XCVI.—*Action of Ethylic β -Iodopropionate on the Sodium Derivative of Ethylic Isopropylmalonate.*

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THESE experiments which were instituted, as explained in the introduction to the preceding paper, with the object of obtaining additional evidence of the constitution of isopropylglutaric acid, were conducted as follows.

Sodium (6 grams) was dissolved in absolute alcohol (75 grams), the solution cooled, and *very carefully purified* ethylic isopropylmalonate (55 grams) and ethylic β -iodopropionate (50 grams) were added, when a somewhat energetic action set in, the mixture becoming quite hot. As soon as the action had subsided, the mixture was heated for four hours on a water bath, in a reflux apparatus, water was then added, the oily product extracted three times with ether, the ethereal solution washed well with water containing a little sulphurous acid, to remove traces of iodine, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure (100 mm.).

Between 150° and 210°, about 20 grams came over, the thermometer then rose rapidly to 220°, most of the residue distilling at 225—235°, and this portion, on refractionation, distilled almost con-

stantly at 228—230° (100 mm.) as a thick, colourless oil, which, on analysis, gave the following numbers.

0·1604 gave 0·3490 CO₂ and 0·1236 H₂O. C = 59·34; H = 8·56.

0·1444 „ 0·3159 „ „ 0·1123 „ C = 59·64; H = 8·65.

C₁₅H₂₆O₆ requires C = 59·60; H = 8·61 per cent.

This *ethylc α-isopropylpropane-ααα₁-tricarboxylate*,

is isomeric with the ethereal salt,

described in the preceding paper, and obtained by the action of ethylic α-bromotrimethylpropionate on the sodium derivative of ethylic malonate, or by condensing ethylic malonate with ethylic isopropylacrylate. Both of these ethereal salts are thick, colourless oils, the former boiling apparently rather higher than the latter.

Hydrolysis of Ethylic α-Isopropylpropane-ααα₁-tricarboxylate. Formation of α-Isopropylpropane-ααα₁-tricarboxylic acid, and of Isopropylglutaric acid.

The hydrolysis of ethylic isopropylpropanetricarboxylate was carried out by boiling the pure substance in a reflux apparatus with twice the calculated quantity of alcoholic potash for four hours; the product was mixed with water, evaporated on a water bath till free from alcohol, acidified, and extracted 10 times with pure ether. The ethereal solution was dried over calcium chloride and evaporated at a low temperature, when an oily acid was obtained which did not crystallise, even when left for some days over sulphuric acid in a vacuum. The analysis gave numbers indicating that the substance consisted of nearly pure α-isopropylpropane-ααα₁-tricarboxylic acid.

0·1423 gave 0·2607 CO₂ and 0·0810 H₂O. C = 49·95; H = 6·33.

C₉H₁₄O₆ requires C = 49·54; H = 6·41 per cent.

This acid differs from its isomeride, described in the preceding paper, in that, when its solution in water is saturated with hydrogen chloride, the acid does not separate in a crystalline form, and it has, so far, not been possible to obtain the substance in a crystalline state by treatment with various solvents.

When heated at 200°, the tribasic acid is decomposed with evolution of carbon dioxide and formation of isopropylglutaric acid; this was best purified as follows:—The crude acid was digested with acetic anhydride, and then converted into its anhydride; this was fractionated under reduced pressure, when almost the whole distilled at 217—222° (100 mm.) as a colourless oil which rapidly solidified on

1508 HEINKE AND PERKIN: ETHYLIC β -IODOPROPIONATE

standing. The crystals were spread on porous porcelain until free from oily mother liquor, and the residual, colourless, crystalline mass recrystallised from light petroleum.

0.1762 gave 0.3969 CO_2 and 0.1210 H_2O . $\text{C} = 61.43$; $\text{H} = 7.63$
 $\text{C}_8\text{H}_{12}\text{O}_3$ requires $\text{C} = 61.54$; $\text{H} = 7.68$ per cent.

This anhydride melts at $53\text{--}54^\circ$, and crystallises from light petroleum in the same characteristic woolly masses as the isopropylglutaric anhydride described in the previous paper. When treated with aniline in benzene solution, it yields isopropylglutaranilic acid (m. p. 158°), which was analysed with the following result.

0.2266 gave 11 c.c. moist nitrogen at 15° and 755 mm. $\text{N} = 5.65$.
 $\text{C}_{14}\text{H}_{19}\text{NO}_3$ requires $\text{N} = 5.62$ per cent.

Lastly, if the anhydride be dissolved in boiling water, the solution concentrated, saturated with hydrogen chloride, and allowed to stand, hard, colourless crystals of isopropylglutaric acid separate, which melt at $94\text{--}95^\circ$, and resemble in all respects the crystals of isopropylglutaric acid obtained in the manner described in the previous paper.

0.1470 gave 0.2963 CO_2 and 0.1067 H_2O . $\text{C} = 55.07$; $\text{H} = 7.93$.
 $\text{C}_6\text{H}_{14}\text{O}_4$ requires $\text{C} = 55.17$; $\text{H} = 8.04$ per cent.

