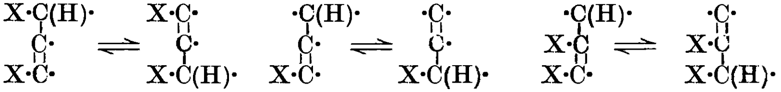
CXCIII.—*The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part I. The Three-carbon System.*

By Christopher Kelk Ingold, Charles William Shoppee, and Jocelyn Field Thorpe.

It has been shown (Birch, Kon, and Norris, J., 1923, **123**, 1361; Birch and Kon, *ibid.*, p. 2440; Kon and Linstead, J., 1925, **127**, 616, 815) that the mobility of the three-carbon system, which reaches a maximum in glutaconic esters (Type I), is also exhibited to a more limited degree in αβ- and βγ-unsaturated esters (Type II), in which only one terminal carbethoxyl group is present, and in analogous unsaturated ketones and nitriles. This paper deals with the general question of the influence of substituents on tautomeric mobility, and includes a study of the case in which, in addition to one terminal carbethoxyl group, a second carbethoxyl group is attached to the central atom of the three-carbon system (Type III).



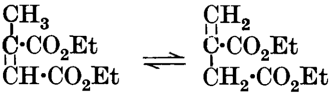
$$\begin{array}{l}X{\cdot}C(H){\cdot}\\ \quad|\\ \quad C{\cdot}\\ \quad\|\\ X{\cdot}C{\cdot}\end{array} \rightleftharpoons \begin{array}{l}X{\cdot}C{\cdot}\\ \quad\|\\ \quad C{\cdot}\\ \quad|\\ X{\cdot}C(H){\cdot}\end{array} \qquad \begin{array}{l}{\cdot}C(H){\cdot}\\ \quad|\\ \quad C{\cdot}\\ \quad\|\\ X{\cdot}C{\cdot}\end{array} \rightleftharpoons \begin{array}{l}{\cdot}C{\cdot}\\ \quad\|\\ \quad C{\cdot}\\ \quad|\\ X{\cdot}C(H){\cdot}\end{array} \qquad \begin{array}{l}{\cdot}C(H){\cdot}\\ \quad|\\ X{\cdot}C\\ \quad\|\\ X{\cdot}C{\cdot}\end{array} \rightleftharpoons \begin{array}{l}{\cdot}C{\cdot}\\ \quad\|\\ X{\cdot}C\\ \quad|\\ X{\cdot}C(H){\cdot}\end{array}$$

(Type I.) (Type II.) (Type III.)

$X = CO_2Et$

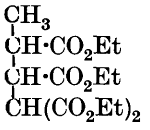
A noteworthy contrast between systems (I) and (II) is that, whilst compounds of type (I) (glutaconic esters) usually attain equilibrium in the absence of an added reagent so that the isomeric forms cannot be isolated as distinct individuals, substances belonging to type (II) frequently require the addition of an alkaline catalyst, such as alcoholic sodium ethoxide, to bring about interconversion of the forms. Type III is found to resemble type II in this respect; on the other hand, there are important differences between these two types in the general character of the equilibria to which they attain.

Citraconic and itaconic esters (IV and V) belong to type III, and they can, of course, be obtained as distinct individuals. There are, however, definite indications of their interconvertibility in the presence of alcoholic sodium ethoxide. Thus Hope found (J., 1912, **101**, 894) that if citraconic ester were treated with ethyl sodiomalonate in ether or benzene, the normal addition compound (VI) was formed; whereas if he used alcohol as solvent, an isomeric ester (VII) was obtained, which could also be prepared directly from itaconic ester.



