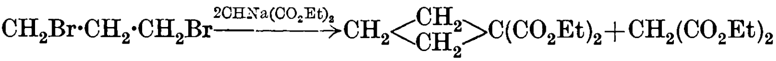
# CXCIX.—*The Action of Certain Dibromotetracarboxylic Esters on the Sodium Derivatives of Ethyl Malonate, Ethyl Ethanetetracarboxylate, and Analogous Substances.*

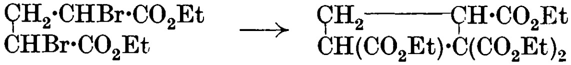
By JOHN JOSEPH LENNON and WILLIAM HENRY PERKIN, jun.

WHEN a dibromo-hydrocarbon reacts with the sodium derivative of ethyl malonate, the decomposition usually proceeds in such a manner that sodium bromide is eliminated and a *cyclo*paraffin dicarboxylic ester is produced; in the case of trimethylene dibromide, for example, the following change occurs:



$$CH_2Br\cdot CH_2\cdot CH_2Br \xrightarrow{2CHNa(CO_2Et)_2} CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C(CO_2Et)_2+CH_2(CO_2Et)_2$$

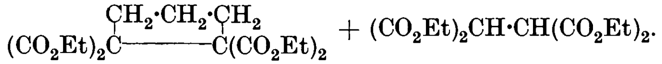
A similar decomposition takes place when the dibromo-hydrocarbon is replaced by the corresponding dibromodicarboxylic ester containing $CO_2Et$ associated with each bromine atom; *e.g.*, $\alpha\gamma$-dibromopropane-$\alpha\gamma$-dicarboxylic ester reacts with ethyl sodiomalonate to yield ethyl *cyclo*butane-1 : 2 : 2 : 3-tetracarboxylate :



$$\begin{array}{l}CH_2\cdot CHBr\cdot CO_2Et\\ CHBr\cdot CO_2Et\end{array} \longrightarrow \begin{array}{l}CH_2\text{———}CH\cdot CO_2Et\\ CH(CO_2Et)\cdot C(CO_2Et)_2\end{array}$$

(Ing and Perkin, J., 1925, **127**, 2389). But if an $\alpha\gamma$-dibromo-$\alpha\alpha\gamma\gamma$-tetracarboxylic ester such as $(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2$ is employed in the place of the $\alpha\gamma$-dibromo-$\alpha\gamma$-dicarboxylic ester, interaction of an entirely different type occurs. The first case of this kind was observed by Perkin and Prentice (J., 1891, **59**, 822), who, in studying the interaction of ethyl $\alpha\epsilon$-dibromopentane-$\alpha\alpha\epsilon\epsilon$-tetracarboxylate with the sodium derivative of ethyl malonate, found that instead of ethyl *cyclo*hexane-1 : 1 : 2 : 2 : 3 : 3-hexacarboxylate being formed as analogy had suggested, the product consisted of a mixture of ethyl *cyclo*pentane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate, the change having evidently taken the following course :

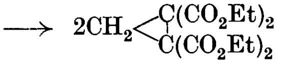
$$(CO_2Et)_2CBr\cdot[CH_2]_3\cdot CBr(CO_2Et)_2 + 2CHNa(CO_2Et)_2 \longrightarrow$$



$$\begin{array}{c}CH_2\cdot CH_2\cdot CH_2\\ (CO_2Et)_2C\text{————}C(CO_2Et)_2\end{array} + (CO_2Et)_2CH\cdot CH(CO_2Et)_2.$$

It was suggested at the time that the curious course taken by this interaction was due to the greater ease of formation of the *cyclo*pentane ring. At a later date (J., 1903, **83**, 782; 1905, **87**, 358) Gregory and Perkin showed that the interaction of ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate with the disodium derivative of ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarboxylate does not lead to the synthesis of the *cyclo*hexane derivative as had been expected but to the formation of two molecules of ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate, the yield being almost quantitative :

$$(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2 + (CO_2Et)_2CNa\cdot CH_2\cdot CNa(CO_2Et)_2$$



$$\longrightarrow 2CH_2{<}\begin{array}{l}C(CO_2Et)_2\\ C(CO_2Et)_2\end{array}$$

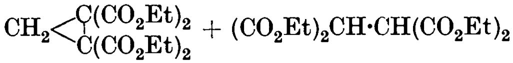
The present investigation was undertaken with the object of studying other decompositions of the kind just mentioned, under as varied conditions as practicable, and it was hoped that it might then be possible to suggest some satisfactory explanation to account for the curious course these interactions take. The following brief summary will indicate sufficiently well the cases which were selected for examination and the course followed by each of the decompositions.

