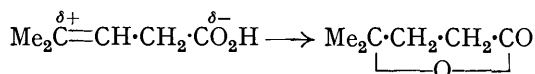**57.** *Investigations of the Olefinic Acids. Part XVI. Additive Reactions and Tautomeric Changes of Cyclic Unsaturated Acids, and Analogous Observations on α-Methylpentenoic Acids.*

By E. J. BOORMAN and R. P. LINSTEAD.

PREVIOUS work (J., 1932, 115; 1933, 580) has shown that the introduction of alkyl groups on the γ-carbon atom greatly increases the readiness with which Δ^β-unsaturated acids form γ-lactones, because it promotes polarisation of the double bond in the sense

$$\overset{\delta+}{Me_2C}=CH\cdot CH_2\cdot \overset{\delta-}{C}O_2H \longrightarrow Me_2C\cdot CH_2\cdot CH_2\cdot CO$$
$$\underset{\textstyle O}{\rule{4cm}{0.4pt}}$$

and possibly because it induces coiling of the chain. In order to assess the relative importance of these two factors we have now studied the effect of γ-alkylation on the ease of lactonisation of some cyclic Δ^β-acids, in which the molecule is more rigid and the polar effect of the γ-alkyl group will be the same as that in the open-chain series but its effect (if any) on the coiling of the molecule must be diminished. For this purpose Δ^2-*cyclo*-hexenecarboxylic (tetrahydrobenzoic) acid and 3-methyl-Δ^2-*cyclo*hexenecarboxylic acid (I and II) have been examined. The configurational changes in these acids are confined to the rotation of the carboxyl group about the bond connecting it to the ring and (possibly) to the oscillation of the ring between the two Sachse (C and Z) forms, and even in the most favoured arrangement an oxygen atom of the carboxyl group cannot approach the γ-carbon atom as closely as is possible in open-chain olefinic acids.

We have also carried out a parallel examination of the tautomeric changes between these Δ^2-acids and their Δ^1-isomerides, and of their reaction with hydrogen bromide.

The preparation of the unmethylated acid (I) and its Δ^1-isomeride (III) (p. 261) presented no special features. The homologous 3-methyl acids (II and IV), previously prepared by Perkin and Tattersall (J., 1905, **87**, 1085; 1907, **91**, 496), were obtained in the present work by the hydrolysis of the unsaturated nitrile resulting from dehydration of the cyano-hydrin of 3-methyl*cyclo*hexanone. This yielded an easily separable mixture of the Δ^1- and the Δ^6-acid (IV and V). The Δ^2-acid was prepared by equilibrating the Δ^1-acid with alkali and was purified by partial esterification. It is conceivable that the Δ^1-acid might isomerise to the Δ^6-acid under these conditions and this in turn might yield the corresponding Δ^β-acid (the Δ^5-acid, VI), which would contaminate the Δ^2-acid. It was found, however, that Δ^1-tetrahydrobenzoic acid showed little or no tendency to pass into the Δ^2-form (see p. 263), and this suggested that the Δ^6-acid of the methylated series (which has a similar
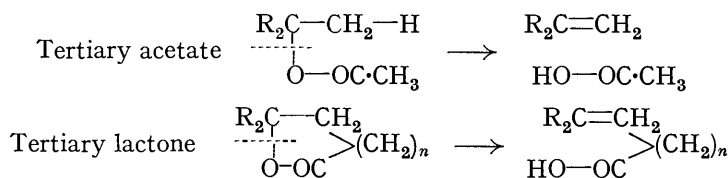
3-carbon system) would also show very little tendency to yield its Δ^β-isomeride. The 3-methyl group, on the other hand, would be expected to promote the formation of the Δ^2-double bond. Hence, even if the Δ^1-acid yielded some Δ^6-acid on equilibration, the Δ^β-acid formed was expected to be almost entirely the Δ^2-isomeride. This was justified experimentally; the isolated Δ^β-acid after careful purification by partial esterification was the Δ^2-isomeride practically free from isomeric impurity.

(III.)   (I.)   (VII.)

(IV.)   (V.)   (VI.)   (II.)   (VIII.)
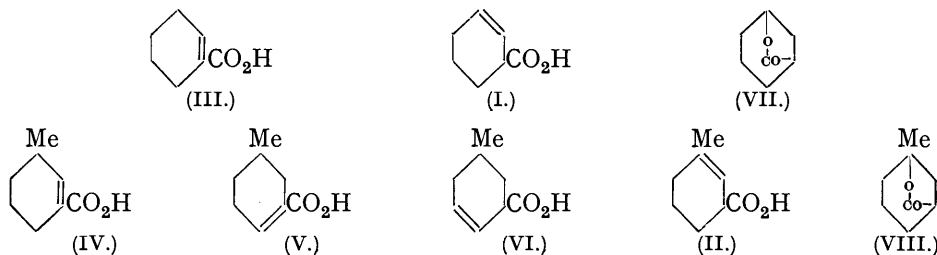
Lactonisation of the Unsaturated Acids.—Δ^2-Tetrahydrobenzoic acid (I) yielded the corresponding γ-lactone on treatment with sulphuric acid with approximately the same facility as Δ^β-hexenoic and -pentenoic acids, and did not lactonise at the b. p. The lactone was identical with the *cis*-1 : 3-*cyclo*hexanolide (VII) of Perkin and Tattersall (*loc. cit.*), which was independently synthesised for comparison. The only abnormality was the instability of the materials to sulphuric acid, the lactone being destroyed by the hot acid and the Δ^β-acid being partly polymerised in the cold.

