

316. 1- Δ^3 -Carene-5 : 6-epoxide, a Constituent of the Oil from
Zieria Smithii.

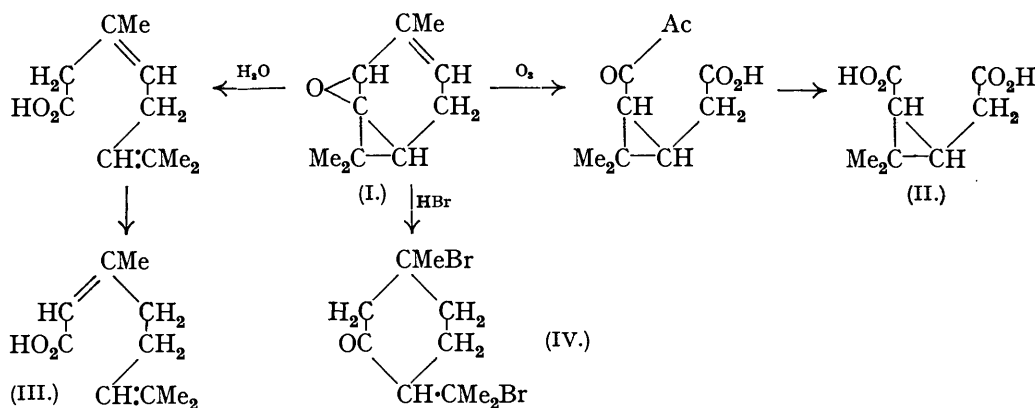
By A. R. PENFOLD, G. R. RAMAGE, and J. L. SIMONSEN.

A constituent of the essential oil from *Zieria Smithii* is shown to be a derivative of Δ^3 -carene, namely, 1- Δ^3 -carene-5 : 6-epoxide (I). It gives *cis*-homocaronic acid (II) on ozonolysis, and geranic acid (III) on digestion with alkali. Hydrogen bromide causes ring fission with the formation of dl-1 : 8-dibromo-p-menthan-3-one (IV), from which by the action of sodium acetate $\Delta^1:4^{(8)}$ -p-menthadien-3-one (X) can be prepared. The epoxide isomerises when heated to 165° to give a mixture of ketones.

ALTHOUGH it is now over forty years since Baeyer (*Ber.*, 1894, **27**, 1919) prepared carone by the action of alkali on dihydrocarvone hydrobromide, only two natural products having this dicyclic structure, Δ^3 - and Δ^4 -carenes, have so far been described. We now record the results of an examination of a third natural carane derivative. During a study of the constituents of the essential oil from *Zieria Smithii*, details of which will be published

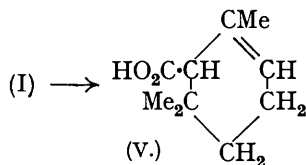
later, a fraction was obtained, b. p. 88—90°/17 mm., which exhibited somewhat unusual properties. On digestion with alkali or if heated with water at 150°, it gave geranic acid in a practically quantitative yield, yet a careful search failed to reveal the presence of an alcohol and analysis showed it to have approximately the composition $C_{10}H_{14}O$. A detailed study of the purified oil has now shown that it is almost certainly 1- Δ^3 -carene-5 : 6-epoxide (I).

The oil, as separated by fractional distillation, contains in a very small amount, linalool and an alcohol, $C_{10}H_{14}O$, characterised by the preparation of a 3 : 5-dinitrobenzoate, m. p. 119°. After the removal of these impurities the oil gave figures on analysis in close accord with those required for $C_{10}H_{14}O$ and titration with perphthalic acid indicated the presence of one ethylenic linkage. The oil gave on ozonolysis *cis*-homocaronic acid (II) in excellent yield, together with a small quantity of what was probably the impure *trans*-acid; evidence of the presence of acetone and formaldehyde in small amount was obtained also. The formation of homocaronic acid on ozonolysis and of geranic acid (III) by the action of alkali can be most satisfactorily explained if the parent substance is represented by (I), the reactions proceeding in accordance with the scheme set out below :