I. Ethyl dibromomalonate and ethyl disodioethanetetracarboxylate interact with the formation of ethyl ethylenetetracarboxylate :

$$2CBr_2(CO_2Et)_2 + 2(CO_2Et)_2CNa\cdot CNa(CO_2Et)_2 \longrightarrow 3(CO_2Et)_2C{:}C(CO_2Et)_2$$

II. Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate and ethyl sodiomalonate yield ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate :

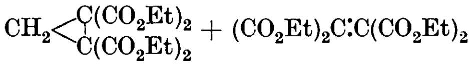
$$(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2 + 2CHNa(CO_2Et)_2 \longrightarrow$$



$$CH_2{<}\begin{array}{l}C(CO_2Et)_2\\ C(CO_2Et)_2\end{array} + (CO_2Et)_2CH\cdot CH(CO_2Et)_2$$

III. Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate interacts with ethyl disodioethanetetracarboxylate to yield ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate :

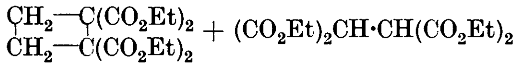
$$(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2 + (CO_2Et)_2CNa\cdot CNa(CO_2Et)_2 \longrightarrow$$



$$CH_2{<}\begin{array}{l}C(CO_2Et)_2\\ C(CO_2Et)_2\end{array} + (CO_2Et)_2C{:}C(CO_2Et)_2$$

IV. Ethyl αδ-dibromobutane-ααδδ-tetracarboxylate and ethyl sodiomalonate yield ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate :

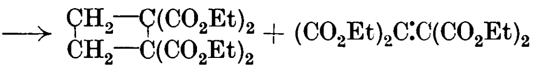
$$(CO_2Et)_2CBr\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2 + 2CHNa(CO_2Et)_2 \longrightarrow$$



$$\begin{array}{l}CH_2-C(CO_2Et)_2\\ CH_2-C(CO_2Et)_2\end{array} + (CO_2Et)_2CH\cdot CH(CO_2Et)_2$$

V. Ethyl αδ-dibromobutane-ααδδ-tetracarboxylate reacts with ethyl disodioethanetetracarboxylate to yield ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate :

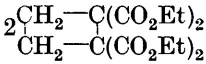
$$(CO_2Et)_2CBr\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2 + (CO_2Et)_2CNa\cdot CNa(CO_2Et)_2$$



$$\longrightarrow \begin{array}{l}CH_2-C(CO_2Et)_2\\ CH_2-C(CO_2Et)_2\end{array} + (CO_2Et)_2C{:}C(CO_2Et)_2$$

VI. Ethyl αδ-dibromobutane-ααδδ-tetracarboxylate and ethyl disodiobutane-ααδδ-tetracarboxylate interact with the formation of two molecules of ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate :

$$(CO_2Et)_2CBr\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2 +$$



$$(CO_2Et)_2CNa\cdot CH_2\cdot CH_2\cdot CNa(CO_2Et)_2 \longrightarrow 2\begin{array}{l}CH_2-C(CO_2Et)_2\\ CH_2-C(CO_2Et)_2\end{array}$$

Various explanations for the apparently anomalous course of these decompositions have been considered from time to time. It has been suggested that in case III, for example, there may in the first place be an interchange of bromine and sodium giving rise to the molecules $(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CNa(CO_2Et)_2$ and

$(CO_2Et)_2CBr{\cdot}CNa(CO_2Et)_2$

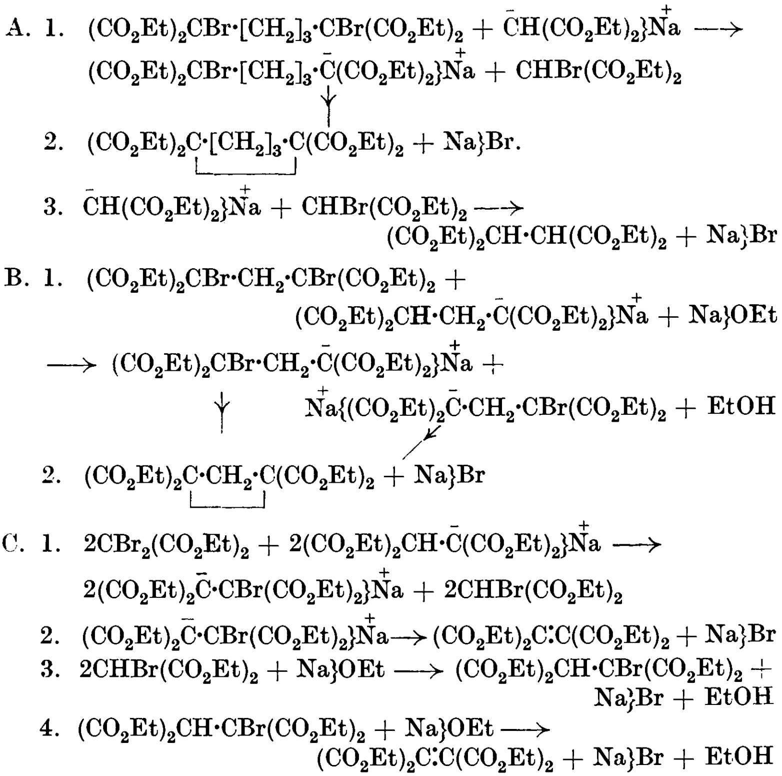
and that each of these might undergo internal elimination of sodium bromide with the formation of ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate respectively. In a similar way, in case VI, ethyl dibromobutanetetracarboxylate and the disodium derivative of ethyl butanetetracarboxylate might undergo intermolecular change yielding two molecules of $(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(CO_2Et)_2$, each of which might then suffer internal elimination of sodium bromide with the formation of ethyl *cyclo*butanetetracarboxylate. Interpreted in accordance with modern conceptions, this suggestion is probably fundamentally correct, but, in this form, it does not appear to be capable of development into an explanation of the whole of the phenomena.