3-Methyl-Δ^2-*cyclo*hexenecarboxylic acid (II), on the other hand, showed the expected resemblance to pyroterebic acid. On treatment with cold sulphuric acid it passed very rapidly indeed into 1-methyl-1 : 3-*cyclo*hexanolide (VIII), identical with material prepared by Perkin and Tattersall's method. The lactonisation appeared to be slightly slower than that of pyroterebic acid. Both lactone and acid were unstable to boiling dilute sulphuric acid. 3-Methyl-Δ^2-*cyclo*hexenecarboxylic acid, like pyroterebic acid, yields the corresponding lactone when boiled alone, but here the formation of lactone is *reversible*. The equilibrium, at about 33% of lactone and 67% of unsaturated acid, was approached from both sides and the system thus provides an example of ring chain tautomerism (lacto-enoic) similar to that occurring between Δ^γ-*iso*heptenoic acid and δ-*iso*heptolactone (Linstead and Rydon, J., 1933, 580). The formation of an isomeric unsaturated acid by the boiling of a γ-lactone is unique. The tautomeric change does not, however, appear to be simple, as the Δ^2-acid formed by boiling the γ-lactone appears to be contaminated with an isomeride, possibly the Δ^3-acid.

The fission of these tertiary lactones into unsaturated acids by the action of heat presents an interesting analogy with Menschutkin's demonstration that the acetates of tertiary alcohols decompose above 100° into acetic acid and an olefin (*Ber.*, 1882, **15**, 2512). Both reactions involve the migration of a hydrogen atom and the fission of a C—O link, but Menschutkin's reaction leads to the disruption of the molecule, and ours only to its rearrangement. The two processes may be represented as follows :

$$\text{Tertiary acetate} \quad \begin{array}{c} R_2C\text{---}CH_2\text{---}H \\ \text{-----} \\ O\text{---}OC\cdot CH_3 \end{array} \longrightarrow \begin{array}{c} R_2C{=}CH_2 \\ HO\text{---}OC\cdot CH_3 \end{array}$$

$$\text{Tertiary lactone} \quad \begin{array}{c} R_2C\text{---}CH_2 \\ \text{-----} \quad {>}(CH_2)_n \\ O\text{-}OC \end{array} \longrightarrow \begin{array}{c} R_2C{=}CH_2 \\ \quad {>}(CH_2)_n \\ HO\text{---}OC \end{array}$$

A comparison of the results obtained with the methylated and the unmethylated acids supports the view that the activity (polarisability) of the double bond is the major factor affecting the ease of lactonisation of an unsaturated acid, providing that suitable approach of the reacting centres is possible in one phase of the molecule.

Addition of Hydrogen Bromide.—This was examined in polar solvents (acetic acid, water). The orientation of the additions was determined quantitatively by methods which were standardised with pure β- and γ-bromo-acids. Owing to the proximity of the double bond to the carboxyl group, the effect of peroxides was neglected (compare Linstead and Rydon, J., 1934, 2001). The observed additions obeyed the Markownikoff rule. Thus, Δ^1-tetrahydrobenzoic acid yielded exclusively 2-bromo*cyclo*hexanecarboxylic acid (probably *trans*-), and Δ^2-tetrahydrobenzoic acid yielded 18% of this acid and 82% of the 3-bromoisomeride, which was isolated in both *cis*- and *trans*-forms. 3-Methyl-Δ^2-*cyclo*-hexenecarboxylic acid, on the other hand, gave exclusively " distant " addition of bromine, the product being 3-*bromo-3-methyl*cyclohexanecarboxylic acid. This was mainly the *cis*-isomeride, as it readily yielded 1-methyl-1 : 3-*cyclo*hexanolide (VIII). 3-Methyl-Δ^1-*cyclo*-hexenecarboxylic acid yielded the isomeric 2-*bromo-3-methyl*cyclohexanecarboxylic acid. These results are similar to those obtained for pentenoic and γ-methylpentenoic acids (Boorman, Linstead, and Rydon, J., 1933, 568) and indicate that the ring has no specific influence on the orientation. Ethyl 2-bromo*cyclo*hexanecarboxylate readily lost hydrogen bromide when treated with ethyl sodiomalonate to yield ethyl Δ^1-tetrahydrobenzoate (compare Cocker, Lapworth, and Peters, J., 1931, 1383; Cook and Linstead, J., 1934, 956), but the esters of the isomeric 3-bromo-acids were unaffected by the same treatment. Ethyl Δ^1-tetrahydrobenzoate added ethyl sodiomalonate (Helfer, *Helv. Chim. Acta*, 1926, **9**, 816), and the product on hydrolysis gave the important *cyclo*hexane-1-carboxylic-2-acetic acid of Windaus, Hückel, and Reverey (*Ber.*, 1923, **56**, 91), which was obtained as the pure *trans*-modification (compare Sircar, J., 1927, 1255).

Tautomeric Changes.—The mobility of the interconversion of both pairs of Δ^1- and Δ^2-acids in alkali was extremely low, as is often the case for more complex α-alkylated acids. The positions of equilibrium were of considerable interest, for in each case the proportion of the Δ^α-form was higher than that anticipated from a study of the analogous acyclic acids, as the following figures show :

>   Tetrahydrobenzoic acids : 95·5% Δ^α-acid at equilibrium.
>   α-Methylpentenoic acid : 89% Δ^α-acid at equilibrium (see p. 267).
>   3-Methyl*cyclo*hexenecarboxylic acids : 75% Δ^α-acid at equilibrium.

The γ-methyl group stabilises the Δ^β-phase to some extent in the usual manner, but no analogous open-chain unsaturated acid carrying one α- and two γ-groups is available to complete the comparison. Owing to the slowness of the tautomeric change neither of the Δ^1-acids gave an appreciable amount of lactone on treatment with sulphuric acid.

