645. *Intermediates in the Conversion of Pinonic Acid into Carbocyclic Compounds.*

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The cyclisation of pinonic acid in acidic media, leading to compounds containing benzene, *cyclo*hexane, and *cyclo*hexene rings, has been investigated. The reactions with bromine and hydrochloric acid, and with phosphoric acid, are believed to follow the courses shown respectively by the left- and the right-hand sides of the scheme (I—XIII).

Barbier and Grignard[1] found 2 : 4-dimethylphenylacetic acid (VII) to be formed by the action of bromine on pinonic acid (I). It is apparent that several consecutive reactions are probably involved in so considerable a change in structure. Harispe[2] increased the yield by allowing bromine and pinonic acid to react in concentrated hydrochloric acid to form a homogeneous solution, then heating it, and subsequently isolating the product (VII) as its methyl ester. By adding the solution, above, to ice, he obtained an oil which, though otherwise unidentified, contained bromine in quantity approximating to that required for a monobromopinonic acid or a monobromo-derivative of 3-(1-hydroxy-1-methylethyl)-6-oxoheptanoic lactone (III). He also converted the ketone (III) into 2 : 4-dimethylphenylacetic acid, an intermediate bromine-containing oil similar to the last again being isolable.

Harispe proposed the following reaction scheme: Pinonic acid is converted into bromopinonic acid (II) which rearranges to the bromo-ketone (IV); this compound, by loss of water and hydrogen bromide, forms the lactone (VIII), hydrolysis of which to the corresponding hydroxy-acid and dehydration of the latter yield 2 : 4-dimethylphenylacetic acid. For the reaction commencing with the ketone (III), bromination to (IV) is the first stage.

The mechanism of the rearrangement of pinonic acid to the ketone (III) having been investigated,[3] it was decided to attempt to elucidate the mechanism of the reaction above by the isolation of intermediates and by separation of the oxidation and acid-catalysis.

Repetition, with (±)-*trans*-pinonic acid, of Harispe's procedure gave 2 : 4-dimethylphenylacetic acid in 50% yield; also, separation by esterification was replaced by direct extraction with dilute ammonia, followed by sublimation, the acid being then obtained in 66% yield. The latter isolation shows 2 : 4-dimethylphenylacetic acid to be the end-product of the reaction and eliminates the possibility that the isomeric lactone (VIII) is the actual product, which on treatment with methanolic hydrogen chloride would be converted into methyl 2 : 4-dimethylphenylacetate. 2 : 4-Dimethylphenylacetic acid (57%) has also been obtained by direct extraction from the reaction commencing with ketone (III).

From the product of bromination of pinonic acid at <30° there was isolated a crystalline bromopinonic acid. On being heated with hydrochloric–hydrobromic acid approximating in composition to the solvent present after bromine-substitution has taken place, it gave 2 : 4-dimethylphenylacetic acid in 56% yield. Reduction of the bromo-acid with zinc and hydrochloric acid gave (±)-*trans*-pinonic acid and the ketone (III), isolated as the oxime and the 2 : 4-dinitrophenylhydrazone respectively; production of the former demonstrates that the bromo-acid has the pinonic acid structure and the *trans*-configuration; the formation of the ketone (III) is ascribed to rearrangement of pinonic acid in the acidic reduction medium. No compound containing a bromomethyl group has been encountered and, further, acid-catalysed bromination of menthone and carvomenthone yields exclusively

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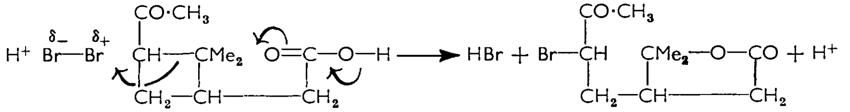
[1] Barbier and Grignard, *Compt. rend.*, 1909, **148**, 646.
[2] Harispe, *Ann. Chim.*, 1936, **6**, 249.
[3] Arcus and Bennett, *J.*, 1955, 2627.

