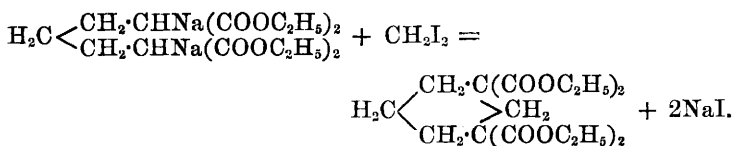


## XII.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

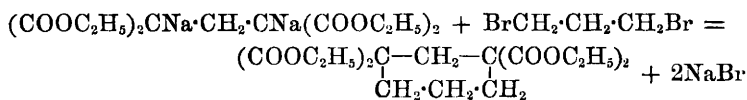
### *Synthesis of Hexahydroterephthalic Acid.*

By J. E. MACKENZIE, B.Sc., and W. H. PERKIN, Jun., Ph.D., F.R.S.

IN a paper published a short time since (Trans., 1891, **59**, 798), it was shown that the disodium compound of ethyl pentanetetracarboxylate, when digested in alcoholic solution with methylene iodide at 100° is, in part, converted into ethyl hexamethylene tetracarboxylate [1 : 1 : 3 : 3], thus :—



The same ethereal salt is also produced by the action of trimethylene bromide on the disodium compound of ethyl propanetetracarboxylate,

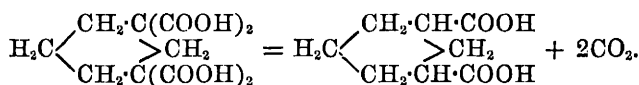


(Trans., 1891, **59**, 990).

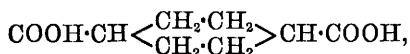
This ethereal salt, on hydrolysis, yields the corresponding tetrabasic acid, and this, when heated at 200—220°, yields a mixture of the two

## SYNTHESIS OF HEXAHYDROTEREPHTHALIC ACID. 173

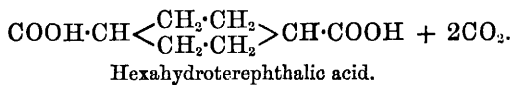
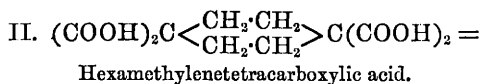
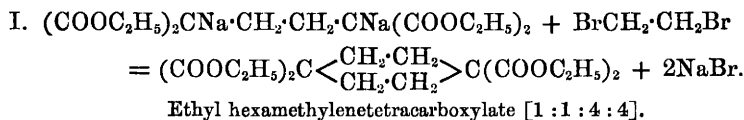
isomeric  $\Gamma^{\text{cis}}$  and  $\Gamma^{\text{cistrans}}$  hexamethylenemetadicarboxylic acids (hexahydroisophthalic acids), with elimination of 2 mols. of carbonic anhydride, thus:—



During the course of the experiments, it was thought probable that the two isomeric hexahydroterephthalic acids,

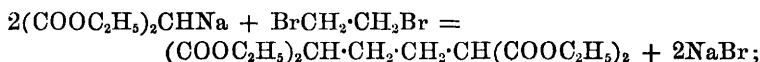


which Baeyer prepared in the course of his beautiful investigations on the reduction of terephthalic acid (*Annalen*, **245**, 169—174), might be synthetically produced in a similar way, from the ethereal salt formed by the interaction of the disodium compound of ethyl butanetetracarboxylate with ethylene bromide, thus:—



On making the experiment, it was found that a considerable quantity of the sparingly soluble  $\Gamma^{\text{cistrans}}$  hexahydroterephthalic acid was produced in this way, and from the mother liquors of this acid a small quantity of an acid melting at 159—162° was with difficulty isolated; the latter is probably the corresponding  $\Gamma^{\text{cis}}$  acid, which melts at 161—162°. Unfortunately, it was not possible to obtain sufficient of the second acid for analysis, owing to the difficulty of preparing ethyl butanetetracarboxylate in large quantities.

This ethereal salt, the preparation of which has been given in a previous paper (*Trans.*, 1887, **51**, 19), is produced in very small quantities when ethylene bromide acts on the sodium compound of ethyl malonate, thus:—



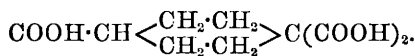
but, in spite of numerous experiments instituted with the object of improving the yield, the largest amount which has as yet been obtained was 35 grams from 1 kilo. of ethyl malonate. For this reason, it was not possible to follow the course of the reaction between the disodium compound of this ethereal salt and ethylene bromide through all its stages, as was the case in the experiments on the synthetical formation of the hexahydroisophthalic acids.

The synthesis of hexahydroterephthalic acid was carried out briefly as follows:—

4 grams of sodium was dissolved in 60 grams of absolute alcohol; the well-cooled solution mixed with 30 grams of pure ethyl butane-tetracarboxylate, 17 grams of ethylene bromide added, and the whole heated in a soda-water bottle at 100° for 10 hours.

