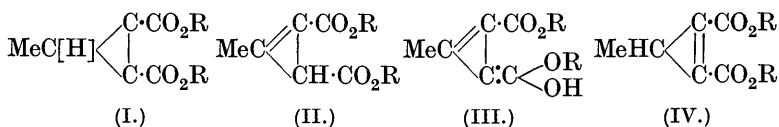


380. *The Structure of the Glutaconic Acids and Esters. Part VII. Derivatives of 3-Methylcyclopropene-1:2-dicarboxylic Acid.*

By G. A. R. KON and H. R. NANJI.

IN 3-methylcyclopropene-1:2-dicarboxylic acid, all three carbon atoms of the propene chain form part of the ring and it therefore resembles the cyclic compounds described in Part IV (this vol., p. 2426) in being capable of three-carbon tautomerism, but not of stereoisomerism, which is precluded by its cyclic structure. Goss, Ingold, and Thorpe (J., 1923, **123**, 327, 3342; 1924, **125**, 1927; 1925, **127**, 460) have suggested that the acid is a true glutaconic derivative,

possessing a mobile hydrogen atom and giving rise to three series of interconvertible esters, termed, respectively, normal (I), labile (II), and enol (III); the acid was also represented by the normal formula (I; R = H). Additional and, in part, contradictory evidence has been contributed by Feist (*Annalen*, 1924, 436, 125).



The existence of the three esters is at variance with the evidence regarding the structure of glutaconic acid derivatives (J., 1931, 560; this vol., pp. 1, 1027, 2426, 2434, 2443). The "normal" formulation of the acid and its ester (I) is, moreover, inconsistent with their resolution into optically active components (Feist; confirmed by Goss, Ingold, and Thorpe); in any case, this mode of formulation has since been abandoned, at any rate as an expression of structure rather than a mode of reaction (McCombs, Packer, and Thorpe, J., 1931, 547). For this reason we have undertaken the revision of the work with the kind permission of Prof. J. F. Thorpe, F.R.S., and Prof. C. K. Ingold, F.R.S.

A re-examination of the facts, together with the new evidence now submitted, shows beyond doubt that the structure of the acid and its solid "normal" ester must be represented by the Δ^2 -formula (II), formerly allotted to the "labile" ester. This leaves the constitution of the latter, assuming it to be an individual compound, to be accounted for, together with that of the enol ester derived from it.

The "labile" ester has been stated to be formed from the "normal" principally in three ways: (i) by distillation under atmospheric pressure; (ii) by treatment with sodium ethoxide; (iii) an equilibrium mixture of all three esters is obtained when any one of them is heated with alcoholic sulphuric acid.

Now it has been shown (Kon and Nanji, J., 1931, 560; Gidvani, Kon, and Wright, this vol., p. 1027) that the action of sodium ethoxide on glutaconic esters leads to the production of equilibrium mixtures and that both the "normal" and the "labile" fractions so obtained are usually mixtures of $\alpha\beta$ - and $\beta\gamma$ -unsaturated esters.

By analogy, therefore, it was to be expected that, if the cyclopropene esters are capable of tautomerism, treatment with sodium ethoxide would produce such a mixture and that the formation of the Δ^1 -ester (IV) would in that case have to be taken into account. For this reason, the equilibration of the Δ^2 -ester was repeated first of all.

Our results differ materially and inexplicably from those recorded in the earlier investigation. We have been unable to obtain the sodio-derivative of the enol ester or the enol ester itself and consequently could not prepare the "labile" ester by the sodium ethoxide process. The formation of the sodio-ethyl ester was merely inferred by the previous investigators from the products obtained from it on acidification, but the sodio-derivative of the methyl ester was actually isolated and analysed. We have repeatedly attempted the preparation of the sodio-derivative both in the ethyl and in the methyl series of esters, but always with negative results.

In our hands, the action of sodium ethoxide on the Δ^2 -ester led in every case to addition of ethyl alcohol to the ester. Dilution with water gave a neutral ester consisting, not of the "normal" ester or of an equilibrium mixture of the Δ^1 - and the Δ^2 -ester, but of the ethoxy-ester, $\text{Me(OEt)C} \begin{matrix} \text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CH}\cdot\text{CO}_2\text{Et} \end{matrix}$ (V), which is easily recognised owing to its high boiling point and low refractive index.

