LXXVII.—*Derivatives of Tetramethylene.*

By W. H. PERKIN, jun.

THE close relationship which exists between tetramethylenecarboxylic acid $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{smallmatrix}$ and the fatty acids, especially the valeric acids, not only in physical properties, but also in general chemical behaviour, has been frequently pointed out; and, in view of this close agreement, the statement of Freund and Gudeman (*Ber.*, **21**, 2695), that the amide of tetramethylenecarboxylic acid on treatment with bromine and potash does not yield more than traces of tetramethyleneamine, $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, seemed remarkable, especially when it is remembered that under similar conditions 90 per cent. of the theoretical yield of isobutylamine is obtained from the amide of isovaleric acid (Hofmann, *Ber.*, **15**, 769).

In order to investigate the cause of this difference in behaviour, numerous experiments on this reaction were made, and it was found that when the *pure* amide of tetramethylenecarboxylic acid (melting at 152—153°) is employed, an excellent yield of tetramethyleneamine is obtained; on the other hand, an impure amide, such as was used by Freund and Gudeman (they give the melting point of 138°), gives only traces of the base under the same conditions.

Tetramethyleneamine, $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, is a colourless liquid which boils at 81°, and closely resembles isoamylamine in general properties; it has a strong, basic odour, mixes with water with development of heat, and gives beautifully crystalline salts, of which the *hydrochloride*, $\text{C}_4\text{H}_9\text{N} \cdot \text{HCl}$, and the *platinochloride*, $(\text{C}_4\text{H}_9\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, were analysed: the former salt, when treated with silver nitrite in aqueous solution, is converted almost quantitatively into hydroxy-tetramethylene.

This secondary alcohol boils at 123° and shows the closest resemblance to the fatty alcohols containing the same number of carbon atoms; it might, indeed, be readily mistaken for normal butylic alcohol.

When digested with fuming hydrobromic acid, hydroxytetramethylene behaves in a remarkable manner, as although it is in part converted into *bromotetramethylene*, a colourless oil boiling at 104°, and closely resembling butylic bromide in properties,

the principal product is a dibromobutane, $\text{C}_4\text{H}_8\text{Br}_2$, boiling at $173-174^\circ$, which must have been formed by the disruption of the four-carbon ring,

a behaviour which, so far, has only been observed in the case of trimethylene and some of its derivatives.

As none of the dibromobutanes,* which had, so far, been prepared, agreed in their properties with the product obtained from hydroxy-tetramethylene, experiments were instituted with the object of synthesising the missing members of the series, and in this way determining with which of them this dibromobutane was identical. Ultimately, the required isomeride was obtained as follows.

Aldol was reduced, in neutral solution, with sodium amalgam and thus converted into 1 : 3-dihydroxybutane,

and this, when treated with hydrobromic acid, yielded 1 : 3-dibromobutane, $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$, which boils at 174° , and was found to be identical in all respects with the dibromide obtained from hydroxytetramethylene.

In the formation of this dibromobutane from hydroxytetramethylene, it is probable that bromotetramethylene is first produced, which then reacts with a further quantity of hydrobromic acid with disruption of the tetramethylene ring, thus :

That the tetramethylene ring may be split in this way is a very interesting fact when taken in connection with Baeyer's view of the stability of rings as developed by him in his well-known "Spannung's Theorie" (*Ber.*, **18**, 2277), which is, briefly stated, as follows.

If it be supposed that the four affinities of the carbon-atom act in the direction of lines drawn from the centre of a tetrahedron to the

* This will be readily seen from the following table, which gives the known isomerides with their boiling points :—

1 : 2 Dibromobutane,	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$	B. p. 166°
1 : 4	„ $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$	„ 190
2 : 2	„ $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CBr}_2 \cdot \text{CH}_3$	„ 145
2 : 3	„ $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$	„ 158
1 : 3 Dibromobutane,	$\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$	obtained as explained above boils at 174° .

corners, then these directions are inclined to one another at an angle of $109^{\circ} 28'$.

When such carbon-atoms combine together to form a closed chain the direction of these affinities must be altered, and to do this a certain strain ("Spannung") must be applied, which may be measured by the angle through which the line of affinity is supposed to be deviated.

In the case of trimethylene $\text{H}_2\text{C} \triangle \text{CH}_2$, for example, in which the carbon-atoms are assumed to be situated at the corners of an equilateral triangle, the angles between two affinities of each carbon-atom forming the ring is 60° , that is to say, the direction of each affinity has been displaced through an angle of $\frac{1}{2}(109^{\circ} 28' - 60^{\circ}) = 24^{\circ} 44'$; in

the formation of the tetramethylene ring, $\text{H}_2\text{C} \square \text{CH}_2$, the angle of displacement is much less, *e.g.*, $\frac{1}{2}(109^{\circ} 28' - 90^{\circ}) = 9^{\circ} 44'$.

The following table, taken from Baeyer's paper, shows the deviation of the direction of each affinity of the carbon-atom necessary in combining with other carbon-atoms to form rings.

$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \triangle \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \quad \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \triangle \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \triangle \\ \text{H}_2\text{C}-\text{CH}_2 \\ \\ \text{CH}_2 \end{array}$
+ $54^{\circ} 44'$	+ $24^{\circ} 44'$	+ $9^{\circ} 44'$	+ $0^{\circ} 44'$	- $5^{\circ} 16'$

In ethylene, the deviation is greatest, and the tendency of the ring to open out with formation of additive products would, therefore, be assumed to be very pronounced; and this is found experimentally to be the case, since ethylene combines with the greatest ease with hydrogen bromide, bromine, chlorine, and even iodine; in the case of trimethylene, the deviation is very much less, and this gas, although it combines with hydrogen bromide and with bromine with disruption of the ring, does so with much greater difficulty than ethylene; chlorine does not act on trimethylene at all except in the presence of sunlight, and then the principal products of the action are the substitution products, monochlorotrimethylene, $\text{C}_3\text{H}_5\text{Cl}$, and dichlorotrimethylene, $\text{C}_3\text{H}_4\text{Cl}_2$, some trimethylene chloride, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$, and other products being, however, also produced (Gustavson, *J. pr. Chem.*, 1894, 50, 380).

In accordance with Baeyer's theory, the tetramethylene ring should be much more stable than the trimethylene ring, and this is clearly proved to be the case from a comparison of the properties of some of the derivatives of these hydrocarbons.

Trimethylenecarboxylic acid, for example, is readily acted on by hydrogen bromide with formation of γ -bromobutyric acid,

whereas tetramethylenecarboxylic acid is not decomposed even when heated with fuming hydrobromic acid at 150° , and many other similar cases might be cited; on the other hand, bromotetramethylene is decomposed by boiling concentrated hydrobromic acid, but comparatively slowly.

This difference in the behaviour of bromotetramethylene and tetramethylenecarboxylic acid is very remarkable, the nature of the substituting groups obviously having a very pronounced effect on the stability of the ring; this same difference of stability is also very marked in the case of the trimethylene compounds, as will be shown in a subsequent paper.

It would be exceedingly interesting to study the behaviour of pentamethylene and hexamethylene and their derivatives towards hydrobromic acid, as, according to Baeyer's theory, the former, owing to the slight strain necessary for its formation, would probably not be attacked; this, moreover, seems to be true, since pentamethylene-1:2-dicarboxylic acid, for example, may be heated with hydrobromic acid at 150° without change.

Hexamethylene and its derivatives might under similar conditions be decomposed, but probably not so readily as tetramethylene compounds, and the behaviour of these substances would be an important test of the value of the "Spannung's Theorie."