The product, which was brownish, and smelt distinctly of ethylene bromide, still had a strongly alkaline reaction; it was mixed with water, extracted four times with ether, the ethereal solution washed well with water, dried over calcium chloride, evaporated, and the residual brownish oil (23 grams) hydrolysed by boiling with a mixture of concentrated sulphuric acid (1 part), water (1 part), and glacial acetic acid (2 parts) for six hours in a reflux apparatus. Steam was next passed through the boiling liquid until all the acetic acid had been removed, the pale-brownish solution cautiously concentrated on a water-bath, and then extracted 30 times with ether. The ethereal solution, after being dried over calcium chloride and evaporated, left 12 grams of a thick, oily acid, which, on standing over sulphuric acid under diminished pressure, rapidly deposited crystals; these, after washing with ether, in which they are sparingly soluble, crystallise from water in cauliflower-like masses, which melt approximately at 152—153°.

The results of the analysis indicate that this substance is hexamethylenetricarboxylic acid,



0.1410 gram substance gave 0.0800 gram H<sub>2</sub>O and 0.2572 gram CO<sub>2</sub>.

	Theory. C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> .	Found.
C. ....	50.00 per cent.	49.75 per cent.
H. ....	5.55     ,,	6.30     ,,
O. ....	44.44     ,,	43.95     ,,

Owing to the small amount of material at our disposal, no further experiments could be made with this acid, and for this reason, it

must in the meantime remain doubtful whether this view of the constitution of this substance is correct.

The remainder of the crude acid was heated at 200—220°, until all evolution of carbonic anhydride had ceased, and the thick, brownish residue, which became almost solid even while quite hot, was allowed to remain in contact with a porous plate for some days; it was then dissolved in dilute sodium carbonate solution, and digested with freshly ignited animal charcoal for two or three hours. The filtered solution after evaporating to a small bulk, and acidifying with hydrochloric acid, deposited on standing about 1·3 grams of a granular precipitate; this, on examination, was found to consist of almost pure  $\Gamma^{\text{cis trans}}$  hexahydroterephthalic acid. The substance, after recrystallisation from water, gave the following numbers on analysis:—

0·1434 gram substance gave 0·0920 gram  $\text{H}_2\text{O}$  and 0·2933 gram  $\text{CO}_2$ .

	Theory. $\text{C}_6\text{H}_{12}\text{O}_4$ .	Found.
C .....	55·81 per cent.	55·77 per cent.
H .....	6·98 „	7·12 „
O .....	37·21 „	37·11 „

This acid melts approximately at 300°, but not sharply; when strongly heated, it sublimes, and this behaviour was especially well observed during the combustion of the substance, when almost the whole sublimed and was deposited in glistening crystals on the cooler portions of the tube. It is readily soluble in warm water, but much more sparingly in cold water; the solution of the sodium salt of the acid does not decolorise potassium permanganate even on standing for some time.

In order, however, to prove conclusively that this acid was identical with the  $\Gamma^{\text{cis trans}}$  hexahydroterephthalic acid obtained by Baeyer from terephthalic acid, the methyl salt was prepared according to Baeyer's directions.

About 0·2 gram of the acid was gently heated in a test-tube with an excess of phosphorus pentachloride for a few seconds, allowed to cool, and the residual solid mass mixed with methyl alcohol. The product was poured into water, the crystalline mass which separated collected, washed with water, and dried on a porous plate over sulphuric acid under diminished pressure. The resulting glistening, crystalline mass melted at 66—68°, and after recrystallisation from light petroleum at 69—70°; Baeyer gives 71° as the melting point of the dimethyl salt of  $\Gamma^{\text{cis trans}}$  hexahydroterephthalic acid.

The mother liquors from the above acid were evaporated to a very small bulk, allowed to stand for some days, the crystalline mass which

separated, collected, washed with a little water, and dried on a porous plate at  $100^{\circ}$ . The resulting crude substance, which, when heated in a capillary tube, began to melt at  $145^{\circ}$ , and was not completely melted at  $190^{\circ}$ , was separated into three substances by conversion into the calcium salt, and repeated recrystallisation of the acids from water: that is, into small quantities of  $\Gamma^{\text{cis trans}}$  hexahydroterephthalic acid, a considerable quantity of an acid melting at  $147\text{--}149^{\circ}$ , probably adipic acid (from the hydrolysis of some unchanged ethyl butanetetracarboxylate), and about 0.028 gram of an acid melting at  $159\text{--}162^{\circ}$ , which is probably  $\Gamma^{\text{cis trans}}$  hexahydroterephthalic acid (m. p.  $161\text{--}162^{\circ}$ ).

The titration of this acid gave the following results:—

0.0271 gram required for neutralisation 3.1 c.c. of potassium hydrate solution (1 c.c. = 0.00559 gram KOH) = 0.0173 gram KOH.

A bibasic acid of the formula  $\text{C}_8\text{H}_{12}\text{O}_4$  requires theoretically 0.0177 gram KOH.

The solution of the potassium salt of this acid, rendered slightly alkaline by the addition of potassium carbonate, did not decolorise potassium permanganate solution.

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