The aqueous solution obtained at the same time contains but little material, consisting for the most part of the ethoxy-acid, m. p. 156° , corresponding to the ester (V) and already isolated by the previous investigators; the remainder is indeed enolic, giving a deep colour with ferric chloride, but analysis of the distilled material shows that it is not isomeric with the Δ^2 -ester and cannot, presumably, be identical with Goss, Ingold, and Thorpe's enol ester.

The formation of the ethoxy-ester (V) is very rapid and there is no evidence of tautomeric change preceding it; indeed, we have not detected any tendency for the formation of the Δ^1 -ester (IV) under any of the experimental conditions tried.

The production of the ester (V) is analogous to the rapid addition of methyl alcohol to the methyl ester, already recorded by Goss, Ingold, and Thorpe and confirmed by us; and if the addition of alcohol to the Δ^2 -esters is the first step in the action of sodium alkoxides on these compounds, it is clearly impossible to speak of the equilibration of the latter in the customary sense, meaning the production of a mixture of isomerides in definite proportions.

The addition of methyl alcohol to the methyl ester is described as being reversible, but the formation of the sodio-derivative in this case must be a reaction of the methoxy-ester, not the *cyclopropene* ester, and is in no way analogous to the formation of sodio-compounds from true glutaconic esters: addition of alcohol to the latter has not yet been observed (compare Kon and Nanji, this vol., p. 2426).

A somewhat similar behaviour has, however, been observed in

the esters of the citraconic-itaconic type (Coulson and Kon, following paper); these do not form sodio-derivatives and it is possible to demonstrate the occurrence of tautomeric change, which is more rapid than the addition of alcohol, although, as already pointed out, this addition makes the actual position of equilibrium uncertain.

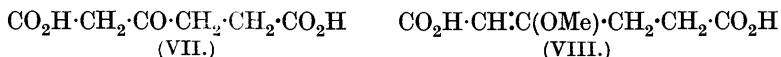
We were also unable to bring about the equilibration of the Δ^2 -ester with alcoholic sulphuric acid; it was recovered unchanged.

The formation of the "labile" ester proceeds readily, however, by the action of heat on the Δ^2 -ester and the properties of the product leave no doubt as to its identity with the "labile" ester previously prepared by the same process, although the boiling point is lower than that recorded. We were, however, unable to confirm the reconversion of this ester into the Δ^2 -ester on keeping or, indeed, under any conditions tried. Our experiments lead to the conclusion that the conversion of the Δ^2 -ester into its isomeride is not only an irreversible process, but one involving a complete rearrangement of the carbon skeleton of the molecule.

The elucidation of the constitution of the "labile" ester presented great difficulties, principally because the results of oxidation with ozone could not be interpreted at first; it is now certain that the compound must be represented by the formula $\text{CO}_2\text{Et}\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (VI) and is therefore a straight-chain acetylene derivative.

This conclusion is based on the following considerations: (i) The "labile" ester is reduced by hydrogen and palladium to an ester which gives a large amount of adipic acid on hydrolysis. This proves the presence of a straight chain of four carbon atoms.

(ii) The ester is hydrolysed by aqueous-methyl alcoholic potassium hydroxide to a mixture of two acids, neither of which, however, is the expected acetylenic acid corresponding to the ester (VI). The principal constituent of the mixture is β -ketoadipic acid (VII); it gives a colour with ferric chloride and yields the semicarbazone of lævulic acid on treatment with semicarbazide, carbon dioxide being eliminated at the same time. The acid is evidently formed by the addition of water to the acetylenic acid (compare Burton and von Pechmann, *Ber.*, 1887, **20**, 145; Perkin and Simonsen, *J.*, 1907, **91**, 816). The second acid, which is only formed in very small amount, appears to be the methoxy-acid (VIII) resulting from the addition of methyl alcohol to the acetylenic acid (compare p. 2559).

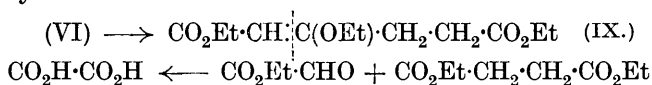


Hydrolysis of the acetylenic ester with dilute hydrochloric acid goes a step further than with alkali and gives a syrupy product, in

which lævulic acid can be easily identified; it is obviously produced by the decarboxylation of the acid (VII).

