XCVII.—*Interaction of Ethylenic Chloride, Ethylic Malonate, and Sodium Ethoxide.*

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It has been shown by W. H. Perkin, jun. (Trans., 1885, 47, 807) that when ethylenic bromide is treated with the monosodium deriva-

tive of ethylic malonate the chief product is 1:1-ethylic trimethylenedicarboxylate, thus:

In a later paper (Trans., 1887, 51, 19) he has shown that at the same time a small quantity of ethylic butanetetracarboxylate is formed, resulting from the action of 1 mol. of ethylenic bromide on 2 mols. of the sodium compound, thus:

In a subsequent paper (Trans., 1894, 65, 578) Perkin has proved that when ethylenic chloride is substituted for ethylenic bromide, the yield of ethylic butanetetracarboxylate can be materially increased.

Having recently had occasion to prepare a large quantity of ethylic butanetetracarboxylate for the purposes of another investigation, we have followed successfully the directions laid down by Perkin (*loc. cit.*), but have found that, in addition to the two products already named, two others, which have hitherto been overlooked, are also formed in small quantities, namely, ethylic butanetricarboxylate and ethylic adipate.

The method followed in establishing this conclusion is described in the present paper.

It will be desirable to repeat the experimental details of this many-sided action *ab initio*.

Sodium (9.2 grams) is dissolved in absolute alcohol (120 c.c.), the solution transferred to a soda-water bottle, ethylic malonate (64 grams) and ethylenic chloride (21 grams) added, and the whole well shaken and tightly corked, the cork being tied down. The bottle is then heated in a water bath, at 100°, for 8 hours, four or six such bottles being usually heated at the same time. When cold, the alcoholic solution is decanted from the sodium chloride, and the alcohol distilled off; the residue, together with that remaining in the bottle, is then mixed with water in order to dissolve the sodium chloride, and extracted three times with ether. The ethereal solution is washed with water, dried over calcium chloride, the ether distilled off, and the residual oil fractionated under diminished pressure (40 mm.) until the thermometer rises to 140°.

The oil which passes over below this temperature consists of a mixture of ethylic trimethylenedicarboxylate with unchanged ethylic malonate; the residue in the flask contains ethylic butanetetracarboxylate (and, as we now find, smaller quantities of ethylic butanetricarboxylate and ethylic adipate).

The distillate of low boiling point is then fractionated under ordinary atmospheric pressure, and, when the object of the preparation is to obtain as much ethylic butanetetracarboxylate as possible, the fraction 180—225° is assumed to contain 50 per cent. of ethylic malonate, and used again; for it is to be noted that the yield of oil boiling above 140° (40 mm.) when prepared from this recovered distillate containing ethylic trimethylenedicarboxylate as well as ethylic malonate, is much larger, and, judging from its colour and consistency, much purer, than that prepared from pure ethylic malonate.

It has been shown by Bone and Perkin (Trans., 1895, 67, 108) that the cause of the increased yield of the ethylic butanetetracarboxylate lies in the fact that it results from the combination of ethylic malonate with the ethylic trimethylenedicarboxylate in the presence of sodium ethoxide, the ethylic trimethylenedicarboxylate behaving like the ethylic salt of an $\alpha\beta$ -unsaturated acid, thus :

The whole of the crude oil boiling above 140° (40 mm.) is refractionated under a pressure of 40 mm. in quantities of about 100 c.c. at a time. The oil commences to boil at about 140° (40 mm.); the thermometer rises gradually to 200°, and more gradually to 230°, between which point and 250° the principal portion distils as an almost colourless oil, a small quantity of a tarry mass remaining in the flask.

The fraction 230—250° (40 mm.) on refractionation gives a small quantity of oil, which boils between 200° and 230° (40 mm.), but the chief part distils again at 230—250°, and consists of almost pure ethylic butanetetracarboxylate (Perkin, *loc. cit.*). As we had in our preparation a large quantity of crude oil boiling above 140° (40 mm.) for fractionation, it was possible for us to obtain a fair quantity of the oil of lower boiling point 140—230° (40 mm.). This on refractionation (at 40 mm.) yielded a further small quantity of ethylic butanetetracarboxylate, but the bulk distilled over between 140° and 210° (40 mm.).

This process of refractionation was repeated two or three times until the oil was separated into two principal fractions, one, A, boiling at 195—210°, and the other, B, at 140—195° (40 mm.). It seemed certain that these two fractions contained substances other than ethylic trimethylenedicarboxylate (b. p. 208° at ordinary atmospheric pressure) on the one hand, or ethylic butanetetracarboxylate (b. p. 240° at 40 mm.) on the other.

(A) *Ethylic butanetricarboxylate*, $(\text{COOEt})_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2(\text{COOEt})$.

