CCXXXIX.—*Muconic and Hydromuconic Acids. Part V. Ester-addition to Ethyl Muconate.*

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It was previously found (Farmer, J., 1922, **121**, 2015; 1923, **123**, 3324) that when alcoholic ethyl sodiomalonate or ethyl sodiocyanoacetate was heated with ethyl muconate a complex mixture of unidentifiable cyclised products was obtained; when, on the other hand, the reactants were kept for several days at room temperature in an ethereal medium (or in an ethereal medium containing only a very small proportion of alcohol) addition took place without the occurrence of serious cyclisation. Under the latter conditions, however, the addition product had suffered double-bond displacement and a considerable proportion thereof consisted of the substance (II) * instead of the normal αβ-addition product (I). It was pointed out that equilibration of the three forms (I), (III), and (II) had

$$\underset{\text{(I.)}}{EtO_2C\cdot CH{:}CH\cdot CHX\cdot CH_2\cdot CO_2Et} \qquad \underset{\text{(II.)}}{EtO_2C\cdot CH_2\cdot CH_2\cdot CX{:}CH\cdot CO_2Et}$$

$$\underset{\text{(III.)}}{EtO_2C\cdot CH_2\cdot CH{:}CX\cdot CH_2\cdot CO_2Et} \qquad \underset{\text{(IV.)}}{EtO_2C\cdot CH_2\cdot CHX\cdot CHX\cdot CH_2\cdot CO_2Et}$$

$$X = CH(CO_2Et)_2 \text{ or } CH(CN)\cdot CO_2Et$$

doubtless taken place (I $\rightleftharpoons$ III $\rightleftharpoons$ II), but no direct evidence of the presence of (I) and (III) was obtained.

Recently, owing to the very numerous ester-additions successfully carried out under " catalytic " conditions, *i.e.*, with the employment of only a small proportion of sodium ethoxide (1/6 to 1/10 mol.), it has seemed advisable to re-investigate the addition in order to discover if the normal αβ-addition product (I) is not indeed obtainable and to prepare, if possible, the double-addition product (IV), which has interesting synthetic applications.

* Since this substance is an αβ-substituted glutaconic ester, it doubtless existed alongside and in equilibrium with its Δβ-(glutaconic) isomeride.

By employing as condensing agent a fractional molecular proportion of sodium dissolved in the minimal quantity of alcohol, the cyclising tendency was entirely checked. The product from ethyl muconate and ethyl malonate was the normal addition product (I), since from both of its fission products (obtained by the action of either neutral permanganate or ozone) good yields of oxalic and tricarballylic acids were obtained. The addition product was, however, not quite free from one or both of the compounds (II) and (III), since its ozone fission product gave a colour with ferric chloride; nevertheless no appreciable amount of either of these was present, since none of the β-keto-esters $EtO_2C{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2$, $EtO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2$, and $EtO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ or their derivatives proved to be isolable.

The normal addition product was easily obtained in good yield, but it could not be induced to combine with a second molecule of the ester-addendum under " catalytic " conditions.

Experimental.

Addition of Ethyl Malonate to Ethyl Muconate.—Ethyl malonate (16 g.) was added to a solution of sodium (0·375 g.) in absolute alcohol (5 c.c.), and the product diluted with dry ether (150 c.c.). Ethyl muconate was then introduced, and the whole refluxed for 5 hours on a water-bath. After cooling, a solution of acetic acid (1 g.) in water (10 c.c.) was added with rapid shaking. The ethereal liquor was thoroughly washed with sodium carbonate solution and with water, dried, and distilled. It yielded *ethyl* Δ^{α}*-butene-*$\alpha\delta$*-dicarboxylate-*γ*-malonate* as a colourless oil which on redistillation boiled at 175—180°/2 mm. (Found: C, 56·9; H, 7·2. $C_{17}H_{26}O_8$ requires C, 57·0; H, 7·2%). Yield, 70%. The constitution of this addition product, which contained a trace of an isomeric ester, followed from the nature of its degradation products (below).

Ozonolysis of the Addition Product.—This was carried out by submitting a chloroform solution of the addition product (10 g.) to a stream of ozonised oxygen until ozone was no longer absorbed. On removal of the solvent from the product a viscous colourless ozonide remained which was not easily decomposed by water except on boiling. The aqueous decomposition product gave a deep colour with ferric chloride, indicating that to some extent double-bond displacement to the $\beta\gamma$- or $\alpha\beta$-position (yielding ethyl $\Delta^{\alpha \text{ or } \beta}$-butene-$\alpha\delta$-dicarboxylate-β-malonate) had taken place. The amount of such displacement was, however, very small, since on complete oxidation of the aldehydic material in the ozonolysis product to the carboxylic acid stage by keeping it for 2 days with perhydrol (30 c.c.) (*i.e.*, until it no longer gave a colour with Schiff's reagent), no neutral

material—and consequently no appreciable quantity of either of the ketonic esters which should be formed from the respective Δ^{α}- or Δ^{β}-form of the addition product—remained. This was ascertained by making the oxidation liquor alkaline with sodium carbonate and extracting it with ether. The dissolved acidic esters were hydrolysed by heating with alkali and then decarboxylated by refluxing with 25% hydrochloric acid for 20 hours. By extraction with ether first of the acid liquor, and then of the residue left on evaporation of the latter to dryness, a mixture of acids was obtained from which oxalic acid was removed as calcium oxalate. The residual acid after regeneration from the mother-liquor was found to be crude tricarballylic acid. This was most conveniently purified by converting it into the lead salt and regenerating the acid therefrom with hydrogen sulphide. The tricarballylic acid thus obtained in good yield melted at 160° [mixed m. p., 160°; *M* (tribasic), 175·5]. The residues were acidified and re-extracted, but no trace of another acid was obtained.

Oxidation of the Addition Product with Permanganate.—To the addition product (9·7 g.), dissolved in acetone and cooled to 0°, 3% permanganate solution (containing excess of magnesium sulphate) was gradually added with mechanical stirring. Reduction of permanganate was very rapid until the equivalent of 4 atoms of oxygen per molecule of the addition product (*i.e.*, 500 c.c.) had been added. At this stage reduction ceased and the product was freed from manganese mud in the usual way. The aqueous liquor was evaporated to dryness, and the residue acidified and extracted with ether. The oil so obtained was hydrolysed with alkali, and afterwards decarboxylated by boiling with 25% hydrochloric acid for 24 hours. The acid liquor was evaporated to dryness, and the residue extracted thoroughly with acetone. A viscous liquid was obtained which soon solidified; this was a mixture of oxalic and tricarballylic acids, from which the individual acids were economically separated in fairly good yield by the method described above.

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