If the "labile" ester used for hydrolysis is not very carefully fractionated, varying quantities of the *cyclopropene* acid are isolated and this may perhaps account for the statement that this acid is the sole hydrolysis product of the "labile" ester, at any rate with hydrochloric acid, since it is the only *solid* acid formed in this case. In addition, the acids (VII) and (VIII) are both sparingly soluble in ether and might be overlooked for this reason.

(iii) The action of sodium ethoxide on the "labile" ester is extremely vigorous, but the formation of a sodio-derivative has not been observed. The principal product is again an ethoxy-ester, $C_{12}H_{20}O_5$, isomeric with the ester (V) and hydrolysable to an acid, m. p. 161° . This was at first thought to be the *trans*-isomeride of the ethoxy-acid, m. p. 156° , since, like the latter, it gave lævulic acid on boiling with hydrochloric acid, but did not give an anhydride. It was later found to be unsaturated and its structure was established by the oxidation of its ester (IX) with ozone. The products were oxalic acid and ethyl succinate. The formation of the latter by the fission of an ozonide was unexpected, but it clearly establishes the constitution of the ester (IX), since this can only be formed from a compound with an ethoxyl group attached to one of the doubly-bound carbon atoms.

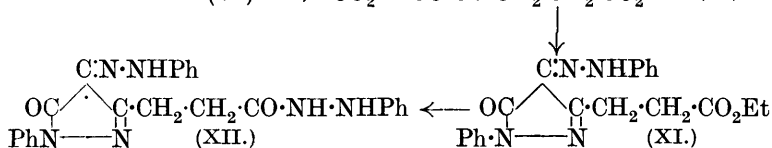


The yield of ethyl succinate in this experiment was 80% and as the yield of the ethoxy-ester from the "labile" ester was on this occasion 64%, it follows that the minimum content of acetylenic ester in the "labile" ester must be 52%, without allowance for manipulative losses and the formation of by-products in the first reaction; it is more probably about 80%.

The formation of the ethoxy-ester (IX) is to be expected and is entirely analogous to the production of ethoxymaleic and fumaric esters from ethyl acetylenedicarboxylate (Michael and Bucher, *Ber.*, 1896, 29, 1792).

(iv) The "labile" ester is ozonised with extreme difficulty and much unchanged initial material is generally recovered in addition to syrupy mixtures of acids (compare Molinari, *Ber.*, 1907, 40, 4154; Harries, *ibid.*, p. 4907); the neutral products are, however, quite distinct from those derived from the Δ^2 -ester, the oxidation of which was repeated for the sake of comparison. The principal product is a yellow ketonic ester, which is neutral or only feebly acidic and is easily characterised by its orange *diphenylhydrazone* (XI);

the latter also gives rise to a *phenylhydrazide*. These compounds are formulated as follows:



The diketonic ester (X), which was not obtained pure, is further oxidised by hydrogen peroxide to succinic acid; attempts to obtain the corresponding acid by hydrolysis were unsuccessful, the only acid isolated being β -keto adipic acid, derived from the "labile" ester itself.

The formation of the diketonic ester containing the original chain of four carbon atoms is unusual, since most acetylenic compounds appear to be oxidised with the rupture of the chain at the triple bond, and led us to retain a cyclic structure for the "labile" ester for some time.

In the earlier experiments, conducted in ethyl acetate solution, small quantities of formaldehyde were usually detected, but these were undoubtedly derived from the solvent (compare Escourrou, *Bull. Soc. chim.*, 1928, 43, 1088; see, however, Dœuvre, *ibid.*, 1929, 45, 140); in later experiments, with chloroform as a solvent, formaldehyde was not detected.

The "labile" ester, unlike the normal, is rapidly attacked by alcoholic sulphuric acid, probably with the addition of alcohol; the nature of the product has not yet been ascertained.

These reactions establish the constitution of the "labile" ester beyond all reasonable doubt, although it must be admitted that the isomerisation of the *cyclopropene* ester into an acetylenic derivative, involving as it does the absorption of the methyl group into the chain, is an unusual reaction and without parallel as far as we know; the disruption of the trimethylene ring in a pyrogenic reaction has, of course, been repeatedly observed.

This isomerisation is clearly a deep-seated decomposition and in no way related to the type of tautomeric change encountered in the glutaconic acids and esters.

The reactions of the Δ^2 -ester, notably the rapid addition of the elements of alcohol to the double bond, also differ materially from those of typical glutaconic esters and suggest that this ester is more nearly related to the esters of the itaconic group; indeed, it is doubtful whether it possesses a mobile hydrogen atom in the ordinary sense, a conclusion already foreshadowed by Feist (*loc. cit.*).