Properties of the Lactones.—When heated with water at 100°, 1 : 3-*cyclo*hexanolide (VII) yielded an equilibrium mixture containing 88% of the corresponding γ-hydroxy-acid. This is an altogether exceptional degree of hydrolysis for a γ-lactone : most members of the class yield less than 10% of hydroxy-acid under these conditions and the highest figure on record is the 25% hydrolysis of γ-butyrolactone (Boorman and Linstead, J., 1933, 580). Nevertheless the lactone undoubtedly belongs to the γ-series from the method of synthesis. Tetrahedral models indicate that the molecule is in a state of strain which can be relieved by the fission of the lactone ring, and it appears very probable that this accounts for the instability. The corresponding 3-methyl lactone (VIII) yields an equilibrium amount of 28% of hydroxy-acid. Here the tendency to fission caused by strain is opposed by the presence of the γ-alkyl group, which has been shown to stabilise monocyclic lactones by Hjelt (*Ber.*, 1896, **29**, 1855) and in earlier papers of this series (compare, for example, the stability of γ-butyrolactone and γ-*iso*hexolactone).

Although the *extent* to which 3-methyl-1 : 3-*cyclo*hexanolide is hydrolysed is unusual, the *velocity* with which it is formed from its hydroxy-acid is quite normal for a γ-lactone and distinguishes it sharply from the lactones of the δ-series.

α-Methylpentenoic Acids and α-Methyl-γ-valerolactone.—The cyclic acids considered above contain in effect a chain branched at the α-carbon atom. No acyclic acids of this type have been studied under similar conditions and in view of this a control examination was made of a typical α-alkylated system—the α-methylpentenoic acids. The experiments

showed that the α-alkyl group had no marked effect on the ease of lactonisation of Δ^β-un-saturated acids. The tautomeric change between Δ^α- and Δ^β-α-methylpentenoic acid has been shown by Goldberg and Linstead to be of normal mobility (J., 1928, 2343).   In support of this it was found that the Δ^α-acid yielded γ-lactone when boiled with dilute sulphuric acid. The lactone was identical with that prepared directly from the Δ^β-acid, and that of Blaise and Luttringer (*Bull. Soc. chim.*, 1905, **33**, 828).   The Δ^β-acid was not lactonised when boiled alone.

It was of particular interest that α-methyl-γ-valerolactone was stable to boiling water, being hydrolysed to only 2%. It was rapidly formed from the corresponding hydroxy-acid and in these respects bore a general resemblance to the isomeric γ-methyl-γ-valero-lactone (*iso*hexolactone). The fact that an α-alkyl group stabilises the γ-lactone ring confirms the view that the instability of the dicyclic lactones studied above is due to strain.

Experimental.

General Methods.—The lactonisation of unsaturated acids and the analysis and separation of the mixtures obtained were carried out by the methods described in J., 1932, 121; bromine additions (*B*) to unsaturated acids by the method of Linstead and Noble (J., 1934, 617), a reaction period of 5 minutes being used; and iodine additions (*J*) by Linstead and May's process (J., 1927, 2565). Recorded densities and refractivities are for $d_4^{20°}$ and $n_D^{20°}$ respectively.

1. *Tetrahydrobenzoic Acids.*

Preparation of the Δ^1-Acid (III).—Δ^1-Tetrahydrobenzonitrile (Ruzicka and Brügger, *Helv. Chim. Acta*, 1926, **9**, 399) was boiled for 17 hours with 10% caustic potash solution (2 equivs.); the product was treated with a slight excess of sulphuric acid and distilled in steam, 9 l. of water being required for the product from 100 g. of nitrile. The distillate was neutralised, evaporated, and extracted with ether to remove neutral and basic impurities. Acidification and extraction with ether then yielded the acid, which, after distillation (b. p. 107°/3 mm.; 138°/14 mm.), partly solidified (yield, 94 g.; 79%) (Equiv. : found, 126·8; calc., 126·1). The solid acid was collected and drained on a porous tile (m. p. 35·5°). The various products reacted with bromine as follows : semi-solid mixture, *B* 21·3%; solid acid (*a*), *B* 13·2%; liquid drainings (*b*), *B* 31·2%. This indicated that the crude acid contained about 20% of the Δ^2-isomeride.

The solid acid (*a*) was partly esterified by treatment with *N*-alcoholic hydrogen chloride (1 vol.) and absolute alcohol (2 vols.) for 3 hours at room temperature and 30 minutes on the steam-bath, and the product separated into acid and ester (Eccott and Linstead, J., 1929, 2153). Pure Δ^1-tetrahydrobenzoic acid was obtained from the acid fraction after distillation as large overlapping plates, m. p. 38° (Found : C, 66·5; H, 7·9; equiv. 126·1, *B* 1·8%. Calc. : C, 66·6; H, 8·0%; equiv., 126·1). Einhorn's preparation from benzoic acid had m. p. 29° (*Ber.*, 1900, **33**, 3455). The liquid acid (*b*) was partly esterified similarly, but for 8 hours in the cold and 1 hour on the steam-bath to ensure the esterification of all the Δ^2-acid. The unesterified acid was the pure Δ^1-isomeride (equiv. 126·1, *B* 1·7%). The combined esters were hydrolysed by cold alkali, and the crude Δ^2-acid isolated by the method described for Δ^β-*iso*hexenoic acid (Linstead, J., 1932, 125). After distillation it was converted into the dibromide, m. p. 167·5° alone or admixed with the derivative of the Δ^2-acid described below.

Ethyl Δ^1-tetrahydrobenzoate, prepared by means of the silver salt, had b. p. 96°/16 mm., *n* 1·4700, *d* 0·9999, $[R_L]_D$ 42·98 (calc., 42·63). An equimolecular mixture of this and ethyl sodio-malonate was left for 3 days in the cold and heated on the steam-bath for 12 hours. The tricarboxylic ester (Helfer, *loc. cit.*) was isolated in 45% yield, b. p. 176—185°/9 mm. (This experiment was carried out before Cook and Linstead, *loc. cit.*, had shown that the corresponding condensation in the *cyclo*pentane series was best effected quickly; the yield could probably be considerably improved.) Hydrolysis with concentrated hydrochloric acid (2 vols.; 28 hours at the b. p.) yielded 92% of pure *trans*-hexahydrohomophthalic acid, m. p. and mixed m. p. 158°, equiv. 93·0 (calc., 93·05).