Another view is that the reason for the course taken in these interactions is to be sought in an extension of the theory of Beasley, Ingold, and Thorpe (J., 1915, **107**, 1080). If in the case of ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarboxylate, for example, it is assumed that the two pairs of carbethoxy-groups cause the fourth valencies of the two carbon atoms to which they are united to be directed together, then it is conceivable that the valencies set free in each of the molecules when sodium bromide is eliminated might, by nature of their proximity, unite directly rather than combine with the second molecule, and that, even in case IV, this might be sufficient to cause the *cyclo*butane derivative to be produced rather than the *cyclo*pentane derivative. Ingold (J., 1921, **119**, 305) has calculated that the carboxyl group attached to a carbon atom decreases the angle between two of the remaining valencies by the same amount as the methyl group, namely, by 2° 8′. It is of course possible that two carbethoxy-groups attached to the same carbon atom might cause a deflexion of more than 5° 6′, but in any case the influence would be too inconsiderable to account for the formation of the small rings in the examples given in this communication.

A much more likely explanation, and one which quite easily meets all the cases under discussion, is the following, for which we are indebted to Professor Robinson.

It seems probable on general grounds that in cases where competing intramolecular and intermolecular reactions of a similar type may occur, there will be a factor favouring the former processes. The inevitable proximity of the reacting centres involves a virtual relative increase of concentration or active mass and obviously there is a stage that is unimolecular in the intramolecular processes, but bimolecular in the intermolecular processes. Thus the action of metals on trimethylene bromide might give either *cyclo*propane or *cyclo*hexane and on the basis of the principle of maximal loss of free energy we should anticipate the formation of *cyclo*hexane. Actually it is *cyclo*propane that is formed and the consideration mentioned above suggests a reasonable explanation of the result. It is not practicable in this instance to augment the concentration of the bromide to such a degree that the intermolecular reaction occurs to a predominating extent, but in cases where the intramolecular reaction proceeds with greater difficulty it should be possible to observe the effects of variations of the concentration on the proportions in which the products are obtained.

We may therefore conclude that substances of the types $(CO_2Et)_2CBr{\cdot}\overset{-}{C}(CO_2Et)_2\}\overset{+}{Na}$, $(CO_2Et)_2CBr{\cdot}[CH_2]_n{\cdot}\overset{-}{C}(CO_2Et)_2\}\overset{+}{Na}$ would be far more likely to give $(CO_2Et)_2C{:}C(CO_2Et)_2$ and $(CO_2Et)_2\underline{C{\cdot}[CH_2]_n{\cdot}C}(CO_2Et)_2$ than to give products arising from intermolecular reactions, provided that *n* is not too great. The intramolecular processes are of a particularly facile character and involve merely the transfer of a negative charge to the bromine atom, a species of oxidation–reduction mechanism being postulated. It is necessary, however, if the results described in this communication are to be accommodated, to recognise in addition that the contrast between the behaviour of ethyl $\alpha\gamma$-dibromoglutarate and its $\alpha\gamma$-dicarbethoxy-derivative (see p. 1514) is due to the fact that it is only the $\alpha$-bromomalonic esters (among substances here considered) that contain a bromine atom analogous to that of the hypobromites and capable of substituting itself for hydrogen in suitably reactive molecules. So avid of electrons is the bromine of the bromomalonic esters of the type $CRBr(CO_2Et)_2$ that the substances behave as oxidising agents, liberating iodine from potassium iodide (compare the behaviour of ethyl $\alpha$-bromoacetoacetate in Kurt Meyer's method of titration of enols with bromine) and oxidising hydrazine to nitrogen (Hirst and Macbeth, J., 1922, **121**, 904, 1116; compare *Ann. Reports*, 1922, **19**, 98—103). Orton and King (J., 1911, **99**, 1185) and Wohl (*Ber.*, 1919, **52**, 51) have suggested the use of halogenated amides in halogenations and Gupta and Thorpe (J., 1922, **121**, 1896) showed that dibromodimethyldihydroresorcinol reacts quantitatively with dimethylaniline with formation of *p*-bromodimethylaniline. Halogenation with the help of bromomalonic esters has, however, not been observed previously and is described in the sequel. All the reactions discussed in this communication can be correlated by the assumption of rapid bromination of substituted sodiomalonic esters by substituted bromomalonic esters, followed by slower double decompositions of the normal type concerned with alkylation of malonic esters. A few examples are symbolised below and other cases appear to conform to these types. (Alternative views may be taken of the course of the interaction of bromine and ethyl sodiomalonate. Two anions from the ester may transfer their charges directly to a bromine molecule or the first phase may be bimolecular, leading to the formation of ethyl bromomalonate and sodium bromide. Schemes analogous to the latter view have been adopted in the text, but the translation into the corresponding schemes employing the direct transfer of charges and formation of bromidions can be made without difficulty. Both courses are possible and may occur simultaneously.)