The statement that the "labile" ester is formed from the normal ester by the action of sodium ethoxide must, in our opinion, be based on a misapprehension.

The constitution of the enol ester must for the present be left an open question; but since this compound is stated to be a derivative of the "labile" ester and not of the normal ester, the formula (III) allotted to it will require revision. Apart from the fact that it appears unlikely that a compound of this constitution would be sufficiently stable to have more than a momentary existence (compare Feist, *loc. cit.*), such a compound could not be produced by the action of sodium ethoxide on the acetylenic ester (VI). In the latter case, it might perhaps be the ester of the ketonic acid (VII), whilst the yellow sodio-derivative isolated and analysed by the previous investigators could have been similarly formed from the corresponding methyl ester (methyl β -keto adipate).

EXPERIMENTAL.

Ethyl 3-Methyl- Δ^2 -cyclopropene-1:2-dicarboxylate ("normal" ester).—The pure ester was prepared from the recryst. acid ($\text{H}\cdot\text{CO}_2\text{H}$ is the best solvent) either through the Ag salt or with the aid of EtOH and H_2SO_4 , both processes giving an ester which solidified completely after distillation, b. p. $115^\circ/11$ mm.; a supercooled specimen had d_4^{20} 1.0651, n_D^{20} 1.4583, $[\alpha]_D^{20}$ 50.78. No high fraction was obtained and the ester did not give the reactions for the "labile" ester mentioned by Goss, Ingold, and Thorpe; such a high fraction was, however, obtained in small amount when the crude, almost black, acid was esterified without previous purification.

The Δ^2 -ester was recovered unchanged and without loss after 3 hrs.' boiling with EtOH (3 vols.) containing 1 vol. of conc. H_2SO_4 ; it boiled at the right temp., solidified completely after distillation, and did not give a colour with FeCl_3 or with 40% KOH aq., and therefore did not contain any "labile" enol ester.

Ozonisation. The ester, dissolved in AcOEt, was treated with ozonised O_3 until no more was absorbed; the solvent was then removed under reduced press., and the ozonide decomposed by shaking with H_2O over-night. The products were AcOH, $\text{H}_2\text{C}_2\text{O}_4$, and ethyl acetyloxaloacetate, as already found by previous investigators. To avoid decomp., the ester was not distilled; on treatment with phenylhydrazine acetate it gave a sparingly sol., colourless pyrazolone, m. p. 230° (Found: C, 67.3; H, 5.4; N, 19.3. $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_6$ requires C, 67.6; H, 5.2; N, 19.7%); no trace of a coloured phenylhydrazine derivative was produced.

Action of sodium ethoxide. (i) The finely ground Δ^2 -ester (15 g.) was added to a solution of 1.15 g. of Na in 15 c.c. of dry EtOH, the reaction mixture being kept, protected from moisture, at approx. 60° for 48 hrs. The dark brown product was then diluted with 200 c.c. of H_2O and extracted with Et_2O (neutral extract), an operation which was very troublesome owing to the formation of an emulsion. The aq. solution was acidified with dil. HCl, rise of temp. being prevented, and again extracted with Et_2O . This extract was shaken with dilute Na_2CO_3 aq. to remove the acid products (the ethoxy-

acid and tar), leaving the quasi-acid (a little brown viscous material) in the ether.

The neutral extract, after thorough washing with H_2O , drying, and evaporation of the Et_2O , gave a residue (about 10 g.), b. p. 145—146°/11 mm. (there was no low fraction corresponding to the unchanged Δ^2 -ester), $d_4^{20.0}$ 1.0353, $n_D^{20.0}$ 1.4389, consisting of ethyl 3-ethoxy-3-methylcyclopropane-1:2-dicarboxylate (V) (Found: C, 58.9; H, 8.8. $C_{12}H_{20}O_5$ requires C, 59.0; H, 8.3%). The ester rapidly decolorised Br in $CHCl_3$ and on hydrolysis with an excess of 10% NaOH aq. and a little EtOH, it gave the ethoxy-acid, m. p. 156° (Goss, Ingold, and Thorpe, *loc. cit.*).