Preparation of the Δ^2-Acid (I).—Aschan's method (*Annalen*, 1892, **271**, 234) gave poor results and the reduced material was always mainly the Δ^1-acid. The following modification gave repeatably good yields : a solution of 15 g. of benzoïc acid in 75 c.c. of aqueous caustic soda was heated (steam-bath) under an air condenser, carbon dioxide passed into the liquid, and 150 g. of 5% sodium amalgam (pea size) added. After 5 hours the mercury was removed and

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50 c.c. of water and another 150 g. of amalgam were added. The process was repeated three more times, and the solution then cooled and acidified with 50% sulphuric acid. Ether extraction removed the partly reduced acid, which was dissolved in caustic soda and the whole process repeated, so that in all 900 g. of amalgam were used. The oily acid was dried, dissolved in chloroform (3 vols.) in a freezing mixture, and a slight excess of 20% bromine in chloroform added. The 2 : 3-dibromo*cyclo*hexanecarboxylic acid (Aschan, *loc. cit.*) obtained by removal of the solvent had m. p. 167·5° after recrystallisation from benzene–petroleum (equiv. 285·6; calc., 286·0). Yield, 160 g. from 225 g. of benzoic acid (15 runs). 80 G. of this in 800 c.c. of absolute alcohol were treated under nitrogen with 30 g. (2 mols.) of zinc for 30 minutes at room temperature and 45 minutes on the steam-bath. The unsaturated acid was isolated in the usual manner; the atmosphere of nitrogen was maintained as far as possible to prevent oxidation to benzoic acid. Pure Δ^2-tetrahydrobenzoic acid (equiv. 126·2; calc., 126·1) was obtained in this way in 84% yield; the properties of two different preparations are given below :

Preparation.	B. p./mm.	M. p.	*n*.	*d*.	$[R_L]_D$ (Calc. 33·40).	*B*, %.
1	120°/10	7·0°	1·4814	1·0820	33·19	92·4
2	130/18	6·5	1·4813	1·0814	33·19	93·2

Aschan describes the acid as an oil, b. p. 234—235° (*loc. cit.*).

cis-1 : 3-cyclo*Hexanolide* (VII) *and* cis-3-*Hydroxy*cyclo*hexanecarboxylic Acid.*—150 G. of *m*-hydroxybenzoic acid (Offermann, *Annalen*, 1894, **280**, 5) were reduced by sodium in boiling alcohol, following Perkin and Tattersall (*loc. cit.*), and gave 100 g. of mixed hydroxy*cyclo*hexane-carboxylic acids. The method of Balas and Srôl (*Coll. Czech. Chem. Comm.*, 1929, **1**, 658), which employs a platinum catalyst, was less satisfactory for large quantities. The mixed hydroxy-acids were heated at 170°/760 mm. for 30 minutes, and the product distilled. The lactone came over at 120—140°/20 mm., and a little *trans*-hydroxy-acid at 177—190°/20 mm. Redistillation of the low fraction gave the pure lactone, b. p. 120—123°/19 mm., forming rather sticky needles from petroleum (b. p. 60—80°), m. p. 119° (equiv., by back titration, 126·0; calc., 126·1). This was heated with a slight excess of caustic soda for 15 minutes, and the solution acidified and extracted with ether. The residue from the ether on recrystallisation from ethyl acetate gave pure *cis*-3-hydroxy*cyclo*hexanecarboxylic acid, m. p. 132° (Perkin and Tattersall give m. p. 130—132°).

Lactonisation of Δ^2-Tetrahydrobenzoic Acid.—Experiments with this acid and its isomeride were performed in an atmosphere of nitrogen. After treatment with boiling 50% sulphuric acid under Fittig's conditions (*Annalen*, 1894, **283**, 47), 73% of material was recovered which contained 63% of 1 : 3-*cyclo*hexanolide, identified by m. p. and mixed m. p. Longer treatment with boiling sulphuric acid resulted in gross decomposition. The acid passed into solution in 60% sulphuric acid (5 vols.) after 42 minutes at room temperature. A large amount of polymeric material was formed, but there was no charring.

	% Recovery		Composition of distillate.	
Time, hrs.	(distillate).	B. p./mm.	% Acid.	% Lactone.
0·75	46	124—128°/15	89·5	10·0
2	33	122/15	73·5	26·0
4	25	125/12	11·0	88·5

After 4 hours the recovery was very poor but the product was almost pure lactone, which was identified by m. p., mixed m. p., and equivalent (126·2; calc., 126·1).

The Δ^2-acid was boiled alone under nitrogen for 1 hour. After distillation the product contained 99% of acid and 0·5% of lactone.

Attempted Lactonisation of Δ^1-Tetrahydrobenzoic Acid.—After 30 minutes' boiling with 50% sulphuric acid (5 vols.), 46% of distillate were recovered, b. p. 132—136°/13 mm., which contained 90% of acid, 8·5% of lactone. The acid was the pure Δ^1-isomeride (m. p. 37°), but insufficient lactone was isolated for identification. No lactone was formed when the Δ^1-acid was kept for 3 days at room temperature with 60% sulphuric acid, and the acid had not isomerised (m. p. 37—38°).

Reactions of 1 : 3-cyclo*Hexanolide.*—The lactone was completely destroyed by 30 minutes' boiling with 50% sulphuric acid. It was partly polymerised after 7 days' standing with 60% acid in the cold, but the monomeric material recovered (60%) was pure (m. p. 120°) and free from acid. The lactone was unchanged by 3 hours' boiling alone.

Hydrolysis and Formation of Hydroxy-acid.—The lactone was boiled with water under the

standard conditions (Boorman and Linstead, *loc. cit.*). Pure *cis*-3-hydroxy*cyclo*hexanecarboxylic acid was treated similarly.