A. 1. $(CO_2Et)_2CBr\cdot[CH_2]_3\cdot CBr(CO_2Et)_2 + \overset{-}{C}H(CO_2Et)_2\}\overset{+}{Na} \longrightarrow$
$(CO_2Et)_2CBr\cdot[CH_2]_3\cdot\overset{-}{C}(CO_2Et)_2\}\overset{+}{Na} + CHBr(CO_2Et)_2$
$\downarrow$
2. $(CO_2Et)_2\underbrace{C\cdot[CH_2]_3\cdot C}(CO_2Et)_2 + Na\}Br.$
3. $\overset{-}{C}H(CO_2Et)_2\}\overset{+}{Na} + CHBr(CO_2Et)_2 \longrightarrow$
$(CO_2Et)_2CH\cdot CH(CO_2Et)_2 + Na\}Br$

B. 1. $(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2 +$
$(CO_2Et)_2CH\cdot CH_2\cdot\overset{-}{C}(CO_2Et)_2\}\overset{+}{Na} + Na\}OEt$
$\longrightarrow (CO_2Et)_2CBr\cdot CH_2\cdot\overset{-}{C}(CO_2Et)_2\}\overset{+}{Na} +$
$\downarrow$ $\overset{+}{Na}\{(CO_2Et)_2\overset{-}{C}\cdot CH_2\cdot CBr(CO_2Et)_2 + EtOH$ $\swarrow$
2. $(CO_2Et)_2\underbrace{C\cdot CH_2\cdot C}(CO_2Et)_2 + Na\}Br$

C. 1. $2CBr_2(CO_2Et)_2 + 2(CO_2Et)_2CH\cdot\overset{-}{C}(CO_2Et)_2\}\overset{+}{Na} \longrightarrow$
$2(CO_2Et)_2\overset{-}{C}\cdot CBr(CO_2Et)_2\}\overset{+}{Na} + 2CHBr(CO_2Et)_2$
2. $(CO_2Et)_2\overset{-}{C}\cdot CBr(CO_2Et)_2\}\overset{+}{Na} \longrightarrow (CO_2Et)_2C{:}C(CO_2Et)_2 + Na\}Br$
3. $2CHBr(CO_2Et)_2 + Na\}OEt \longrightarrow (CO_2Et)_2CH\cdot CBr(CO_2Et)_2 +$
$Na\}Br + EtOH$
4. $(CO_2Et)_2CH\cdot CBr(CO_2Et)_2 + Na\}OEt \longrightarrow$
$(CO_2Et)_2C{:}C(CO_2Et)_2 + Na\}Br + EtOH$

In order to bring further evidence of the oxidising action of bromo-esters containing the α-bromo-αα-dicarboxylic group, the action of ethyl αγ-dibromopropane-ααγγ-tetracarboxylate and of ethyl αδ-dibromobutane-ααδδ-tetracarboxylate on phenol was investigated.

When the former was heated to boiling with a large excess of phenol, the phenol was brominated and the product, on hydrolysis, yielded *propane-ααγ-tricarboxylic acid*, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2H)_2$, m. p. 125°, which on heating, decomposed into carbon dioxide and glutaric acid (m. p. 97—98°). Clearly the products of this decomposition are brominated phenol and ethyl propane-ααγγ-tetracarboxylate, bromination of the phenol and reduction of the dibromo-ester having taken place. In a similar manner, ethyl αδ-dibromobutane-ααδδ-tetracarboxylate and phenol interacted smoothly to yield brominated phenol and an ester which was clearly ethyl butane-ααδδ-tetracarboxylate because on hydrolysis by boiling with hydrochloric acid an almost quantitative yield of adipic acid was obtained.