In connection with this point, it should be noted that benzene, when heated at 260 – 270° , with hydriodic acid containing iodine, yields hexane (comp. Baeyer, *Annalen*, **278**, 89) with disruption of the ring. Possibly, in this case, hexamethylene iodide, $\text{C}_6\text{H}_{12}\text{I}_2$, or diiodide, $\text{C}_6\text{H}_{12}\text{I}_2$, may first be produced, and then reduced to hexane by the further action of the hydriodic acid.

Chlorotetramethylene, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CHCl} \end{array}$, may be readily obtained by the action of phosphorus pentachloride on hydroxytetramethylene. It is a colourless oil which boils at 85° , and when treated with potassium iodide in alcoholic solution yields *iodotetramethylene*, $\text{C}_4\text{H}_8\text{I}$ (b. p. 138°), although the action does not take place readily. The last-named substance was prepared in considerable quantity (30 grams), in the hope that tetramethylene might be obtained from it by reduction under suitable conditions, and that by treatment with quinoline (Baeyer, *Annalen*, **278**, 107), dihydrotetrene* might be formed, thus.

* With regard to this nomenclature, see *Trans.*, 1890, **57**, 214.

The preliminary experiments gave results which seemed to bear out these suppositions; but, on the other hand, it was soon evident that a detailed examination of such hydrocarbons, which would probably boil at about 20° and 35° respectively, could only be carried out with such quantities of material as it would be almost impossible to obtain by the methods described in this paper, and therefore this part of the subject was not further investigated.

The close resemblance of chloro-, bromo-, and iodo-tetramethylene to the corresponding butyl compounds is very marked, as will be seen from a comparison of their properties. The tetramethylene compounds all boil somewhat higher than the butyl compounds, and this is also noticeable in the case of other tetramethylene derivatives, which all, without exception, boil higher than the corresponding saturated fatty compounds, as is seen from the following table, in which the symbol $\square$ is used for $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \end{array}$.

Tetramethylene derivatives.	B. p.	Butane derivatives.	B. p.	Diff.
$\square \cdot \text{COOH} \dots\dots\dots$	195°	$\text{C}_4\text{H}_9 \cdot \text{COOH} \dots\dots\dots$	186°	+ 9°
$\square \cdot \text{NH}_2 \dots\dots\dots$	81	$\text{C}_4\text{H}_9 \cdot \text{NH}_2 \dots\dots\dots$	76	+ 5
$\square \cdot \text{OH} \dots\dots\dots$	122°	$\text{C}_4\text{H}_9 \cdot \text{OH} \dots\dots\dots$	116	+ 7
$\square \cdot \text{Cl} \dots\dots\dots$	85	$\text{C}_4\text{H}_9\text{Cl} \dots\dots\dots$	77	+ 8
$\square \cdot \text{Br} \dots\dots\dots$	104	$\text{C}_4\text{H}_9\text{Br} \dots\dots\dots$	100	+ 4
$\square \cdot \text{I} \dots\dots\dots$	138	$\text{C}_4\text{H}_9\text{I} \dots\dots\dots$	131	+ 7

Other examples illustrating the same point might also be given.

In the second part of this paper, the results of a detailed investigation of the action of bromine on tetramethylenedicarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$, are described, an investigation which was undertaken in the first instance in the hope of obtaining tetrenedicarboxylic acid, $\begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{COOH} \\ | \quad | \\ \text{CH} \cdot \text{C} \cdot \text{COOH} \end{array}$, the study of which, in consideration of the similarity of its constitution to that of phthalic acid, must have given very interesting results; but this acid could not be isolated. Nevertheless, many other substances were obtained which are of considerable interest.

When tetramethylenedicarboxylic anhydride is treated with excess of bromine in presence of phosphorus, substitution takes

place, and the crystallised product of the reaction, after treatment with water, is found to consist principally of *cis*-dibromotetramethylenedicarboxylic acid,

This acid melts at 202—205°, and when treated with acetic anhydride yields an anhydride (m. p. 104°); as this is reconverted into the original acid when dissolved in water, the latter must be the *cis*-dicarboxylic acid.

Trans-dibromotetramethylenedicarboxylic acid could not be obtained by heating the *cis*-acid in sealed tubes with concentrated hydrochloric or hydrobromic acid at 180°; the product from these experiments melted at 200—203°, and could not be distinguished from the *cis*-acid. The *trans*-acid is therefore either not formed in this way, or is very similar to the *cis*-acid in physical properties; the latter alternative is by no means improbable, as the *cis*- and *trans*-modifications of tetramethylenedicarboxylic acid are themselves so very similar that a careful examination of their chemical properties is necessary before they can be distinguished (*Trans.*, this vol., 572).

It would be very remarkable if dibromotetramethylenedicarboxylic acid were found to exist in only one form, not only from the fact that the parent substance tetramethylenedicarboxylic acid itself exists in the *cis*- and *trans*-modifications, but also because succinic acid, which is similar to these acids in constitution, when treated with bromine, yields a mixture of stereoisomeric dibromo-acids.

The study of the action of alkalis on dibromotetramethylenedicarboxylic acid has yielded very unexpected results, as, when this acid is treated with either strong or weak bases, such as potash, baryta, silver oxide, quinoline, or dimethylaniline, under various conditions, the principal product of the action, and indeed, in most cases the only product which could be isolated, was bromodihydrotetrane-carboxylic acid, the formation of which may be represented thus

That the constitution of this new acid is represented as above, and not by the formula $\begin{array}{c} \text{CH} : \text{CH} \\ | \\ \text{CH}_2 \cdot \text{CBr} \cdot \text{COOH} \end{array}$, is rendered very probable from an

examination of the properties of the acid. Its most remarkable property is its stability; when, for example, it is boiled for some time with strong potash (sp. gr. 1.3), or treated with silver oxide, it is not decomposed to any extent, and, on acidifying, the unchanged acid separates in crystals; this fact can only be explained on the assumption that the bromine-atom is attached to doubly bound carbon: in bromomaleic acid, $\text{COOH} \cdot \text{CH} : \text{CBr} \cdot \text{COOH}$, the bromine-atom is not removed by boiling with baryta water (Carius, *Annalen*, **149**, 264), whereas in saturated bromo-acids, as, for example, in the case of bromosuccinic acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{COOH}$, the bromine-atom is readily eliminated by boiling with alkalis. The tendency of dibromotetramethylenedicarboxylic acid to be converted into bromodihydro-tetrenedicarboxylic acid is very remarkable, this change taking place, with separation of iodine, when the aqueous solution of the dibromo-acid is warmed with potassium iodide, a change which it is difficult to represent by an equation.

Bromodihydro-tetrenedicarboxylic acid melts at 121—122°, and shows all the properties of an unsaturated acid; thus, it readily decolorises permanganate solution, and combines with bromine to form tribromotetramethylenedicarboxylic acid.

When silver oxide acts on an aqueous solution of dibromotetramethylenedicarboxylic acid, bromodihydro-tetrenedicarboxylic acid is formed in considerable quantities, but the principal product of the action is a thick, syrupy acid, which, although it could not be obtained quite pure, is obviously dihydroxytetramethylenedicarboxylic acid,

The reaction is in fact very similar to the formation of bromofumaric acid and tartaric acid from isodibromosuccinic acid under the same conditions.

The behaviour of methylic dibromotetramethylenedicarboxylate towards alkalis is, on the other hand, quite different from that of the free acid; when treated with alcoholic potash, for example, a curious action takes place; since bromine, and not, as was to be expected, hydrogen bromide is eliminated, dihydro-tetrenedicarboxylic acid being formed thus.