Material.	Time, hrs.	% Acid.	% Lactone in product.
Lactone	24	74·7	25·5
,,	48	86·8	14·6
,,	96	90·1	12·6
,,	144	89·5	13·5
Hydroxy-acid	24	88·0	12·0
,,	72	87·3	14·2

Where the total of the values for acid and lactone exceeds 100%, it is probable that the direct titration figure (% acid) is more correct. A trace of ψ-acidic impurity appears to be formed in the longer experiments. The formation of lactone from hydroxy-acid under Hjelt's conditions was not measured owing to the very high proportion of hydroxy-acid at equilibrium.

Tautomeric Change between the Δ^1- *and the* Δ^2-*Acid in Alkali.*—This was followed under standard conditions (Linstead, J., 1927, 2579), but owing to the instability of the Δ^2-acid the boiling with alkali was carried out in sealed bulbs and the equilibrated acid was distilled in nitrogen. The composition of the mixture was determined by bromine addition, the following reference figures being used :

% Δ^2-acid	0·0	4·4	9·1	12·9	16·7
% Bromine added	1·7	6·5	10·8	14·0	18·2

The Δ^1-acid yielded 78% of a mixture of isomerides with equiv. 126·1 (calc., 126·1), *B* 5·9%, whence % Δ^2-acid = 4·1. The Δ^2-acid gave 74% of a mixture with equiv. 126·4, *B* 6·2%; % Δ^2-acid = 4·4. Both samples gave a considerable quantity of solid Δ^1-acid, m. p. 37°. The mobility was not determined.

trans-2-*Bromocyclohexanecarboxylic Acid.*—Passage of dry hydrogen bromide into Δ^1-tetrahydrobenzoic acid in acetic acid yielded the 2-bromo-acid, which crystallised from petroleum in rosettes of flattened needles, m. p. 108° (equiv. 206·6; calc., 207·0). Aschan (*loc. cit.*) prepared this acid (m. p. 108—109°) by heating the same components in a sealed tube, which suggests that the acid has the *trans*-configuration. The acid was esterified by cold alcoholic sulphuric acid at room temperature (2 days) to the *ethyl* ester, which could not be distilled without decomposition (Found : Br, 33·9. $C_9H_{15}O_2Br$ requires Br, 34·0%).

cis-3-*Bromocyclohexanecarboxylic Acid.*—The method of Perkin and Tattersall was improved as follows : A mixture of *cis*-1 : 3-*cyclo*hexanolide and water ($1\frac{1}{2}$ vols.) was saturated with hydrogen bromide at 0°, kept in a closed vessel for 1 day, and again saturated at 0° and kept for a further 3 days. Water was added and the solid upper layer was crushed, collected, and dried on a tile over sulphuric acid in a vacuum desiccator. Yield, 85% of burr-like clusters of needles from light petroleum, m. p. 65° (lit. 62°) (equiv. 207·0; calc., 207·0). The *ethyl* ester, prepared in the same manner as the 2-bromo-isomeride in 96% yield, distilled without decomposition at 143°/25 mm. (Found : Br, 34·2%).

Addition of Hydrogen Bromide to Δ^2-*Tetrahydrobenzoic Acid.*—Analysis of the products was complicated by the possible formation of *cis*- and *trans*-bromo-acids, but a modification of the method previously used (Boorman, Linstead, and Rydon, *loc. cit.*) gave satisfactory results. A solution of the acid in alcohol (20 vols.) and water (40 vols.) was exactly neutralised with $N/10$-baryta, warmed on the steam-bath under reflux for 15 minutes, and again neutralised with baryta. The pure 2-bromo-acid gave figures corresponding to the formation of 77 $\pm$ 1% of hydroxy-acid, and a little pseudo-acid. *cyclo*Hexene was also formed. The *cis*-3-bromo-acid was converted quantitatively into lactone and the *trans*-isomeride was unaffected. A known excess of baryta was then added, and the mixture warmed on the steam-bath for 1 hour. This hydrolysed the γ-lactone and decomposed the salt of the *trans*-γ-bromo-acid. The excess of baryta was again titrated. This method was applied to the analysis of unknown mixtures in two ways; first directly, and secondly after the proportion of β-bromo-acid had been artificially increased by the addition of a known amount, about 25 or 30%. Typical results obtained by the two methods are tabulated below under the headings " Direct " and " Indirect."

The addition of hydrogen bromide was slow to dry Δ^2-tetrahydrobenzoic acid, but more rapid when $\frac{1}{2}$% of water was present. The products were left in a vacuum until the weight was constant and then gave the following analytical figures :

No.	Condition of acid.	Equivalent (Calc., 207·0).	Bromo-acid in product.			
			Direct.		Indirect.	
			% 2-.	% 3-.	% 2-.	% 3-.
1	Dry	207·5	17·5	86·5 (?)	18·0	82·0
2	,,	205·4	13·0	81·0	19·0	81·0
3	Moist	210·0	16·5	82·0	18·5	82·0
4	,,	205·0	17·0	83·0	18·0	82·0

The product from experiment 1 contained 38·6% Br (calc. for $C_7H_{11}O_2Br$, 38·6%).

These results were confirmed as follows. The pure 2-bromo-ester was boiled with ethyl sodiomalonate in benzene for 24 hours; the product, b. p. 95°/15 mm., was identified as Δ^1-tetra-hydrobenzoic ester by conversion into *trans*-hexahydrohomophthalic acid (m. p. and mixed m. p. 158°). The products of experiments (2) and (3) were esterified, and the mixed bromo-esters boiled with ethyl sodiomalonate in benzene for 24 hours. The unchanged 3-bromo-ester was isolated by distillation [Found : for a synthetic mixture containing 78% of *cis*-3-bromo-ester, 79% of 3-bromo-ester; for the ester from (2), 83·5% of 3-bromo-ester, for the ester from (3), 83·0% of 3-bromo-ester].

