twice its volume of phosphorus trichloride for about 10 minutes, and after allowing the mixture to stand for about an hour, decanting the liquid from the layer of phosphorous acid, and submitting it to fractional distillation. As soon as the phosphorus trichloride had passed over, the thermometer rose rapidly to 160°,

between which temperature and 162° the whole distilled. This fraction was analysed by Carius' method.

0.1571 gave 0.1652 AgCl. Cl = 26.09.

C_6H_9OCl requires Cl = 26.79 per cent.

This chloride has a very similar smell, and is generally very similar in properties to the corresponding chloride of tetramethylenecarboxylic acid $\begin{array}{c} CH_2-CH_2 \\ | \quad | \\ CH_2-CH \cdot COCl \end{array}$ which boils at 139° .

Anilide of Pentamethylenecarboxylic acid, $C_5H_9 \cdot CO \cdot NH \cdot C_6H_5$.—In order to prepare this, the chloride of pentamethylenecarboxylic acid was added drop by drop to a large excess of pure aniline, the whole being stirred with a glass rod during the operation. As soon as the vigorous action had moderated, the mixture was heated on a water bath for a few minutes, poured into water, and dilute hydrochloric acid added to dissolve the excess of aniline. The resulting crystalline precipitate was well washed with water, dried on a porous plate, recrystallised several times from alcohol, and analysed.

0.1975 gave 13.1 c.c. moist nitrogen at 17° and 762 mm. N = 7.71.

$C_5H_9 \cdot CO \cdot NH \cdot C_6H_5$ requires N = 7.40 per cent.

The anilide of pentamethylenecarboxylic acid crystallises from alcohol in magnificent glistening prisms, resembling sugar in appearance. It melts at 159 — 160° , and when strongly heated distils apparently without decomposing. It is readily soluble in alcohol, benzene, chloroform, and acetic acid, less so in ether and light petroleum.

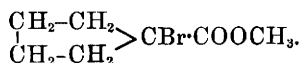
Professor Wislicenus was kind enough to send us a small quantity of pure pentamethylenecarboxylic acid prepared from the ketone of adipic acid (p. 89). In order to determine whether this was identical with our acid, we converted it into the acid chloride by treatment with phosphorus trichloride, and prepared from the fractioned chloride the anilide under exactly the same conditions as those given above. The anilide, after two crystallisations from alcohol, melted at 159 — 160° , and gave the following results on analysis.

0.2200 gave 13.9 c.c. moist nitrogen at 17° and 766 mm. N = 7.39.

$C_5H_9 \cdot CO \cdot NH \cdot C_6H_5$ requires N = 7.40 per cent.

A very careful comparison of this product with the anilide obtained from our acid proved that the substances were identical.

Methylic α -Monobromopentamethylenecarboxylate,



The action of bromine on pentamethylenecarboxylic acid was studied in the first instance, with the view of showing that, when treated in this way, the acid behaved as a saturated acid, forming a monobromo-substitution and not a dibrom-additive product. 5 grams of pentamethylenecarboxylic acid (b. p. 214—217°) was mixed with 0.3 gram of dry amorphous phosphorus in a flask connected with a reflux condenser, and 15 grams of dry bromine added in small portions at a time. The decomposition took place at once, quantities of hydrogen bromide being evolved. As soon as the violence of the action had moderated, the whole was heated on a water bath for five hours, the condenser then removed, and the heating continued until the excess of bromine had been driven off.

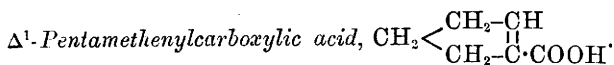
The dark-coloured product was converted into the methylic salt and not into the acid, as it was thought that the former would be more readily purified. For this purpose, the oil was added to excess of methylic alcohol, and after standing for an hour, the alcoholic solution was poured into water. The oily methylic salt was now extracted with ether, and the ethereal solution, after being well washed with water and dilute sodium carbonate solution, was dried over anhydrous potassium carbonate. On distilling off the ether, a dark brown oil was left, which, on being purified by fractionation under reduced pressure, yielded a colourless oil; this, on analysis, gave the following results.

0.3203 gave $\text{AgBr} = 0.2960$. Br = 39.3.

0.2326 „ $\text{AgBr} = 0.2165$. Br = 38.8.

$\text{C}_6\text{H}_7\text{Br} \cdot \text{COOCH}$ requires Br = 38.8 per cent.

Methylic α -bromopentamethylenecarboxylate is a colourless oil which boils at 122—125° (60 mm.), and is specifically heavier than water. In its odour and general properties it closely resembles the corresponding tetramethylene derivative (Trans., 1892, **61**, 43).



