# LXIV.—*The Use of Tetramethylene Dibromide in the Synthetical Formation of Closed Carbon Chains.*

By LEONARD JAMES GOLDSWORTHY.

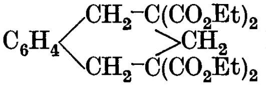
TETRAMETHYLENE dibromide, formerly obtainable with difficulty, is now accessible in quantity either from *cyclo*hexanol (von Braun and Lemke, *Ber.*, 1922, **55**, 3526) or from ethyl succinate (Müller, *Monatsh.*, 1928, **49**, 27).

The present communication is concerned with its action on the sodium compounds of ethyl malonate, ethyl ethanetetracarboxylate and ethyl propanetetracarboxylate.

Haworth and Perkin (J., 1894, **65**, 96), when investigating the action of pentamethylene dibromide, prepared from pentamethylenediamine, on the sodium compound of ethyl malonate, isolated from the products of the reaction ethyl *cyclo*pentane-1 : 1-dicarboxylate. They concluded from this that their pentamethylene dibromide was a mixture of tetramethylene and pentamethylene dibromides and showed how the tetramethylene compound might have been formed during the preparation of the pentamethylenediamine. The authors commented on the remarkable difference in behaviour of pentamethylene and tetramethylene dibromides towards the sodium compound of ethyl malonate : whereas the former dibromide yielded ethyl *cyclo*hexane-1 : 1-dicarboxylate and ethyl heptane-ααωω-tetracarboxylate, the latter under precisely similar conditions gave only ethyl *cyclo*pentane-1 : 1-dicarboxylate, no ethyl hexane-ααωω-tetracarboxylate being formed. The author has investigated the action of ethyl sodiomalonate on pure tetramethylene dibromide, and his results are in complete accord with those obtained in the experiments with the mixed dibromides.

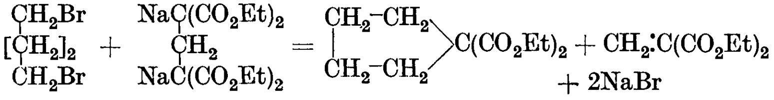
From the product of the action of tetramethylene dibromide on ethyl sodioethanetetracarboxylate, a reaction analogous to those by which hexahydroterephthalic and hexahydro*iso*phthalic acids have been synthesised by Perkin and his collaborators, the author has obtained *cis*- and *trans*-hexahydrophthalic acids, identical with the acids obtained by Baeyer (*Annalen*, 1890, **258**, 213) by the reduction of tetrahydrophthalic acid.

According to Kötz (*J. pr. Chem.*, 1903, **68**, 148) the compound



$C_6H_4\left\langle\begin{matrix}CH_2\text{-}C(CO_2Et)_2\\ CH_2\text{-}C(CO_2Et)_2\end{matrix}\right\rangle CH_2$

has been synthesised by Speiss by the action of *o*-xylylene dibromide on ethyl sodiopropanetetracarboxylate. By the analogous reaction of tetramethylene dibromide with this sodium compound the author has attempted to synthesise ethyl *cyclo*heptane-1 : 1 : 3 : 3-tetracarboxylate, with totally unexpected results. The products of the reaction were ethyl *cyclo*pentane-1 : 1-dicarboxylate and the polymeride of ethyl methylenemalonate, prepared first by Zelinsky (*Ber.*, 1889, **22**, 3296) by the action of methylene iodide on ethyl sodiomalonate and later by Perkin (J., 1898, **73**, 340), who gave to it the name "para-ethylic methylene malonate." From the former compound a dicarboxylic acid, identical with that synthesised by the action of ethyl sodiomalonate on tetramethylene dibromide, was obtained. It would appear, therefore, that the reaction which takes place is that represented by the equation



$$\begin{matrix}CH_2Br\\ [CH_2]_2\\ CH_2Br\end{matrix} + \begin{matrix}NaC(CO_2Et)_2\\ CH_2\\ NaC(CO_2Et)_2\end{matrix} = \begin{matrix}CH_2\text{-}CH_2\\ |\\ CH_2\text{-}CH_2\end{matrix}\!\!>C(CO_2Et)_2 + CH_2{:}C(CO_2Et)_2 + 2NaBr$$

Another striking example is thus afforded of the ease of formation of 5-carbon ring structures.