While these experiments were in progress and nearly completed, we heard from Professor Auwers that he had instituted similar experiments in conjunction with Mr. A. W. Titherley.*

These chemists studied the action of ethylic β -iodopropionate on the sodium derivative of ethylic isopropylmalonate, and thus obtained an ethereal salt boiling at 197° (33 mm.), which, although not analysed, was obviously identical with the ethylic α -isopropylpropane-*aaa*₁-tricarboxylate obtained by us, and which distilled, as stated above, at $228\text{--}230^\circ$ (100 mm.).

This ethereal salt was then hydrolysed by boiling with hydrochloric acid, and thus converted into a remarkably stable crystalline diethyl salt of the formula

(m. p. $68\text{--}69^\circ$), which appears to resist the further action of the acid; when boiled with alcoholic soda, however, it is hydrolysed, with formation of a syrupy acid, which evidently consists of not quite pure isopropylglutaric acid. As soon as Professor Auwers heard that we were investigating this subject and had already obtained pure isopropylglutaric acid, he did not continue his experiments, but kindly left the completion of the research to us.

* The results of these experiments have since been published in the *Annalen*, 1896, 292, 217.

Pentane- $\alpha\gamma\gamma\alpha_1$ -tetracarboxylic acid, $(\text{COOH})_2\text{C}(\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH})_2$.

In our first experiments on the action of ethylic β -iodopropionate on the sodium derivative of ethylic isopropylmalonate, a sample of the latter was employed which boiled at $209\text{--}211^\circ$, and which, although it had been carefully prepared, must evidently, from the results subsequently obtained, have contained some unchanged ethylic malonate. This fraction was treated with sodium and ethylic β -iodopropionate, as described on p. 1506, and the product distilled under reduced pressure (30 mm.), when, after the ethylic isopropylpropanetricarboxylate had passed over, a considerable fraction was obtained, boiling at $230\text{--}235^\circ$. After again fractionating, this oil gave the following results on analysis.

0.1411 gave 0.2957 CO_2 and 0.1019 H_2O . C = 57.13; H = 8.03.

$\text{C}_{17}\text{H}_{28}\text{O}_8$ requires C = 56.67; H = 7.78 per cent.

The further examination of this substance showed that it was ethylic pentane- $\alpha\gamma\gamma\alpha_1$ -tetracarboxylate, identical with the compound obtained by Emery (*Ber.*, 1891, **24**, 282) by treating the sodium compound of ethylic malonate with ethylic β -bromopropionate.

Emery gives the boiling point of his ethereal salt as 215° (13 mm.). From the ethereal salt, the corresponding tetracarboxylic acid, which is not described by Emery, may be obtained in the following way. It is hydrolysed by boiling with an excess of alcoholic potash for two hours in a reflux apparatus, the solution mixed with water, boiled until free from alcohol, evaporated to a small bulk, acidified, and extracted at least 30 times with pure ether, as the acid is only sparingly soluble in ether and very difficult to extract. After drying the ethereal solution over calcium chloride and evaporating to a small bulk, crystalline crusts are deposited on standing; these were collected, washed with ether, dissolved in a very little water, and the solution saturated with hydrogen chloride, when almost the whole of the acid separated as a colourless, sandy powder, which gave the following results on analysis.

0.1321 gave 0.2112 CO_2 and 0.0594 H_2O . C = 43.61; H = 4.99.

$\text{C}_9\text{H}_{12}\text{O}_8$ requires C = 43.55; H = 4.84 per cent.

Pentane- $\alpha\gamma\gamma\alpha_1$ -tetracarboxylic acid, when heated in a capillary tube, decomposes rapidly at about $185\text{--}187^\circ$ with vigorous evolution of gas, and formation of pentane- $\alpha\gamma\alpha_1$ -tricarboxylic acid.

Pentane- $\alpha\gamma\alpha_1$ -tricarboxylic acid, $\text{COOH}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH})_2$.

This acid was prepared by heating the corresponding tetracarboxylic acid at 200° until the evolution of carbon dioxide had ceased. The syrupy residue was dissolved in hot water, and the solution, after cooling, saturated with hydrogen chloride, but no crystallisation took place even on long standing; when, however, the solution was placed over solid potash in a vacuum desiccator, beautiful colourless prisms separated after some days; these were collected, dried at 90° , and analysed.

- I. 0.1785 gave 0.3078 CO_2 and 0.1001 H_2O . $\text{C} = 47.03$; $\text{H} = 6.29$.
 II. 0.1431 „ 0.2478 „ „ 0.0768 „ $\text{C} = 47.23$; $\text{H} = 5.97$.
 $\text{C}_8\text{H}_{12}\text{O}_6$ requires $\text{C} = 47.06$; $\text{H} = 5.88$ per cent.

Pentane- $\alpha\gamma\alpha_1$ -tricarboxylic acid melts at 114 — 115° with slight previous softening. Emery (*Ber.*, 1891, **24**, 284) gives the melting point at 106 — 107° .