

CCLIII.—*Constitution of the Yellow Sodium Compounds formed from Ethyl Citraconate (or Itaconate) and Ethyl Sodiomalonate.*

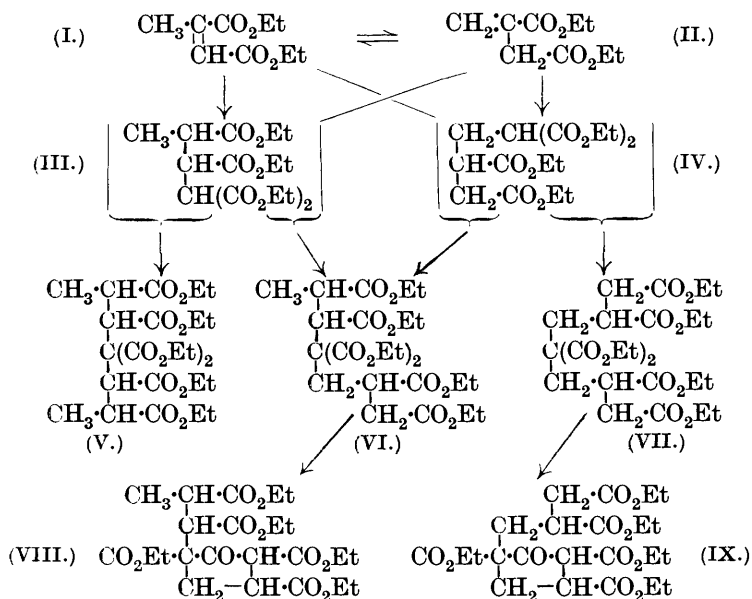
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THE action of ethyl sodiomalonate on ethyl citraconate has been examined by Michael (*Ber.*, 1900, **33**, 3757), by Hope (*J.*, 1912, **101**, 892), and by Ingold, Shoppee, and Thorpe (this vol., p. 1477). The combined results of these investigations show that, in alcoholic solution under the conditions of the condensation, ethyl citraconate (I) and ethyl itaconate (II) are directly interconvertible, so that whichever is used as the initial substance, products are obtained which are derived from both. It has also been proved that the primary addition product of ethyl malonate to ethyl citraconate has constitution (III), and the primary addition product to ethyl itaconate has constitution (IV).

Owing principally to the reactivity of the addition products (III) and (IV), the whole reaction is actually much more complex than the above simple statement indicates, and amongst the by-products described by Ingold, Shoppee, and Thorpe was an insoluble, remarkably stable, yellow sodio-derivative, the constitution of which was left undetermined. This substance has now been investigated, and the elucidation of its structure forms the subject of the present communication.

Actually, the sodium "compound" is a difficultly separable mixture of two closely similar isomerides. On acidification, the corresponding ketonic esters are obtained. One is a liquid characterised by an acid, m. p. 149°, which it yields on hydrolysis. The second, present in greater quantity, is a solid, m. p. 83°; on hydrolysis, it gives an acid, m. p. 173°.

Analysis shows that these two ketonic esters are derived by the elimination of alcohol from one or more of the products of the further addition to ethyl citraconate or ethyl itaconate (I, II) of either of the primary addition products (III or IV), both of which are mono-substituted malonic esters. If it may be assumed that these substituted malonic esters would add to citraconic and itaconic esters in the same directions as have been established for the addition of malonic ester itself, then it follows that the three possible addition compounds must have the structures (V), (VI), and (VII). Now these three esters might conceivably lose alcohol in a large number of ways, giving a variety of derivatives of *cyclopentanone* and *cyclohexanone*; there are, nevertheless, only two structurally isomeric formulæ (VIII and IX) which are consistent with the properties of the ketonic esters obtained.