## EXPERIMENTAL.

*Preparation of Tetramethylene Dibromide.*—Tetramethylene glycol was converted into the dibromide in better yield (85%) by the following method than by that employed by Müller (*loc. cit.*). To a mixture of 48% hydrobromic acid (155 c.c.) and concentrated sulphuric acid (36 c.c.), the glycol (48 g.) was added and then gradually, with cooling, concentrated sulphuric acid (58 c.c.). The mixture was refluxed for one hour and then distilled until no more drops of the dibromide appeared in the distillate. The crude dibromide was washed successively with water, cold concentrated sulphuric acid, a 10% solution of sodium carbonate and water, dried over calcium chloride, and distilled, practically wholly at 97°/30 mm.

*Action of Tetramethylene Dibromide on Ethyl Sodiomalonate.*—Tetramethylene dibromide (21·8 g.) and ethyl malonate (32 g.) were added to a solution of sodium (4·6 g.) in dry alcohol (80 c.c.). When the mixture was warmed slightly, a vigorous reaction set in, which was completed by 4 hours' heating on the water-bath. The alcohol was then distilled off, the residue mixed with water and extracted with ether, the ethereal solution washed and dried, the ether removed, and the residual oil distilled under diminished pressure. Two fractions were collected, of which the first distilled below 135°/30 mm. and consisted mainly of ethyl malonate, and the second passed over at 135—190°/30 mm. (mostly at 160—180°). The latter on redistillation at the ordinary pressure gave a small fraction below 210°, consisting mainly of ethyl malonate, and a fraction 210—227°. This was hydrolysed with methyl-alcoholic potash in the usual way, and after removal of the methyl alcohol was acidified, and the residue evaporated to dryness at the ordinary temperature over solid potash in a vacuum desiccator. The *cyclo*pentane-1 : 1-dicarboxylic acid was extracted from the nearly colourless, dry residue with ether and twice crystallised from water; m. p. 185° (Haworth and Perkin, *loc. cit.*, give 184—185°) [0·1664 neutralised 0·1800 $Ba(OH)_2$; calc., 0·1801]. When it was heated just above the m. p., the acid was converted into an oil with an unpleasant rancid odour, which was clearly identical with *cyclo*pentanemonocarboxylic acid (Wislicenus, *Annalen*, 1898, **275**, 337).

*Action of Tetramethylene Dibromide on Ethyl Sodiomethanetetracarboxylate.*—Dry alcoholic solutions of ethyl ethanetetracarboxylate (38·2 g. in 60 c.c.) and of sodium (5·5 g. in 70 c.c.) were mixed and well shaken, tetramethylene dibromide (26·2 g.) was added, and the mixture refluxed for 4 hours and, as it still had an alkaline reaction, heated for 2 hours in a sealed bottle at 100°. The bulk of the alcohol was then distilled off, water added, and the residual oil extracted with ether. From the washed and dried ethereal solution, an oil was obtained which on distillation gave a small fraction below 100°/30 mm., two small fractions at 100—210° and 210—220°, and a large fraction (27·3 g.) at 220—240°. A further small quantity of oil distilling at 220—240°/30 mm. was obtained by redistillation of the fractions 100—210° and 210—220°. One more fractionation yielded 26·5 g. of an oil, b. p. 225—235°/30 mm., which was hydrolysed by refluxing with methyl-alcoholic potash. After removal of the methyl alcohol, acidification with hydrochloric acid, and evaporation to dryness, the product was extracted with ether in a Soxhlet apparatus. The ether was then distilled off and the brown viscous residue of *cyclo*hexane-1 : 1 : 2 : 2-tetracarboxylic acid was converted into the dicarboxylic acid by ½ hour's heating at 200°. During the heating, impure crystals of the *cis*-acid, m. p. 170—183°, formed by the reunion of the *cis*-anhydride and water encrusted the cool parts of the apparatus (0·0780 neutralised 0·0500 KOH; calc., 0·0508).