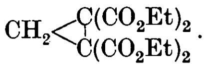
It is therefore each $CBr(CO_2Et)_2$ grouping which is equivalent to a molecule of bromine in these reactions. If, for example, ethyl αδ-dibromobutane-ααδδ-tetracarboxylate could be regarded as equivalent to a molecule of the *cyclo*butane ester plus a molecule of bromine, the experiment just described should have yielded the ring-ester and hydrogen bromide. That this was not the case supports the view that the ring formation, observed in the reactions previously discussed, is dependent on the intermediate production of the sodio-derivative of ethyl monobromobutanetetracarboxylate. In order to test this hypothesis still further, the following experiment was instituted :

Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate (1 mol.) was heated in alcoholic solution with β-naphthol (1 mol.) and sodium ethoxide (2 mols.) on the steam-bath. The product, after being boiled with dilute hydrochloric acid and concentrated, gave a large yield of *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylic acid, the interaction having evidently taken place on these lines :

$$C_{10}H_7{\cdot}ONa + NaOEt + (CO_2Et)_2CBr{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 \longrightarrow$$

$$C_{10}H_6Br{\cdot}ONa + (CO_2Et)_2CH{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 \longrightarrow$$

$$C_{10}H_6Br{\cdot}OH + (CO_2Et)_2CNa{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 \longrightarrow$$



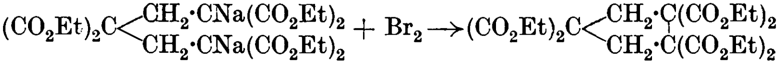
$$CH_2{<}\begin{matrix}C(CO_2Et)_2\\ |\\ C(CO_2Et)_2\end{matrix}.$$

This experiment emphasises the necessity for the formation of the sodio-bromo-derivative before the ring can be closed.

Included in this investigation are some further experiments on the abnormal behaviour of the disodium derivative of ethyl pentanehexacarboxylate, one of the substances produced in considerable quantity during the condensation of ethyl malonate with formaldehyde (Bottomley and Perkin, J., 1900, **77**, 298). In the course of that investigation it was shown that the disodium derivative of this ester does not react normally when heated with methylene iodide to yield ethyl *cyclo*hexane-1 : 1 : 3 : 3 : 5 : 5-hexacarboxylate but is almost completely decomposed into ethyl paramethylenemalonate, probably thus,

$$(CO_2Et)_2CNa\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CNa(CO_2Et)_2 \longrightarrow 2CH_2{:}C(CO_2Et)_2 + Na_2C(CO_2Et)_2$$

the disodium derivative of ethyl malonate then reacting with the methylene iodide to yield a further quantity of ethyl paramethylenemalonate. That the disodium derivative of ethyl pentanehexacarboxylate is in fact capable of existence was demonstrated by its conversion into ethyl *cyclo*pentane-1 : 1 : 3 : 3 : 4 : 4-hexacarboxylate by the action of bromine (*loc. cit.*, p. 303).

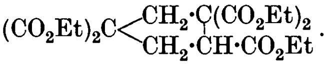


$$(CO_2Et)_2C\Big<\begin{matrix}CH_2\cdot CNa(CO_2Et)_2\\ CH_2\cdot CNa(CO_2Et)_2\end{matrix} + Br_2 \longrightarrow (CO_2Et)_2C\Big<\begin{matrix}CH_2\cdot C(CO_2Et)_2\\ \vert \\ CH_2\cdot C(CO_2Et)_2\end{matrix}$$

A characteristic of this ester is that, on hydrolysis and elimination of carbon dioxide, it yields *trans-cyclo*pentane-1 : 2 : 4-tricarboxylic acid, m. p. 129—130°.

We have now found that the disodium derivative of ethyl pentanehexacarboxylate on heating with ethyl αβ-dibromopropionate, instead of reacting normally with the formation of the *cyclo*heptane derivative, yields ethyl *cyclo*pentanepentacarboxylate. The product was again identified by conversion into *trans-cyclo*pentanetricarboxylic acid, m. p. 129—130°. The probable explanation of this curious synthesis is that the disodium derivative of ethyl pentanehexacarboxylate is, on heating, first decomposed into ethyl paramethylenemalonate and the disodium derivative of ethyl propane-ααγγ-tetracarboxylate, which then reacts with the ethyl αβ-dibromopropionate to yield ethyl *cyclo*pentane-1 : 2 : 2 : 4 : 4-pentacarboxylate :

$$(CO_2Et)_2CNa\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CNa(CO_2Et)_2 \longrightarrow CH_2{:}C(CO_2Et)_2 + (CO_2Et)_2CNa\cdot CH_2\cdot CNa(CO_2Et)_2 \xrightarrow{CH_2Br\cdot CHBr\cdot CO_2Et}$$



$$(CO_2Et)_2C\Big<\begin{matrix}CH_2\cdot C(CO_2Et)_2\\ \vert \\ CH_2\cdot CH\cdot CO_2Et\end{matrix}.$$

Goldsworthy and Perkin (J., 1914, **105**, 2671) have already shown that an excellent yield of ethyl *cyclo*pentanepentacarboxylate may be obtained by treating the disodium derivative of ethyl propanetetracarboxylate with ethyl dibromopropionate. The ease with which ethyl pentanehexacarboxylate loses a molecule of ethyl paramethylenemalonate when its disodium derivative is heated still requires explanation.