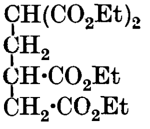
$$\begin{array}{l}CH_3\\ |\\ C{\cdot}CO_2Et\\ \|\\ CH{\cdot}CO_2Et\end{array} \rightleftharpoons \begin{array}{l}CH_2\\ \|\\ C{\cdot}CO_2Et\\ |\\ CH_2{\cdot}CO_2Et\end{array}$$

(IV.) (V.)



$$\begin{array}{l}CH_3\\ |\\ CH{\cdot}CO_2Et\\ |\\ CH{\cdot}CO_2Et\\ |\\ CH(CO_2Et)_2\end{array}$$

(VI.)



$$\begin{array}{l}CH(CO_2Et)_2\\ |\\ CH_2\\ |\\ CH{\cdot}CO_2Et\\ |\\ CH_2{\cdot}CO_2Et\end{array}$$

(VII.)

A re-examination of this reaction has shown that *both* the ester (VI) and its isomeride (VII) are formed from either citraconic or itaconic ester under a considerable variety of conditions, *e.g.*, by treatment with an equivalent or a large excess of sodium ethoxide in cold or in hot ethyl alcohol, or with sodium in boiling benzene. Under other conditions, only one isomeride could actually be isolated in the pure condition, the formation of the other being established by the production of derivatives.

These experiments, a fuller account of which is given below, strongly emphasise the suggestion that citraconic and itaconic esters are tautomeric in the presence of sodium ethoxide, just as are the esters (and nitriles, etc.) of type II previously discussed. Hope, however, advanced the opinion that the interconversion in the presence of sodium ethoxide might take place through the adding on and splitting off of alcohol in accordance with the following scheme, and he succeeded in isolating an ethoxy-derivative to which formula (VIII) was assigned.

$$\text{(IV.)} \rightleftharpoons CH_3{\cdot}C(OEt)(CO_2Et){\cdot}CH_2{\cdot}CO_2Et \ \text{(VIII.)} \rightleftharpoons \text{(V.)}$$

This view has, of course, the same mechanical simplicity as other " adding on and splitting off " theories of isomeric change, and it is necessary to explain why we regarded it as improbable. First it has been shown (E. H. Ingold, J., 1925, **127**, 469) that although, in reversible addition reactions, fission corresponding with addition in the direction favoured by polar influences is in general readily effected, yet fission corresponding with addition in a non-favoured direction takes place with difficulty or not at all. The conversion of (VIII) into (V), involving as it does the removal of a β-ethoxyl group along with an α-hydrogen atom, would be a fission of the latter class, and would certainly not take place under the experimental conditions employed. Secondly, in all alcohol-additions to unsaturated esters, the ethoxyl group takes up the same position as does the $-CH(CO_2Et)_2$ group in the corresponding additions of ethyl malonate. Hence, regarding the malonic ester addition products (VI) and (VII) as derived from (IV) and (V), respectively, we see that if citraconic ester formed an ethoxy-compound it should have formula (IX), whilst if itaconic ester gave one it should have formula (X); and either of these on losing alcohol would, of course, pass back into the ester from which it was derived. Thus, not only would an ester of constitution (VIII) not be formed, but, even if it were, it would not undergo the changes which it was invented to explain.

$$CH_3{\cdot}CH(CO_2Et){\cdot}CH(OEt){\cdot}CO_2Et \qquad OEt{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$$

(IX.) (X.)

Proof that Hope's ethoxy-ester has in reality formula (X) was obtained by converting the corresponding ethoxy-acid (XI) with hydrobromic and hydriodic acids into the bromo-acid (XII) and the iodo-acid (XIII), respectively, and into the lactone (paraconic acid) of the hydroxy-acid (XIV), all of which were identified by comparison with specimens synthesised for the purpose. The isomeric bromo- and hydroxy-acids corresponding with the ethoxy-esters (VIII) and (IX) are known and their m. p.'s and properties are such that they could not be confused with the substances obtained.*

$OEt{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (XI.)

$CH_2Br{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (XII.)

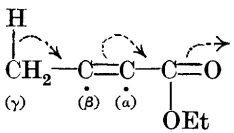
$CH_2I{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (XIII.)

$OH{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ (XIV.)

Thus, there is no evidence that an ethoxy-ester intervenes in the conversion of citraconic ester into itaconic ester; on the contrary, itaconic ester obviously must intervene in the conversion of citraconic ester into the ethoxy-ester obtained; and, naturally, the same ethoxy-ester can be obtained from itaconic ester directly.