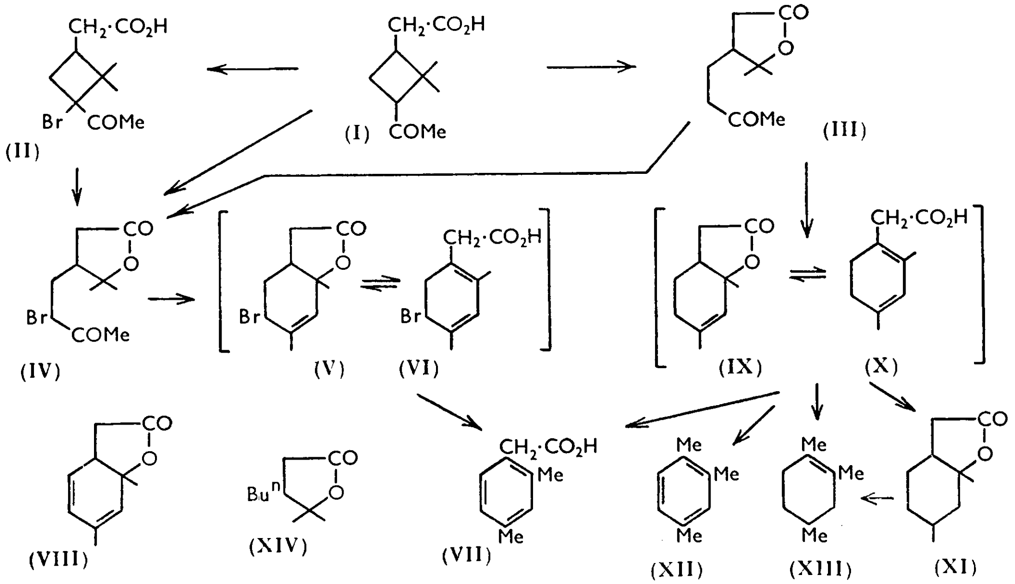
the tertiary bromo-derivatives;[4] the bromopinonic acid is therefore assigned the structure (II).

Further, it has been found that conversion of pinonic acid into the ketone (III) is too slow for this to be the main course of reaction (the ketone, once formed, is rapidly brominated). It is concluded that the bromo-ketone is largely formed either by rearrangement of bromopinonic acid (which rapidly disappears if the temperature is not kept below 30°) or directly by the reaction of bromine with pinonic acid under acidic conditions:



this mechanism is analogous to that deduced[3] for the acid-catalysed rearrangement of pinonic acid to the ketone (III).

From Harispe's and the present results, the scheme (I—VII) is deduced. The bromoketone (IV), regarded as the essential precursor to 2 : 4-dimethylphenylacetic acid, is formed from pinonic acid by three routes: through bromopinonic acid (II), through the ketone (III), and directly, as above. Ring-closure yields the lactone (V), in equilibrium with the acid (VI), and from these 2 : 4-dimethylphenylacetic acid is formed by elimination of hydrogen bromide.



The ketone (III) is rapidly formed when pinonic acid is heated in phosphoric acid at 100° (92—95% in 5 min.[3]), and cyclisation occurs on further heating at higher temperatures, analogously to the change (IV) ⟶ (V) + (VI).

(±)-*trans*-Pinonic acid was heated in phosphoric acid to 165°, evolution of carbon dioxide commencing at 150°; 2 : 4-dimethylphenylacetic acid was obtained in 3·5% yield; there was isolated also a lactone which, from the analytical data, equivalent on hydrolysis, and oxidation by bromine to 2 : 4-dimethylphenylacetic acid, is considered to have structure (XI) (yield 7·5%); there were also a hydrocarbon mixture (yield 25%, calc. as C_9H_{16}), a higher-boiling hydrocarbon fraction (not identified), and considerable neutral resin. The first mixture is considered, on the following grounds,

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[4] Kotz and Steinhorst, *Annalen*, 1911, **379**, 13.