The hydrobromides after several weeks deposited first the impure *trans*-3-bromo-acid, m. p. 153—157° (compare Perkin and Tattersall, J., 1907, **91**, 495), and then the *cis*-3-bromo-acid, m. p. and mixed m. p. 65°.

2. 3-*Methyl*cyclo*hexenecarboxylic Acids.*

Δ^1-*Acid* (IV*).—This was prepared from 3-methyl*cyclo*hexanone by the method used for Δ^1-tetrahydrobenzoic acid with the minor differences noted below. The ketone tended to yield high-boiling compounds in the presence of mineral acids and the cyanohydrin was therefore made as follows : The sodium bisulphite compound from 170 g. of ketone was treated with a solution of 104 g. (1 mol.) of potassium cyanide in 200 c.c. of water, together with 300 c.c. of ether, which removed a coating of cyanohydrin from the surface of the bisulphite compound. The mixture was shaken for 30 minutes in ice and then over-night mechanically. The cyanohydrin was isolated by means of ether and was not distilled in bulk, although it could be distilled in small quantities in the presence of a few drops of concentrated sulphuric acid at 133°/16 mm. The crude cyanohydrin was dehydrated by the method used by Ruzicka and Brügger (*loc. cit.*) for the lower homologue. 103 G. of unsaturated nitrile, presumably Δ^1- + Δ^6-, were obtained, b. p. 88—95°/17 mm. 50 Hours' boiling with 2 mols. of 10% aqueous caustic potash were required for its hydrolysis. The product was acidified in ice with hydrochloric acid *very cautiously* on account of the ease with which the Δ^2-acid lactonises. A 77% yield of crude acid, b. p. 126—128°/7 mm. or 145—146°/15 mm., was obtained (equiv., 141·0; calc., 140·1). Bromine titration indicated that this contained about 22% of Δ^β-acid. The acid was partly esterified in the cold for 20 hours by the method described for the lower homologue; the ester (A) was retained and the unesterified acids (Δ^1- and Δ^6-) were separated through the calcium salts by the method of Perkin and Tattersall (*loc. cit.*). The less soluble calcium salt after crystallisation yielded 50 g. of 3-methyl-Δ^1-cyclo*hexenecarboxylic acid, b. p. 130°/7 mm., which solidified in ice and melted at 26°. Perkin and Tattersall state that they were unable to obtain a completely solid acid by the calcium salt separation, and in view of this a small amount of the acid was converted into 1 : 2-*dibromo*-3-*methyl*cyclo*hexanecarboxylic acid*, which formed small white plates from formic acid, m. p. 119° (Found : Br, 53·2; equiv., 300·0. $C_8H_{12}O_2Br_2$ requires Br, 53·3%; equiv., 300·0). On reduction with zinc and alcohol this regenerated an unsaturated acid identical in properties with the initial material. Hence, purification by partial esterification and through the calcium salt suffices to yield the homogeneous Δ^1-acid, which has m. p. 26—27°, n 1·4917, d 1·0501, $[R_L]_D$ 38·62 (calc., 38·02), B 2·0%.

Δ^2-*Acid* (II).—This was obtained by Perkin and Tattersall (*loc. cit.*) in an impure form from the corresponding 3-bromo-acid. The crude ester (A) obtained during the purification of the hydrolysis product of the unsaturated nitrile described above (24 g.) was hydrolysed in the manner described for *iso*hexenoic acid (J., 1932, 125). The acid had b. p. 123°/7 mm. (equiv., 140·9; calc., 140·1). As the low bromine addition (79·4%) suggested that some Δ^a-acid was still present, the acid was separated by partial esterification for 4 hours into an ester (B) and an acid (C).

* Perkin and Tattersall call this the Δ^6-acid, the acid (V) being the Δ^1-; but this is inconvenient for the present purpose.

The acid (C) was in turn esterified for 6 hours to give an ester (D). Both (B) and (D) gave on hydrolysis the almost pure Δ^2-acid with bromine additions of 96·1 and 95·1%. Total yield, 11·2 g. A solid dibromide was not obtained, but the acid readily yielded a *p*-toluidide, tufted needles from light petroleum, m. p. 108—109°.

1-*Methyl*-1 : 3-cyclo*hexanolide* (VIII).—This was prepared from *cis*-3-hydroxy*cyclo*hexane-carboxylic acid following Perkin and Tattersall. The 3-hydroxy-3-methyl*cyclo*hexanecarboxylic acid from this was distilled slowly in a vacuum, 4·6 g. of a fraction, b. p. 128°/22 mm., being obtained (Perkin and Tattersall give b. p. 145°/20 mm.). This was dissolved in ether, washed with sodium bicarbonate solution, and left in contact with potassium carbonate in a vacuum. Distillation then yielded pure *cis*-1-methyl-1 : 3-*cyclo*hexanolide, b. p. 120—121°/20 mm., which solidified to a mass of overlapping plates, m. p. 45° (Found : C, 68·3; H, 8·5. Calc. : C, 68·4; H, 8·6%). Another preparation of the same solid lactone is described below.

No lactonisation of the Δ^1-acid was effected by the action of sulphuric acid either at the boiling point for 15 minutes or in the cold for 7 days under the usual conditions.

Lactonisation of the Δ^2-Acid.—(i) The acid was charred by hot dilute sulphuric acid. It rapidly dissolved in 5 vols. of 60% sulphuric acid at 20°, with a rise in temperature of 5°. The following samples were analysed :

Time, mins.	% Recovery (distillate).	B. p./mm.	Composition of distillate.	
			% Acid.	% Lactone.
5	89	118/18	15·5	86·0
15	86	,,	12·5	88·5
60	83	,,	8·5	92·5

The products were combined and separated into acid and lactone. The small amount of acid had the bromine addition of the unchanged Δ^2-acid (96%). The lactone had m. p. 44°, alone or mixed with 1-methyl-1 : 3-*cyclo*hexanolide (equiv., 139·8; calc., 140·1). This showed that the Δ^2-acid was substantially free from the Δ^6-isomeride.

