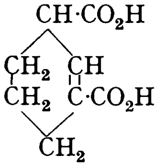
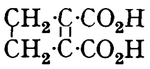
386. *The Structure of the Glutaconic Acids and Esters. Part VIII. Some Cyclic Compounds of the Glutaconic and the Citraconic Acid Series.*

By G. A. R. Kon and B. L. Nandi.

The experiments described below were undertaken with the object of investigating several cyclic compounds related to the glutaconic acids and also to 3-methyl*cyclo*propene-1 : 2-dicarboxylic acid, the chemistry of which was found to present some unusual features (J., 1932, 2557). These compounds are :

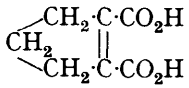


(I.)

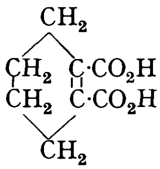


$$\begin{array}{l} CH_2{\cdot}C{\cdot}CO_2H \\ CH_2{\cdot}C{\cdot}CO_2H \end{array}$$

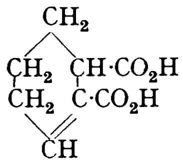
(II.)



(III.)



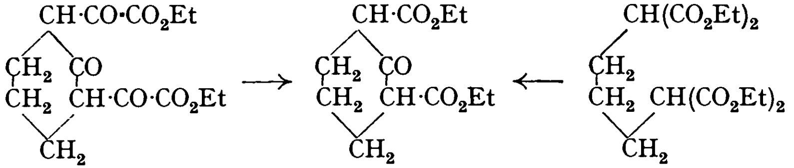
(IV.)



(V.)

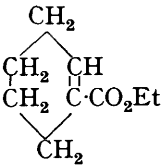
Δ^2-*Tetrahydro*iso*phthalic acid* (I) should behave like an $\alpha\gamma$-disubstituted glutaconic acid, except that it is incapable of stereoisomerism owing to its cyclic structure. Perkin and Pickles (J., 1905, **87**, 294) claimed to have isolated an acid of this structure by the reduction of *iso*phthalic acid; subsequently, Farmer and Richardson (J., 1926, 2172; 1927, 59) showed that this acid was in reality the *cis*-Δ^4-isomeride, but their efforts to prepare the true Δ^2-acid were fruitless. This preparation has now been effected by two different methods:

(i) *cyclo*Hexanone condenses with two molecules of ethyl oxalate in the presence of two molecules of sodium ethoxide, giving, in addition to ethyl *cyclo*hexanone-2-glyoxylate, a small amount of the diglyoxylate (VI). This on distillation gives the ester (VII); a better method for the preparation of this compound by the cyclisation of ethyl dicarboxypimelate (VIII) is due to Uschakov (*J. Russ. Phys. Chem. Soc.*, 1929, **61**, 795). The ketonic ester is then reduced, and the *hydroxy-ester* dehydrated to the *ester* of the acid (I).

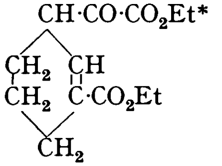


(VI.) (VII.) (VIII.)

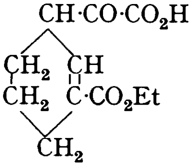
(ii) Ethyl oxalate condenses with ethyl tetrahydrobenzoate (IX) in the same way as ethyl crotonate and other similar esters (Lapworth, J., 1901, **79**, 1265), giving rise to the *ester* (X); curiously enough, the reaction requires the presence of sodium ethoxide, unlike the cases studied by Lapworth, who employed sodium in a neutral solvent. The ester (X) yields on mild hydrolysis in the cold the *half-ester* (XI); the carbethoxyl group marked * has been hydrolysed, because the new compound gives off carbon monoxide on heating. Further hydrolysis gives the *acid* (XII), from which the Δ^2-acid is obtained on oxidation with alkaline hydrogen peroxide.



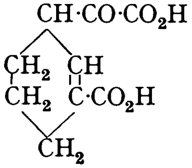
(IX.)



(X.)



(XI.)



(XII.)

The acid so obtained is different from any of the hydrophthalic acids previously described; the position of the double bond is proved by oxidation of the ester with ozone, glutaric acid being ultimately obtained. The new acid is a true glutaconic acid derivative, for, although it forms neither a neutral nor an enolic anhydride, the ester can be readily alkylated; the presence of a " mobile " hydrogen atom is thus proved.