to be composed of ψ-cumene (XII) and 1 : 2 : 4-trimethyl*cyclo*hexene (XIII) in approximately equal amounts: (*a*) Nitration gave 3 : 5 : 6-trinitro-ψ-cumene in 23% yield; ψ-cumene itself gave 60%. (*b*) A series of fractions showed the following properties: the highest-boiling gave 49% of the same trinitro-compound, those of lower b. p.s 5%; but a fraction boiling below these last gave, after aromatisation with palladised charcoal, 28%. Analytical data for a lower-boiling fraction are consistent with the presence of much trimethyl*cyclo*hexene together with some ψ-cumene. (*c*) Rates of hydrogenation of *cyclo*hexene, 1-methyl*cyclo*hexene, 1 : 2-dimethyl*cyclo*hexene, and the (unfractioned) hydrocarbon were found to be related as follows: *cyclo*hexene $\gg$ 1-methyl*cyclo*hexene $\gg$ 1 : 2-dimethyl*cyclo*hexene $\approx$ hydrocarbon. It is concluded that the ethylenic part of the molecule is fully alkylated, and hence that 1 : 2 : 4-trimethyl*cyclo*hexene is present, but not its isomers or trimethyl*cyclo*hexadienes, all of which contain the more readily hydrogenated CH:CH or CH:CMe groups.

The reaction scheme (I—XIII), accounting for the formation of the products described, is put forward. Pinonic acid is converted into the ketone (III), which cyclises to the lactone (IX), an equilibrium existing between this compound and the acid (X). The lactone (XI) is formed by addition of hydrogen to (IX), while dehydrogenation of (X) [or (IX) directly] yields 2 : 4-dimethylphenylacetic acid (VII). Decarboxylation of (IX) [or (X)] together with addition of hydrogen yields 1 : 2 : 4-trimethyl*cyclo*hexene (XIII); accompanied by dehydrogenation it yields ψ-cumene (XII).

It is not intended to imply that there necessarily occurs a dismutation of, or hydrogen transfer between, (IX) or (X); such transfer may involve compounds which condense or polymerise to form the resin.

Some alternative reaction routes have been investigated by a study of rates of carbon dioxide evolution by the following compounds in phosphoric acid at 160°.

Pinonic acid, rapidly converted into the ketone (III), yielded 54% of carbon dioxide in 5 min., but thereafter the rate of evolution slackened. To gain insight into the stability of the lactone ring in the ketone (III), cyclisation was prevented by reduction of the keto- to a methylene group; β-*n*-butyl-γγ-dimethyl-γ-butyrolactone (XIV), obtained by the Huang-Minlon procedure, gave 5% of the possible carbon dioxide in 30 min. It is thus improbable that the ketone itself undergoes rapid decarboxylation; so decarboxylation is referred to one or more of the later compounds (IX, X, XI, or VII).

The lactone (XI) gave 39% of carbon dioxide in 60 min., and a hydrocarbon which gave correct analyses for 1 : 2 : 4-trimethyl*cyclo*hexene (XIII) was isolated in small yield; thus, this hydrocarbon is probably formed partly from this lactone.

2 : 4-Dimethylphenylacetic acid (VII) was almost unaffected by such treatment, so ψ-cumene is not formed by decarboxylation of this compound.

EXPERIMENTAL

Hydrochloric and phosphoric acid refer respectively to the acid of *d* 1·18 and *d* 1·74. Extraction, unless otherwise stated, was by methylene chloride.

Bromine–Hydrochloric Acid Reactions.—(*a*) In each of the following experiments (±)-*trans*-pinonic acid[3] (18·4 g.) was suspended in hydrochloric acid (30 ml.), and bromine (16·5 g.) was added in one portion; the flask was shaken vigorously, the temperature reaching 48° in 10 min., with disappearance of the pinonic acid and bromine. The solution was heated in a steam-bath for 4 hr., then cooled. Either of two procedures was then used.

(i) Water (70 ml.) was added, and the resin which separated was dissolved in methylene chloride (30 ml.); the aqueous solution was repeatedly extracted (total solvent, 80 ml.). The combined methylene chloride solutions were washed with water, excess of dilute aqueous ammonia, then again water, and on evaporation gave an unidentified oil (1·3 g.); the ammoniacal solution and the succeeding washings were acidified with hydrochloric acid and extracted (3 × 30 ml.). The extract was washed with water and the solvent distilled; the product (15·3 g.) was sublimed at 100°/0·01 mm. during 5 hr., and yielded 2 : 4-dimethylphenylacetic acid (10·8 g.), m. p. 101°; after recrystallisation from *cyclo*hexane it (10·2 g.) had m. p. 104°.