The easy preparation of lactone by this process suggested that it might also be obtainable from the mixture of methyl*cyclo*hexenecarboxylic acids obtained from 3-methyl*cyclo*hexanone through the cyanohydrin, which was known to contain about 22% of Δ^β-acid (p. 264). 55 G. of this mixture were shaken vigorously for 15 minutes with 60% sulphuric acid (5 vols.). The lactone, isolated and freed from acid as usual, boiled at 100°/8 mm. (7·5 g.), and had m. p. 44° and mixed m. p. 45°. The fact that the lactone was the pure 1 : 3-isomeride shows that there was no tendency for any other isomeric acid to lactonise under these conditions. Moreover the amount of lactone isolated (corrected for experimental losses obtained when lactonising the pure Δ^2-acid under the same conditions) corresponded to a content of 19% of Δ^2-acid in the original mixture, *i.e.*, nearly as much as that indicated for the *total* Δ^β-acid by bromine titration. Hence the amount of Δ^5-acid present in the mixture must be very small.

(ii) The acid was boiled gently in an all-glass apparatus in an inert atmosphere with the following results :

Time, mins.	30	90	120 *	300
Product { % acid	74	68	72	65
% lactone	26	31·5	32	30·5

* This product was distilled before analysis. The lactone, separated in the usual manner, had m. p. and mixed m. p. 44°.

Reactions of 1-Methyl-1 : 3-cyclohexanolide.—(i) The lactone was boiled under the same conditions as the Δ^2-acid and the products were analysed without distillation.

Time, mins.	75	255	375
Product { % acid	42·5	61·5	57·5
% lactone	58	36·5	36·5

A sample of lactone was boiled for 300 minutes and the acid that had been produced was separated in 63% yield. It had a bromine addition of 94%. This was converted into the *p*-toluidide, which crystallised from light petroleum as a mixture, m. p. about 100°. Owing to lack of material the nature of the isomeric acid could not be determined more precisely.

(ii) The lactone was charred by the action of hot dilute sulphuric acid, but not so readily as the isomeric Δ^2-acid. It was unaffected by cold 60% sulphuric acid.

(iii) When boiled with water, it yielded the corresponding hydroxy-acid as follows :

Time, hrs.	42	48	72
Product { % hydroxy-acid	21·6 (?)	27·1	28·7
{ % lactone	74·0	75·2	69·3

The formation of the lactone from the hydroxy-acid at 100° was followed by the usual method (J., 1932, 128), with these results :

Time, mins..............................	20	65	185	365	545
% Lactone formed.....................	5·2	15·2	35·1	47·7	54·1

The time of half-change to the equilibrium is 198 minutes.

Tautomeric Change of the Δ^1- into the Δ^2-Acid in Alkali.—The mobility was remarkably low. Pure Δ^1-acid was boiled for 16 hours (copper flask) with 2 mols. of 25% caustic potash solution. The acid was isolated as usual : 90%, equiv., 140·4 (calc., 140·1), B 6·2%. After further treatment with 2 mols. of 40% caustic potash solution for 64 hours, 84% was recovered with equiv. 141·0, B 13·0%. This was finally boiled for 90 hours with 3 mols. of 33% caustic potash solution and then had equiv. 141·1, B 27·0% ; 84% recovery. A second sample was boiled successively with caustic potash as follows : (i) 9 hours with 10 mols. of 25% ; 63 hours with 2 mols. of 40% ; 114 hours with 3 mols. of 33%. An overall yield of 55% was obtained with equiv. 140·4, B 26·0%. The second treatment was much more drastic, but the final products had very similar bromine additions and were therefore presumed to have reached the equilibrium at a value of 74·8% of Δ^1-acid. The Δ^2-acid was isolated from the equilibrium mixture in the manner described under its preparation and gave the same *p*-toluidide, m. p. and mixed m. p. 109°.

2-Bromo-3-methylcyclohexanecarboxylic acid (probably *trans*-) was prepared by saturating a mixture of 3-methyl-Δ^1-*cyclo*hexenecarboxylic acid and an equal part of glacial acetic acid at 0° with hydrogen bromide and keeping the solution for a few days. The solvent was removed, and the resulting solid pressed on a porous tile and crystallised from light petroleum. The bulk of the product formed needles, but small amounts of a second form crystallising in long prisms were obtained (? the *cis*-acid). The needles melted at 144·5° (Found : Br, 36·2; equiv., 221·3. $C_8H_{13}O_2Br$ requires Br, 36·2% ; equiv., 221·0).

cis-*3-Bromo-3-methylcyclohexanecarboxylic acid* was made by treating 3-methyl-1 : 3-*cyclo*-hexanolide with 2 vols. of aqueous hydrogen bromide, saturated at 0°, for 48 hours. The bromo-acid, isolated by means of ether, soon solidified to a mass of needles, m. p. 45° after being drained on a tile (Found : Br, 35·8. $C_8H_{13}O_2Br$ requires Br, 36·2%). The substance very readily re-formed the lactone with loss of hydrogen bromide. It was soluble with immediate decomposition in water (like γ-bromo*iso*hexoic acid) and the equivalent could not be determined.

Addition of Hydrogen Bromide to 3-Methyl-Δ^2-cyclohexanecarboxylic Acid.—Mixtures of the 2- and the 3-bromo-acid were analysed by the following process. A weighed amount of the bromo-acid was dissolved in alcohol and water and neutralised with N/10-baryta. The solution was boiled under reflux for 30 minutes and again titrated with baryta. The pure 2-bromo-acid yielded 97·5% of hydroxy-acid, no ψ-acid, and a trace of unsaturated hydrocarbon. The 3-bromo-acid yielded no acidic material, the barium salt being stable. For an artificial mixture containing 90·5% of the 3-bromo-acid, the percentage found was 90·4.