I have not been able to find a case exactly analogous to this, and illustrating the unstable nature of the bromine-atoms in this position, but it may be mentioned that dimethylsuccinic acid

which, in constitution, closely resembles tetramethylenedicarboxylic acid, when treated with bromine and phosphorus, yields the anhydride of pyrocinchonic acid $\begin{array}{c} \text{CH}_3 \cdot \text{C} \cdot \text{CO} \\ || \\ \text{CH}_3 \cdot \text{C} \cdot \text{CO} \end{array} > \text{O}$; the intermediate dibromodimethylsuccinic acid which is probably formed, in the first instance, losing the two bromine atoms (Zelinsky, Krapiw *Berichte*, **22**, 653).

Dihydrotetrenedicarboxylic acid is sparingly soluble in cold water, melts at 178° , and when heated at 200° loses 1 mol. H_2O , and is converted into an anhydride $\begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{CO} \\ || \\ \text{CH}_2 \cdot \text{C} \cdot \text{CO} \end{array} > \text{O}$, a resinous substance which could not be obtained in a crystalline form, and which dissolves in water with formation of a crystalline acid of the same empirical formula as dihydrotetrenedicarboxylic acid, from which, however, it differs in a very marked manner, notably in being excessively soluble in water. Whether these two acids are stereoisomeric or whether a change in the position of the double bond has taken place during the above treatment, has not yet been satisfactorily determined, owing to the small amount of material available for investigation.

The constitution of dihydrotetrenedicarboxylic acid is proved in the following way.

The methylic salt of this acid is formed quantitatively when methylic dibromotetramethylenedicarboxylate is digested in alcoholic solution with potassium iodide, iodine being liberated.

It is a beautifully crystalline substance which melts at 46° , and when exposed to bromine vapour is reconverted into methylic dibromotetramethylenedicarboxylate; it must therefore have the constitution represented above; dihydrotetrenedicarboxylic acid itself, on the other hand, may be exposed to bromine vapour for some days without change.

This has already been prepared by Freund and Gudeman (*Ber.*,

21, 2694), but not in a pure condition, as these chemists give the melting point 138° , whereas the pure amide melts at 153° .

In preparing large quantities of this amide, the following method was generally employed.

Pure tetramethylenecarboxylic chloride (10 grams) prepared as described in a previous paper (Trans., 1891, 59, 41) is added slowly through a dropping funnel to the strongest aqueous ammonia (100 c.c.), the whole being well cooled during the operation.

As each drop of the chloride comes in contact with the ammonia solution, a very vigorous action takes place, accompanied by volumes of white fumes, and, after about half has been added, the amide commences to separate in glistening plates which ultimately quite fill the liquid. The crystals are collected by means of the pump, washed once or twice with strong ammonia solution, dried on a porous plate in the air, and, if necessary, recrystallised from ether, in which the substance is sparingly soluble.

The amide is thus obtained in the form of magnificent, silky plates, which, on analysis, gave the following results.*

	Theory. $C_4H_7 \cdot CO \cdot NH_2$.	Found.
C	60.60 per cent.	60.75 per cent.
H	9.09 ,,	9.30 ,,
N	14.15 ,,	14.30 ,,

The amide of tetramethylenecarboxylic acid melts at $152-153^{\circ}$, and is very readily soluble in water and alcohol, but only sparingly in ether; when heated, it sublimes in iridescent plates, which are very like sublimed benzoic acid in appearance; it is volatile even at 100° , and cannot be dried in a water oven without loss.

* Considerable difficulty was experienced in determining the nitrogen in this substance, as, when burnt in a stream of carbon dioxide in the manner usually adopted, the result was always much too high, in two cases the analysis indicating 20 per cent. of nitrogen.

Obviously, during the combustion of this amide, very stable gases (ethylene?) are evolved, which pass away with the nitrogen into the eudiometer, and, in order to obviate this, an experiment was made, in which the tube was kept at a bright red heat and the combustion conducted slowly, but even then the result was 2 per cent. too high; the above nitrogen determination, which gave correct numbers, was carried out as follows.

The substance was digested with pure concentrated hydrochloric acid for five minutes, the solution then mixed with water and boiled until the odour of tetramethylenecarboxylic acid was imperceptible; the amount of ammonium chloride in the solution was then determined as ammonium platinochloride in the usual manner.

In several other cases it has been noticed that closed chain compounds are exceedingly difficult to analyse, and accurate results have only been obtained when the tube was kept very hot, and the combustion conducted throughout in a stream of oxygen.

It is very stable, as is illustrated by the fact that it was not entirely decomposed even after boiling for half an hour with strong potash, some of the unchanged amide separating in crystals on cooling; it is, however, very readily hydrolysed by boiling concentrated hydrochloric acid.

In preparing this amide in the manner described above, a considerable quantity remains in the ammoniacal mother liquors, but most of this may be recovered by repeated extraction with ether; any loss of valuable product is avoided by passing air through the aqueous solution until the bulk of the ammonia has been expelled, and then hydrolysing the dissolved amide by boiling with hydrochloric acid. The regenerated tetramethylenecarboxylic acid can be extracted with ether in the usual manner, and used for a subsequent operation.

This interesting substance is formed when the pure amide of tetramethylenecarboxylic acid is treated with bromine and potash, according to the well-known method devised by Hofmann (*Ber.*, **15**, 762); the details of the preparation are as follows.

Bromine (16.2 grams) is weighed out into a flask of about 500 c.c. capacity, and then the pure, finely-powdered amide (10 grams) is added in two or three portions with constant shaking, the whole gradually dissolving with evolution of very little heat.*

At the end of two hours, potash (10 per cent.) is slowly added, the whole being well cooled during the operation; after a time, a reddish-brown, crystalline precipitate separates. On adding more alkali, very little rise of temperature takes place, but the precipitate becomes colourless, and doubtless consists of the bromamide of tetramethylenecarboxylic acid, $\text{C}_4\text{H}_7 \cdot \text{CO} \cdot \text{NHBr}$. On continuing to add strong potash (about 30—35 per cent.) in small quantities at a time with constant shaking, the bromamide gradually passes into solution; as now much heat is developed, the flask must be cooled from time to time by plunging it into water; when all the crystals have disappeared, the whole is distilled in a current of steam until the condensed water is no longer alkaline, and the distillate is then rendered slightly acid by the addition of hydrochloric acid, and evaporated to dryness.

The residue, which consists of a mixture of tetramethyleneamine hydrochloride and ammonium chloride, is extracted with absolute alcohol, the extract filtered from undissolved ammonium chloride, eva-

* Freund and Gudeman (*loc. cit.*), using the impure amide, noticed the development of a considerable amount of heat.

porated to dryness, and the extraction with alcohol repeated. The crude hydrochloride obtained on evaporating the second extract is sufficiently pure for use in the preparation of hydroxytetramethylene, &c.

In order to isolate the base itself, the hydrochloride is transferred to a small retort, mixed with powdered potash, and distilled, the aqueous distillate is dehydrated with potash, and the oily base separated and fractioned; almost the whole of it distils between 81° and 83°, and, on refractionation, boils constantly at 82°.

On analysis the following numbers were obtained.

	Theory. C_4H_9N .	Found.	
		I.	II.
C	67.60 per cent.	67.25	67.13 per cent.
H	12.67 „	12.60	12.58 „
N	19.72 „	19.58	— „

Tetramethyleneamine boils at 82°, and possesses a very pungent basic odour somewhat similar to that of isoamylamine; it absorbs carbon dioxide from the air fumes strongly in contact with hydrogen chloride, and mixes with water with development of heat. The *hydrochloride*, $C_4H_9N.HCl$, was prepared by neutralising an aqueous solution of the base with hydrochloric acid, and evaporating to dryness. It crystallises from alcohol, in which it is readily soluble, in long, striated, prismatic needles, closely resembling crystals of ammonium chloride in appearance, and very readily soluble in water. The results of analysis gave

	Theory. $C_4H_9N.HCl$.	Found.
Cl.	33.02 per cent.	33.24 per cent.