The acid is recovered unchanged after 7 days' boiling with 20% potassium hydroxide solution, but heating with hydrochloric acid in a sealed tube causes a rapid change and after 4 hours at 180° the product is the pure Δ^3-acid. This change is noteworthy, since it provides yet another example of the passage of the double bond *outside* the three-carbon system (compare Kon and Watson, J., 1932, 1; Gidvani, Kon, and Wright, *ibid.*, p. 1027), and it must be inferred that the stability of the glutaconic propene system is not as great as formerly believed. Moreover, we find that the Δ^3-acid is not isomerised into the Δ^2- on treatment with either acids or alkalis and thus appears to represent the most stable arrangement; and Farmer and Richardson (J., 1927, 59) failed to alkylate the Δ^3-ester, so there can be little or no tendency for this ester to pass into the Δ^2-isomeride, which, as already stated, is readily alkylated.

The remaining acids, as was expected, conform to the itaconic–citraconic, not the glutaconic, acid type; they nevertheless present several special features. For instance, the *cyclo*butene (II) and the *cyclo*pentene (III) acids have the double bond in the Δ^1-position, unlike the methyl*cyclo*propene acid; their esters do not add on alcohol or suffer isomerisation on treatment with sodium ethoxide; indeed, no indication has up to the present been obtained of the existence of isomerides with a different position of the double bond. The esters are also stable to heat.

The tetrahydrophthalic acids exist in Δ^1- and Δ^2-modifications, as already shown by Baeyer (*Annalen*, 1890, **258**, 145). The Δ^1- is rapidly converted into the Δ^2-acid on boiling with alkali, the extent of the change being about 75%; this figure was estimated by taking advantage of the widely different solubilities of the cadmium salts of these acids in water: current bromo- and iodo-metric methods were found to be inapplicable. The occurrence of the reverse change (from Δ^2 to Δ^1) in the presence of alkali could not be detected, although Goss and Ingold state (J., 1926, 1471) that it does occur; there appears to be no experimental proof of this statement.

The esters of these two acids show no sign of mobility and are stable to heat; they do, however, slowly add on the elements of alcohol on treatment with sodium ethoxide.

The 1 : 2-dicarboxylic acids now examined thus differ from 3-methyl*cyclo*propene-dicarboxylic acid in a radical manner and they do not appear to share the great mobility of the itaconic acid group (compare Linstead and Mann, J., 1931, 726).

EXPERIMENTAL.

Ethyl cyclo*Hexanone-2 : 6-dicarboxylate.*—(i) *cyclo*Hexanone was condensed with ethyl oxalate as described by Kötz and Michels (*Annalen*, 1907, **350**, 210), but the amounts of sodium ethoxide and ethyl oxalate were doubled. The product was worked up as usual; on distillation, 30 g. of ethyl *cyclo*hexanonecarboxylate were obtained, together with 17 g. of a fraction, b. p. 130—170°/17 mm.; at that point the distillation had to be stopped owing to decomposition. On refractionation at 10 mm. the following fractions were obtained: (1) 154—157° (Found: C, 60·2; H, 7·3%); (2) 157—161° (Found: C, 58·6; H, 7·4%); (3) 161—168°, $d_{4^\circ}^{20^\circ}$ 1·124, n_D 1·4681 (Found: C, 59·5; H, 7·4. Calc. for $C_{12}H_{18}O_5$: C, 59·5; H, 7·4%). Fractions (2) and (3) thus consisted mainly of the desired ester, which was characterised by the formation, by the action of phenylhydrazine, of a *pyrazolone*, m. p. 148° after crystallisation from benzene–petroleum (Found: C, 67·2; H, 5·9. $C_{16}H_{18}O_3N_2$ requires C, 67·1; H, 6·3%).

Attempts to effect the condensation of *cyclo*hexanone or ethyl *cyclo*hexanonecarboxylate and ethyl oxalate in a neutral solvent were unsuccessful.