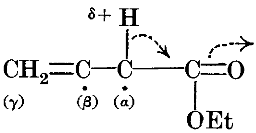
Our view of the effect of sodium ethoxide and other alkaline reagents in promoting the interconversion of these and the other three-carbon tautomerides is best made clear by reference to a recent paper by Holmes and Ingold (this vol., p. 1305), in which it is shown that a hydrogen atom attached to a hydrocarbon radical may be extracted in the form of its ion (that is, the nucleus only) by the action of a powerful negative ion such as hydroxyl, and that this process is facilitated if the hydrogen atom is already in a state of *incipient* ionisation owing to the presence in the molecule of a group (electron-sink) which exerts a pull on the electrons involved in binding the hydrogen atom. Now the carbethoxyl group, like all groups which are *m*-directive in aromatic substitution, is regarded as a powerful electron-sink (compare Allen, Oxford, Robinson, and Smith, this vol., p. 401; Ingold and Ingold, *ibid.*, p. 1310), and hence the "mobile hydrogen atom" in citraconic and itaconic ester, and in similar pairs of three-carbon tautomerides, may be assumed to be in a state of incipient ionisation owing to small electron displacements in the directions

(XV.) †



$$\overset{\delta+\ \mathrm{H}}{\underset{(\gamma)}{\mathrm{CH_2}}}-\underset{(\beta)}{\underset{\bullet}{\mathrm{C}}}=\underset{(\alpha)}{\underset{\bullet}{\mathrm{C}}}-\underset{\mathrm{OEt}}{\mathrm{C}}=\mathrm{O}$$

and



$$\underset{(\gamma)}{\mathrm{CH_2}}=\underset{(\beta)}{\underset{\bullet}{\mathrm{C}}}-\overset{\delta+\ \mathrm{H}}{\underset{(\alpha)}{\underset{\bullet}{\mathrm{C}}}}-\underset{\mathrm{OEt}}{\mathrm{C}}=\mathrm{O}$$

(XVI.)†

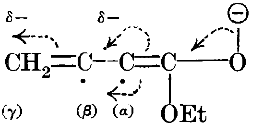
The former scheme is precisely similar to that given by Ingold and Ingold for *m*-substitution in the benzene ring (*loc. cit.*, Case 2, p. 1312). The conditions under which the isomeric change may occur will now depend entirely on the extent to which this preliminary loosening of the potential hydrogen ion has taken place.

---

* Dr. Hope, to whom these data were privately communicated, is in complete agreement with the structural conclusions.

† For explanation of symbols, see Ingold and Ingold, *loc. cit.*, p. 1312, footnote.

If incipient ionisation is considerable, mere loose combination with neutral solvent molecules (ordinary hydrion solvation) will be sufficient to draw the hydrogen nucleus away. If, on the other hand, it is slight, the more powerful attraction of a negative ion will be required to effect removal, and it is in this way, we believe, that sodium ethoxide, a source of negative ethoxyl ions, acts in facilitating the interconversion of three-carbon tautomerides. As the hydrogen nucleus is drawn away, so the electron displacements, originally minute, are enabled to progress in the sense of formulæ (XV) and (XVI), until, when ionic dissociation is complete, the displacement also is complete, the negative ionic charge appearing on the oxygen atom; thus (XV) and (XVI) give the common ion (XVII).



(XVII.)

The second half of the process, the recombination of the negative ion (XVII) with hydrion, is similarly comparable with *op*-substitution, the ion (XVII) corresponding in structure with a phenoxide ion (*loc. cit.*, Case 1, p. 1312). In each of these ions there is assumed to be a weak tendency towards a return of the electrons, giving (in different electromeric phases) small negative charges in the α- and γ- (or *o*- and *p*-) positions, to which, therefore, either positive ions, or the positive ends of incipiently ionised molecules, become attracted. In the case now under consideration, the positive ions would be solvated hydrions, and as combination proceeds, so the electrons would be drawn back in the sense of formula (XVII) until either the neutral molecule (XV) or its isomeride (XVI) is regenerated (compare with diazo-coupling).* Or, an incipiently ionised molecule, such as water or alcohol, may be attracted, and the positive end of it (hydrogen) transferred to the three-carbon system by reaction in a cycle (compare with *op*-nitration, *loc. cit.*).