On adding platinic chloride to a strong solution of the hydrochloride, the *platinochloride*, $(C_4H_9N)_2H_2PtCl_6$, is obtained as a deep yellow, crystalline precipitate, which dissolves readily in hot water, and separates on cooling in groups of deep orange octahedra. For analysis, the salt was dried at 100°.

	Theory. $(C_4H_9N)_2H_2PtCl_6$.	Found.	
		I.	II.
Pt.	34.87 per cent.	34.79	34.82 per cent.

This salt is rather sparingly soluble in cold water; when heated in a capillary tube, it begins to darken at 200°, and becomes quite black at 210—215°.

The hydrochloride of tetramethyleneamine reacts readily with silver nitrite, evolving nitrogen and forming hydroxytetramethylene

fortunately the reaction takes place with the formation of traces only of bye-products, and the yield of the hydroxy-compound obtained is, therefore, very good. The experiment was conducted as follows :—Crude tetramethyleneamine hydrochloride (20 grams), which had been freed from ammonium chloride by treatment with alcohol, as explained on p. 959, was dissolved in water (80 c.c.), and to the well-cooled solution a slight excess of freshly precipitated silver nitrite (prepared from 40 grams of silver nitrate), added in small quantities at a time. Effervescence soon began, and after remaining for one hour at the ordinary temperature the whole was heated on a water bath for a few minutes, until the vigorous evolution of gas had almost ceased. The product was then well cooled, mixed with anhydrous potassium carbonate, and extracted five times with pure ether; the ethereal solution was dried over anhydrous potassium carbonate, filtered, and the ether very slowly distilled off; a rectifying column being used so as to obviate, as far as possible, loss of the hydroxy-derivative by evaporation. The residual, almost colourless, oil (12 grams), after twice fractioning, boiled constantly at 123° , and gave the following results on analysis.

	Theory. $C_4H_7\cdot OH$.	Found.	
		I.	II.
C	66.66 per cent.	66.52	66.41 per cent.
H	11.11 „	11.10	11.23 „

Hydroxytetramethylene is a colourless oil, which smells like butylic alcohol; it is readily soluble in water, and dissolves sodium with evolution of hydrogen and formation of a white sodium compound.

Action of Hydrobromic acid on Hydroxytetramethylene. Formation of

Having thus obtained hydroxytetramethylene, the next point was to investigate its behaviour with the halogen acids, in order, if possible, to prepare halogen derivatives of the hydrocarbon; the first experiments instituted were with hydrobromic acid.

Hydroxytetramethylene dissolves in fuming hydrobromic acid (saturated at about 10°), with slight development of heat; as, however, little action appeared to take place in the cold, a large excess of the acid was added, and the whole heated to boiling in a flask, into the neck of which a reflux condenser had been ground. During the operation, a heavy oil separated on the surface of the liquid; but as the action continued and the hydrobromic acid became weak, the oil sank; after

heating for an hour, the product was poured into water the heavy, brownish oil extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, and the ether evaporated. The residual oil was then repeatedly fractioned, and thus readily separated into two fractions, boiling at 102—104° and 173—174° (737 mm.) respectively; of these, the latter was present in by far the larger quantity. The substance boiling at 102—104° is evidently bromotetramethylene, as is shown by the following analyses.

	Theory. C_4H_7Br .	Found.		per cent.
		I.	II.	
C	35.55	35.02	—	
H	5.19	5.06	—	
Br	59.26	58.77	58.85	

Bromotetramethylene is a colourless oil, which boils at about 104° (760 mm.); it is specifically heavier than water, and has an odour which can scarcely be distinguished from that of isobutylic or isoamyl bromide.

The substance boiling at 173—174° (737 mm.) is a very heavy oil, possessing in a marked degree the odour of trimethylene bromide; it gave, on analysis, the following numbers.

	Theory. $C_4H_5Br_2$.	Found.		per cent.
		I.	II.	
C	22.22	22.00	—	
H	3.71	3.70	—	
Br	74.07	74.32	74.21	

These analyses show that this substance must be a dibromobutane, and its formation proves that, under the conditions of the experiment, the tetramethylene ring in bromotetramethylene has been split, addition of hydrogen bromide simultaneously taking place. As explained in the introduction, this dibromobutane is different from any of the known isomerides; and experiment proved that it is identical with the 1:3-dibromobutane, which is obtained when 1:3-dihydroxybutane, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot OH$, is treated with hydrobromic acid (see next section).

Preparation of 1:3-Dibromobutane, $CH_3 \cdot CHBr \cdot CH_2 \cdot CH_2Br$.

This new substance was prepared in order to ascertain whether it was identical with the dibromobutane obtained by the action of hydrobromic acid on hydroxytetramethylene, as described in the last section, and the method employed was briefly as follows.*

* Compare Orndorff and Newbury, *Monatshefte für Chemie*, **13**, 516.

Aldehyde (200 grams) was mixed with an equal volume of water, and then a strong solution of potassium carbonate (12 grams) added drop by drop, the whole being kept at 0° during the addition, which extended over about two hours; after standing for two days at the ordinary temperature, the mixture was neutralised with hydrochloric acid, extracted three times with ether, and the ethereal solution evaporated.

In order to convert the residue, which consisted of crude aldol (98 grams), into the corresponding 1 : 3-dihydroxybutane, it was dissolved in water (1 litre), and reduced in flat, porcelain basins with nearly twice the calculated quantity of $2\frac{1}{2}$ per cent. sodium amalgam, the solution being kept neutral by the constant addition of small quantities of dilute hydrochloric acid, a rapid stream of carbon dioxide being also passed through the liquid, to prevent the accidental accumulation of any large quantity of alkali arising from rapid decomposition of the amalgam.

During the reduction, a sticky substance separated, and the solution also acquired a very penetrating and irritating odour, due possibly to the formation of crotonaldehyde; in order to remove these bye-products, the solution was filtered, and extracted with a small quantity of ether. The filtrate was then slowly concentrated to about 250 c.c. in a flask connected with a long, rectifying column, and the residue saturated with hydrogen bromide, without cooling, loss being prevented by using a reflux apparatus.

After 24 hours, the product was diluted with twice its volume of water, extracted five times with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, and the ether distilled off; the residual dark brown oil was then twice fractionated, and yielded 40 grams of 1 : 3-dibromobutane boiling at $172-175^{\circ}$, of which the greater portion passed over between 173° and 174° . Analysis—

	Theory. $C_4H_8Br_2$.	Found.	
		I.	II.
Br	74.07 per cent.	73.52	73.67 per cent.

The 1 : 3-dibromobutane obtained in this way boiled at the same temperature, and showed all the properties of the substance obtained by treating hydroxytetramethylene with hydrobromic acid, so that there can be no doubt the two products are identical.

I have to thank Messrs. G. H. Cross and J. N. Goldsmith, students in the Owens College, for help in carrying out these experiments.

This substance was prepared by the action of phosphorous pentachloride at moderate temperatures on hydroxytetramethylene, and not by heating this hydroxy-derivative with hydrochloric acid, as it appeared possible that, in the latter case, the chlorotetramethylene formed might be further acted on by the halogen acid with formation of dichlorobutane (see previous section).

Pure hydroxytetramethylene (11 grams) was placed in a flask fitted with a reflux condenser, and pure phosphorous pentachloride (35 grams) gradually introduced in small portions at a time; each successive quantity being allowed to entirely disappear before any more was added; the action, which is very vigorous and accompanied by the evolution of torrents of hydrogen chloride, was moderated by cooling the flask with ice-cold water; at the close, however, the temperature was allowed to rise to 60°.