The residue from sublimation was boiled with chloroform, then cooled and an insoluble powder was filtered off; this material was twice crystallised from aqueous ethanol, and its solution in acetone decolorised by passage through a column of charcoal, followed by washing of the column with this solvent. The product (0·47 g.) yielded, after three recrystallisations from acetone, an acid (*A*), m. p. 214° [Found: C, 72·95; H, 6·9%; *M* (Rast), 309].

(ii) The solid which separated when the hydrochloric acid solution was cooled was collected on a sintered-glass filter, washed with hydrochloric acid, and added to methanol (15 ml.). The liquid was saturated with hydrogen chloride and boiled under reflux for ½ hr.; next day it was again saturated, and boiled for 1 hr. Water was added and the whole extracted; the extract was washed with water and dried (Na_2SO_4). It yielded methyl 2 : 4-dimethylphenylacetate (10·0 g.), b. p. 174—178°/95 mm.; a portion, left in contact with potassium carbonate, gave on distillation the ester, b. p. 124—126°/13 mm.; a further portion (5·0 g.) was boiled under reflux for 1 hr. with potassium hydroxide (2·0 g.), water (20 ml.), and ethanol (5 ml.). After cooling and acidification, recrystallisation of the product from hot water yielded 2 : 4-dimethylphenylacetic acid (4·1 g.), m. p. 105·5°. S-*Benzylthiuronium* 2 : 4-*dimethylphenylacetate*, plates (from water), had m. p. 164·5° (Found: S, 9·45. $C_{18}H_{22}O_2N_2S$ requires S, 9·7%).

(*b*) (±)-*trans*-Pinonic acid (19·0 g.) was added to bromine (16·5 g.) and hydrochloric acid (30 ml.) with cooling so that the temperature did not rise above 30°. After 10 min. the solution was poured on ice, and the aqueous liquid was decanted from a heavy oil, which was taken up in methylene chloride (50 ml.); this solution was washed with water, dried (Na_2SO_4), and evaporated; by filtration of the semi-solid residue, crystals (5·9 g.) were separated. After three recrystallisations from methylene chloride the product (2·85 g.) had m. p. 114·5—115°, and further recrystallisation yielded *bromopinonic acid*, m. p. 116·5—117° (Found: C, 45·9; H, 5·65; Br, 30·25%; equiv., 258. $C_{10}H_{15}O_3Br$ requires C, 45·65; H, 5·75; Br, 30·35%; equiv., 263).

To a vigorously stirred solution of the bromo-acid (0·25 g.) in hydrochloric acid (50 ml.) was added zinc dust (0·70 g.); subsequently water (50 ml.) and further zinc dust (0·70 g.) were added; stirring was continued for 5 hr., and the whole was kept overnight, then filtered. The filtrate was extracted; the extract was washed with dilute aqueous ammonia and with water, and gave a product (20 mg.) which was converted into its 2 : 4-dinitrophenylhydrazone (35 mg.) which, after recrystallisation from ethanol, had m. p. 162°, and m. p. 163° when mixed with the derivative, m. p. 163·5°, of the authentic ketone (III). The ammoniacal and aqueous washings were acidified and extracted; the product (50 mg.) from the extract was converted[3] into its oxime; the latter (10 mg.), m. p. 146—147°, had, after recrystallisation from ethyl acetate–carbon tetrachloride, m. p. 148—149°, and m. p. 149—150° when mixed with authentic (±)-*trans*-pinonic acid oxime of m. p. 152°.

Hydrogen chloride (17·5 g.) was passed into ice-cooled hydrochloric acid (69 ml.) and hydrobromic acid (*d* 1·48; free from bromine; 43 ml.); the product is referred to as hydrochloric–hydrobromic acid. Bromopinonic acid (0·50 g.) was heated under reflux on a steam-bath with this acid (2·0 ml.). From the clear solution first obtained, an oil separated; after 4 hr. water (3 ml.) was added and the whole was chilled. The oil solidified; the product was collected, washed with water, and dried. It (0·30 g.; m. p. 98—100°) yielded on sublimation 2 : 4-dimethylphenylacetic acid (0·25 g.), m. p. 103°, mixed m. p. 104°.