A small portion of the first fraction (A), boiling at $195\text{--}210^\circ$ (40 mm.), was collected at $200\text{--}205^\circ$ (40 mm.), and the colourless oil analysed.

(1) 0.1793 gave 0.3740 CO_2 and 0.1293 H_2O . $\text{C} = 56.84$; $\text{H} = 8.06$.

(2) 0.1661 „ 0.3461 CO_2 „ 0.1208 H_2O . $\text{C} = 56.78$; $\text{H} = 8.13$.
 $(\text{COOEt})_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2(\text{COOEt})$ requires $\text{C} = 56.87$; $\text{H} = 8.09\%$.

While we were engaged on this investigation, we learnt from an abstract (Abstr., 1897, i, 19) that Montemartini had prepared ethylic butanetricarboxylate by treating ethylic γ -chlorobutyrate with ethylic sodiomalonate, thus:

He described it as a colourless liquid boiling at $175\text{--}176^\circ$ under 18 mm. pressure.

The oil boiling at $200\text{--}205^\circ$ (40 mm.) appeared, therefore, to be ethylic butanetricarboxylate.

We proceeded to confirm this conclusion by forming the derivatives described below.

This was prepared by treating the sodium compound of ethylic butanetricarboxylate with ethylic iodide.

Sodium (0.84 gram) was dissolved in absolute alcohol (12 c.c.), and ethylic butanetricarboxylate (10 grams), ethylic iodide (5.7 grams) added, and the whole heated on a water bath for 4 hours in a flask connected with a reflux condenser. On working up the product in the usual way, 7 grams of a yellow oil was obtained, which was fractionated under diminished pressure and found to boil at $200\text{--}205^\circ$ (32 mm.); a small portion boiling at $200\text{--}202^\circ$ (32 mm.) was collected as a colourless oil, and analysed.

0.1424 gave 0.3091 CO_2 and 0.1139 H_2O . $\text{C} = 59.16$; $\text{H} = 8.94$.

$(\text{COOEt})_2\text{CEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2(\text{COOEt})$ requires $\text{C} = 59.53$; $\text{H} = 8.67\%$.

It may be observed that one of us has previously shown (Trans., 1894, 65, 997) that it is not possible to prepare *mono*-alkyl derivatives of ethylic butanetetracarboxylate by the action on it of 1 mol. of sodium ethoxide and an alkylic haloid, since, instead of a monalkyl derivative, a mixture of the dialkyl derivative with unchanged ethylic salt is produced.

Montemartini (*loc. cit.*) also prepared this monalkyl derivative of ethylic butanetricarboxylate, by treating ethylic γ -chlorobutyrate with ethylic ethylsodiummalonate. He described it as boiling at 205—208° under a pressure of 35 mm.

a-Ethylbutanetricarboxylic Acid, $(\text{COOH})_2\text{CET}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2(\text{COOH})$.

This acid was obtained by the hydrolysis of ethylic *a*-ethylbutanetricarboxylate with hydrochloric acid, the ethylic *a*-ethylbutanetricarboxylate mixed with excess of concentrated hydrochloric acid after being boiled for 10 hours was evaporated to a small bulk on the water bath and saturated with hydrochloric acid, when a white, crystalline substance was precipitated on vigorous stirring. This was collected on a filter, washed with a little concentrated hydrochloric acid, spread on a porous tile, and dried in a vacuum over potassium hydroxide. It melted at 155—158°, with evolution of carbonic anhydride, and on analysis gave the following result:

0.1462 gave 0.2649 CO_2 and 0.0882 H_2O . C = 49.38; H = 6.74.
 $(\text{COOH})_2\text{CET}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2(\text{COOH})$ requires C = 49.50; H = 6.47 %.

Montemartini (*loc. cit.*) obtained this acid by hydrolysis with alcoholic solution of potassium hydroxide, but described it as an oil.

The silver salt was prepared by pouring a neutral aqueous solution of the ammonium salt into excess of strong solution of silver nitrate; the white amorphous precipitate, dried over sulphuric acid in a vacuum, gave the following results:

- (1) 0.2050 gave on ignition 0.1204 Ag. Ag = 58.72.
- (2) 0.1262 „ „ 0.0742 Ag. Ag = 58.79.
- (3) 0.1964 „ „ 0.1152 Ag. Ag = 58.65.
- (4) 0.1730 gave 0.1304 CO_2 and 0.0379 H_2O and 0.1012 Ag.
 C = 20.58; H = 2.45; Ag = 58.50.

$\text{C}_9\text{H}_{11}\text{O}_6\text{Ag}_3$ requires C = 19.94; H = 2.05; Ag = 60.27 per cent.