The product was slowly fractioned, everything which passed over below 105° being collected,* the distillate was agitated with water to decompose the phosphorous oxychloride which it contained, and the supernatant oily layer separated, dried over calcium chloride and fractionated; almost the whole of it (11·5 grams) passed over between 83° and 87°.

After refractionation, a colourless oil boiling constantly at 85° and specifically lighter than water, was obtained. On analysis it gave the following results.

	Theory. $\text{C}_4\text{H}_7\text{Cl}$.	Found.
C	53·10 per cent.	53·07 per cent.
H	7·74 ,,	7·53 ,,
Cl	39·16 ,,	38·73 ,,

Chlorotetramethylene possesses a not disagreeable odour, very similar to that of isoamyl chloride.

In order to prepare this substance, chlorotetramethylene (8 grams) was heated with finely powdered potassium iodide (18 grams) and methylic alcohol (20 c.c.) in a sealed tube at 120—125° for five hours; the product, which was discoloured by iodine, was mixed with water, and the heavy oil which separated extracted with ether; the ethereal solution, washed with dilute sodium hydrogen sulphite, was dried over calcium chloride, evaporated, and the residue carefully fractioned.

* On decomposing the residue with water, a very small quantity of oil separates; this was neglected.

It was then found that the oil contained about 50 per cent. of unchanged chlorotetramethylene; after this had passed over, the thermometer rose rapidly to 130°, between which temperature and 140° the remainder distilled as a colourless oil; on refractionation, it boiled almost constantly at 138°, and gave the following results on analysis.

	Theory. C ₄ H ₇ I.	Found.
C	26·37 per cent.	26·85 per cent.
H	3·85 ,,	4·05 ,,
I	69·78 ,,	69·22 ,,

Iodotetramethylene is a colourless, heavy oil, which in its properties shows the greatest resemblance to isobutylic or isoamylic iodide; its odour can scarcely be distinguished from that of the latter, and, when exposed to light, it quickly turns brown owing to separation of iodine. It is readily reduced by zinc dust and hydrochloric acid with formation of a very volatile hydrocarbon, which is probably tetramethylene; unfortunately the amount of material at my disposal was too small to allow of the systematic examination of this reaction.

Action of Quinoline on Iodotetramethylene.—This action (compare Baeyer, *Annalen*, 278, 107) was investigated with the view of obtaining the unsaturated hydrocarbon dihydrotetrene, $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH} \end{array}$, as explained in the introduction, but the results were not very satisfactory.

Iodotetramethylene (8 grams) was mixed with pure quinoline (15 grams) and the whole heated in a sealed tube at 180° for two hours; the product was then distilled from the tube, every precaution being taken to avoid loss of the volatile hydrocarbon by cooling the condenser and the receiver with a freezing mixture.

In this way, a small quantity of a colourless oil was obtained which boiled between 30° and 45°, and contained halogen; after heating in a small sealed tube with sodium and refractioning, the greater portion distilled between 33° and 35°, but it was not quite free from halogen. This substance is instantly oxidised by potassium permanganate and decolorises bromine; on analysis it gave numbers agreeing only approximately with the formula C₄H₆, owing not only to the presence of traces of halogen, but especially to the great difficulties attending the analysis of a hydrocarbon of this low boiling point.

Dibromotetramethylenedicarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CBr} \cdot \text{COOH} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CBr} \cdot \text{COOH} \end{array}$

This acid is produced when the anhydride of tetramethylenedicarboxylic acid (this vol., 581) is treated with a large excess

of bromine and amorphous phosphorus, according to the Hell-Volhard-Zelinsky method.

Tetramethylenedicarboxylic anhydride (10 grams) is ground up in a mortar with amorphous phosphorus (3 grams), transferred to a flask, into the neck of which a condensing tube has been ground, and *dry* bromine (70 grams) then gradually added, the very vigorous action which takes place being moderated from time to time by cooling with water. On heating the mixture on a water bath, torrents of hydrogen bromide are evolved during the first hour; the action then slackens considerably, and at the end of six hours, a second quantity of phosphorus (3 grams) and bromine (70 grams) is added, and the heating continued for about 15 hours; air is then blown through the mass in order to remove excess of bromine, and the dark-coloured liquid residue, which on cooling frequently deposits crystals of phosphorus pentabromide, is decomposed cautiously by means of ice-cold water. After standing some time, the thick, dark brown product is extracted with ether, the ethereal solution, well washed with water containing a little sodium hydrogen sulphite, dried over calcium chloride, the ether distilled off, and the residual oil fractionated under reduced pressure (70 mm.).

The mass froths a good deal at first, and a considerable quantity of water distils over; the thermometer then rises rapidly, the greater portion distilling between 185 and 190° as an almost colourless oil, which solidifies in the receiver; a good deal of a dark brown residue is, however, left behind in the distilling flask.

The distillate is ground up and digested with sufficient hydrobromic acid (sp. gr. 1.49) to dissolve it, the solution filtered through glass wool and allowed to cool slowly; the mass of glistening crystals which separates is collected, washed with hydrobromic acid, drained on a porous plate, and recrystallised from the same solvent. The purified substance, after drying first over sticks of potash in a vacuum, and then at 100°, gave the following results on analysis.

	Found.		Theory. $C_6H_6Br_2O_4$.
	I.	II.	
C	24.10	24.05 per cent.	23.84 per cent.
H	2.10	2.20 ,,	1.99 ,,
Br	52.71	— ,,	52.98 ,,

When rapidly heated in a capillary tube, dibromotetramethylenedicarboxylic acid melts at about 202—205° with evolution of gas, probably due to the formation of its anhydride; it dissolves readily in alcohol or ether, and also in boiling hydrobromic acid, but is only sparingly soluble in the latter solvent in the cold. It is remarkable

that it is readily soluble in water; a strong, hot aqueous solution, on cooling, deposits the substance in beautiful glistening plates.

A moderately concentrated aqueous solution of this acid gives, with silver nitrate, a copious crystalline precipitate of a silver salt, which contains no silver bromide, as it is completely dissolved by dilute nitric acid. On boiling, however, decomposition sets in with separation of silver bromide in abundance.

Considerable quantities of this methylic salt were necessary for many of the experiments described in this paper, and in the first instance it was prepared from the pure dibromo-acid by treating it with methylic alcohol and hydrogen chloride in the usual way; ultimately, however, it was found that the best method of preparation was the following.

The crude product of the action of bromine and phosphorus on tetramethylenedicarboxylic anhydride (from which the excess of bromine had been removed by blowing in air, as described on p. 966), was poured in a thin stream, and without cooling, into a large excess of methylic alcohol; after the vigorous action had subsided, and the product cooled down, water was added, and the methylic salt extracted twice with ether. The ethereal solution was well washed with dilute sodium carbonate, dried over calcium chloride, the ether evaporated, and the residual dark brown oil fractionally distilled under reduced pressure (50 mm.).

With the exception of a small quantity of a substance of low boiling point, nearly the whole of the oil distilled between 180° and 205°, undergoing slight decomposition and evolving some hydrogen bromide; on redistilling, two principal fractions were obtained boiling at 185—195° and 195—200° (50 mm.) respectively. Both of these, after 14 days, deposited hard, prismatic crystals, which were separated from the oil by filtration through glass wool, left in contact with porous porcelain until quite dry and colourless, ground up, and then recrystallised twice from boiling light petroleum (b. p. 60—70°); in this way the methylic salt was obtained in magnificent, colourless prisms, which on analysis gave the following result.