(*c*) Reaction as in (*b*), but without cooling, gave a syrup from which, in spite of seeding with bromopinonic acid, none of the latter was isolated.

(*d*) The (±)-ketone (III) (18·4 g.) was allowed to react with bromine and hydrochloric acid as in (*a*); reaction was rapid, the temperature rose to 50°, and a homogeneous solution was obtained; it was cooled. One half was treated as in (*a*, i) and yielded 2 : 4-dimethylphenylacetic acid (4·7 g.), m. p. 104° (105·5° after recrystallisation from *cyclo*hexane), and the acid *A* (0·25 g.), m. p. 203—205°. The rest was poured on ice and extracted. The extract, after being washed with water, dried (Na_2SO_4), and evaporated at reduced pressure, gave a syrup (12·7 g.), n_D^{25} 1·4984; a portion (0·50 g.), heated on a steam-bath for 4 hr. with hydrochloric–hydrobromic acid (2·0 ml.), yielded 2 : 4-dimethylphenylacetic acid (0·19 g.), m. p. 100°, and the acid *A* (5 mg.), m. p. 202—203°. Attempts to isolate the ketone (IV), as such and as derivatives, from the syrup did not succeed.

(*e*) A stirred suspension of (±)-*trans*-pinonic acid (3·0 g.) in hydrochloric–hydrobromic acid (3·0 ml.) was immersed in a thermostat bath at 48°. After 10 min. the clear solution was poured into water (100 ml.) and aqueous ammonia (*d* 0·88; 10 ml.) was added; extraction yielded the ketone (III) (0·78 g.), and, by extraction of the aqueous liquid after acidification with hydrochloric acid, pinonic acid (1·88 g.) was recovered.

Reaction in Phosphoric Acid.—(±)-*trans*-Pinonic acid (80 g.) and phosphoric acid (200 g.), in a distillation flask, were immersed in an oil-bath previously heated to 180°; the pinonic acid dissolved; thereafter, at 150°, evolution of carbon dioxide and separation of an oil commenced; the temperature of the mixture rose to 165°, heating of the oil-bath having been discontinued latterly, and an oil and water distilled. Water (150 ml.) was added to the flask, and the contents were distilled in steam. The aqueous distillate (*B*) was separated from the oil (*C*), and the aqueous phosphoric acid (*D*) was decanted from a resin (*E*).

[In the account below, (VII) and (XI) refer respectively to (impure) specimens of 2 : 4-dimethylphenylacetic acid and 2-hydroxy-2 : 4-dimethyl*cyclo*hexylacetic lactone.]

The distillate *B* (4 l.) was repeatedly extracted (total solvent, 400 ml.); the extract yielded an oil (7·5 g.), which was washed in methylene chloride (25 ml.) with aqueous sodium carbonate. The latter on acidification with dilute sulphuric acid gave (VII) (1·5 g.), m. p. 98°. The solution was evaporated and the product boiled under reflux for 2 hr. with ethanolic 0·5N-potassium hydroxide (75 ml.). After dilution with water (100 ml.) and extraction of non-hydrolysable material (0·1 g.), the alkaline solution was acidified and extracted; the lactone (XI) (5·6 g.) was obtained.

The oil *C* was washed in methylene chloride with aqueous sodium carbonate and separated through a short distillation column into volatile and involatile portions. The former was kept over, then distilled from, sodium, and yielded a colourless distillate (F_2) (11·8 g.), b. p. 150—170°, n_D^{25} 1·4780. Treatment of the involatile portion with ethanolic potassium hydroxide (50 ml.), as above, gave a viscous non-hydrolysable oil (*G*) (5·8 g.) and (XI) (1·3 g.).

The aqueous material *D*, on treatment as for *B*, gave (VII) (0·2 g.), m. p. 101°.

The resin *E* was washed in methylene chloride with water, recovered, and heated at 100°/0·2 mm. for 6 hr. in a sublimation-apparatus; solution of the sublimate in methylene chloride and extraction with aqueous sodium carbonate effected separation into a neutral gum (1·0 g.) and (VII) (0·8 g.), m. p. 101—102°. A soft, brown, clear resin (28·9 g.) remained in the apparatus.

