LXXVIII.—1 : 2-*Pentamethylenedicarboxylic Acid*.

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THE anhydride of α 's-pentamethylenedicarboxylic acid behaves towards bromine, in the presence of phosphorus, in a manner similar to the anhydride of *cis*-tetramethylenedicarboxylic acid (see preceding paper), the principal product of the action being *dibromopentamethylenedicarboxylic acid*,

but the yield of this acid is comparatively small, as much carbonaceous matter is produced during the bromination and during the subsequent purification of the substance by recrystallisation from hydrobromic acid.

This tendency to decompose into carbon and hydrogen bromide, when heated with bromine, has been previously observed in the case of pentamethylenedicarboxylic acid (Trans., 1887, 51, 247), and may possibly be characteristic of pentamethylene derivatives; in the experiment referred to here, the pure bibasic acid was heated with bromine water at 180° for four hours, at the end of which time it had completely decomposed into carbon and hydrogen bromide.

Dibromopentamethylenedicarboxylic acid is a colourless, crystalline substance, which melts at 183—184°; it cannot be distilled, and all attempts to obtain an anhydride with the aid of acetyl chloride, &c., failed, owing to the instability of the acid; when treated with alkalis, it is readily decomposed with formation of *bromodihydropentenecarboxylic acid*, thus—

just as under similar conditions dibromotetramethylenedicarboxylic acid yields bromodihydotetrenecarboxylic acid.

This new acid crystallises from water in needles, melts at about 130°, and, in contact with bromine vapour, is rapidly converted into *tribromopentamethylenecarboxylic acid*,

Dihydropentenedicarboxylic acid is produced when methylic dibromopentamethylenedicarboxylate is digested with potassium iodide in alcoholic solution, and the product hydrolysed with potash.

It crystallises in colourless prisms, melts at 178°, and is much less readily converted into an anhydride than the corresponding dihydro-tetrenedicarboxylic acid, from which it also differs in that it is converted by contact with bromine vapour into dibromopentamethylenedicarboxylic acid, whereas under these circumstances the tetrene acid remains unchanged.

Experiments are also described in this paper, made with the object of preparing the anhydride of *trans*-pentamethylenedicarboxylic acid; as this anhydride should, according to Baeyer's views (*Annalen*, **257**, 179), be capable of existence, and should, indeed, be as readily produced as the anhydride of *trans*-hexahydrophthalic acid. As, however, *trans*-pentamethylenedicarboxylic acid is not appreciably acted on by acetyl chloride at 100° (this vol., 587), and at 140° yields the anhydride of the *cis*-acid, results which Baeyer was kind enough to confirm, it seemed unlikely that the *trans*-anhydride could be isolated even if it existed.

However, at Baeyer's suggestion, we systematically studied the action of acetic anhydride on the pure *trans*-acid, and as the result of a large number of experiments we find that the almost pure *trans*-anhydride is formed when the acid is digested with acetic anhydride for 25 minutes and the excess of acetic anhydride removed by passing a current of dry air through the product heated at 120° under 20 mm. pressure; it is an oil which contains traces of the anhydride of the *cis*-acid, into which it is completely converted by distillation.

The analogy between the dimethylsuccinic acids, the hexahydrophthalic acids, and the pentamethylenedicarboxylic acids is now complete, the only remarkable point being that whereas the anhydrides of the *trans*-modifications of the two first-named acids are so easily formed, *trans*-pentamethylenedicarboxylic acid can only be converted into its anhydride with considerable difficulty.

In order to prepare this substance, *cis*-pentamethylenedicarboxylic anhydride (10 grams) was mixed with amorphous phosphorus (2 grams), dry bromine (60 grams) gradually added, with constant cooling, and the whole heated in a reflux apparatus for six hours to boiling; torrents of hydrogen bromide were given off, and the action appeared to proceed in much the same way as in the case of the formation of dibromotetramethylenedicarboxylic acid (p. 966). A further quantity of bromine (30 grams) and amorphous phosphorous (1 gram) was then added, and the heating continued for six hours longer; the product, after being freed from excess of bromine by blowing in air, was poured into a large quantity of water, care being taken to keep the temperature below 30° by cooling with water. After about an hour, the heavy oil was extracted with ether, the ethereal solution filtered from a considerable quantity of carbonaceous matter, washed with a little dilute sodium hydrogen sulphite solution to remove the last traces of bromine, dried by calcium chloride,

evaporated, and the dark-coloured, oily residue allowed to stand over sulphuric acid in a vacuum for about a week. At the end of that time, the thick, prismatic crystals which had separated were freed as far as possible from the dark, oily, mother liquor by decantation, allowed to remain in contact with porous porcelain until quite colourless, ground up, and recrystallised twice from fuming hydrobromic acid.