This view of activation in tautomeric change represents a rational development of principles previously formulated by E. H. Ingold (*Chem. and Ind.*, 1923, **42**, 1246),† and we would apply it not only

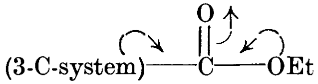
---

* The hydrions will, of course, also approach and combine with the negatively charged oxygen atom, but this produces no new isolable isomeride and is easily reversible (ordinary ionic dissociation). It is the circumstance that, when the hydrion approaches C_α or C_γ the electrons return along the chain to that point and so *bind* the hydrion, which (according to this view) gives to the $\alpha\beta$- and $\beta\gamma$-unsaturated isomerides their stability as individuals.

† Read to Section B of the British Association at Liverpool, September, 1923.

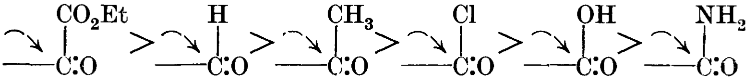
to three-carbon tautomerism, but also, with appropriate modifications, to all other mobile-hydrogen tautomeric systems, including ring-chain systems. Illustrations of its applications are, however, now confined to certain effects of structure on three-carbon tautomerism.

The effect of the terminal groups on the *mobility* of the three-carbon system (compare *inter alia*, Ingold and Piggott, J., 1922, **121**, 2381; Birch, Kon, and Norris, *loc. cit.*) may readily be correlated with directive action in benzene substitution. Thus the smaller mobility of systems terminated by a carbethoxyl or carboxyl group, as compared with similar systems terminated by an acetyl group, is regarded as due to the competition :



$$(\text{3-C-system})\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OEt$$

This is only a particular case of the general principle that the greater the electron-giving tendency possessed by a group R (as indicated by its *op*-directive power in aromatic substitution) the smaller will be the mobility of a three-carbon system terminated by ·CO·R. Thus the sequence $NH_2 > OH > Cl > CH_3 > H > CO_2Et$ for *op*-directive power leads to the sequence

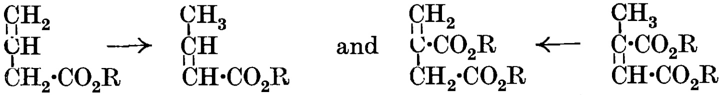


$$\text{—}\overset{\overset{\displaystyle CO_2Et}{|}}{C}{:}O > \text{—}\overset{\overset{\displaystyle H}{|}}{C}{:}O > \text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}{:}O > \text{—}\overset{\overset{\displaystyle Cl}{|}}{C}{:}O > \text{—}\overset{\overset{\displaystyle OH}{|}}{C}{:}O > \text{—}\overset{\overset{\displaystyle NH_2}{|}}{C}{:}O$$

for the enhancement of three-carbon mobility. Similar series apply to related phenomena discussed by E. H. Ingold (*loc. cit.*) and, in passing, it may be noticed that the difference –CO·Cl>–CO·OH is utilised in the Hell-Volhard method of brominating aliphatic acids through their chlorides. The reason for the greater mobility of three-carbon systems in which there are two terminal carbethoxyl groups (glutaconic esters, type I) as compared with those in which there is only one (types II and III) is too obvious to require elaboration.

A general discussion of the effect of groups on the three-carbon *equilibrium* would necessarily be lengthy, but the method of treatment can be illustrated by means of a few examples. In the simple case of a three-carbon system activated by one terminal group, say a carboxyl group, six types of modification by substitution are possible, since either an *op*-directive group (electron source) or a *m*-directive group (electron-sink) might be introduced into either the α-, or the β-, or the γ-position.