This interesting unsaturated acid is formed when methylic monobromopentamethylenecarboxylate is acted on by aqueous potash, as explained in the introduction (p. 90). In order to prepare it, methylic monobromopentamethylenecarboxylate was mixed with strong potash solution (sp. gr. 1.2) and shaken from time to time until it had almost entirely dissolved, an operation which took about

two days. The solution was then heated to boiling for half an hour, cooled well, acidified, and extracted five times with pure ether. The ethereal solution was dried with calcium chloride, and evaporated, when a light brown oil was left, which, after a time, solidified almost entirely. The crystals were freed from oily impurity by spreading the mass on a porous plate, and recrystallising three times from water to which a little purified animal charcoal was added. In this way beautiful, colourless crystals were obtained.

0.1352 gave 0.3144 CO_2 and 0.0870 H_2O . $\text{C} = 64.22$; $\text{H} = 7.25$.

$\text{C}_6\text{H}_5\text{O}_2$ requires $\text{C} = 64.28$; $\text{H} = 7.14$ per cent.

The analysis and general properties of this acid, and especially its behaviour when treated with bromine (see below), leave scarcely any doubt that it is Δ^1 -pentamethenylcarboxylic acid. When heated in a capillary tube, the acid softens at about 115° , and melts not quite sharply at 119 – 121° . It is readily soluble in hot water, alcohol, ether, and light petroleum, but only sparingly in cold water. It dissolves easily in alkalis and alkali carbonates, the cold solution in dilute sodium carbonate decolorising permanganate instantaneously, showing that the acid is unsaturated.

Pentamethenylcarboxylic acid crystallises from its solution in hot water or hot light petroleum in glistening plates, which very closely resemble benzoic acid in appearance. It is also remarkable that not only are the melting points of the two acids identical, but also that pentamethenylcarboxylic acid sublimes with great readiness even at 100° in very much the same way as benzoic acid. Pentamethenylcarboxylic acid is, without doubt, identical with the acid $\text{C}_6\text{H}_5\text{O}_2$, of which Wislicenus and Gärtner (*Annalen*, **275**, 337) obtained an almost quantitative yield by heating hydroxy-pentamethylenecarboxylic acid with feebly fuming hydriodic acid and phosphorus at 150° (see p. 91).

Dibromopentamethylenecarboxylic acid, $\text{CH}_2 \begin{array}{c} \text{CH}_2\text{-CHBr} \\ | \\ \text{CH}_2\text{-CBr-COOH} \end{array}$.

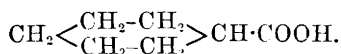
In order to obtain further evidence in support of the view of the constitution of pentamethenylcarboxylic acid adopted in the preceding section, the action of bromine on this acid was carefully investigated. 0.06 gram of the pure acid was placed on a watch glass under a bell jar, and exposed to the action of bromine vapour for 10 hours; the excess of bromine was then removed by allowing the dark brown liquid product to remain over potash in a vacuum for 24 hours. In this way an almost colourless, crystalline mass was obtained, which, after recrystallisation from light petroleum, gave, on analysis, numbers agreeing with the formula of dibromopentamethylene-carboxylic acid.

0.0984 gave 0.1358 AgBr. Br = 58.81.

$C_6H_8Br_2O_2$ requires Br = 58.82 per cent.

Dibromopentamethylenecarboxylic acid is readily soluble in ether, alcohol, chloroform, benzene, and hot light petroleum, sparingly so in the latter solvent in the cold, and almost insoluble in water. It crystallises from light petroleum in colourless leaflets, which, when heated in a capillary tube, soften at 127° , and melt at about 134° . A freshly prepared solution of the acid in sodium carbonate does not decolorise permanganate, but it does so after standing for some time owing to slight decomposition. When boiled with water, the acid first melts, and then dissolves completely, the solution now containing much hydrobromic acid.

Hexamethylenemonocarboxylic acid (Hexahydrobenzoic acid),



When crude pentamethylenedicarboxylic acid is distilled, and the oily distillate repeatedly fractioned, the principal product obtained is pentamethylenecarboxylic acid, boiling at $214-215^\circ$. But there is also a considerable quantity of a higher fraction, boiling between 215° and 235° ; this, when submitted to repeated and careful fractionation, gave about 3 grams of a colourless oil, which distilled between 232° and 234° . On analysis, it gave the following numbers.

0.1320 gave 0.3164 CO_2 and 0.1116 H_2O . C = 65.37; H = 9.39.

$C_6H_{11} \cdot COOH$ requires C = 65.62; H = 9.38 per cent.

The silver salt of this acid was obtained as a white, amorphous precipitate on adding silver nitrate to the neutral solution of the ammonium salt; after washing it well with water, and drying over sulphuric acid in a vacuum, it was analysed.

0.2010 gave 0.2613 CO_2 , 0.0868 H_2O , and 0.0926 Ag. C = 35.45;

H = 4.79; Ag = 46.07.

$C_6H_{11} \cdot COOAg$ requires C = 35.74; H = 4.69; Ag = 45.95 per cent.