In this way, colourless, glistening crystals were obtained, which, after drying at 100°, gave the following results on analysis.

	Found.			Theory.
	I.	II.		$C_5H_6Br_2(COOH)_2$.
C	26.71	27.24	per cent.	26.58 per cent.
H	2.84	2.95	„	2.53 „
Br	50.21	49.69	„	50.63 „

Dibromopentamethylenedicarboxylic acid melts at 183—184° with evolution of gas; it is readily soluble in warm water, alcohol, and ether, and in hot concentrated hydrochloric or hydrobromic acids, but only sparingly in the cold acids. In general properties, it resembles the corresponding dibromotetramethylenedicarboxylic acid, except that it is less stable and very readily carbonises when treated with reagents or when heated; thus, for example, all attempts to prepare its anhydride by distillation under diminished pressure failed, owing to the acid decomposing into a carbonaceous mass with evolution of hydrogen bromide in abundance. When heated with acetic anhydride in a reflux apparatus, the solution rapidly darkened and ultimately became almost black, hydrogen bromide being evolved; on distilling the product under reduced pressure (20 mm.) decomposition set in as soon as the acetic anhydride had passed over; many other experiments were made with the object of preparing the anhydride, but in no case could a crystalline compound be isolated.

This is formed when alcoholic potash acts on dibromopentamethylenedicarboxylic acid. The pure dibromo-acid (5 grams) was added in small quantities at a time to a strong boiling solution of pure potash (10 grams) in ethylic alcohol; a vigorous action set in, potassium bromide separated, and at the same time the mass became dark coloured. After boiling for a few minutes, using a reflux condenser, water was added, the dark brown solution, filtered from small quantities of carbonaceous matter, was acidified, and extracted five times with ether; the ethereal solution, after being washed well with

water, and dried over calcium chloride, was evaporated, and the crystalline residue left in contact with porous porcelain for some hours until free from oily mother liquor. The crude residual substance was then purified by repeated recrystallisation from water with the aid of animal charcoal, and the colourless crystals analysed.

	Found.		Theory.
	I.	II.	C ₅ H ₆ Br·COOH.
C	38·15	38·02 per cent.	37·69 per cent.
H	4·08	3·94 „	3·66 „
Br	42·13	42·01 „	41·88 „

Bromodihydropentenecarboxylic acid melts at about 130°, but softens a few degrees lower, and, when strongly heated, distils without leaving any residue and apparently without undergoing decomposition; it is readily soluble in alcohol, ether, benzene, chloroform, formic acid, and hot water or light petroleum, but only sparingly in the two latter solvents in the cold; it crystallises best from hot water.

The solution of the acid in dilute sodium carbonate decolorises permanganate rapidly.

Bromodihydropentenecarboxylic acid is apparently not the only product of the action of alcoholic potash on dibromopentamethylenedicarboxylic acid, but the other substance or substances present in the mother liquor of this acid could not be isolated in quantity sufficient for analysis.

This acid is formed quantitatively when bromodihydropentenecarboxylic acid is exposed to the action of bromine vapour.

0·5546 gram of pure bromodihydropentenecarboxylic acid left in contact with *dry* bromine vapour for 24 hours, and then freed from excess of bromine by exposure over potash in a vacuum, had gained 0·481 gram in weight, whereas, in the formation of the tribromo-acid, according to the above equation, theoretically 0·464 gram of bromine should have been taken up. The product is highly unstable, but, with care, it may be recrystallised from formic acid, and is thus obtained in colourless nodular masses, about half of the substance remaining in the mother liquor.

The pure substance, on analysis, gave the following result.

	Found.	Theory. C ₆ H ₈ ·Br ₂ O ₂ .
Br.	68·04 per cent.	68·37 per cent.

Tribromopentamethylenedicarboxylic acid is readily soluble in ether and alcohol, but only sparingly in water, formic acid, or light petroleum; it is very readily decomposed when boiled with water, hydrogen bromide being eliminated.

The freshly-prepared solution of the acid in cold sodium carbonate does not decolorise permanganate instantaneously, but oxidation takes place slowly on standing, and very rapidly if the solution is warmed, due doubtless to the gradual decomposition of the tribromo-acid into unsaturated compounds.

In order to prepare this beautiful crystalline substance, the following method was employed.