(ii) The Δ^2 -ester was similarly treated, but the reaction product was kept at room temp. for 15 mins. only before being worked up as above. The neutral ester ($d_4^{20.0}$ 1.0428, $n_D^{20.0}$ 1.4411) again consisted of the ethoxy-ester (Found: C, 58.6; H, 8.1%), the addition of EtOH being apparently complete.

(iii) As (ii), but the mixture was heated under reflux on the steam-bath for 15 hrs. The neutral ester again consisted of the ethoxy-ester; the quasi-acid product, which gave a deep violet colour with $FeCl_3$, was formed in somewhat greater amount. This was combined with that obtained in the first experiment and distilled; about 1 g. of a yellow oil was collected at 140°/11 mm.; this had $d_4^{20.0}$ 1.07, $n_D^{20.0}$ 1.4529 and was thus quite different from the "labile" ester (see below); it decolorised Br in $CHCl_3$ almost instantaneously (neither the Δ^2 -ester nor the "labile" ester did so in a control expt.), gave a faint colour with $FeCl_3$ even after a few days, and was evidently not isomeric with the Δ^2 -ester (Found: C, 57.4; H, 7.7. Calc. for $C_{11}H_{18}O_5$: C, 57.8; H, 7.8%).

(iv) Na (0.95 g.) was dissolved in 10 c.c. of dry EtOH, the excess evaporated under reduced press., dry Et_2O and 10 g. of the ethoxy-ester, prepared as described under (i), added, and the whole kept for 2 days; the ethoxy-ester was recovered completely unchanged.

(v) The following expts. were kindly carried out by Mr. E. H. Coulson, M.Sc.: the "normal" ester (5 g.), dissolved in 20 c.c. of EtOH, was added to 0.6 g. of Na in 20 c.c. of EtOH, and the ester recovered after 5 mins. keeping at room temp.; it had b. p. 138—140°/28 mm., $d_4^{20.0}$ 1.0608, $n_D^{20.0}$ 1.4558. 4.7 G. of the ester so obtained were hydrolysed by boiling with aq.-alc. NaOH for 30 mins., the EtOH removed in vac., and the acid (3.12 g.) recovered by acidification and continuous extraction with Et_2O . It had m. p. about 198° and contained 16.3% of ethoxy-acid according to the OEt estimation; this agrees with the result of titration (Found: *M*, 148.5. Calc. for 16.3% ethoxy-acid, 149.7).

Ethoxy-acid, m. p. 156°.—The acid obtained in the above expts. was evidently identical with that described by Goss, Ingold, and Thorpe; it gave lævulic acid on boiling with HCl aq. as described by them (semicarbazone, m. p. 187°. Found: C, 41.6; H, 6.4. Calc.: C, 41.6; H, 6.3%). The acid, m. p. 156°, when boiled with AcCl gave an *anhydride*, which solidified in an evacuated desiccator; m. p. 49° (Found: C, 56.3; H, 5.8. $C_8H_{10}O_4$ requires C, 56.4; H, 5.8%).

Reduction of the Δ^2 -Ester.—The ester, dissolved in aq. EtOH, was shaken with colloidal Pd and gum arabic in H under 2 atms.; the reduction was complete in 48 hrs. The catalyst was then coagulated by warming and removed, and the ester isolated from the diluted filtrate by means of Et_2O . It did not decolorise $KMnO_4$ and on hydrolysis with alc. KOH gave an acid, m. p.

131—132° after two crystals from $\text{AcOEt}-\text{C}_6\text{H}_6$; after being kept for some time over P_2O_5 , the acid had m. p. 147° (compare Feist, *loc. cit.*; Goss, Ingold, and Thorpe, *loc. cit.*) (Found: C, 50.0; H, 5.5. Calc.: C, 50.0; H, 5.6%).

Ethyl Δ^{α} -Butine- α -dicarboxylate ("labile" ester) (VI).—The Δ^2 -ester was rapidly distilled in portions of not more than 20 g. over a free flame. The liquid first assumed a yellow colour at about 180°; there was usually a flash of blue flame above the liquid just before it began to boil. Decomp. set in towards the end of the distillation, with the evolution of EtOH (analysed and identified) and gases possessing a strong garlic-like odour. The distillate was refractionated under reduced pressure with a column, the purest "labile" ester being collected at 137°/20 mm.; it had d_4^{20} 1.0709, n_D^{20} 1.4661, $[R_L]_D$ 51.24. The low fractions obtained were again distilled under atmospheric pressure, more of the required fraction being produced.