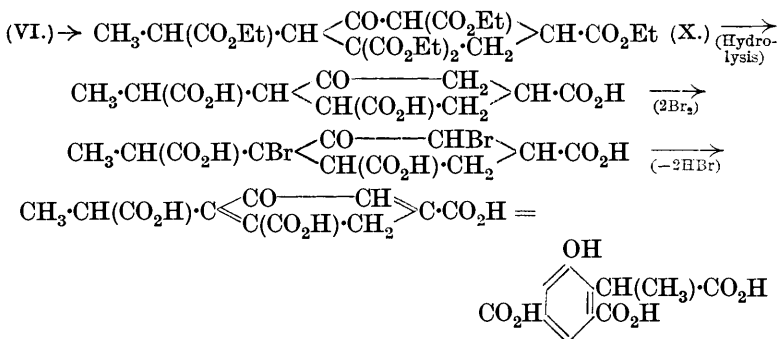


Both these esters give a colour with ferric chloride and form insoluble yellow sodio-compounds; they must, therefore, each contain the grouping $\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$. This might arise in a Dieckmann

reaction by the elimination of alcohol either from $\text{CO}(\text{OEt}) + (\text{H})\text{CH}\cdot\text{CO}_2\text{Et}$, or from $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CO}(\text{OEt}) + (\text{H})\text{C}\cdot\text{CO}_2\text{Et}$. The second alternative is, however, excluded in the present case, since the group $\cdot\text{CH}(\text{CO}_2\text{Et})_2$ is not contained in any of the esters (V), (VI), (VII). The loss of alcohol must therefore take place from $\text{CO}_2\text{Et} + \text{CH}_2\cdot\text{CO}_2\text{Et}$, and this at once removes formula (V) from consideration, since it does not contain the group $-\text{CH}_2\cdot\text{CO}_2\text{Et}$.

Both ketonic esters, on hydrolysis by mineral acids, evolve two molecules of carbon dioxide along with five of ethyl alcohol, two carboxyl groups being thus completely eliminated in each case. This is taken to show the presence of the system $\text{CO}_2\text{Et}\cdot\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{CO}_2\text{Et}$, which can only be formed from $\cdot\text{CO}_2\text{Et} + \cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (preceding paragraph) if the carboxyl group concerned in the elimination of alcohol is itself part of the system $\text{CO}_2\text{Et}\cdot\text{C}\cdot\text{CO}_2\text{Et}$. In this case, ring closure must take place between the groups $\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and $>\text{C}(\text{CO}_2\text{Et})_2$ in (VI) and (VII), the cyclic products having the structures (VIII) and (IX) respectively.

There is one remaining possibility, namely, that the loss of two carboxyl groups on hydrolysis arises from the independent occurrence in the molecule of the groups $\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ and $>\text{C}(\text{CO}_2\text{Et})_2$. *cyclo*Butane, *cyclo*heptane, and *cyclo*octane structures being ignored, there is only one formula containing these groups which is consistent with the properties already mentioned, namely, the *cyclohexane* structure (X), which might conceivably arise from (VI). We exclude it, however, on the grounds that neither of the tribasic acids obtained by acid hydrolysis of the two ketonic esters could be converted into a phenolic acid by bromination :



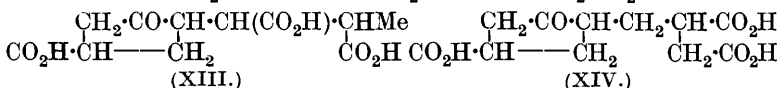
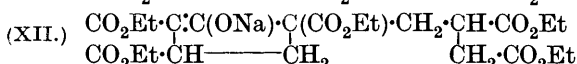
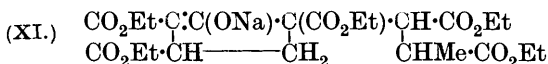
It does not, of course, follow immediately that, of the two ketonic esters isolated, one has formula (VIII) and the other formula (IX), since each of these obviously represents several possible stereoisomeric forms, including, in each case, forms which could give different

tribasic acids on hydrolysis. There remain, therefore, three alternatives: either the two ketonic esters are stereoisomeric modifications of (VIII) (hypothesis *a*), or they are stereoisomeric forms of (IX) (hypothesis *b*), or one is a form of (VIII) and the other is a form of (IX) (hypothesis *c*).