(ii) A short description of Uschakov's preparation (*loc. cit.*) may prove useful: a mixture of ethyl malonate (320 g.) and trimethylene bromide (210 g.) was slowly added to an ice-cold solution of 46 g. of sodium in 500 c.c. of absolute alcohol with cooling. After 2 hours water and dilute sulphuric acid were added and the oil was extracted in ether, recovered, and distilled in steam until no more oily drops of the initial material and ethyl tetramethylenedicarboxylate collected in the distillate. The residue in the flask was isolated by means of ether and distilled, the fraction of b. p. 140—220°/12 mm. being refractionated and giving 227 g., b. p. 215—220°/10 mm.

120 G. of the above ester were added to 11 g. of sodium in 215 c.c. of alcohol (dried over calcium) and boiled under reflux for 3 hours, the alcohol and ethyl carbonate were removed under reduced pressure, 200 c.c. of water added, and the solution cooled in a freezing mixture and slowly decomposed by addition of 50 c.c. of 20% sulphuric acid. The oil was extracted, washed (sodium carbonate, then water), and dried in ether, recovered, and distilled; some unchanged initial material was obtained, together with a lower fraction, b. p. 155—200°/10 mm., which on refractionation gave 25 g. of the ester (VI), b. p. 162—172°/10 mm.

Ethyl cyclo*Hexanol-2 : 6-dicarboxylate.*—25 G. of the ketonic ester in 200 c.c. of rectified spirit, 1 c.c. of ferrous chloride solution (0·13 g. per l.), and 2 g. of platinum oxide catalyst ("Organic Syntheses," vol. 8, p. 92) were shaken with hydrogen. The catalyst was reactivated by shaking with air after 12 hours and the operation was complete after a further 8 hours; the theoretical volume of hydrogen (2250 c.c.) had then been absorbed. The catalyst was filtered off, the solvent removed under reduced pressure, and the residue distilled, b. p. 145—147°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·1202, n_D 1·4679, $[R_L]_D$ 60·63; yield, 17 g.

*Ethyl Δ^2-Tetrahydro*iso*phthalate.*—18 G. of the hydroxy-ester in 14 g. of pyridine were cooled in a freezing mixture, and 11·6 g. of thionyl chloride introduced drop by drop with constant shaking. After 12 hours, water was added and the *ester* (9 g.) was extracted with ether; it had

b. p. 149—151°/12 mm., $d_{4^\circ}^{20^\circ}$ 1·0771, n_D 1·4720, $[R_L]_D$ 58·76 (calc., 58·58) (Found : C, 63·2; H, 7·7. $C_{12}H_{18}O_4$ requires C, 63·7; H, 7·9%).

Ethyl 3-Carbethoxy-Δ^2-cyclo*hexeneglyoxylate* (X).—Ethyl tetrahydrobenzoate was prepared essentially as described by Ruzicka and Brugger (*Helv. Chim. Acta*, 1926, **9**, 399), but the preparation of *cyclo*hexanone cyanohydrin was found to proceed better with a more dilute solution of potassium cyanide (200 g. of 95% single salt in 900 c.c. of water for 260 g. of *cyclo*hexanone) than that recommended by Tarbouriech (*Compt. rend.*, 1909, **149**, 604).

All attempts to condense ethyl tetrahydrobenzoate with ethyl oxalate in the presence of sodium or potassium in a neutral solvent failed. A mixture of the two esters (101 g. of each was added to an ice-cold solution of 15·1 g. of sodium in 200 c.c. of alcohol with constant shaking), and the mixture kept in ice-water for 24 hours. Water (1 l.) was added to the deep yellow solution, then 300 c.c. of 5% sulphuric acid. The precipitated solid *ester* (141 g.), washed with water until colourless and recrystallised from alcohol, formed silky needles, m. p. 105° (Found : C, 61·3; H, 7·1. $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%).

Hydrolysis. (i) 7 G. of the above ester were left at room temperature with 2·3 g. of sodium hydroxide in 16 c.c. of water and 22 c.c. of alcohol. After 2 days the alcohol was removed under reduced pressure, and the solution diluted and acidified with sulphuric acid; 4 g. of the *acid ester* (XI) separated, m. p. 178° after crystallisation from dilute alcohol (Found : C, 58·5; H, 6·2. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%).

