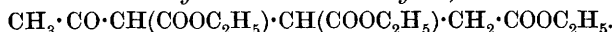


LXXX.—*Formation of Ethereal Salts of β -Ketonic Acids*

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SINCE Michael (*J. pr. Chem.*, 1887, 35, 349) made the interesting observation that the ethereal salts of the sodium derivatives of ethylic acetoacetate and ethylic malonate have the property of uniting with the ethereal salts of unsaturated acids, this reaction has been applied, especially by Auwers (*Ber.*, 1891, 24, 307, 2887) to ethylic malonate, but it has scarcely been used for the production of ethereal salts of β -ketonic acids. In the course of our researches on this class of compounds, we have prepared several members of the group in this way.

The experiments were carried out as follows. The ethereal salt of the β -ketonic acid was added to an equivalent quantity of dry sodium ethoxide suspended in ether which was free from water and alcohol, and the solution thus obtained mixed with the corresponding weight of the ethereal salt of the unsaturated acid. The mixture, after 2 to 3 days, was acidified with dilute sulphuric acid, the ethereal layer shaken with sodium carbonate, and the oil remaining after removal of the ether fractionated under diminished pressure.

Ethylic α -Acetotricarballylate,

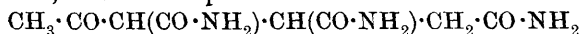
On adding ethylic fumarate to ethylic sodioacetoacetate, heat is evolved; the ethereal solution, after being allowed to stand overnight, is treated in the manner mentioned above. The oily residue left on evaporating the ether, when fractionated under diminished pressure, yields 75 per cent. of the theoretical quantity of ethylic α -acetotricarballylate, boiling at 187—188° under a pressure of 11 mm.

0.2538 gave 0.5154 CO_2 and 0.1614 H_2O . C = 55.38; H = 7.06.

$\text{C}_{14}\text{H}_{22}\text{O}_7$ requires C = 55.26; H = 7.23 per cent.

This ethereal salt had already been obtained by Emery (*Ber.*, 1890, 23, 3757) by the interaction of ethylic sodioacetoacetate and ethylic monochlorosuccinate, and the boiling point found was 175° under a pressure of 9 mm.

Ferric chloride gives a red violet coloration with an alcoholic solution of the ethereal salt. Concentrated aqueous ammonia dissolves ethylic α -acetotricarballylate if left in contact with it for a short time, and the solution after 3 to 4 days deposits crystals, whilst the ammoniacal liquor turns red; these crystals dissolve in boiling water, and, on cooling, are deposited in colourless prisms, which become darkened, and melt at 248° with evolution of gas. Its aqueous solution gives a violet coloration with ferric chloride, this indicating that the substance still contains the grouping of acetoacetic acid. This conclusion is, moreover, supported by the following analytical data, which correspond with the formula



for the amide of acetotricarballylic acid.

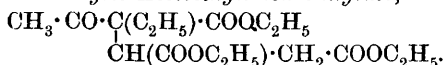
0.2301 gave 0.3771 CO_2 and 0.1280 H_2O . $\text{C} = 44.69$; $\text{H} = 6.18$.

0.1428 „ 25 c.c. nitrogen at 25° and 760 mm.; $\text{N} = 19.53$.

$\text{C}_8\text{H}_{13}\text{N}_3\text{O}_4$ requires $\text{C} = 44.65$. $\text{H} = 6.05$; $\text{N} = 19.53$ per cent.

The yield of the amide is very small; the greater part of the ethereal salt being decomposed by the ammonia and transformed into a dark tarry substance, which is left on evaporating the ammoniacal mother liquor.

Ethylic Acetoethyltricarballylate,

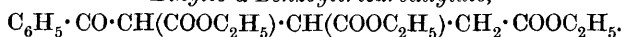


Like ethylic sodioacetoacetate, the sodium derivatives of the mono-substitution products of the ethereal salt combine with ethereal salts of unsaturated acids. We have chosen ethylic acetoacetate and, proceeding as before, have found that, in the presence of sodium ethoxide, it combines with ethylic fumarate. After repeated fractional distillation, the product, ethylic acetoethyltricarballylate, is obtained as a colourless oil which boils at 194 — 196° under a pressure of 9 mm., and has a density $d_{19^\circ/19^\circ} = 1.0996$.

0.2244 gave 0.4780 CO_2 and 0.1598 H_2O . $\text{C} = 58.10$; $\text{H} = 7.91$.