	Found.	Theory. $\text{C}_4\text{H}_4\text{Br}_2(\text{COOCH}_3)_2$.
C	29·21 per cent.	29·09 per cent.
H	3·30 ,,	3·03 ,,
Br	48·48 ,,	48·48 ,,

Methylic dibromotetramethylenedicarboxylate melts at 88—89°

and is readily soluble in alcohol, chloroform, benzene, and hot, light petroleum, but only sparingly so in the latter solvent in the cold. It separates from dilute methylic alcohol in colourless groups of glistening, feathery crystals.

The oily mother liquor which was separated from the crystals, as explained above, was refractioned, and in this way a further, though small, quantity of crystalline methylic salt was obtained. After separating this, and again refractioning the mother liquor, no further crystallisation took place, even after the oil had been left for months in contact with a crystal of the methylic salt; analyses of two samples of this oil boiling at 190—195° and 195—200° (50 mm.) respectively, gave the following results.

	Found.		Theory.
	I.	II.	$C_4H_4Br_2(COOCH_3)_2$.
Br.	46·30	47·10 per cent.	48·48 per cent.

It is possible that this product contains some impurity which retards crystallisation. As the analysis, however, seems to show that it can contain, at the most, only traces of such impurity, and as this would hardly prevent the separation of a substance characterised, like the methylic salt, by great facility for crystallising, it is possible that the liquid methylic salt is a stereoisomeride of the crystalline salt.

That there is a considerable difference between the solid and liquid methylic salt is shown clearly in their behaviour with potash (see p. 973).

Anhydride of Dibromotetramethylenedicarboxylic acid,

It has been shown in a previous communication (this vol., 572) that tetramethylenedicarboxylic acid [1:2] exists in two well-defined *cis*- and *trans*-modifications, and it might be supposed that its dibromo-derivative would show the same behaviour. In order to investigate this point, it was necessary, in the first place, to prepare the anhydride of this acid, which was ultimately accomplished in the following way. Nearly pure dibromotetramethylenedicarboxylic acid (m. p. 185—190°) was distilled under a pressure of 40 mm., when almost the whole of it passed over at 180—185°, and solidified on cooling to a hard crystalline cake; this was dissolved in freshly distilled acetic anhydride, the solution boiled for five minutes in a reflux apparatus, and then placed over potash in a vacuum dessicator. As the excess of acetic anhydride evaporated, beautiful, colourless, prismatic

crystals separated; these were collected, washed with acetic anhydride, and dried over potash and sulphuric acid in a vacuum; they gave the following result on analysis.

	Found.	Theory. C ₆ H ₄ Br ₂ O ₃ .
C	25.21 per cent.	25.31 per cent.
H	1.72 ,,	1.41 ,,
Br	56.43 ,,	56.33 ,,

Dibromotetramethylenedicarboxylic anhydride melts at 103–104°, and is readily soluble in alcohol, ether, benzene, and boiling light petroleum (b. p. 100°), but only sparingly in the latter in the cold. In contact with moisture, it is readily converted into the acid from which it was derived; some of the powdered substance which was left exposed to the air for a few days had almost entirely changed, and then melted at about 180°. The anhydride dissolves readily in warm water, and the solution on cooling deposits pure dibromotetramethylenedicarboxylic acid in glistening crystals (m. p. 204–205°). This acid is therefore the *cis*-modification.

In order to determine whether the corresponding *trans*-modification existed, some of the pure anhydride was dissolved in warm hydrobromic acid solution (sp. gr. 1.49) and heated in a sealed tube at 190–200° for two hours. On cooling, the tube was found to be filled with glistening crystals, very little discoloration and no charring having taken place; these crystals were collected and recrystallised from hydrobromic acid; they melted then at about 200°, and were exactly similar in appearance to the original *cis*-acid.

It appears, therefore, that the *trans*-modification of dibromotetramethylenedicarboxylic acid does not exist: unless indeed it is so similar in properties to the *cis* form that it could only be identified on very prolonged investigation.

Action of Alkalis on Dibromotetramethylenedicarboxylic acid.

Bromodihydropentenedicarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CBr} \\ | \\ \text{CH}_2 \cdot \text{C} \cdot \text{COOH} \end{array}$

As explained in the introduction, these experiments were instituted with the object of obtaining tetrenedicarboxylic acid, $\begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{CH} \cdot \text{C} \cdot \text{COOH} \end{array}$; but, although the conditions were varied as far as possible, this acid could never be isolated; the reaction proceeded in all cases in the same way, carbon dioxide and hydrogen bromide being eliminated, and bromodihydropentenedicarboxylic acid formed, thus:

1. *Experiments with Barium Hydroxide.*—Pure dibromotetramethylenedicarboxylic acid (about 5 grams) was dissolved in a little warm water and the solution mixed with a large excess of hot, strong barium hydroxide; this caused the separation of a white, glistening, crystalline precipitate which was very sparingly soluble even in boiling water, and probably consisted of the barium salt of the dibromo-acid; on continued boiling, however, this was gradually decomposed and passed into solution, much hydrogen bromide being eliminated, as was proved by testing the solution with silver nitrate. After filtering from a small quantity of insoluble matter, carbon dioxide was passed through the boiling liquid to precipitate the excess of baryta, and the whole filtered hot; the filtrate, on being evaporated to a small bulk and allowed to cool, deposited colourless crystals which, after recrystallisation from water and drying at 100° , gave the following results on analysis.

	Found.		Theory.
	I.	II.	$C_{10}H_8Br_2O_4Ba$.
Ba	28.03	28.02 per cent.	28.02 per cent.
Br*	33.01	— „	32.72 „

On drying at 100° , the air-dry glistening crystals become opaque and lose 9.77 per cent. in weight, which appears to show that the freshly prepared salt has the composition, $C_{10}H_8Br_2O_4Ba + 3H_2O$ (containing 9.96 per cent. H_2O). This water of crystallisation is gradually given off, when the crystals are left exposed over sulphuric acid in a dessicator for a long time.

The barium salt is sparingly soluble in cold, but readily in hot water: on adding hydrochloric acid to the hot solution, and allowing it to cool slowly, bromodihydrotetrenecarboxylic acid separates in colourless needles which, after recrystallising from water, gave the following results on analysis.

	Found.	Theory.
		$C_4H_4BrCOOH$.
C	34.20 per cent.	33.90 per cent.
H	2.97 „	2.83 „
Br	45.23 „	45.18 „

The acid melts at 121 — 122° , and is sparingly soluble in cold water, readily in hot water, chloroform, alcohol, ether, benzene, and hot light petroleum; it is best crystallised from hot water or light petroleum. That it is an unsaturated acid is shown firstly by the behaviour of the cold solution of its sodium salt with a drop of permanganate, which it instantaneously decolorises, and, secondly, by

* In order to determine the bromine in this salt, it was found necessary to heat the substance with fuming nitric acid and silver nitrate for 5 hours at 200 — 220° .

its conversion into tribromotetramethylenecarboxylic acid when treated with bromine.

The bromine-atom in bromodihydrotetrenecarboxylic acid is very firmly bound, and is only very slowly eliminated by boiling with silver hydroxide, potash, quinoline, and other alkalies; the acid dissolves also in fuming nitric acid, and the solution may be warmed almost to the boiling point without elimination of bromine; ultimately, however, vigorous oxidation sets in, and the acid is rapidly decomposed.

Action of Potash on Dibromotetramethylenedicarboxylic acid.—If this acid be digested with excess of potash instead of with baryta, and the solution acidified and extracted with ether, a yellow, semi-solid acid is obtained on evaporating the ethereal solution. If left in contact with porous porcelain, this becomes quite hard and almost colourless, and, after recrystallisation from water with the aid of animal charcoal, yields colourless crystals of bromodihydrotetrenecarboxylic acid. It melted at 122° , and on analysis gave the following result.