Characterisation of products. Specimens of (VII) were combined and recrystallised from *cyclo*hexane, yielding 2 : 4-dimethylphenylacetic acid (1·97 g.), m. p. 101—103°, and, after recrystallisation from water, m. p. and mixed m. p. 105°. A 1 : 1 mixture of (±)-*trans*-pinonic acid (m. p. 105—105·5°) and 2 : 4-dimethylphenylacetic acid had m. p. 77—80°.

The material (3·4 g.) from combination and distillation of specimens of (XI) gave, on redistillation, *2-hydroxy-2 : 4-dimethyl*cyclo*hexylacetic lactone*, b. p. 102—103°/0·7 mm., n_D^{25} 1·4693 (Found: C, 71·5; H, 9·55%; equiv., 169·2. $C_{10}H_{16}O_2$ requires C, 71·45; H, 9·55%; equiv., 168·2). The lactone (0·091 g.), hydrochloric acid (0·17 ml.), and bromine (0·061 g.) were heated at 100° for 1 hr. in a sealed tube. The organic acidic product, separated by aqueous sodium carbonate, on being heated for 2½ hr. at 100°/0·1 mm., gave a sublimate (0·049 g.) which on recrystallisation yielded 2 : 4-dimethylphenylacetic acid, m. p. and mixed m. p. 103°.

The oil *G*, on redistillation, gave an unsaturated hydrocarbon fraction, b. p. 125—128°/3·5 mm., n_D^{25} 1·5084 (Found: C, 88·1; H, 11·6%).

The ψ-cumene contents of the hydrocarbon F_2 and similar fractions were estimated by the following nitration procedure. The hydrocarbon (0·290 g.) was added dropwise with shaking to a cooled mixture of nitric acid (*d* 1·42; 2·0 ml.) and sulphuric acid (3·0 ml.). After being heated in a steam-bath for 10 min., with occasional shaking, the mixture was poured into water (100 ml.). The product was collected, washed with water (100 ml.), then with ethanol (4 ml.), and dried *in vacuo*; the yield and, after one recrystallisation from ethanol where necessary, the m. p., and m. p. when mixed with 3 : 5 : 6-trinitro-ψ-cumene having m. p. 188—189°, were determined. The m. p.s and mixed m. p.s of the specimens lay in the ranges 183—185° and 185—187°. In a control experiment ψ-cumene, b. p. 167—169°, n_D^{25} 1·5020, gave 60% of the nitro-compound; F_2 yielded 23%.

The volatile hydrocarbon mixture from a preceding decomposition, F_1, b. p. 149—167°, n_D^{25} 1·4811, was investigated as follows. (i) A portion was separated into fractions. The lower-boiling showed strong unsaturation to bromine in carbon tetrachloride. The fraction of b. p. 165—166°, n_D^{25} 1·4967, gave 49% of trinitro-ψ-cumene, which was recrystallised to constant m. p. 188°, mixed m. p. 188—189°. Fractions of b. p. 155·5—157°, n_D^{25} 1·4699, and b. p. 153—154°, n_D^{25} 1·4650, each gave 5%. The fraction of b. p. 149—150°, n_D^{25} 1·4583 (0·38 g.), was boiled for 5 hr. with 7% palladised charcoal (0·039 g.). The product, b. p. 154—170°, n_D^{25} 1·4683, gave a 28% yield of trinitro-ψ-cumene. For the fraction of b. p. 151—153°, n_D^{25} 1·4587, there was found: C, 87·65; H, 12·45 (Calc. for C_9H_{16}: C, 87·0; H, 13·0. Calc. for C_9H_{12}: C, 89·85; H, 10·05%).

(ii) Ozonolysis in acetic acid gave no identified product. This finding may be due to the formation of stable polymeric ozonides similar to those obtained by Criegee and his co-workers from 1 : 2-dimethyl*cyclo*hexene.[5]

(iii) Material F_1 and the following olefins (0·004 mole) were hydrogenated in methanol (20 ml.) in the presence of platinum (from, for each run, 15 mg. of Adams platinic oxide) at slightly above atmospheric pressure, with the following absorptions: *cyclo*hexene 86% in 20 min. at 23°; 1-methyl*cyclo*hexene 27% in 20 min., 49% in 120 min. at 23°; 1 : 2-dimethyl*cyclo*hexene 3% in 20 min., 5% in 120 min. at 21°; material F_1 (assumed for calculation to be half 1 : 2 : 4-trimethyl*cyclo*hexene and half ψ-cumene) 6% in 20 min., 8% in 120 min. at 21°.