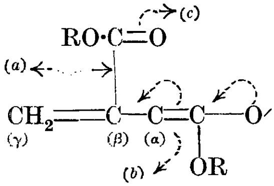
As illustration, we may consider the introduction of an electron sink into the β-position, the effect of which is to displace the equilibrium in the direction favouring the βγ-unsaturated isomeride. For example, the isomeric changes



$$\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2\cdot CO_2R \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ | \\ CH \\ \| \\ CH\cdot CO_2R \end{matrix} \quad \text{and} \quad \begin{matrix} CH_2 \\ \| \\ C\cdot CO_2R \\ | \\ CH_2\cdot CO_2R \end{matrix} \longleftarrow \begin{matrix} CH_3 \\ | \\ C\cdot CO_2R \\ \| \\ CH\cdot CO_2R \end{matrix}$$

(Type II.) (Type III.)

form a striking contrast (compare also Baeyer, *Annalen*, 1890, **258**, 165; Hassell and Ingold, this vol., p. 1465; Goss and Ingold, *ibid.*, p. 1471). The reason for this effect is clearly seen if we consider the return of the electrons in the ion (XVII). Two routes are originally open, (*a*) and (*b*) (XVIII), but one of these (*a*) clashes with path (*c*) provided by the β-group; hence the hydrogen ion combines preferentially at the α-carbon atom :



(XVIII.)

Similarly, in aromatic substitution, the introduction of a *m*-directing group in the *m*-position to a powerful *op*-directing group tends to facilitate substitution in the position *between* the two groups.

Again, the introduction of an *op*-directing group (electron source) in the γ-position will oppose (*a*), and in the absence of disturbing factors should therefore favour the βγ-unsaturated isomeride. γ-Alkyl groups are known to have this effect (compare *inter alia*, Wallach, *Annalen*, 1912, **394**, 376; Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080; Birch, Kon, and Norris, *loc. cit.*; Kon and Linstead, *loc. cit.*). Analogous considerations may be applied to other cases, and the comparison with aromatic substitution obviously gives great scope for the prediction of the relative magnitude as well as the direction of the effect to be expected from different substitutions in different positions.

The analogy between tautomerism and reversible additive reactions has been emphasised in a number of recent memoirs, and a discussion of the application of these views to that subject will be given in an ensuing paper.

EXPERIMENTAL.

Citraconic anhydride was obtained (3 kg.) from citric acid, and the fraction, b. p. 204—205°/760 mm., esterified as described by Hope. It is important to distil the anhydride under ordinary pressure to isomerise any itaconic anhydride. The ethyl citraconate had b. p. 118—120°/20 mm. (yield, 80%). Ethyl itaconate, b. p. 119—120°/20 mm., was prepared from itaconic acid.

Addition of Ethyl Sodiomalonate to Ethyl Citraconate and Ethyl Itaconate and Separation of the Products.—Ethyl sodiomalonate was prepared in the usual manner, with ethyl alcohol as solvent and the theoretical quantity of sodium, and the ethyl citraconate (1 mol.) added, the temperature being kept at 15°. After 24 hours, the pale yellow product was poured into water, and the product extracted with ether and washed with sodium carbonate. The residue obtained on evaporation of the ether was subjected to a long series of fractional distillations, as a result of which it was partly separated into two products : (*a*) b. p. 198—199°/10 mm., and (*b*) b. p. 190—191°/10 mm. The former (*a*) was ethyl *n*-butane-αβδδ-tetracarboxylate, since on hydrolysis by hydrochloric acid it gave *n*-butane-αβδ-tricarboxylic acid, m. p. 121°, which was identified by comparison with a specimen prepared by hydrolysing the product of condensing ethyl sodioethanetricarboxylate with ethyl β-iodopropionate. The fraction (*b*) consisted of ethyl *n*-butane-ααβγ-tetracarboxylate, since on hydrolysis it gave *trans*-α-methyltricarballylic acid, m. p. 185°.