The crude product of the action of bromine and phosphorus on pentamethylenedicarboxylic acid, after removal of excess of bromine by blowing in air (p. 980), was treated with methylic alcohol; and as soon as the mixture had cooled down it was poured into water; and the crude methylic salt which separated as a dark-coloured heavy oil extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution, dried over anhydrous potassium carbonate, filtered, and evaporated. The dark-coloured, oily residue, consisting of crude methylic dibromopentamethylenedicarboxylate, did not deposit crystals, even after standing for some days over sulphuric acid in a vacuum, and therefore no analysis was made.

This crude methylic salt was dissolved in alcohol, a large excess of powdered potassium iodide added, and the whole heated in a reflux apparatus for two hours; iodine was liberated in abundance, and the action appeared to proceed exactly as in the case of the decomposition of methylic dibromotetramethylenedicarboxylate under similar conditions (p. 974). To the product, mixed with water, sufficient dilute sodium hydrogen sulphite solution was added to remove the free iodine, and the oily methylic salt extracted twice with ether; the ethereal solution was then dried over calcium chloride, evaporated, and the residual, oily, ethereal salt at once converted into the corresponding acid by hydrolysis with potash. After boiling with excess of alcoholic potash for about five minutes, the solution was diluted with water, evaporated on a water bath till free from alcohol, acidified, and extracted 15 times with ether; the dark, crystalline mass which remained after distilling off the ether was purified by recrystallisation,

first from water with the aid of animal charcoal, and then from ether. Analysis,

	Found.		Theory.
	I.	II.	$C_5H_6(COOH)_2$.
C	53.90	53.77 per cent.	53.84 per cent.
H	5.46	5.33 „	5.13 „

Dihydropentenedicarboxylic acid crystallises in hard, glistening, transparent crystals, and melts unaltered at about 178° ; it is readily soluble in hot water, alcohol, acetic acid, and acetic anhydride, moderately in ether, but only sparingly in benzene, light petroleum, and cold water. It is a strong acid; its aqueous solution is strongly acid to litmus, and even thick crystals effervesce vigorously when brought in contact with sodium carbonate solution; a dilute solution of its sodium salt decolorises permanganate, although not so instantaneously as the sodium salts of many other unsaturated acids. In its behaviour towards bromine vapour, this acid appears to differ in a very marked manner from the corresponding dihydrotetrenedicarboxylic acid; a small quantity of the former was exposed to dry bromine vapour under a bell-jar during two days, the reddish-coloured product was freed from bromine over potash in a vacuum dessicator, and the residue recrystallised from hydrobromic acid. The crystals obtained melted and decomposed at 180° , and as they contained bromine, they probably consisted of dibromopentamethylenedicarboxylic acid; unfortunately the identity could not be proved by analysis, owing to the small quantity of material at our disposal; under similar conditions, dihydrotetrenedicarboxylic acid remains unchanged.

In its behaviour when heated, dihydropentenedicarboxylic acid differs also in a marked manner from the corresponding tetrene derivative; the latter, on distillation, carbonises and is entirely decomposed, whereas the former, if rapidly heated, distils without decomposition, the solid distillate melting at 175 – 177° . If, however, the pentene acid be heated for 10 minutes in a narrow test-tube in such a way that the distillate constantly runs back, and the product be then distilled, an oily distillate will be obtained which, on long standing, becomes opaque from separation of a small quantity of a crystalline substance, and, on warming with water, it first melts and then gradually passes into solution. On standing over sulphuric acid in a vacuum, the aqueous solution deposits a small quantity of dihydropentenedicarboxylic acid, and the filtrate from these crystals, on evaporation, dries up to a gummy residue, which resembles the product obtained on dissolving the anhydride of dihydrotetrenedicarboxylic acid in water; it could not be analysed, the quantity being insufficient.

Salts of Dihydropentenedicarboxylic acid.

Hydrogen Silver Salt, $\text{COOH} \cdot \text{C}_7\text{H}_6 \cdot \text{COOAg}$.—One of the most characteristic properties of dihydrotetrenedicarboxylic acid is the tendency which it shows to form a hydrogen silver salt, and this property is even more pronounced in the case of dihydropentenedicarboxylic acid.

The pure acid was dissolved in water, the solution rendered slightly alkaline with ammonia, warmed to about 40° , and excess of silver nitrate added, when a white precipitate separated, which was collected, washed with water, and dried over sulphuric acid in a vacuum.