Now, according to the scheme on p. 1913, the condensation of the pure ester (III) with either citraconic or itaconic ester (experiment A) should yield forms of (VIII) only, whereas the condensation of the isomeric ester (IV) with either ethyl citraconate or ethyl itaconate (experiment B) might give modifications of both (VIII) and (IX). Hence, according to hypothesis (*a*), experiment A should yield the two known ketonic esters, whilst experiment B should give not only these but also new isomerides. According to hypothesis (*b*), experiment A could only yield new isomerides, whilst experiment B would be expected to give the known substances. Finally, according to hypothesis *c*, experiment A should give one of the known isomerides only (that which has formula VIII), whilst experiment B should yield a mixture of both, similar to the mixture formed in the original condensations of citraconic and itaconic esters with malonic ester.

Actually the observations accorded with hypothesis *c*, experiment A yielding only the liquid ester corresponding with the tribasic acid, m. p. 149°. Experiment B gave a mixture of the same liquid ketonic ester and the solid isomeride, m. p. 83°, the latter being formed in larger proportion as in the original condensation. Hence the liquid ester has formula (VIII) and the solid one formula (IX).

It follows that the original insoluble yellow sodio-derivative is a mixture of (XI) and (XII) containing an excess of (XII), and that the tribasic acids, m. p.'s 149° and 173°, have formulæ (XIII) and (XIV) respectively.



On oxidation with permanganate, the acid (XIV) yields an acid $\text{C}_{10}\text{H}_{14}\text{O}_8$, which appears to be the glutaric acid,

$\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$
(XV), to be expected from the oxidative fission of a cyclopentanone.

E X P E R I M E N T A L.

The various methods of condensing ethyl sodiomalonate with ethyl citraconate have been described by Ingold, Shoppee, and Thorpe (*loc. cit.*). In order to obtain the sodium compounds, the product from 105 g. of ethyl citraconate, 91 g. of ethyl malonate, and 26 g. of sodium in 300 g. of alcohol was poured into water. After vigorous shaking to coagulate the precipitate, this was collected, washed with a little alcohol and with water, and dried. The best yields (10 g.) were obtained when the original mixture was heated on the steam-bath for at least 4 hours before being worked up. The mixture of sodium compounds is sparingly soluble in alcohol and the alcoholic solution gives a bright crimson colour with ferric chloride.

Ethyl ω -1 : 3 : 4-*Tricarbethoxy-2-keto-cyclopentylmethylsuccinate* (IX).—(a) The mixed sodio-derivatives (30 g.) were shaken with hydrochloric acid and ether until no solid remained. The nearly colourless oil obtained from the ethereal layer (dried with sodium sulphate) soon crystallised and then separated from ether-ligroin or alcohol in colourless needles, m. p. 83° (Found : C, 56·7; H, 6·8. $C_{23}H_{34}O_{11}$ requires C, 56·7; H, 7·0%). The ester gives a cherry-red colour with aqueous alcoholic ferric chloride.

(b) Ethyl citraconate (4 g.) and ethyl butane- $\alpha\beta\delta\delta$ -tetracarboxylate (7 g.) were heated together for 3 hours in presence of alcoholic sodium ethoxide (sodium, 1 g.; ethyl alcohol, 12 g.). The paste of crystals obtained was mixed with water, and the solid collected, from which the esters were regenerated, and the isomeride, m. p. 83°, separated, as in the preceding experiment.

ω -4-*Carboxy-2-ketocyclopentylmethylsuccinic Acid* (XIV).—The above ester was heated for 1 hour on the steam-bath with 30% hydrochloric acid under a condenser short enough to permit the escape of alcohol vapour. The solution so obtained was evaporated in an open basin on the steam-bath, and the solid residue crystallised from hydrochloric acid; tufts of needles were then obtained, m. p. 173° (yield, 85%) (Found : C, 51·1; H, 5·5; *M*, by titration, 257. $C_{11}H_{14}O_7$ requires C, 51·1; H, 5·5%; *M*, 258).