	Found.	Theory. $C_3H_5BrO_2$.
Br.....	45.32 per cent.	45.18 per cent.

Many experiments were then made with the object of eliminating hydrogen bromide from this monobromo-acid by boiling with aqueous and alcoholic solutions of potash of various degrees of concentration, but in no case could the desired tetrenecarboxylic acid, $\begin{array}{c} CH:CH \\ | \quad | \\ CH:C-COOH \end{array}$ be isolated.

Action of Quinoline and of Dimethylaniline on Dibromotetramethylenedicarboxylic Anhydride.—When this anhydride is gently heated with quinoline, a vigorous action sets in, and a good deal of charring takes place; on examining the product, the only crystalline substance which could be isolated was found to be bromodihydrotetrenecarboxylic acid melting at 122° , showing that the quinoline had acted much in the same way as the baryta water and the potash, 1 mol. of hydrogen bromide only being eliminated.

A similar result was obtained with dimethylaniline, but the action proceeded much more smoothly, and with little charring; 0.5 gram of the pure anhydride was dissolved in 10 grams of pure dimethylaniline, and the solution heated gently until the vigorous action which soon sets in had subsided; the temperature was then raised to the boiling point of the liquid for a few seconds.

The product was then digested with alcoholic potash for 10 minutes, the dimethylaniline removed by distillation in steam, the alkaline solution filtered, acidified and extracted with ether; the residue left on distilling the ether gave colourless needles, which when crystallised

from water melted at 122° , and showed all the properties of bromodihydrotetrenecarboxylic acid.

Action of Silver Oxide on Dibromotetramethylenedicarboxylic acid.—

As it was not found possible to remove all the bromine from this acid by means of baryta or potash, experiments on the action of silver oxide were instituted.

About 5 grams of the pure dibromo-acid was dissolved in half a litre of water, and freshly prepared silver oxide was added in small quantities to the solution heated nearly to boiling, until, after standing for some time and filtering, the solution was found to contain a considerable quantity of silver on testing it with hydrochloric acid; when this point was reached it was found to be disadvantageous to warm any further, otherwise the organic silver salt present decomposes with deposition of silver. A stream of hydrogen sulphide was then passed through the warm filtered liquid until the whole of the silver had been precipitated, and the clear solution was evaporated to a small bulk and allowed to stand over sulphuric acid in a vacuum. After two days, the crystalline precipitate which had separated was collected and recrystallised from water; it then melted at 122° and consisted of bromodihydrotetrenecarboxylic acid, as the following analysis shows.

	Found.	Theory. $C_4H_4Br \cdot COOH$.
Br	45.41 per cent.	45.18 per cent.

The dark coloured filtrate from these crystals was digested with carefully purified animal charcoal and allowed to evaporate to dryness over sulphuric acid in a vacuum, the resulting syrupy mass was then rubbed up with a little water, a few crystals which remained undissolved removed by filtration, and the filtrate again allowed to evaporate, the treatment with cold water being repeated until the solution contained only traces of bromine.

The pale yellow syrup ultimately obtained on evaporation showed no signs of crystallising even after standing in a dessicator for a fortnight; when heated at 100° , it lost water and yielded a brittle, transparent resin which on analysis gave the following results.

	Found.		Theory.
	I.	II.	$CH_2C(OH) \cdot COOH$ $CH_2C(OH) \cdot COOH$
C	40.41	40.46 per cent.	40.91 per cent.
H	4.34	4.51 „	4.55 „

As these analyses were carried out with the product from two distinct experiments, it seems probable that this substance is slightly impure dihydroxytetramethylenedicarboxylic acid, the formation of which was to be expected from the conditions of the experiment :

and the behaviour of the acid favours this view. When heated, it readily chars, giving off a strong smell of burnt sugar; sulphuric acid also quickly chars the acid when the mixture is gently warmed; the acid is very readily soluble in water and reduces ammoniacal silver solution rapidly at 80—100°, in these respects behaving very like tartaric acid. On the other hand, it does not appear to form a sparingly soluble potassium salt.

Action of Potash on liquid Methyl Dibromotetramethylenedicarboxylate.—A quantity of this substance which boiled constantly at 190—195° (50 mm.) was digested with alcoholic potash, the product diluted with water, evaporated till free from alcohol, acidified and extracted with ether. The residue left on distilling off the ether, when repeatedly recrystallised from water with the aid of animal charcoal, yielded considerable quantities of bromodihydrotetrenecarboxylic acid, also a mixture of acids melting about 150°, which were not further investigated, and traces only of dihydrotetrenedicarboxylic acid. This difference in the behaviour of the liquid and solid methyl salt towards potash is remarkable, and shows that there must be a considerable difference in their constitutions.

A solution of bromodihydrotetrenecarboxylic acid in chloroform is only very slowly attacked by bromine. Addition, however, readily takes place if the finely divided acid is left under a bell-jar in contact with *dry** bromine vapour, the reaction proceeding quantitatively as is shown by the following experiment.

0.1074 gram of substance left in contact with dry bromine vapour during 24 hours yielded a red liquid, which, after standing over potash in a vacuum dessicator until the excess of bromine had evaporated, became quite hard and almost colourless, and weighed 0.2044 gram, an increase of 0.0970 gram. On the assumption that addition takes place according to the equation

the increase should have been 0.0971 gram. The product was analysed by heating it with fuming nitric acid and silver nitrate at 210° for 5 hours, and gave the following results agreeing with the formula of tribromotetramethylenecarboxylic acid

* If the bromine vapour be moist, oxidation sets in, and an uninviting sticky substance is formed.

	Found.	Theory. $C_4H_4Br_3 \cdot COOH$.
Br.....	70·96 per cent.	71·21 per cent.

Tribromotetramethylenecarboxylic acid is readily soluble in benzene and alcohol, sparingly in water and light petroleum; but attempts to recrystallise the substance were unsuccessful, as it readily decomposes when warmed with solvents.

This beautiful substance is formed when methylic dibromotetramethylenedicarboxylate is digested in alcoholic solution with potassium iodide, thus

Pure methylic dibromotetramethylenedicarboxylate (2 grams) is dissolved in absolute alcohol (20 c.c.) finely powdered potassium iodide (4 grams) added, and the mixture heated to boiling in a flask connected with a reflux apparatus; the solution very soon begins to darken in colour owing to the separation of iodine, and after boiling for 2 hours the decomposition is complete. In order to isolate the product of the action, water is added, the dark oily mass extracted four times with ether, the ethereal solution washed with dilute sodium hydrogen sulphite until colourless, and then with water; after drying over calcium chloride, and evaporating, a thick colourless oil is obtained, which, on cooling, solidifies to a mass of crystals.

The crystalline mass after being left in contact with porous porcelain until quite free from oily mother liquor, was recrystallised twice from light petroleum (b. p. 50—60°), when magnificent glistening crystals were obtained. On analysis, these gave the following results.

	Found.		Theory. $C_4H_4(COOCH_3)_2$.
	I.	II.	
C.....	56·14	56·21 per cent.	56·47 per cent.
H.....	5·93	5·95 „	5·88 „

Methylic dihydrotetrenedicarboxylate melts at 44—46° and is readily soluble in methylic or ethylic alcohols, ether, benzene, and hot light petroleum, but only sparingly in the latter solvent in the cold; it crystallises from most solvents with great facility.

A small quantity of the finely powdered substance was exposed under a bell glass to the vapour of dry bromine for 15 hours; after removal of the excess of bromine over potash in a vacuum, a colourless mass was left which crystallised in needles melting at 84—86°.

and showed all the properties of methylic dibromotetramethylenedicarboxylate; it was doubtless identical with the latter, but no analysis of the product could be made owing to the small amount of substance available.