When an attempt was made to distil the Δ^2 -ester slowly, a glycerol bath being used to maintain a steady temp. and minimise charring, hardly any "labile" ester was obtained, the product, apart from EtOH and gases, consisting of an undistillable dark gum giving an intense colour with FeCl_3 .

We have failed to obtain the "labile" ester by the action of "molecular" K in xylene on ethyl 2:3-dibromo-3-methylcyclopropane-1:2-dicarboxylate as described by Goss, Ingold, and Thorpe; the action was vigorous and much decomp. took place, but the neutral material recovered still contained a good deal of unchanged bromo-ester. The action of NaOEt was also tried without success.

A specimen of the "labile" ester, d_4^{20} 1.0719, n_D^{20} 1.4650, was kept for over 6 months in sealed glass tube; it then had d_4^{20} 1.0740, n_D^{20} 1.4649, so that no appreciable change had occurred. It gave no colour with FeCl_3 either before or after the expt.

Hydrolysis of the "Labile" Ester.—The first expts. were conducted with a somewhat low-boiling preparation of the "labile" ester, and the cyclopropene acid was the principal product isolated; this was not the case when the high-boiling fraction was employed.

(i) *With hydrochloric acid.* The ester was boiled under reflux with 7 vols. of 10% HCl aq. until all the oil had passed into solution (about 1 hr.), and the solution evaporated to dryness on the steam-bath. The residue did not solidify in a vac. over KOH and on treatment with phenylhydrazine acetate gave an immediate ppt. of the phenylhydrazone of levulic acid, fine needles, m. p. and mixed m. p. 107—108° after one crystal from dil. MeOH: the semicarbazone was also readily obtained.

(ii) *With potassium hydroxide.* The ester (9.6 g.), dissolved in 20 c.c. of MeOH, was added to a warm solution of 7 g. of KOH in 15 c.c. of H_2O ; a violent reaction occurred, causing the solution to boil, and a brown colour was immediately developed. The solution was warmed for 30 mins., freed from MeOH under reduced pressure, extracted once with Et_2O , acidified with HCl aq., and repeatedly extracted with a large quantity of Et_2O (the acids formed are sparingly soluble in Et_2O), the extract being dried and evaporated. The crystal residue was a mixture of two acids, which were separated by fractional crystallisation first from acetone and finally from AcOEt. The less soluble constituent was present in very small quantity and separated as a microcryst. powder, m. p. 186° (decomp.), probably consisting of the *methoxy-acid* (VIII) (Found: C, 48.4; H, 5.9. $\text{C}_7\text{H}_{10}\text{O}_5$ requires C, 48.3; H, 5.8%).

The more soluble acid, which formed the bulk of the hydrolysis product,

separated from AcOEt in flattened needles, m. p. 124—125° (decomp.), and was distinguished by its reaction with FeCl_3 , a reddish-violet colour being produced. It was β -keto adipic acid (VII) (Found: C, 45.4; H, 5.2. $\text{C}_8\text{H}_8\text{O}_5$ requires C, 45.0; H, 5.0%). The acid reacted with semicarbazide acetate with evolution of CO_2 and the formation of the semicarbazone of lævulic acid, m. p. 184° after one crystn. from dil. EtOH (Found: C, 41.8; H, 6.4. Calc.: C, 41.6; H, 6.4%).

Reduction of the "Labile" Ester.—This was carried out as described on p. 2564. The acid obtained on hydrolysis of the reduced ester still reduced KMnO_4 to some extent. It was recryst. from AcOEt-petroleum and finally from acetone; after several crystns., adipic acid, m. p. 149°, representing more than half the original product, was obtained and identified by direct comparison (Found: C, 49.2; H, 6.8. Calc.: C, 49.3; H, 6.9%).

Action of sodium ethoxide. The expts. were carried out and the products isolated as described on p. 2563. Great care must be taken to keep the reaction mixture in ice and to add the alc. solution of the ester to the NaOEt a drop at a time, otherwise the reaction is very vigorous and much darkening occurs. The reaction is complete in about an hr.

The neutral fraction (75% yield) boiled at 155°/15 mm. and had $d_4^{20.0}$ 1.0493, $n_D^{20.0}$ 1.4586, $[\alpha]_D^{20}$ 61.9; it consisted of practically pure ethyl β -ethoxy- Δ^{α} -butene- α,δ -dicarboxylate (IX) (Found: C, 59.3; H, 8.1. $\text{C}_{12}\text{H}_{20}\text{O}_5$ requires C, 59.0; H, 8.3%); it gave no colour with FeCl_3 , rapidly absorbed Br in CHCl_3 , and reduced alkaline KMnO_4 .