Ethyl α -1 : 3 : 4-*Tricarbethoxy-2-keto-cyclopentyl- β -methylsuccinate* (VIII).—(c) Ethyl citraconate (4 g.), ethyl butane- $\alpha\alpha\beta\gamma$ -tetracarboxylate (7 g.), and alcoholic sodium ethoxide (sodium, 1 g.; ethyl alcohol, 12 g.) were heated on the steam-bath for 3 hours, and the flocculent product obtained on dilution with water was treated with hydrochloric acid and ether. The oil thus obtained (Found : C, 56·4; H, 6·7. $C_{23}H_{34}O_{11}$ requires C, 56·7; H, 7·0%) gave a bright red colour with ferric chloride. The ester was characterised by conversion into the tribasic acid described below.

(d) The same substance may be obtained from the oily by-product accompanying the ester of m. p. 83° in experiments (a) and (b) above.

α -4-Carboxy-2-ketocyclopentyl- β -methylsuccinic Acid (XIII).—The ester (VIII) was hydrolysed with hydrochloric acid as in the preparation of the isomeric acid (XIV). The acid so obtained crystallised from acetone–benzene in needles, m. p. 148 – 149° (Found: C, 51.1; H, 5.8. $C_{11}H_{14}O_7$ requires C, 51.1; H, 5.5%).

Ethyl ω -4-Carboxy-2-ketocyclopentylmethylsuccinate, prepared by esterification of the acid (XIV) with alcoholic sulphuric acid in the usual manner, had b. p. $247^{\circ}/18$ mm. and gave no colour with ferric chloride (Found: C, 59.6; H, 7.5. $C_{17}H_{26}O_7$ requires C, 59.6; H, 7.6%).

The *semicarbazone*, obtained from the ester and semicarbazide acetate in cold aqueous alcoholic solution, had m. p. 105° after crystallisation from dilute alcohol (Found: C, 54.1; H, 7.4. $C_{18}H_{29}O_7N_3$ requires C, 54.1; H, 7.3%).

$\beta\delta$ -Dicarboxysuberic Acid (XV).—A solution of the acid (XIV) (2 g.) in aqueous sodium hydrogen carbonate was treated with 3% potassium permanganate in the cold. The reaction, slow initially, accelerated, and then became slow again when 29 c.c. had been added. A further 29×2.2 c.c. were then added rapidly, and the mixture was kept over-night. After treatment of the manganese oxides with steam, the combined filtrates were evaporated to small bulk, and the liquid was made acid with hydrochloric acid, boiled, and rendered alkaline with ammonia; addition of calcium chloride then gave calcium oxalate. The filtrate was strongly acidified and extracted with ether. On concentration of the dried ethereal solution, a crystalline acid was obtained, but complete evaporation yielded a gum which frothed and filled the desiccator when the attempt was made to pump off the last traces of ether. The solid acid had m. p. 206 – 207° and was stable to permanganate (Found: C, 45.7; H, 4.8. $C_{10}H_{14}O_8$ requires C, 45.8; H, 5.3%).

The ethyl butane- $\alpha\alpha\beta\gamma$ -tetracarboxylate and ethyl butane- $\alpha\beta\delta\delta$ -tetracarboxylate used in these experiments were characterised through their amides, of which *butane- $\alpha\alpha\beta\gamma$ -tetracarboxyamide* is a new compound. It is readily obtained from the ester and aqueous ammonia, and, after crystallisation from boiling water, has m. p. 267° (decomp.) (Found: C, 41.8; H, 6.3. $C_8H_{14}O_4N_4$ requires C, 41.7; H, 6.1%).

We desire to thank the Royal Society for a grant with the aid of which the expenses involved in this work have been met.