(ii) 10 G. of the ester were boiled with 35 c.c. of 20% potassium hydroxide solution for 2 hours. The solution was cooled in a freezing mixture and cautiously acidified with very dilute sulphuric acid (acidification at room temperature causes some evolution of carbon dioxide). The *acid* (XII) was isolated by means of ether; it formed silky needles from dilute alcohol, m. p. 224° with evolution of gas (Found : C, 54·4; H, 5·2. $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%).

Δ^2-*Tetrahydro*iso*phthalic Acid* (I).—The ester (X) can be distilled unchanged, b. p. 188°/16 mm., but loses carbon monoxide when kept at 115—120° for 2 hours. The resulting mass was hydrolysed with an excess of potassium hydroxide; the acid obtained, which partly solidified in a vacuum desiccator after a week, was drained and recrystallised from acetone–petroleum; it melted at 187° and was evidently the somewhat impure acid (I) (Found : C, 57·2; H, 5·9%). It was obtained in a pure state by hydrolysis of 10 g. of the ester (X) as described under (ii) above and addition of 20 c.c. of 20 vol. hydrogen peroxide to the cooled alkaline solution. This was acidified after 24 hours, and the acid (6 g.) recovered by means of a continuous ether extractor; it was still somewhat coloured and the m. p. could not be raised above 192° by recrystallisation from water (charcoal). It was boiled for an hour with 10% alkali solution; the recovered acid was colourless and had m. p. 197—198° after crystallisation from water (Found : *M*, by titration, 169·4. Calc., 170·1). The same *acid* was also obtained by the hydrolysis of its ester (p. 1630) with 15% potassium hydroxide solution (Found : C, 56·7; H, 5·9. $C_8H_{10}O_4$ requires C, 56·5; H, 5·9%). The ethyl ester, prepared through the silver salt, had b. p. 150°/12 mm., $d_{4^\circ}^{20^\circ}$ 1·0772, n_D 1·4722, $[R_L]_D$ 58·78 (calc., 58·58) (compare above).

Ozonisation. 5 G. of the pure ester were ozonised in chloroform solution and the ozonide was freed from solvent under reduced pressure and decomposed by shaking with water, the product being taken up in ether. The residue after removal of the solvent gave a colour with Schiff's reagent; it was hydrolysed in the cold with 10% aqueous potassium hydroxide, and an excess of 20 vol. hydrogen peroxide added to the solution. After 24 hours this was acidified and extracted with ether; glutaric acid (3·1 g.) was then obtained and identified by the usual means.

Ethylation. 10 G. of the pure ester were left over-night with 1·2 g. of " molecular " sodium in 100 c.c. of benzene; as only a part of the metal had dissolved, the mixture was boiled on the steam-bath for 6 hours. An excess of ethyl iodide was then added, and the vigorous reaction completed by heating for an hour. The *ester* isolated had b. p. 145—150°/9 mm., $d_{4^\circ}^{20^\circ}$ 1·0448, n_D 1·4682, $[R_L]_D$ 67·60 (calc., 67·82) (Found : C, 65·7; H, 8·5. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%). The ester was hydrolysed to 1-*ethyl*-Δ^2-cyclo*hexene*-1 : 3-*dicarboxylic acid*, m. p. 162° after crystallisation from dilute alcohol (Found : C, 60·4; H, 6·9. *M*, by titration, 197·8. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; *M*, 198·1).

Isomerisation of the Acid (I).—(i) The acid (5 g.) was heated with 50 c.c. of 25% potassium hydroxide solution in a sealed tube at 100° for 18 hours; in another experiment the solution was boiled in a copper flask for a week. The acid was recovered unchanged in both cases.

(ii) 4 G. of the acid were heated in a sealed tube with 10 c.c. of hydrochloric acid at 180—190° for 4 hours. The liquid was filtered from carbon and evaporated, and the solid residue recrystallised from water. It melted at 227°, rising to 244° after two more crystallisations (mixed m. p. with Δ^3-acid, 244°) (Found : C, 56·3; H, 5·8. Calc. : C, 56·5; H, 5·9%).

Methyl Δ^1-cyclo*Butene*-1 : 2-*dicarboxylate*.—This ester was prepared essentially as described by Perkin (J., 1894, **67**, 950); for the preparation of *cyclo*butane-1 : 2-dicarboxylic acid, Fuson and Kao's method (*J. Amer. Chem. Soc.*, 1929, **51**, 1536) was employed.