The quasi-acid fraction consisted of a few drops of a brown gum giving a dirty brown colour with FeCl_3 .

No ethoxy-acid was isolated from the acid fraction, but on one occasion, when a somewhat low-boiling specimen of "labile" ester had been used, some of the cyclopropene acid, m. p. 200°, was found.

Structure of the Ethoxy-ester (IX).—The ethoxy-ester obtained from the "labile" ester was hydrolysed with alc. KOH; the acid crystallised from H_2O in small needles, m. p. 161°, which depressed the m. p. of the isomeric acid, m. p. 156°. It did not yield an anhydride on boiling with AcCl for some hrs. and rapidly reduced alkaline KMnO_4 (Found: C, 51.2; H, 6.5. $\text{C}_8\text{H}_{12}\text{O}_5$ requires C, 51.1; H, 6.4%).

The acid, m. p. 161°, was boiled with HCl aq. (1:1) for 3 hrs., the liquid evaporated, and the residue extracted with Et_2O ; the extract on evaporation gave lævulic acid, identified by means of the semicarbazone and the phenylhydrazido-phenylhydrazone, m. p. 180° (Found: C, 58.8; H, 6.9; N, 19.1. Calc.: C, 68.9; H, 6.8; N, 18.9%).

The ethoxy-ester was oxidised by means of O_3 as described on p. 2563. The aq. and the alkaline extracts of the product contained large quantities of $\text{H}_2\text{C}_2\text{O}_4$. The neutral portion (more than 80% yield) had b. p. 103°/14 mm., $d_4^{15.4}$ 1.0501, $n_D^{15.4}$ 1.4319, and was almost pure ethyl succinate (Found: C, 54.8; H, 8.0. Calc.: C, 55.1; H, 8.1%). On hydrolysis, succinic acid was obtained from it in good yield and in a high state of purity (Found: C, 40.6; H, 5.2. Calc.: C, 40.6; H, 5.1%).

Ozonisation of the "Labile" Ester.—Many expts. were carried out, of which the following is typical. The purest available ester (15 g.) was dissolved in AcOEt (90 c.c.) and kept ice-cold while ozonised O_3 was passed through it for a week. After removal of the solvent in a vac., the ozonide was decomposed by shaking with 100 c.c. of H_2O over-night, the Et_2O -sol. products

being repeatedly extracted with Et_2O ; the extract was washed with 5% NaHCO_3 aq., dried, and evaporated.

The aq. solution after extraction with Et_2O still contained some formaldehyde, which was identified by bubbling H through the warm solution and passing the gas through a solution of dimethyldihydroresorcinol; the condensation product, m. p. and mixed m. p. 188° , was obtained in small amount.

The aq. and the alkaline washings contained AcOH and $\text{H}_2\text{C}_2\text{O}_4$.

The neutral extract gave on evaporation of the Et_2O a yellow oil, giving a faint colour with FeCl_3 and a marked reaction with sodium nitroprusside. With phenylhydrazine acetate the *phenylhydrazone* (XI) was almost immediately pptd.; this crystallised from MeOH in orange plates or flattened needles, m. p. 120° (Found: C, 65.7; H, 5.5; N, 15.4. $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_4$ requires C, 65.9; H, 5.5; N, 15.4%). The filtrate from this phenylhydrazone, when heated with a further small amount of phenylhydrazine acetate and kept for some time, deposited a second crop of the phenylhydrazone together with another solid which could be readily separated owing to its sparing solubility in MeOH ; it crystallised from much boiling EtOH in reddish-brown plates, m. p. $225\text{--}226^\circ$, and appeared to be the *phenylhydrazide* of the lower-melting compound (XII) (Found: C, 67.2; H, 5.5; N, 19.2. $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_6$ requires C, 67.7; H, 5.2; N, 19.7%).