In order to prepare this acid, the pure methylic salt was digested for 10 minutes with an excess of alcoholic potash, the solution of the potassium salt mixed with water, evaporated until free from alcohol, acidified and extracted at least 10 times with ether; the ethereal solution was then dried by calcium chloride, evaporated, and the residual almost colourless acid purified by recrystallisation from water. Analysis

	Found.		Theory.
	I.	II.	$\text{C}_4\text{H}_4(\text{COOH})_2$.
C	50.49	50.60 per cent.	50.70 per cent.
H	4.15	4.25 „	4.23 „

Dihydotetrenedicarboxylic acid crystallises from water in colourless needles which melt and decompose at about 178° forming the anhydride. It is readily soluble in hot water and alcohol, sparingly in cold water, benzene, or ether, and almost insoluble in light petroleum. It dissolves readily in dilute sodium carbonate, and the solution decolorises permanganate very rapidly, a proof that the acid is unsaturated.

When exposed to dry bromine vapour, it is either not acted on at all or action takes place with extreme slowness, which is rather remarkable as the methylic salt under the same conditions is readily converted into methylic dibromotetramethylenedicarboxylate. If a little of the acid be carefully heated in a test tube, water is given off at first, and the residue then rapidly decomposes, a carbonaceous mass being left: in this respect the acid differs widely from compounds of analogous constitution, such as fumaric acid or pyrocinchonic anhydride which distil without decomposition.

Silver Salt $\text{C}_4\text{H}_4(\text{COOAg})_2$.—This salt is obtained as a white amorphous precipitate on adding a large excess of silver nitrate to a warm, slightly alkaline, solution of the ammonium salt; it was collected, washed with warm water, dried over sulphuric acid in a vacuum and then at 100° , and analysed with the following result.

	Found.	Theory.
		$\text{C}_6\text{H}_4\text{Ag}_2\text{O}_4$.
C	20.22 per cent.	20.22 per cent.
H	0.95 „	1.12 „
Ag	60.32 „	60.67 „

This silver salt is very sparingly soluble in water; when heated it decomposes all at once, yielding a very voluminous mass of silver, for which reason the above silver determination had to be carried out in the wet way.

Hydrogen Silver Salt, $\text{COOH} \cdot \text{C}_4\text{H}_4 \cdot \text{COOAg}$.—The warm mother liquors from the above salt, after two days, deposited magnificent, glistening needles of the hydrogen silver salt; these were collected, washed with water, dried over sulphuric acid in a vacuum and then at 100° , and analysed.

	Found.		Theory. $\text{C}_6\text{H}_5\text{AgO}_4$.
	I.	II.	
Ag	42.94	43.12 per cent.	43.35 per cent.

It is remarkable that the corresponding dihydropentenedicarboxylic acid (p. 983) should give a similarly constituted hydrogen silver salt, and that both salts, when they have once crystallised, should be so sparingly soluble in water.

Dihydrotetrenedicarboxylic acid is also produced when methylic dibromotetramethylenedicarboxylate (p. 967) is treated with alcoholic potash, the action in this case being quite different from that which takes place when dibromotetramethylenedicarboxylic acid itself is heated with alkalis.

The pure methylic salt (5 grams) was dissolved in a little boiling alcohol, and a strong solution of potash (7 grams) in alcohol gradually added; a vigorous action took place, and in a short time the whole solidified to a crystalline mass.

On subsequently warming on a water bath, most of the crystals gradually disappeared, and the colour of the liquid changed to dark brown; after two hours' digestion in a reflux apparatus, water was added, the solution evaporated until free from alcohol, filtered, acidified, and extracted 10 times with ether; the ethereal solution was then dried over calcium chloride, filtered, and the ether slowly distilled off. During the distillation, and after the bulk of the ether had distilled over, crystals separated; these were collected, washed with a little ether to remove the dark-coloured mother liquor, and purified by recrystallisation from water with the aid of animal charcoal. The colourless crystals thus obtained melted at 178° , and consisted of pure dihydrotetrenedicarboxylic acid, as the following analysis shows.

	Found.		Theory. $\text{C}_4\text{H}_4(\text{COOH})_2$.
C	50.35	per cent.	50.70 per cent.
H	4.31	„	4.23 „

This reaction does not afford a convenient means of preparing this acid, as the yield is not good, and the product is much more difficult to purify than that obtained from the pure methylic salt, as previously explained (p. 975).

In the first experiments made with the object of preparing this anhydride, the pure acid was digested with acetyl chloride and with acetic anhydride for one hour endeavours to purify the dark-coloured product by distillation under reduced pressure (20 mm.) were fruitless, because as soon as the excess of acetic anhydride or acetyl chloride had passed over and the temperature rose above 150°, rapid decomposition set in, and the whole mass became quite black. When, however, the pure acid was heated in a test tube at 190–200°, vigorous effervescence took place, water was eliminated, and the action was complete in five minutes; the product, which on cooling set to a hard, transparent resin, was analysed, two distinct preparations giving the following numbers.

	Found.			Theory.
	I.	II.		$\text{C}_4\text{H}_4\text{C}_2\text{O}_3$.
C	57.47	57.55	per cent.	58.06 per cent.
H	3.29	3.27	„	3.23 „

This substance is obviously the anhydride of dihydotetrenedicarboxylic acid. It is a resinous substance, which melts in the steam oven, and could not be obtained in a crystalline form; when boiled with water, it melts and gradually dissolves, forming a clear solution, and this, if allowed to evaporate over sulphuric acid in a vacuum leaves a syrupy residue which, on long standing, deposits crystals.

In contact with porous porcelain, these crystals lose the adherent, syrupy mother liquor, and become quite colourless, but all attempts to recrystallise the substance failed; two distinct preparations were dried at 100°, and analysed with the following results.

	Found.			Theory.
	I.	II.		$\text{C}_4\text{H}_4(\text{COOH})_2$.
C	50.63	50.59	per cent.	50.70 per cent.
H	4.10	4.25	„	4.23 „

This acid is, therefore, isomeric with dihydotetrenedicarboxylic acid (m. p. 178°), and it differs from this in a most marked manner; it is, for example, excessively soluble in water and ether, and cannot be recrystallised, whereas the acid of melting point 178° is sparingly soluble in these solvents, and is remarkable for the great

facility with which it crystallises. Unfortunately the small quantity of material at my disposal made it impossible for me to further investigate this substance.

*Action of Potassium Iodide on Dibromotetramethylenedicarboxylic acid.
Formation of Bromodihydrotetrenedicarboxylic acid.*

The formation of methylic dihydrotetrenedicarboxylate by the action of potassium iodide on methylic dibromotetramethylenedicarboxylate made it interesting to determine whether dihydrotetrenedicarboxylic acid itself might be produced by treating the dibromo-acid with potassium iodide.

The pure dibromo-acid (2 grams) was mixed with a strong solution of potassium iodide (10 grams) and allowed to stand, when it was noticed that even in the cold the solution gradually acquired a yellow tint, due to liberation of iodine; at 100°, in a sealed tube, decomposition took place rapidly, and after two hours the liquid had become dark brown. On allowing the tube to remain over night in a cool place, crystals were deposited, and when the tube was opened a slight pressure was noticeable, due to carbon dioxide. The crystals were collected, washed with water, and recrystallised several times from this solvent, when they became colourless. The substance melted at 122°, and, on analysis, was found to consist of bromodihydrotetrenedicarboxylic acid.

	Found.	Theory.
Br	44·95 per cent.	45·18 per cent.

It is remarkable that there should be such a difference between the behaviour of dibromotetramethylenedicarboxylic acid and that of its methylic salt, when treated with potassium iodide.

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