$\text{C}_{16}\text{H}_{26}\text{O}_7$ requires $\text{C} = 58.18$; $\text{H} = 7.88$ per cent.

Ethylic α -Benzoyltricarballylate,



The reaction between ethylic fumarate and the sodium derivative of ethylic benzoylacetate is complete after 2 days; the ethereal solution of the product is treated first with dilute sulphuric acid and then with sodium carbonate, and on removal of the ether leaves a viscous, yellow oil which exhibits a green fluorescence, and distils at 244 — 245°

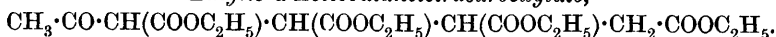
under a pressure of 10 mm. On analysis, the following numbers were obtained.

0.2331 gave 0.5370 CO_2 and 0.1345 H_2O . $\text{C} = 62.82$; $\text{H} = 6.41$.

$\text{C}_{19}\text{H}_{24}\text{O}_7$ requires $\text{C} = 62.63$; $\text{H} = 6.59$ per cent.

The same compound had previously been prepared by Emery (*J. pr. Chem.*, 1896, 53, 312) by the action of ethylic chlorosuccinate on ethylic sodiobenzoylacetate, and he found the boiling point to be 250° under a pressure of 16 mm.

Ethylic α -Acetobutanetetracarboxylate,



Ethylic aconitate combines with the sodium derivative of ethylic acetoacetate with the same readiness as ethylic fumarate; this is effected by adding to a solution of ethylic acetoacetate in dry ether the equivalent quantity of sodium ethoxide, dried in a vacuum at 180° , and then, as soon as the latter has dissolved, the calculated amount of ethylic aconitate. The mixture is left for 3 days, and the red ethereal solution thus obtained subjected to the treatment already described. The oily residue left on distilling off the ether, on being fractionated, boils at 222 – 223° under a pressure of 10 mm.

0.2242 gave 0.4577 CO_2 and 0.1436 H_2O . $\text{C} = 55.67$; $\text{H} = 7.11$.

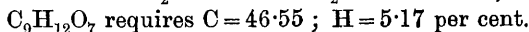
$\text{C}_{18}\text{H}_{28}\text{O}_9$ requires $\text{C} = 55.67$; $\text{H} = 7.21$ per cent.

Ethylic α -acetobutanetetracarboxylate is a pale yellow oil with a green fluorescence, and has a density $d_{26^\circ/26^\circ} = 1.1462$.

Concentrated aqueous ammonia dissolves the ethereal salt in the course of some hours, the solution becoming red, and after 3–4 days it deposits a solid which is obtained in colourless plates on crystallisation from boiling water; it decomposes at about 268° without melting. The yield of this substance was so small that, although 5 grams of the ethereal salt had been used, it did not suffice for establishing its composition by an analysis. There can, however, be no doubt that it is the amide of acetobutanetetracarboxylic acid. The ammoniacal filtrate from the solid is strongly fluorescent, and on evaporation leaves a dark, tarry residue.

Acetonyltricarballic Acid.

The hydrolysis of acetobutanetetracarboxylate is best effected by boiling with hydrochloric acid (diluted with an equal volume of water) in a reflux apparatus. After 3 hours heating, the oil disappears, and on evaporating the solution on the water bath, an oily residue is left which slowly solidifies to a hard, amorphous mass. This becomes



$C_9H_{11}AgO_7$ requires Ag = 58.59 per cent.

formed by adding 20 grams of benzoylacetone to a solution of 2.85 grams of sodium in 100 c.c. of absolute alcohol, and then 25.5 grams

of ethylic chlorofumarate. After 2 hours digestion on the water bath, the mixture ceases to be alkaline to litmus; the product is then poured into water, and the oil which separates extracted with ether. On evaporating the ether, an oil is left which distils at $233\text{--}235^\circ$ under a pressure of 10 mm.; it is very viscous, of a yellow colour, and gives in alcoholic solution a wine-red coloration with ferric chloride.

0.3058 gave 0.7320 CO_2 and 0.1645 H_2O . $\text{C} = 65.26$; $\text{H} = 5.97$.

$\text{C}_{18}\text{H}_{20}\text{O}_6$ requires $\text{C} = 65.06$; $\text{H} = 6.02$ per cent.

We propose to continue this investigation, and to examine whether the union of ethereal salts of β -ketonic acids with those of unsaturated acids takes place under conditions similar to those of ethylic malonate and its homologues.

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