These results agree closely with those required for hexahydrobenzoic acid, and there is every reason to believe that the two are identical. Aschan (*Annalen*, **271**, 260), who prepared hexahydrobenzoic acid from benzoic acid, gives the boiling point of the former as $232-233^\circ$, and the melting point at 28° , and states that the acid does not decolorise potassium permanganate in dilute sodium carbonate solution. Our acid distilled at $232-234^\circ$, and was also indifferent to permanganate. When cooled in a freezing mixture, it solidified, but gradually liquefied again at ordinary temperatures. This difference in melting point is obviously due to the presence of some slight

impurity; but, owing to the small amount of material at our disposal, we were not able to remove it.

Ethyllic Heptane- w_2w_2 -tetracarboxylate,
 $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2.$

In fractioning the product of the action of the crude dibromides on ethylic sodiomalonate, a thick oil was obtained boiling at 180—285° (50 mm.), and from this, on redistilling, an almost colourless fraction boiling at 270—275° (50 mm.) was isolated. This, on analysis, gave the following results.

0.1758 gave 0.3754 CO_2 and 0.1291 H_2O . $\text{C} = 58.24$; $\text{H} = 8.16$.

$\text{C}_{19}\text{H}_{32}\text{O}_8$ requires $\text{C} = 58.76$; $\text{H} = 8.25$ per cent.

This substance is ethylic heptane- w_2w_2 -tetracarboxylate, formed by the action of pentamethylene dibromide on 2 mols. of ethylic sodiomalonate, as explained in the introduction (p. 92).

It is an almost colourless oil which appears to undergo very slight decomposition when distilled under the ordinary pressure. When added to an ethereal solution of sodium ethoxide, a yellow, flocculent sodium derivative is precipitated; this probably has the constitution $(\text{COOC}_2\text{H}_5)_2\text{CNa}\cdot[\text{CH}_2]_3\cdot\text{CNa}(\text{COOC}_2\text{H}_5)_2$.

Hydrolysis of Ethylic Heptanetetracarboxylate. Synthesis of Azelaic acid, $\text{COOH}\cdot[\text{CH}_2]_7\cdot\text{COOH}$.

This ethereal salt was readily hydrolysed by boiling with excess of alcoholic potash, the action being complete after heating for half an hour on a water bath. In order to isolate the product, water was added, the solution evaporated on a water bath until free from alcohol, acidified, and extracted several times with pure ether. The ethereal solution after drying over calcium chloride and evaporating deposited a thick, pale yellow oil, probably heptanetetracarboxylic acid; it did not crystallise, and therefore was not analysed.

When heated at 200°, this thick, oily acid readily decomposed, with evolution of carbon dioxide; the residual oil, which became nearly solid on standing, was readily purified by dissolving it in boiling water and decolorising by means of animal charcoal. Beautiful, colourless crystals separated from the hot concentrated solution as it cooled; after recrystallisation, it melted at 105—107°. Its identity with azelaic acid was established by a direct comparison with a sample of the latter, prepared by the oxidation of Chinese wax. The analysis gave the following results.

0.1102 gave 0.2301 CO_2 and 0.842 H_2O . $\text{C} = 57.03$; $\text{H} = 8.49$.

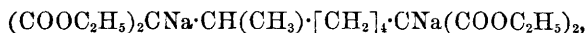
$\text{C}_9\text{H}_{16}\text{O}_4$ requires $\text{C} = 57.44$; $\text{H} = 8.51$ per cent.

The silver salt, prepared from the neutral solution of the ammonium salt by precipitating with silver nitrate, is a white, amorphous powder, and gave the following results on analysis.

- I. 0.1298 gave 0.1240 CO₂, 0.0434 H₂O, and 0.0686 Ag. C = 26.06; H = 3.75; Ag = 53.60.
 II. 0.2296 gave 0.2232 CO₂, 0.0740 H₂O, and 0.1230 Ag. C = 26.53; H = 3.58; Ag = 53.57.
 C₉H₁₄O₄Ag₂ requires C = 26.86; H = 3.48; Ag = 53.73 per cent.

Action of Bromine on the Disodium Derivative of Ethylic Heptanetetracarboxylate.

The action of bromine on the disodium derivative of ethylic isooctanetetracarboxylate,



was studied by Freer and Perkin (Trans., 1888, 53, 220), with the object of preparing a heptamethylene derivative, but no such substance could be isolated; a similar want of success has attended our experiments on the action of bromine on the disodium derivative of ethylic heptanetetracarboxylate.

In carrying out this experiment, ethylic heptanetetracarboxylate (1 mol.) was mixed with an ethereal solution of sodium ethylate (2 mols.), and the calculated quantity of bromine (1 mol.) was gradually added, the whole being well agitated and cooled during the addition. The whole of the bromine disappeared, and the action was then evidently not at an end, as on adding iodine a considerable quantity of this was also absorbed; in fact, the action evidently proceeds in a very different way from that which takes place when the disodium derivatives of ethylic butane- and pentane-tetracarboxylate are acted on by bromine.

On hydrolysis, the product gave an oily acid, and this, when heated at 200°, yielded an oil from which a small quantity of a crystalline substance was obtained melting at 106°, and having all the properties of azelaic acid. The oily products were not further investigated.

*Chemical Laboratories of the
Owens College, Manchester.*