Ozonisation. 10 G. of the pure solid ester in 100 c.c. of chloroform were treated with ozonised oxygen until no more was absorbed (60 hours), the ozonide was freed from solvent under reduced pressure and decomposed with water, the product dissolved and washed (sodium carbonate) in ether and recovered, and the residue treated with phenylhydrazine acetate; the diphenylhydrazone of methyl αα′-diketoadipate (Kon and Nandi, J., 1932, 2958) was obtained, m. p. 130° (Found : C, 62·5; H, 5·9. Calc. : C, 62·3; H, 5·7%).

Behaviour with sodium methoxide and towards heating. 5 G. of the ester were kept over-night with 0·8 g. of sodium in 30 c.c. of methyl alcohol at room temperature and then recovered by addition of water and extraction with ether. Washing with sodium carbonate removed a little *cyclo*butene-1 : 2-dicarboxylic acid formed by hydrolysis, but the ester was otherwise unchanged (proved by ozonisation).

5 G. of the pure ester were twice distilled at atmospheric pressure, then fractionated under reduced pressure. Some polymerisation and charring took place, but the ester which was recovered was unchanged (ozonisation).

Ethyl 1 : 2-*dibromo*cyclo*butane*-1 : 2-*dicarboxylate* was prepared in the same way as the methyl ester (Perkin, *loc. cit.*), except that the product of bromination of *cyclo*butane-1 : 2-dicarboxylic anhydride was poured into ethyl alcohol. The crude product distilled at 140—167°/15 mm., and at 150—158°/14 mm. after refractionation; yield, 33% (Found : C, 33·5; H, 3·9; Br, 44·7. $C_{10}H_{14}O_4Br_2$ requires C, 33·5; H, 3·9; Br, 44·7%).

Ethyl Δ^1-cyclo*Butene*-1 : 2-*dicarboxylate*.—Treatment of the dibromo-ester with potassium iodide in acetone or alcohol led to a complicated reaction. 13 G. of the ester in 60 c.c. of alcohol were gradually treated with 5 g. of zinc dust and the mixture was gently boiled for 3 hours. The alcohol was then distilled off under reduced pressure, and the residue diluted with water and extracted with ether. The *ester* (6 g.) had b. p. 136—139°/23 mm., $d_{4^\circ}^{20^\circ}$ 1·0870, n_D 1·4571, $[R_L]_D$ 49·63 (calc., 49·37) (Found : C, 60·6; H, 7·1. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). Its behaviour towards sodium ethoxide and also when heated was like that of the methyl ester. The above method has been successfully used for the preparation of the methyl ester.

Ozonisation. The ethyl ester, ozonised exactly as described above, gave ethyl αα′-diketoadipate (Found : C, 63·7; H, 6·4. Calc. : C, 64·2; H, 6·4%), identified by means of its phenylhydrazone, m. p. 150° (Kon and Nandi, *loc. cit.*).

Attempt to prepare Δ^2- *or* Δ^3-cyclo*Butene*-1 : 2-*dicarboxylic acid*.—(i) Ethyl ethanetetracarboxylate (14 g.) was warmed with 2 g. of " molecular " sodium in 100 c.c. of benzene until all the metal had dissolved (12 hours). The mixture was cooled, 5 g. of chloroacetyl chloride gradually added, and the whole heated for 3 hours. The product, worked up in the usual way, was a viscous brown liquid which gradually deposited the solid unchanged ester. This was filtered off (9 g.), and the mother-liquor distilled. It boiled with much decomposition at 155—185°/7 mm. and gave a *phenylhydrazone*, m. p. 128° after crystallisation from acetone (Found : C, 62·6; H, 6·4. $C_{22}H_{28}O_8N_2$ requires C, 62·7; H, 6·7%); it was therefore presumably derived from ethyl *cyclo*butan-3-one-1 : 1 : 2 : 2-tetracarboxylate. A somewhat better yield of the liquid fraction, which is a mixture of the above ketonic ester with initial material, was obtained by carrying out the condensation in a pressure bottle at 100° for 12 hours; the use of bromoacetyl bromide also appears to be advantageous. No reaction took place in the presence of sodium ethoxide.