When heated in a crucible, this salt decomposes suddenly with formation of voluminous threads of silver, and the amount of silver contained in the salt was found to be only 44.3 per cent., whereas the neutral salt, $\text{C}_7\text{H}_6\text{O}_4\text{Ag}_2$, would contain 58.38 per cent.; indeed, this analysis agrees very much better with the composition of the hydrogen silver salt, $\text{C}_7\text{H}_7\text{O}_4\text{Ag}$, which contains 41.08 per cent. of silver.

The mother liquors from this salt, on standing, deposited long, colourless needles which in appearance closely resemble the crystals of the hydrogen silver salt of dihydrotetrenedicarboxylic acid. They were collected, washed with water, and analysed with the following result.

	Found.	Theory. $\text{C}_7\text{H}_7\text{O}_4\text{Ag}$.
Ag	41.41 per cent.	41.08 per cent.

This salt is, therefore, evidently the hydrogen silver salt.

A neutral solution of the ammonium salt of dihydropentenedicarboxylic acid shows the following behaviour with reagents.

Lead acetate; a white, gelatinous precipitate.

Copper sulphate and barium nitrate; no precipitate.

Calcium chloride; no precipitate at first, but, on standing, the calcium salt separates slowly in magnificent four-sided, glistening, tabular crystals.

Anhydride of Trans-pentamethylenedicarboxylic acid.

As explained in the introduction to this paper, considerable interest attaches to the preparation of an anhydride of *trans*-pentamethylenedicarboxylic acid, and many experiments were made with the object of obtaining this substance, of which only one or two can be described here.

The *trans*-acid used in these experiments was very carefully purified by repeated recrystallisation; it was then heated in sealed tubes

at 200° with concentrated hydrochloric acid, in order to free it from traces of the *cis*-acid which might possibly be present (compare this vol., 590), and then quantities of about 1 gram were heated with pure acetic anhydride to boiling on a reflux apparatus for 5, 10, 15, 20, and 25 minutes respectively. After standing for several days over potash in a vacuum, and until free from acetic anhydride, a very thick, oily residue was in all cases, obtained, which, even when the heating had been continued for 25 minutes, gradually deposited varying quantities of unchanged acid, and all the samples, on standing, exposed to the air completely solidified to a cake of the pure acid in a few days.

Ultimately, a substance consisting evidently of nearly pure *trans*-pentamethylenedicarboxylic anhydride was obtained as follows.

The pure acid was heated with 10 times its weight of pure acetic anhydride on a reflux apparatus for 25 minutes, so that the liquid just boiled; the product was then transferred to a small Würtz flask, heated at 120° under a pressure of 20 mm., and a slow stream of carefully dried air allowed to pass through the liquid until the excess of acetic anhydride had been completely removed.

The slightly brownish residue gave, on analysis, the following numbers, which agree with those required for the anhydride of *trans*-pentamethylenedicarboxylic acid.

	Found.		
	I.	II.	Theory.
C	59.73	59.81 per cent.	$C_5H_8C_2O_3$. 60.00 per cent.
H	5.90	5.87 „	5.71 „

This substance is, however, not quite pure, and contains traces of the *cis*-anhydride, as was shown by the fact that when it was dissolved in hot water, and the solution allowed to cool, crystals were obtained which did not melt quite sharply at 160° (the m. p. of the *trans*-acid), and the mother liquor was found to contain traces of the *cis*-acid; nevertheless, there can be no doubt that the greater portion of the substance must have consisted of the anhydride of the *trans*-acid.

In its properties, this anhydride differs in many ways from the beautifully crystalline anhydride of the *cis*-acid; it dissolves, for example, in sodium carbonate very rapidly with effervescence, and when exposed to the air on a watch-glass, it gradually solidifies to a solid cake consisting principally of the *trans*-acid; the *cis*-anhydride, on the other hand, is stable in the air, and dissolves only very slowly in sodium carbonate.

Possibly this tendency to combine with water may account for the gradual deposition of *trans*-acid from the products of the time ex-

periments described above, as it is difficult to be certain that potash is dry, and, moreover, water would be produced by the absorption of the acetic acid.

The remainder of the *trans*-anhydride was distilled under reduced pressure, when a colourless distillate was obtained, which solidified in the manner so highly characteristic of the *cis*-anhydride; the distillate was dissolved in acetic anhydride and allowed to slowly evaporate over potash in a vacuum, when crystals gradually separated which melted at 70—71° (the *cis*-anhydride melts at 73°), and gave on analysis the following result.

	Found.	Theory. $C_5H_8C_2O_3$.
C	59·68 per cent.	60·00 per cent.
H	5·89 „	5·71 „

It is, therefore, obvious that *trans*-pentamethylenedicarboxylic anhydride, on distillation, is converted into the anhydride of the *cis*-acid.

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