In view of the unsatisfactory character of this separation, the crude product obtained from the condensation of 525 g. of citraconic ester and 455 g. of ethyl malonate was treated in the following manner. An ethereal solution was shaken with 2*N*-aqueous sodium hydroxide and then mixed with 100 c.c. of ice-water and 50 c.c. of 50% potassium hydroxide. This alkaline solution was extracted twice with ether, the combined ethereal extracts were evaporated, and the residue was fractionally distilled. A first fraction (8 g.) had b. p. 140—180°/12 mm., and the main fraction (22 g.) b. p. 180—192°/12 mm.; on redistillation, this gave a colourless oil (20 g.), b. p. 189—190°/11 mm., consisting of ethyl *n*-butane-ααβγ-tetracarboxylate (Found : C, 55·5; H, 7·5. Calc. : C, 55·5; H, 7·5%), since it yielded *n*-butane-αβγ-tricarboxylic acid on hydrolysis. The potassium hydroxide solution was acidified and extracted with ether, and the extract washed thoroughly with saturated aqueous sodium hydrogen carbonate. On evaporation of the extract, an oil (15 g.) was obtained, which on distillation gave a fraction (6·5 g.), b. p. 205—210°/15 mm., consisting of ethyl *cyclo*pentan-3-one-1 : 2 : 4-tricarboxylate. On boiling this with hydrochloric acid for one hour and evaporating the solution, *cyclo*pentanone-3-carboxylic acid, m. p. 62—64°, b. p. 170—174°/17 mm., was obtained. The more volatile ester fraction (5 g.), b. p. below 200°/15 mm., contained the ethyl *cyclo*pentanonedicarboxylate and ethyl *cyclo*pentanonecarboxylate described below. The sodium hydrogen carbonate solution was acidified with hydrochloric acid and extracted with ether, and the residue (60 g.) from the extract esterified with ethyl alcohol and sulphuric acid in the usual manner. An ethereal solution of the esters so obtained was washed with aqueous sodium hydrogen carbonate and then with aqueous potassium hydroxide at 0°. The ester (20 g.) on fractional distillation gave 12 g. of an oil, b. p. 200—204°/12 mm., consisting of ethyl *n*-butane-αβδδ-tetracarboxylate (Found: C, 54·7; N, 7·4. Calc.: C. 55·5; H, 7·5%), since on hydrolysis only *n*-butane-αβδ-tricarboxylic acid was obtained. The sodium hydroxide solution was acidified with hydrochloric acid and extracted with ether, and the extract washed with aqueous sodium hydrogen carbonate and then with ice-cold 10% aqueous potassium hydroxide. The ether extract on evaporation gave a resin. The potassium hydroxide solution was acidified and extracted with ether; ethyl *cyclo*pentanone-1 : 2 : 4-tricarboxylate was then obtained. The sodium hydrogen carbonate solution was reacidified with hydrochloric acid, and the product obtained on extraction with ether was esterified with alcohol and sulphuric acid. The esters, after being washed in ethereal solution with aqueous sodium hydroxide and distilled, yielded, in addition to a small amount of substance, b. p. below 140°, a main fraction, b. p. 210—245°/12 mm., consisting essentially of ethyl dicarboxy*cyclo*pentenylmalonate (see below). The sodium hydroxide solution was treated at 0° with excess of carbon dioxide, and the oil thus precipitated was extracted with ether. The residue from the ether on distillation gave a small fraction, b. p. below 145°/12 mm., and a main fraction, b. p. 145—154°/12 mm., consisting of ethyl *cyclo*pentanonedicarboxylate (see below). The carbonated solution was rendered acid, and the product extracted with ether and re-esterified with alcohol and sulphuric acid. The esters so obtained, after being washed in ethereal solution with alkali and distilled, gave principally a fraction, b. p. 230—240°/12 mm., consisting mainly of ethyl dicarboxy*cyclo*pentenylmalonate.

The various "low" fractions mentioned in the course of the foregoing account were combined and examined. They consisted principally of unaltered ethyl malonate, ethyl mesaconate, and ethyl itaconate, a possible indication of the reversibility of the reaction.