The addition of hydrogen bromide to dry Δ^2-acid and to acid containing $\frac{1}{2}$% of water was carried out in the usual manner, and the product analysed by the above method [Found : (dry addition) 99·1, 99·1% of 3-bromo-acid; (moist addition) 99·0% of 3-bromo-acid]. The combined products were boiled with caustic soda for 10 minutes, acidified, and extracted with ether. The product was distilled, freed from traces of acid with sodium bicarbonate, and re-distilled. 1-Methyl-1 : 3-*cyclo*hexanolide was obtained, m. p. and mixed m. p. 45°, which showed that a considerable quantity of the 3-bromo-acid had the *cis*-configuration.

3. α-*Methylpentenoic Acids.*

Preparations (Goldberg and Linstead, *loc. cit.*).—190 C.c. of propaldehyde yielded 34 g. of Δ^α-acid. This was not appreciably purified by partial esterification. It had m. p. 101°/9 mm., m. p. 21°, n 1·4583, d 0·9829, $[R_L]_D$ 31·71 (calc., 30·98), J 0·6%, equiv. 113·9 (calc., 114·1). Reduction of ethyl α-methyl-β-acetosuccinate yielded 57% of αγ-dimethylparaconic acid, which was pyrolysed to crude α-methyl-Δ^β-pentenoic acid. This was partly esterified for 5 hours, and the ethyl ester hydrolysed to the pure acid (25% yield from the paraconic acid), b. p.

90°/10 mm., n 1·4360, d 0·9619, $[R_L]_D$ 31·02, J * 75·0%, equiv. 113·9, which failed to solidify after 24 hours at − 80°.

Lactonisations.—(1) Δ^α-*Acid.* There was no gross decomposition with boiling 50% sulphuric acid and the formation of lactone proceeded as follows :

Time, mins.	% Recovery (distillate).	B. p./mm.	% Acid.	% Lactone.
15*	90	98—102°/7	96·0	5·5
90	89	85—108/11	44·5	55·5
360	84	85/11	2·5	97·0

Composition of distillate above % Acid and % Lactone columns.

* Fittig's conditions (*loc. cit.*).

The products were combined and separated into acid and lactone. The acid had b. p. 103°/10 mm., n 1·4579, d 0·9826, J 0·6%, equiv. 114·1. It melted at 20° alone or mixed with the Δ^α-acid. The lactone had b. p. 81°/10 mm., n 1·4289, d 1·0036, whence $[R_L]_D$ 29·29 (calc., 29·37), equiv. 114·2 (calc., 114·1). It solidified in solid carbon dioxide–ether to a crystalline mass, m. p. − 36°. The identity with the α-methyl-γ-valerolactone of Blaise and Luttringer (*loc. cit.*) was confirmed by preparation of the hydrazide, m. p. 118°, from ethyl acetate (lit., 115°). Cold dilute sulphuric acid had no action on the acid.

(2) Δ^β-*Acid.* After treatment under Fittig's condition the acid yielded 89% of distillate, b. p. 84°/10 mm., containing 2% of acid and 98·5% of lactone. After purification the lactone was proved to be identical with α-methyl-γ-valerolactone by m. p. and mixed m. p. (− 37°) and other physical constants, which were almost the same as those given above. Treatment with cold 60% sulphuric acid gave the following results : there was no rise in temperature and the two acids mixed only slowly.

Time, hrs.	% Recovery (distillate).	B. p./mm.	% Acid.	% Lactone.
2	75	84—90°/10	55·5	45·5
5	81	82/9	26·5	74·5
24	83	87/9	3·5	98·5

Composition of distillate above % Acid and % Lactone columns.

The unlactonised acid was identified as the Δ^β-isomeride by its physical properties and iodine addition. The lactone was identical with that already described (m. p. and mixed m. p. − 36°).

The Δ^β-acid was boiled for 3 hours under atmospheric pressure and then distilled at 92°/11 mm. There was hardly any lactonisation (acid, 98·2% ; lactone, 2·5%).

Reactions of α-*Methyl-γ-valerolactone.*—The lactone was unchanged after treatment for a week at room temperature with 60% sulphuric acid or for 90 minutes at the b. p. with 50% acid. The hydrolysis of the lactone by boiling water (*a*) and the velocity of its formation from the hydroxy-acid (*b*) were determined by the standard methods :

(a) Time, hrs.	24					48		
% Acid	2·0					2·0		
% Lactone	—					96·0		

(b) Time, mins.	5	10	15	30	45	60	120	240
% Lactone formed	18·4	34·5	43·3	61·8	71·4	78·2	87·0	93·0

Preliminary experiments on the addition of hydrogen bromide to α-methyl-Δ^β-pentenoic acid indicated that about 90% of the γ-bromo-acid was formed. The product was converted in good yield into α-methyl-γ-valerolactone, identified by m. p. and mixed m. p.

* This iodine addition is considerably higher than that observed by Goldberg and Linstead and partial esterification has obviously eliminated some Δ^α-isomeride. In view of the fact that unsaturated acids are isomerised at high temperatures (Linstead, *J.*, 1930, 1603; Linstead and Noble, *loc. cit.*), it is not surprising that some Δ^β-acid should have changed into the stable Δ^α-form at the temperature of pyrolysis (290°). On the basis of the new value for the iodine addition of the Δ^β-acid the position of the three-carbon equilibrium has to be corrected from 81% αβ- to 89% αβ-. If this is compared with the figure for the *n*-pentenoic acids (68% αβ- ; Linstead and Noble, *loc. cit.*), it will be seen that the effect of the α-methyl group in stabilising the αβ-position of the double bond is even greater than at first thought.