(ii) As the mixture of esters could not be separated by distillation, the initial material was frozen out as far as possible and filtered off. 13 G. of the residual liquid were dissolved in 100 c.c. of alcohol and hydrogenated in the presence of 2 g. of platinum oxide as described on p. 1630, except that a pressure of 3 atmospheres had to be employed. No further absorption took place after 9 hours. The product recovered no longer reacted with phenylhydrazine; it was hydrolysed by boiling for 2 hours with a concentrated solution of 26 g. of barium hydroxide, and 8 g. of a barium salt were collected and decomposed with the theoretical amount of sulphuric acid. The filtered solution was evaporated to dryness, and the solid residue crystallised thrice from acetone. It had m. p. 191° and probably consisted of 3-hydroxy*cyclo*butane-1 : 1 : 2 : 2-tetracarboxylic acid (Found : C, 38·7; H, 3·2; *M*, 247·6. $C_8H_8O_9$ requires C, 38·7; H, 3·2%; *M*, 248). The yield of this material was so poor that the synthesis was abandoned at this stage.

Ethyl Δ^1-cyclo*Pentene*-1 : 2-*dicarboxylate*.—This ester was prepared as described by Willstätter (*Ber.*, 1895, **28**, 663) and had b. p. 140°/16 mm., $d_{4^\circ}^{20^\circ}$ 1·0805, n_D 1·4652, $[R_L]_D$ 54·26 (calc., 53·97) (Found : C, 62·3; H, 7·3. Calc. : C, 62·3; H, 7·5%). It does not decolorise bromine in chloroform, but rapidly reduces permanganate. It was kept for 2 days at room temperature with $1\frac{1}{2}$ times the theoretical amount of 30% aqueous potassium hydroxide and enough alcohol to give a homogeneous solution. The alcohol was removed under reduced pressure, and the acid recovered from the acidified solution, m. p. 178° after crystallisation from ethyl acetate, was re-esterified through the silver salt; the ester had b. p. 138°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·0807, n_D 1·4656.

Ozonisation. The pure ester was ozonised in chloroform solution. The product was identified as ethyl αα′-diketopimelate by means of the phenylhydrazone, m. p. 147° (Blaise and Gault, *Bull. Soc. chim.*, 1907, **1**, 81) (Found : C, 64·9; H, 6·6. Calc. : C, 65·1; H, 6·6%); and by hydrolysis, followed by treatment with hydrogen peroxide, as described on p. 1631, glutaric acid being obtained. The ester prepared by Willstätter's method behaved in exactly the same way on oxidation.

Action of sodium ethoxide. 10 G. of the ester were kept over-night with 1·1 g. of sodium in 50 c.c. of alcohol (dried over calcium) at room temperature. The neutral ester recovered (6 g.) had b. p. 142—144°/18 mm., $d_{4^\circ}^{20^\circ}$ 1·0801, n_D 1·4642, and was therefore unchanged (Found : C, 62·2; H, 7·5%). The alkaline washings yielded an oil, b. p. 135—140°/13 mm., which was evidently the *acid ester* (Found : C, 58·5; H, 6·4. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%). The ester thus had not undergone isomerisation or addition of alcohol.

Attempted Isomerisation of the Δ^1-Acid.—5 G. of the pure acid (m. p. 178°) were heated with 20 c.c. of 25% potassium hydroxide solution in a sealed tube at 100° for 12 hours; 4·6 g. of the unchanged acid were recovered. Similarly, no change was produced by 12 hours' heating in a sealed tube with concentrated hydrochloric acid.

Δ^2-Tetrahydrophthalic Acid.—Baeyer's method of preparation (*loc. cit.*) being very laborious, the following alternative was devised.

Ethyl 1-*hydroxy*-1-*cyano*cyclo*hexane*-2-*carboxylate*.* 100 G. of potassium cyanide in 600 c.c. of water were mixed with 100 g. of ethyl *cyclo*hexanonecarboxylate cooled in ice, and 200 c.c of hydrochloric acid were added drop by drop with constant shaking. After 12 hours, the oil formed was extracted, washed (sodium carbonate), and dried in ether, recovered, and distilled with the addition of a drop of sulphuric acid. The product (105 g.) had b. p. 147—150°/10 mm. and gave an intense red colour with ferric chloride.

