XLIII.—*The Action of Ethyl Dibromopropanetetracarboxylate on the Disodium Derivative of Ethyl Propanetetracarboxylate. A Correction.*

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A SHORT time ago (Trans., 1903, **83**, 780), T. W. D. Gregory and the author published the results of a research on the action which takes place when the disodium derivative of ethyl propanetetracarboxylate is digested with ethyl dibromopropanetetracarboxylate. It was shown that the decomposition proceeds almost quantitatively with elimination of sodium bromide and formation of a beautifully crystalline ester which melts at 46°.

Some years previously, Perkin and Prentice (Trans., 1891, **59**, 990) had investigated a very similar decomposition, namely, the action which takes place when the disodium derivative of ethyl propanetetracarboxylate is digested with trimethylene bromide. Since the product obtained in this latter case yielded, on hydrolysis and subsequent elimination of carbon dioxide, the *cis*- and *trans*-modifications of hexahydroisophthalic acid, there can be no doubt that it was ethyl hexamethylenetetracarboxylate, the formation of which is readily understood from the equation

Arguing from this experience, as well as from the results which had been obtained in the investigation of many other analogous ring syntheses, Gregory and the author concluded that the decomposition which had taken place when the disodium derivative of ethyl propanetetracarboxylate was digested with ethyl dibromopropanetetracarboxylate was to be represented as follows:

that is to say, the ester melting at 46° was ethyl hexamethyleneoctocarboxylate. On hydrolysis, this ester yielded the corresponding acid (m. p. 220°), which, when heated above its melting point, was decomposed into carbon dioxide and an acid melting at 175°. This

acid was described as *trans*-hexamethylenetetracarboxylic acid, the change just mentioned being represented in the following way :

Lastly, on treatment with acetic anhydride, the *trans*-acid yielded the anhydride of the corresponding *cis*-acid, which melted at 60°, and was, on hydrolysis, readily converted into the *cis*-acid (m. p. 139—140°).

During the course of a series of experiments similar to those just described, Dr. Max Guthzeit requested Mr. Martin Lobeck* to repeat the above research, with the result that, while able to confirm our experimental work in every detail, he came to the conclusion that the interpretation of the results given by Gregory and the author is certainly incorrect. After carrying out a series of molecular weight determinations, he arrived at the remarkable conclusion that the compounds just mentioned are, without exception, trimethylene derivatives, that is to say, the molecular weights are exactly half those of the hexamethylene derivatives which Gregory and the author assumed had been produced. There is no doubt that Dr. Guthzeit's view is correct, since most of the trimethylene derivatives in question have been obtained by other means, and a careful comparison shows that their properties agree almost exactly with those of the substances obtained by Gregory and the author. The following corrections are therefore necessary in the original paper (Trans., 1903, 83, 780).

For "ethyl hexamethyleneoctocarboxylate" read "ethyl trimethylenetetracarboxylate."

For "hexamethyleneoctocarboxylic acid" read "trimethylenetetracarboxylic acid."

For "*cis*- and *trans*-hexamethylenetetracarboxylic acids" read "*cis*- and *trans*-trimethylenedicarboxylic acids."

The quantitative formation of a trimethylene derivative by the action of ethyl dibromopropanetetracarboxylate on the disodium derivative of ethyl propanetetracarboxylate is most extraordinary, and, as far as the author knows, entirely without analogy.

When a bromoethereal salt acts on a sodium derivative, the reaction proceeds in such a way that sodium bromide is eliminated and the two residues join together. Thus, for example, when ethyl bromoacetate reacts with the sodium derivative of ethyl malonate, ethyl ethanetricarboxylate is formed :

But the action which takes place between ethyl dibromopropanetetra-

* The account of these experiments will shortly appear.

carboxylate and the disodium derivative of ethyl propanetetracarboxylate is very different from this. The elimination of sodium bromide leads, apparently, to the formation of two unsaturated molecules which, instead of combining in the usual way to form ethyl hexamethyleneoctocarboxylate (p. 358), are each converted into ethyl trimethylenetetracarboxylate by internal saturation :

This reaction is another instance of the remarkable ease with which trimethylene derivatives are formed during the course of reactions which might be expected to yield either unsaturated compounds or hexamethylene derivatives.

Many such cases are now known, and the following may be instanced in illustration of this point.

(1) Trimethylene bromide reacts with zinc to form trimethylene,

and apparently no traces either of propylene (Gustavson, *J. pr. Chem.*, 1899, [ii], 59, 302) or of hexamethylene are formed during the reaction.

(2) Acetyltrimethylene is produced quantitatively when acetylpropyl bromide is digested with caustic potash (Lipp, *Ber.*, 1889, 22, 1207; Idzowska and E. Wagner, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 259, 269; *Chem. Centr.*, 1898, ii, 474) :

(3) Ethyl α -bromoglutarate is converted by treatment with alcoholic potash or quinoline into trimethylenedicarboxylic acid or its ethyl salt :

(Bowtell and Perkin, *Proc.*, 1899, 15, 241; see also the following paper by Perkin and Tattersall, p. 362).

Caronic acid is formed in an exactly similar way when ethyl bromodimethylglutarate is digested with alcoholic potash :

(Perkin and Thorpe, *Trans.*, 1899, **75**, 50).

Preliminary experiments, which have already been made, seem to show that tetra-, penta-, and hexa-methylene rings are not readily formed, if at all, when bromo-compounds similar to those mentioned above are treated with alcoholic potash.

Observations such as these tend to throw doubt on the general applicability of the "Spannungs Theorie" because, according to that theory, four, five, and six membered saturated carbon rings ought to be produced with much greater ease and be much more stable than the three membered carbon ring.

In conclusion, I have to thank Dr. Guthzeit for his kindness in communicating with me privately in regard to this matter and for allowing me to make this correction.

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