## EXPERIMENTAL.

*Preparation of the Materials employed in the Following Experiments.*—"Absolute alcohol" was dehydrated as completely as possible by boiling under reflux over quicklime for at least 8 hours and then distilled.

Ethyl ethanetetracarboxylate, $(CO_2Et)_2CH\cdot CH(CO_2Et)_2$, was prepared by the action of an ethereal solution of iodine on the sodium derivative of ethyl malonate under the conditions described by Bischoff and Rach (*Ber.*, 1884, **17**, 2781). Ethyl propane-ααγγ-tetracarboxylate, $(CO_2Et)_2CH\cdot CH_2\cdot CH(CO_2Et)_2$, was obtained by the action of formaldehyde on ethyl malonate in the presence of diethylamine (Knoevenagel, *Ber.*, 1894, **27**, 2346; Haworth and Perkin, J., 1897, **71**, 1063) and distilled at 195—197°/14 mm. Ethyl butane-ααδδ-tetracarboxylate, $(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$, was prepared by the action of ethyl sodiomalonate on ethylene chloride and on ethyl *cyclo*propane-1 : 1-dicarboxylate (Perkin, J., 1894, **65**, 578; Bone and Perkin, J., 1895, **67**, 111; compare Lean and Lees, J., 1897, **71**, 1063). It distilled at 211—215°/14 mm.

Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate,

$$(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2,$$

was obtained by the action of bromine on ethyl propane-ααγγ-tetracarboxylate in chloroform solution (Gregory and Perkin, J., 1903, **83**, 782). This substance is best purified by cooling a saturated solution in warm petroleum (b. p. 60—80°) to —20° and melts at 55°. Ethyl αδ-dibromobutane-ααδδ-tetracarboxylate, $(CO_2Et)_2CBr\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2$, m. p. 83—85°, was prepared by the action of bromine on ethyl butanetetracarboxylate under conditions similar to those used in the preparation of the corresponding dibromopropane ester (compare Lean, J., 1900, **77**, 107). Ethyl dibromomalonate was obtained by the action of bromine on ethyl malonate as described by Conrad and Bruckner (*Ber.*, 1891, **24**, 3001) and was collected at 128—132°/15 mm.

The decompositions briefly outlined in the introduction were carried out under the following conditions :

I. Ethyl dibromomalonate (31·8 g.) was added to an alcoholic solution of the disodium derivative from ethyl ethanetetracarboxylate (31·8 g.); the mixture became warm and sodium bromide separated. After the whole had been heated under reflux on the steam-bath for 2 hours, water was added, and the product isolated by extraction with ether as usual. A colourless syrup was obtained which largely solidified when it was cooled to —15° and well stirred. The solid was collected with the aid of a pump, left in contact with porous porcelain, and recrystallised from petroleum; it then melted at 56° and was found to be ethyl ethylenetetracarboxylate. The oil which passed through the filter yielded on distillation a further quantity of ethyl ethylenetetracarboxylate, the yield of this ester being about 60% of that possible. The final mother-liquor contained the same ester and yielded on hydrolysis and elimination of carbon dioxide, besides fumaric acid, about 3 g. of succinic acid derived evidently from some unchanged ethyl ethanetetracarboxylate.

II. When ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate (1 mol.) was added to an alcoholic solution of ethyl sodiomalonate (2 mols.), the mixture became warm and sodium bromide separated. The reaction was complete after 2 hours' refluxing and the product, isolated by addition of water and extraction with ether, was a viscid oil which gradually deposited crystals; after recrystallisation from light petroleum, the substance melted at 75—76° and consisted of ethyl ethanetetracarboxylate. The oily mother-liquor solidified on being cooled to $-15°$ and, after contact with porous porcelain, and several crystallisations from petroleum, a substance, m. p. 40—41°, was obtained which was shown to be ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate by analysis and by the undepressed melting point of its mixture with an equal amount of this substance prepared as explained on p. 1514.

III. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate (24·5 g.) was added to ethyl ethanetetracarboxylate (15·9 g.) dissolved in an alcoholic solution of sodium ethoxide (2·3 g. Na). The interaction which set in on standing, was complete after 1 hour's heating under reflux on the steam-bath. The product, diluted with water, was extracted with ether and the ethereal solution was washed with sodium carbonate, dried over calcium chloride, and evaporated; a solid was then obtained which was separated into its two components by fractional crystallisation from petroleum. The less soluble substance, m. p. 55—57°, was ethyl ethylenetetracarboxylate and the other substance, m. p. 42—44°, was proved by careful comparison to be ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate.