The same nine substances, namely, ethyl malonate, itaconate, mesaconate, butane-ααβγ-tetracarboxylate, butane-αβδδ-tetracarboxylate, *cyclo*pentanone-mono-, -di-, and -tri-carboxylate, and dicarboxy*cyclo*pentenylmalonate, were obtained, by the same method of separation, when the original condensation was carried out at 80°, and also when ethyl itaconate was substituted for ethyl citraconate in either experiment. Similar condensations carried out with itaconic and with citraconic ester, both at 15° and at 80°, with the difference that the quantity of sodium employed was twice the theoretical, yielded the same products, together with a pale yellow mixture of sodium compounds the nature of which has not yet been elucidated. Other condensations were carried out in boiling benzene as the solvent, the ethyl sodiomalonate being prepared from "molecular" sodium and ethyl malonate. When ethyl citraconate was used, not only ethyl butane-ααβγ-tetracarboxylate, but also αβδδ-tetracarboxylate and the *cyclo*pentane-esters were obtained. The use of excess of sodium made no difference to these results, and the yellow sodium compounds were not obtained as when alcohol was used as solvent. Other condensations were effected by the aid of molecular sodium (1 mol.) in dry ether. In this case, using ethyl citraconate, ethyl butane-ααβγ-tetracarboxylate was obtained in 80% yield, and the αβδδ-ester was not isolated; but it must have intervened in the production of ethyl *cyclo*pentanonetricarboxylate, which was identified by hydrolysis to *cyclo*pentane-3-carboxylic acid, m. p. 62°. The use of excess of sodium did not affect this result. Similar experiments using ethyl itaconate in place of ethyl citraconate led to 65—75% yields of ethyl *n*-butane-αβδδ-tetracarboxylate, which was identified through its amide (m. p. 255°; compare Michael and Schulthess, *J. pr. Chem.*, 1892, **45**, 57) and hydrolysis product. The *cyclo*pentane esters were also obtained, but ethyl *n*-butane-ααβγ-tetracarboxylate could not be identified. The presence of excess of sodium did not affect this result.

It appears, therefore, that the mobility of the unsaturated esters is less in benzene and ether than in alcoholic sodium ethoxide, and that in ether particularly, possibly on account of its low b. p., there is very little interchange.

The following compounds are new.

Ethyl cyclo*pentanone*-3-*carboxylate* is a colourless oil, b. p. 109—111°/10 mm. It gives no colour with ferric chloride (Found: C, 61·4; H, 7·7. $C_8H_{12}O_3$ requires C, 61·5; H, 7·7%). The *semicarbazone* was prepared by means of semicarbazide acetate and crystallised from ethyl alcohol in needles, m. p. 153·5° (Found: C, 50·6; H, 7·2. $C_9H_{15}O_3N_3$ requires C, 50·7; H, 7·0%). The ester can be prepared by way of the acid chloride, which is obtained when phosphorus pentachloride acts on *cyclo*pentanone-3-carboxylic acid.

Ethyl cyclo*pentanone*-2 : 4 (*or* 2 : 3)-*dicarboxylate* has b. p. 150°/10 mm. and 160°/18 mm. It gives a deep red colour with ferric chloride (Found: C, 57·6; H, 7·3. $C_{11}H_{20}O_5$ requires C, 57·8;

H, 7·0%). A semicarbazide could not be prepared. On hydrolysing the ester with hydrochloric acid, *cyclo*pentanonecarboxylic acid, m. p. 64°, was obtained.