The crude acid in the flask was dissolved in water, and the solution decolorised with animal charcoal. On evaporation, colourless crystals were obtained, which even after several recrystallisations melted indefinitely at 175—180° and were apparently a mixture of the *cis*- and *trans*-acids. As these are not easily separated by fractional crystallisation (compare Baeyer, *loc. cit.*), the mixture of acids was distilled and so converted into the *cis*-anhydride, which was obtained as a colourless oil mixed with water, a small amount of a brown impurity remaining behind in the distilling flask. When the anhydride was dissolved in hot water, and the solution evaporated, crystals of the *cis*-acid were formed, m. p. 192° after softening and sintering at 182° in the manner described by Baeyer (0·1133 neutralised 0·1121 KOH; calc., 0·1127).

For the preparation of the *trans*-acid the mother-liquors from the crystallisation of the mixture of *cis*- and *trans*-acids were evaporated and the residue, a yellow viscous mass, was distilled. From the distillate of crude *cis*-anhydride, by solution in water and evaporation, crystals of the *cis*-acid were obtained, which were nearly pure after one recrystallisation. These were heated with concentrated hydrochloric acid in a sealed tube for 4 hours at 180° and so converted into the *trans*-acid, of which crystals mixed with specks of carbon separated on cooling. The acid after purification with animal charcoal and one recrystallisation from water was pure, m. p. 215—221° [0·0984 neutralised 0·0976 $Ba(OH)_2$; calc., 0·0978].

*Action of Tetramethylene Dibromide on Ethyl Sodiopropanetetracarboxylate.*—Sodium (5·5 g.) was dissolved in dry alcohol (68 c.c.)

in a pressure bottle provided with a reflux condenser, by heating at 130°. The solution was cooled to about 40°, and the semi-solid mass obtained was well shaken with ethyl propanetetracarboxylate (39·8 g.) until it became entirely fluid. When tetramethylene dibromide (26·2 g.) was added to the cold solution, a reaction set in with considerable evolution of heat. This was completed on the next day by closing the pressure bottle and heating for 3 hours at 130°. From the reaction mixture, after distillation of the alcohol and addition of water, ether extracted an oil (43 g.), which was distilled under reduced pressure, the following fractions being collected: below 140°/30 mm., 6·4 g.; 140—150°, 7·0 g.; 150—180°, 3·8 g.; 180—210°, 16·2 g.; 210—240°, 6·3 g. During the collection of the last fraction decomposition set in and the pressure rose to 80 mm., several grams of a tarry substance remaining in the distilling flask. On standing for 24 hours, the fraction 180—210°/30 mm. almost completely solidified, forming a colourless wax-like mass, the appearance of which suggested that it might be the polymeride of ethyl methylenemalonate. After being washed with light petroleum and dried on a porous plate, the substance melted at 155—160° (Zelinsky, *loc. cit.*, found 155—156°), and when heated above the m. p. slowly decomposed with evolution of a gas, the decomposition taking place rapidly above 200° (Found: C, 55·3; H, 6·3. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0%). These figures and the properties of the substance, *viz.*, its behaviour when heated, its sparing solubility in alcohol, ether, light petroleum, and benzene, and its reducing action on potassium permanganate, left no doubt as to its identity with the polymeride of ethyl methylenemalonate.

The other product of the reaction, *viz.*, ethyl *cyclo*pentane-1 : 1-dicarboxylate (see equation on p. 483), was found in the fractions which distilled at 140—150° and 150—180°. From these, by refractionation first under reduced pressure (30 mm.) and finally at the ordinary pressure, 7·6 g. of an oil, b. p. 223—225°/761 mm., were obtained. This ester was converted in the usual way into the corresponding acid, m. p. 183—184° after four recrystallisations from water [0·1900 neutralised 0·2037 $Ba(OH)_2$; calc., 0·2056]. The identity of the acid was further established by heating it above its m. p. and distilling the monocarboxylic acid formed. The distillate was an oil having the characteristic rancid odour of *cyclo*pentanemonocarboxylic acid.

UNIVERSITY COLLEGE, RANGOON.

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