IV. On adding ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate (25·2 g.) to a solution of ethyl malonate (16 g.) in alcoholic sodium ethoxide (2·5 g. Na), sodium bromide was quickly precipitated; the decomposition was complete after 2 hours' heating under reflux. The product, isolated in the usual way, was a pale brown syrup which, on cooling, partly solidified. The solid, collected by means of the pump and crystallised from petroleum, melted at 75—76° and proved to be ethyl ethanetetracarboxylate. The oily mother-liquor was hydrolysed by boiling with dilute hydrochloric acid for several hours, and the solution concentrated first on the steam-bath and then over caustic potash in a vacuum desiccator. The solid which had separated after some days was collected and crystallised from hydrochloric acid; a small quantity of adipic acid was isolated and the mother-liquor contained some succinic acid. The former resulted evidently from the hydrolysis of some ethyl butanetetracarboxylate which had been produced by the reduction of the dibromo-derivative, and the latter from some unchanged ethanetetracarboxylate which had not crystallised. The hydrochloric acid mother-liquor from these acids yielded, on evaporation to dryness, a syrupy acid which was converted, by boiling with excess of acetyl chloride, into an anhydride which distilled at 165—170°/20 mm., solidified, and melted at 71—73°. This was identified as the anhydride of *cis-cyclo*butane-1 : 2-dicarboxylic acid by conversion into the acid, m. p. 136—138°, by boiling with water (Perkin, J., 1894, **65**, 582).

V. On mixing equimolecular proportions of ethyl αδ-dibromobutane-ααδδ-tetracarboxylate and ethyl disodioethanetetracarboxylate in alcoholic solution, interaction set in at once; it was completed by heating under reflux for ½ hour. The product, isolated in the usual manner, was a viscid oil which at −10° gradually deposited a solid; this, after recrystallisation, melted at 55—57° and proved to be ethyl ethylenetetracarboxylate. The oily mother-liquor was hydrolysed by boiling with dilute hydrochloric acid for some hours and concentrated; a little fumaric acid then separated and was identified by conversion into maleic anhydride. The mother-liquor was evaporated to dryness and the syrupy residue was heated in an oil-bath at 180° until evolution of carbon dioxide had ceased and then digested with excess of acetyl chloride for 2 hours. On distillation, an anhydride was obtained which boiled at 165°/20 mm. and solidified to a crystalline mass, m. p. 62—70°. This was decomposed by boiling with water, and the solution allowed to evaporate over sulphuric acid in a vacuum desiccator; a solid was then obtained from which, by crystallisation from hydrochloric acid, *cis-cyclo*butane-1 : 2-dicarboxylic acid, m. p. 136—137°, was isolated in quantity.

VI. On the addition of ethyl dibromobutanetetracarboxylate (25·2 g.) to a solution of ethyl butanetetracarboxylate (17·3 g.) in alcoholic sodium ethoxide (2·3 g. Na), the mixture became warm and sodium bromide separated. The action was completed by heating under reflux for 1 hour and the product was treated with water and extracted with ether. The syrup remaining after evaporation of the ether was hydrolysed by boiling with dilute hydrochloric acid for several hours, the solution was evaporated, and the syrupy residue heated at 180° until evolution of gas had ceased and then refluxed for 2 hours with acetyl chloride. On distillation, an oil,

b. p. 148°/14 mm., was obtained which quickly solidified and after contact with porous porcelain had m. p. 72—74°. When this anhydride was boiled with water, and the solution allowed to concentrate over sulphuric acid in a vacuum desiccator, *cis-cyclo*butane-1 : 2-dicarboxylic acid was obtained, m. p. 137—138° (Found : C, 49·9; H, 5·7. Calc. for $C_6H_8O_4$ : C, 50·0; H, 5·6%).

*The Action of Phenol on* (i) *Ethyl* $\alpha\gamma$*-Dibromopropane-*$\alpha\alpha\gamma\gamma$*-tetracarboxylate and* (ii) *Ethyl* $\alpha\delta$*-Dibromobutane-*$\alpha\alpha\delta\delta$*-tetracarboxylate.*—(i) Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate (22 g.), mixed with phenol (70 g.), was gently boiled under reflux for 5 hours and the product, which, on cooling partly crystallised, was distilled; a mixture of phenol and brominated phenol passed over at 185—190° and crystallised, a thermometer placed in the solidifying mass remaining at 35°. The residue above 190° was boiled for 6 hours with concentrated hydrochloric acid (30 c.c.) and water (40 c.c.) and then distilled in steam to remove phenol, etc., and the solution, after being filtered from a viscid insoluble substance, was evaporated to a small bulk and left over solid potash in a vacuum desiccator for 2 weeks, during which the syrup deposited nearly pure *propane-*$\alpha\alpha\gamma$*-tricarboxylic acid*, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2H)_2$, in balls of needles which, after contact with porous porcelain, melted at 115—118°. This acid is almost completely miscible with water, but a concentrated solution left over sulphuric acid gradually deposits needles which melt at about 125° and lose carbon dioxide at 128—135° (Found : C, 41·0; H, 4·6. $C_6H_8O_6$ requires C, 40·9; H, 4·5%). The acid was heated in a test-tube in a sulphuric acid bath at 150—160° until effervescence had ceased; the residue solidified, melted at 95—97° and, after crystallisation from a few drops of water, at 97—98° and consisted of glutaric acid (method of mixed melting point).