In later experiments the Et_2O solution of the neutral oxidation product was washed with ice-cold 5% KOH aq. until it no longer gave a colour with FeCl_3 . The yellow alkaline washings contained a small quantity of succinic acid (m. p. and mixed m. p. 185°); the neutral oil still gave a marked reaction with sodium nitroprusside and an abundant ppt. of the compound (XI), thus showing that the latter is not derived from an enolisable β -keto ester. In one expt. the neutral product was distilled, but boiled rather indefinitely. The fraction, b. p. $110\text{--}120^\circ/4$ mm., consisted mainly of the diketonic ester with some 25% of unchanged initial material (Found: C, 53.8; H, 6.5. $\text{C}_{10}\text{H}_{14}\text{O}_6$ requires C, 52.2; H, 6.1%).

An attempt was made to oxidise the keto ester further; the crude ester was mixed with 4 times the calc. amount of 10% KOH aq., with the addition of enough EtOH to give a homogeneous solution, and the mixture kept for 2 hrs.; the hydrolysis then appearing to be complete, an excess of 30% H_2O_2 was added, and the solution kept over-night. After removal of the EtOH under reduced press., the solution was acidified and repeatedly extracted with Et_2O , which removed a mixture of acids, the principal constituent being succinic acid, m. p. and mixed m. p. 185° (Found: C, 40.6; H, 5.1. Calc.: C, 40.6; H, 5.0%).

The ozonisation of the "labile" ester was repeated in CHCl_3 solution; the O_2 issuing from the apparatus was passed through two bubblers containing H_2O . No CH_2O was detected in this or in the water used for the decomp. of the ozonide. The neutral oil obtained (4.7 g. from 10.3 g. of ester) gave no colour with FeCl_3 and formed an immediate ppt. of the compound, m. p. 120° , with phenylhydrazine. It was hydrolysed with an excess of 20% KOH in MeOH , the MeOH evaporated, the diluted solution extracted with Et_2O , acidified, and repeatedly extracted with a large quantity of Et_2O ; on evaporation of the dried extract a semi-solid mass was obtained, which gradually solidified and crystallised from acetone- CHCl_3 in plates, m. p. 122° (decomp.), of β -keto adipic acid, recognised by the violet colour it gave with FeCl_3 (Found: C, 45.3; H, 5.2. Calc.: C, 45.0; H, 5.0%).

Action of Alcoholic Sulphuric Acid on the "Labile" Ester.—The expt. was carried out exactly as with the Δ^2 -ester; the product boiled somewhat indefinitely, the greater part at about $126^\circ/11$ mm., $d_4^{20.0^\circ}$ 1.0520, $n_D^{20.0^\circ}$ 1.4430, and instantly decolorised Br in CHCl_3 . In this respect it resembled the other ethoxy-esters described, and analysis clearly shows that it is not isomeric with the initial material (Found: C, 58.0, 58.0; H, 7.4, 7.7. $\text{C}_{10}\text{H}_{14}\text{O}_4$ requires C, 60.6; H, 7.8%); we have not yet succeeded in separating the constituents of this mixture.

Methyl 3-Methyl- Δ^2 -cyclopropene-1:2-dicarboxylate.—The methyl ester of the acid, m. p. 200° , was prepared in the same way as the ethyl ester; it had b. p. $105^\circ/9$ mm., $d_4^{20.0^\circ}$ 1.1410, $n_D^{20.0^\circ}$ 1.4668, $[R_L]_D$ 41.34 (compare Feist, *loc. cit.*).

Action of sodium methoxide. The ester (8.5 g.) was added to a solution of 1.15 g. of Na in 20 c.c. of dry MeOH, and the mixture kept for 2 days at room temp.; it did not darken appreciably. A cryst. solid which had separated was filtered off and proved to be the methoxy-ester, m. p. 94° ; the filtrate was worked up as described on p. 2563. The neutral portion of the product consisted entirely of the same ester. No quasi-acid portion was obtained. The acid portion contained a small amount of solid, m. p. 130 — 132° , probably the hydrogen methyl ester (Goss, Ingold, and Thorpe, *loc. cit.*). No Na derivative was formed.

"Labile" Methyl Ester.—The Δ^2 -ester was distilled as described on p. 2565; there was very little decomposition. The ester on refractionation had b. p. 106 — $108^\circ/12$ mm., $n_D^{20.0^\circ}$ 1.1453, $n_D^{20.0^\circ}$ 1.4684, $[R_L]_D$ 41.40; it was evidently largely composed of unchanged Δ^2 -ester. It was treated with NaOMe as described above and gave the same products, which were doubtless derived from the Δ^2 -ester contained in it; no Na derivative was formed.

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