Ethyl 2 : 4 (*or* 2 : 3)-*Dicarboxy*cyclo*pentenylmalonate* (*or Ethyl* 2 : 4 [*or* 2 : 3]-*dicarboxy*cyclo*pentylidenemalonate*).—A number of crude specimens of this ester (51 g.) were combined and carefully distilled; 43 g. of a pure fraction, b. p. 240—245°/16 mm., were then obtained (Found: C, 58·3; H, 7·1. $C_{18}H_{26}O_8$ requires C, 58·3; H, 7·1%). The ester was unsaturated and gave no colour with ferric chloride. It showed an exaltation of refractivity of 1·9 units for sodium light ($n_D^{21°}$ 1·46719; *d* 1·13273). The acid obtained on hydrolysis was a syrup, and may have been a mixture of the endocyclic and exocyclic unsaturated acids, since the parent ester would almost certainly be tautomeric. From the first fractions obtained in the distillation of the above ester, a semicarbazone was obtained which was identified with that described above, m. p. 153·5°.

Formation and Constitution of Ethyl ω-Ethoxymethylsuccinate.—This ester may be prepared either from citraconic ester, as described by Hope, or from itaconic ester. Using Hope's method, we found some difficulty in obtaining the ethoxy-ester free from unsaturated esters, but after a series of careful fractionations, about 15—20% of an ester, b. p. 137—140°/23 mm., was obtained which decolorised permanganate only slowly. It gave correct figures on analysis and on treatment with aqueous ammonia yielded *ω-ethoxymethylsuccinamide*, which was isolated by evaporating the ammonia solution in a vacuum and crystallising the residue from water. Thus obtained, the amide formed prisms, m. p. 149—150° (Found: C, 48·4; H, 7·8. $C_7H_{14}O_3N_2$ requires C, 48·3; H, 8·0%). By the use of itaconic ester (20 g.), sodium (0·16 g.), and alcohol (96 c.c.), and by keeping the mixture at the ordinary temperature overnight, a product was obtained which, after four fractional distillations, yielded 3 g. of an unsaturated ester, b. p. 130—135°/23 mm., and 5 g. of an ester, b. p. 137—140°/23 mm., which only slowly decolorised alkaline permanganate. The unsaturated ester, on treatment with ammonia, was converted into mesaconamide, m. p. 176—177° (Found: C, 47·0; H, 6·3. Calc.: C, 46·9; H, 6·2%) and must therefore have consisted largely of mesaconic ester. The saturated ester was evidently the same ethoxy-ester as that obtained from citraconic ester, since it gave the same amide, m. p. 149—150°, on treatment with ammonia and the same acid on hydrolysis (Found: C, 56·6; H, 8·6. Calc.: C, 56·9; H, 8·6%). The ethoxy-acid obtained on hydrolysis had the m. p. and properties described by Hope.

α-Iodopropane-βγ-dicarboxylic Acid.—The ethoxy-acid (2 g.) was boiled for 2 hours with "Zeisel" hydriodic acid, and the ethyl iodide formed allowed to escape. The resulting solution was extracted with ether, and the extract washed with thiosulphate solution, dried, and evaporated. The residue immediately solidified with evolution of heat, and after crystallisation from ethyl acetate–ligroin had m. p. 138° (Found: C, 23·9; H, 2·7. Calc.: C, 23·2; H, 2·7%). It was identified by direct comparison and a mixed m. p. determination with a specimen of α-iodopropane-βγ-dicarboxylic acid prepared for the purpose.

α-Bromopropane-βγ-dicarboxylic Acid.—The ethoxy-acid was boiled for 3 hours with hydrobromic acid (*d* 1·49), and the product extracted with ether. The residue obtained at once solidified, and after crystallisation from ethyl acetate–petrol had m. p. 137°. It was identified by the m. p. of a mixture with a genuine specimen.

Paraconic Acid.—Both the iodo- and the bromo-acid were treated with excess of silver oxide in aqueous suspension; heat was generated and the silver halide precipitated. The acid extracted with ether after addition of mineral acid solidified in an evacuated desiccator and then melted at 50—53°. After crystallisation from ether–chloroform, paraconic acid was obtained, m. p. 57°, and identified by direct comparison and a mixed m. p. determination with an authentic specimen.

We take this opportunity to record our thanks to both the Chemical Society and the Royal Society for grants with the aid of which the cost of this investigation has been defrayed.

THE UNIVERSITY, LEEDS.
THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

[*Received, March 2nd, 1926.*]