β-n-*Butyl-γγ-dimethyl-γ-butyrolactone.*—The (±)-ketone (III) (12·5 g.) was dissolved in a warm solution of potassium hydroxide (12·5 g.) in diethylene glycol (90 ml.), and aqueous hydrazine hydrate (*d* 1·013; 5 ml.) was added; the whole was boiled under reflux for 1½ hr., raised to 205° while distillation was allowed to proceed, then kept under reflux at this temperature for 4½ hr. After cooling, water (150 ml.) was added and neutral material (0·6 g.) removed by extraction. The alkaline liquid was acidified with dilute sulphuric acid, then repeatedly extracted; the extract was washed with water, and dried (K_2CO_3). It yielded an oil (6·5 g.), b. p. 136—141°/13 mm., repeated fractionation of which gave β-n-*butyl-γγ-dimethyl-γ-butyrolactone* (1·1 g.), b. p. 99·5°/1·2 mm., n_D^{25} 1·4470 (Found: C, 70·3; H, 10·6%; equiv., 168·6. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·7%; equiv., 170·2).

Decarboxylations.—The compound (240 mg.) and phosphoric acid (1·0 ml.) were placed in a 5 ml. flask attached, *via* a short reflux condenser, to an oil-filled gas-burette. The flask was immersed in an oil-thermostat at 160°; periodically it was removed and allowed to cool, the increase in gas-volume was observed, and the percentage decarboxylation calculated.

	Decarboxylation (%) in		
Compound	5 min.	10 min.	30 min.
Pinonic acid	54	59	60
2-Hydroxy-2 : 4-dimethyl*cyclo*hexylacetic lactone	—	16	39
β-n-Butyl-*γγ*-dimethyl-*γ*-butyrolactone	—	1	5

2-Hydroxy-2 : 4-dimethyl*cyclo*hexylacetic lactone (3·25 g.), in solution in phosphoric acid (13 ml.), was heated for 3 hr. under reflux at 160°; an oil separated. The mixture was cooled, then diluted with water, and the oil extracted with ether; repeated fractionation, and drying with sodium, yielded a hydrocarbon, probably 1 : 2 : 4-*trimethyl*cyclo*hexene* (0·25 g.), b. p. 144—145°, n_D^{25} 1·4430 (Found: C, 86·75; H, 13·55. C_9H_{16} requires C, 87·0; H, 13·0%).

2 : 4-Dimethylphenylacetic acid (1·00 g.) was heated with phosphoric acid (10 ml.) for 1 hr. at 160—170°; it (0·95 g.) was recovered, having m. p. 104—105°.

2-Hydroxy-2 : 4-dimethyl*cyclo*hexylacetic lactone and β-*n*-butyl-*γγ*-dimethyl-*γ*-butyrolactone differ notably in their rates of hydrolysis: for complete hydrolysis the former lactone required 2 hours' boiling under reflux with ethanolic 0·5N-potassium hydroxide, whereas the latter was completely hydrolysed in 30 min. at room temperature with this reagent.

The olefins used for determination of hydrogenation rates were distilled from sodium. *cyclo*Hexene had b. p. 81·5—82°, n_D^{25} 1·4440; 1-methyl*cyclo*hexene, prepared by dehydration of a mixture of *cis*- and *trans*-2-methyl*cyclo*hexanol with phosphoric acid, had b. p. 109—109·5°, n_D^{20} 1·4484, n_D^{25} 1·4458; 1 : 2-dimethyl*cyclo*hexene, prepared by slow distillation of a mixture of *cis*- and *trans*-1 : 2-dimethyl*cyclo*hexanol with iodine, had b. p. 136·5—137°, n_D^{25} 1·4574.

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[5] Criegee and Lohaus, *Chem. Ber.*, 1953, **86**, 1; Criegee, *Annalen*, 1953, **583**, 1.