$\text{C}_9\text{H}_{12}\text{O}_6\text{Ag}_2$ „ C = 24.90; H = 2.79; Ag = 50.17 „

These analyses seemed to show that this silver salt consisted of a mixture of the tribasic and dibasic silver salts of *a*-ethylbutanetricarboxylic acid; a mixture containing six parts of the tribasic and one part of the dibasic silver salt would have the following percentage composition, C = 20.65; H = 2.15; Ag = 58.83.

Such acid silver salts are not unknown, for one of us has shown (*Trans.*, 1894, 65, 998) that dicetyl- and dibenzyl-butane-tetracarboxylic acids give dibasic silver salts.

0.0246 gram of the acid, when titrated with a standard solution of barium hydroxide, using phenolphthalein as the indicator, required 0.0292 $\text{Ba}(\text{OH})_2$ for neutralisation.

0.0246 gram of α -ethylbutanetricarboxylic acid would require 0.0290 $\text{Ba}(\text{OH})_2$ to form a tribasic barium salt.

α -Ethyladipic Acid, $\text{COOH} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

This acid was obtained by heating 1 gram of α -ethylbutanetricarboxylic acid in a test-tube, in an oil bath at 170 — 210° , until evolution of carbonic anhydride had ceased; there was little or no charring. The product was dissolved in a small quantity of water, saturated with hydrochloric acid, and vigorously stirred, when the acid was precipitated in small, white crystals; these were collected, washed with a little concentrated hydrochloric acid, drained on a porous tile, and dried over potassium hydroxide and sulphuric acid in a vacuum. The acid melted at 48 — 50° , and an analysis gave the following result:

0.1176 gave 0.2382 CO_2 and 0.0848 H_2O . $\text{C} = 55.20$; $\text{H} = 8.06$. $\text{COOH} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ requires $\text{C} = 55.13$; $\text{H} = 8.13\%$.

Montemartini (*loc. cit.*), who also obtained this α -ethyladipic acid, gave the melting point as 46 — 49° .

(B.)—*Ethylic Adipate*.

It was stated above that, in fractionating the crude oil boiling above 140° (40 mm.), the lower boiling portion was itself separated by fractionation at 40 mm. pressure into two fractions, called respectively A and B. The latter, (B), boiling at 140 — 195° (40 mm.), was fractionated several times under ordinary atmospheric pressure, the main portion distilling between 230° and 250° . In view of what has gone before, it seemed probable that this consisted mainly of ethylic adipate, the more so as ethylic adipate boils at 245° (ordinary pressure). On submitting it to hydrolysis by boiling it with concentrated hydrochloric acid, and evaporating the solution, a white, crystalline substance was obtained which, after purification, melted at about 150° , and did not evolve carbonic anhydride on raising the temperature. Adipic acid melts at 149° .

Action of Sodium Ethoxide on Ethylic Butanetetracarboxylate.

The most probable explanation of the formation of ethylic butanetricarboxylate and of ethylic adipate during the preparation of ethylic butanetetracarboxylate, as described above, is that it is due to partial hydrolysis and elimination of one or two molecules of carbonic anhydride under the action of sodium ethoxide, or perhaps of sodium hydroxide, since the materials cannot be entirely free from moisture. Again, the digestion under pressure is performed in corked bottles which are

entirely submerged in water, and it is probable that, with the shrinking of the cork, a little water enters the bottles and so forms sodium hydroxide. In order to test this, 20 grams (1 mol.) of ethylic butanetetracarboxylate (b. p. 240° at 40 mm.) were mixed with sodium ethoxide (2 mols.), formed by dissolving 2.65 grams of sodium in 32 c.c. of absolute alcohol, and heated in a corked soda-water bottle in a water bath at 100° for 7 hours. The alcohol was then distilled off, water added, and the whole extracted four times with ether; the ethereal solution, after being well washed with water and dried over calcium chloride, was evaporated, and the residual dark yellow oil was distilled under diminished pressure (40 mm.). It passed over entirely between 160° and 215° , a small quantity of charred matter remaining in the distilling flask.

It was thus shown that the product of the action of sodium ethoxide on ethylic butanetetracarboxylate contained none of the original ethylic butanetetracarboxylate, but consisted entirely of a mixture of ethylic butanetricarboxylate with ethylic adipate.

We have thus proved that, unless ethylic butanetetracarboxylate is carefully fractionated, it will certainly contain a small amount of both ethylic butanetricarboxylate and ethylic adipate. We may add that the unsuspected presence of these substances had been the cause of anomalous results in an investigation which is still in hand.

It cannot be doubted that a similar action is of frequent occurrence, in a greater or lesser degree, whenever substances containing two alkylic carboxylic groups are heated in the presence of sodium ethoxide.

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