Ethyl 1-*cyano*cyclo*hexene*-2-*carboxylate*. 36 G. of the hydroxy-ester were dehydrated exactly as described on p. 1630; the product (24 g.), consisting of the above ester, b. p. 135—137°/10 mm., was boiled over-night with 100 c.c. of 30% aqueous potassium hydroxide and enough alcohol to give a clear solution. The alcohol was removed under reduced pressure, and the liquid strongly acidified and extracted with ether; a 72% yield of Δ^2-tetrahydrophthalic acid was obtained.

Ethyl Δ^2-tetrahydrophthalate, prepared through the silver salt, had b. p. 155°/12 mm., $d_{4^\circ}^{20^\circ}$ 1·0760, n_D 1·4700, $[R_L]_D$ 58·96 (calc., 58·58) (Found : C, 63·7; H, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

The ester was also prepared by the action of alcoholic sulphuric acid on the acid. The product was not homogeneous; the lowest fraction had b. p. 158—160°/12 mm., $d_{4^\circ}^{20^\circ}$ 1·0859, n_D 1·4768, and the highest, b. p. 162—164°/12 mm., $d_{4^\circ}^{20^\circ}$ 1·0974, n_D 1·4847.

The pure ester was unchanged after three distillations at atmospheric pressure, after boiling for 4 hours in a Geisler flask, after treatment with sodium ethoxide as described on p. 1632, and after the last solution had been boiled for 4 hours.

Ethyl Δ^1-Tetrahydrophthalate.—The Δ^1-acid was prepared from the Δ^2-acid as described by Baeyer (*loc. cit.*) and esterified through the silver salt; the *ester* had b. p. 160°/14 mm., $d_{4^\circ}^{20^\circ}$ 1·0782, n_D 1·4743, $[R_L]_D$ 59·31 (calc., 58·58) (Found : C, 63·7; H, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%). Like the Δ^2-ester, it has no tendency to react with iodine chloride or bromine; it was recovered unchanged after two distillations at atmospheric pressure.

Action of sodium ethoxide. After 4 hours' heating with sodium ethoxide as described above, the neutral ester recovered had b. p. 164—170°/18 mm., $d_{4^\circ}^{20^\circ}$ 1·0612, n_D 1·4616 (Found : C, 61·2; H, 8·3%). The change in physical properties and in composition shows that some alcohol had been added on. The ester was therefore hydrolysed : an estimation of ethoxyl in the mixture of acids obtained showed that some 12·4% of an ethoxy-acid had been formed.

Interconversion of the Δ^1- and the Δ^2-Acids.—Attempts to devise an iodometric method for the estimation of mixtures of these two acids failed because both add on bromine in chloroform almost instantaneously, but do not react with iodine. The insolubility of the cadmium salt of the Δ^1-acid allowed a rough analysis of mixtures to be made.

---

* The authors are indebted to Mr. K. Sams of this College for details of the preparation, which was first carried out by him.

Preliminary experiments showed that the anhydride of the Δ^1-acid was rapidly hydrolysed by alkali to the Δ^2-acid. 1 G. portions of the anhydride were heated for different periods with 11 equivalents of 12% potassium hydroxide solution under reflux. The solution was rapidly cooled and acidified, and the acid recovered by means of ether. After removal of the solvent the acid was exactly neutralised with 2*N*-ammonia and made up to 100 c.c., 10 c.c. of a concentrated solution of cadmium sulphate were added, and the solution was boiled for 5 minutes. The precipitated salt was washed with water and then with alcohol, dried at 100°, and weighed. The solubility of the salt at 21° is 0·0696%. The following results were obtained :

Time (mins.)	15	30	60	120
Δ^1-Acid recovered, %	28·0	27·7	27·1	24·7

The equilibration is thus practically complete at the end of 15 minutes.

2 G. of the pure Δ^2-acid (m. p. 215°) were heated with 50 c.c. of 25% potassium hydroxide solution in a sealed tube at 100° for 6 hours; 1·96 g. of acid were recovered, m. p. 212—214°, 215° after one crystallisation. No insoluble cadmium salt was obtained by the process described above, so no conversion into the Δ^1-acid had occurred.

The authors' thanks are due to the Chemical Society for a grant.

IMPERIAL COLLEGE, LONDON, S.W. 7.

[*Received, November 7th,* 1933.]