(ii) A mixture of ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate (20 g.) and phenol (60 g.) was heated to boiling for 6 hours and the portion boiling at 184—190°, containing much bromine, was distilled off. The residue was boiled with hydrochloric acid (30 c.c.) and water (40 c.c.) for 3 hours, the alcohol eliminated being allowed to escape; the solution was then filtered from the dark gum and evaporated to dryness. The solid residue separated from hydrochloric acid in flat needles, m. p. 150—152°, and consisted of adipic acid, the yield being almost quantitative (Found : C, 49·2; H, 6·9. Calc. for $C_6H_{10}O_4$ : C, 49·3; H, 6·9%).

*The Action of Ethyl* $\alpha\gamma$*-Dibromopropane-*$\alpha\alpha\gamma\gamma$*-tetracarboxylate on* $\beta$*-Naphthol in the Presence of Sodium Ethoxide.*—The dibromo-ester (21 g.) was added to a solution of β-naphthol (6 g.) in alcoholic sodium ethoxide (Na, 2 g.), the clear liquid soon becoming cloudy. After heating for an hour on the steam-bath, the alcohol was evaporated, and the residue was boiled with concentrated hydrochloric acid (20 c.c.) and water (50 c.c.) for 2 days, the alcohol produced being allowed to escape. The filtered product was evaporated to dryness, leaving a syrup which largely crystallised, and this was extracted with ether. After filtration, and distillation of the ether, an almost solid mass remained which, in contact with porous porcelain, left a colourless crystalline mass of nearly pure *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylic acid, m. p. 205—210° and after crystallisation from a little water, 210—212° (vig. eff.) (Found: C, 38·7; H, 2·9. Calc. for $C_7H_6O_8$: C, 38·5; H, 2·7%). The identity of this acid, obtained in large yield in this process, was demonstrated by conversion into the *cis*- and *trans*-modifications of *cyclo*propane-1 : 2-dicarboxylic acid.

*The Action of Ethyl* αβ-*Dibromopropionate on Ethyl* αε-*Disodiopentane*-ααγγεε-*hexacarboxylate.*—The ethyl pentanehexacarboxylate used in this experiment was obtained from the high-boiling oil produced during the preparation of ethyl propane-ααγγ-tetracarboxylate by the condensation of ethyl malonate with formaldehyde (Bottomley and Perkin, J., 1900, **77**, 298). Ethyl αβ-dibromopropionate was prepared by the addition of bromine to acraldehyde, oxidation of the product to αβ-dibromopropionic acid, and esterification of this with alcoholic hydrochloric acid. The material used distilled at 95—97°/13 mm.

A concentrated alcoholic solution of the pentane ester (25 g.) was added to a solution (50 c.c.) of sodium ethoxide (2·5 g. Na) previously mixed with an equal volume of dry ether. Ethyl dibromopropionate (13 g.) was then added, the mixture kept cool during 24 hours, the bulk of the solvents distilled off, and the residue mixed with water and extracted with ether. After being well washed, and dried over calcium chloride, the extract left on evaporation an oil, which was separated into two main fractions by distillation under reduced pressure. That boiling below 180°/15 mm. set to a wax-like solid on standing, and after contact with porous porcelain and crystallisation from alcohol, the crystals melted at 145—148° and were identified as ethyl paramethylenemalonate (Haworth and Perkin, J., 1898, **73**, 340). The other fraction, b. p. 225—245°/15 mm., was boiled with hydrochloric acid until a clear solution resulted, the water and hydrochloric acid were then removed by distillation under reduced pressure, and the residual syrup was heated in an oil-bath at 180—200° for several minutes. When the solution of the product in concentrated hydrochloric acid was kept for several days over solid potash in a vacuum desiccator, crystals gradually separated; these, after being in contact with porous porcelain and recrystallised from hydrochloric acid, melted at 127—130° (Found : C, 47·2 ; H, 4·7. Calc. for $C_8H_{10}O_6$ : C, 47·5 ; H, 4·9%). That this substance was *trans*-*cyclo*pentane-1 : 2 : 4-tricarboxylic acid was established by direct comparison with a specimen of this acid which had been prepared from the product of the action of ethyl αβ-dibromopropionate on the disodium derivative of ethyl propane-ααγγ-tetracarboxylate (Goldsworthy and Perkin, J., 1914, **105**, 2673).

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