The interaction of the oil with the halogen acids and with cold ethyl-alcoholic potassium hydroxide afforded evidence in support of this structure. With hydrogen chloride a dihydrochloride, decomp. 72°, was obtained, and hydrogen bromide yielded a dihydrobromide, decomp. 74°. These are almost certainly *dl*-1 : 8-dichloro- and *dl*-1 : 8-dibromo-*p*-menthan-3-one (IV) respectively, since the latter yields on catalytic hydrogenation *dl*-menthone. The formation of these dihalides is comparable with the conversion of Δ^3 - and Δ^4 -carenes into dipentene dihydrochloride under similar conditions, the ring fission in this case being accompanied by the isomerisation of the epoxide to a ketone. Such isomerisation is common, two recent examples being the conversion of the epoxide, auraptene, into the ketone, *isoauraptene* (Böhme and Pietsel, *Ber.*, 1939, **72**, 778) and of 2- β -phenylethylcyclohexeneoxide into 2- β -phenylethylcyclohexanone (Grewé, *ibid.*, p. 1316). The very facile isomerisation of the epoxide to carbonyl derivatives is described further on p. 1498.

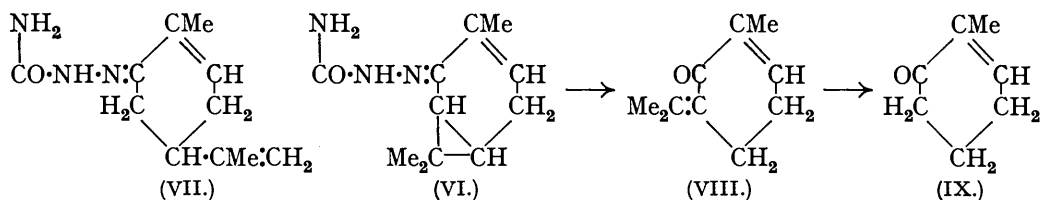
Reference was made above to the fact that the epoxide gave on digestion with alkali geranic acid, but it was found that with cold ethyl-alcoholic potassium hydroxide solution



the reaction proceeded in a different manner, yielding a crystalline acidic product which was optically active. The acid was, however, a mixture, from which by fractional crystallisation, a homogeneous acid, $C_{10}H_{16}O_2$, m. p. 83—84°, was obtained. We think that there can be little doubt that this acid is one of the optically active modifications of Δ^2 -cyclogeranic acid (V), the *dl*-form of which was prepared by Tiemann (*Ber.*, 1900, **33**, 3712). In agreement with this was the observation that catalytic hydrogenation showed the presence of one ethylenic linkage. It is proposed to resolve *dl*- Δ^2 -cyclogeranic acid to confirm the above suggestion.

Although the evidence outlined above is in full accord with the suggested structure (I), direct evidence of the presence of the oxide ring by conversion into the glycol could not be obtained owing to the facile formation of geranic acid. Nor was it possible by catalytic hydrogenation to confirm the presence of only one ethylenic linkage, since this was obviously again accompanied by ring fission, as commonly occurs with dicyclic compounds containing the cyclopropane ring (Iyer and Simonsen, J., 1926, 2049; Short and Read, J., 1938, 2016; this vol., p. 1040).

Furthermore, certain observations did not eliminate the possibility that the oxide was in reality a dicyclic ketone with a somewhat inert carbonyl group, although all previous attempts to prepare carenones have failed (Baeyer, *Ber.*, 1894, **27**, 810; 1898, **31**, 2067; Clarke and Lapworth, J., 1910, **97**, 15). If the oxide was kept in the cold with semicarbazide acetate in aqueous methyl-alcoholic solution for some days, a semicarbazone, in a yield of approximately 50%, was obtained which analysis showed to be derived from a ketone $C_{10}H_{14}O$. This semicarbazone, which was optically active, was not homogeneous, since, although fractional crystallisation did not cause any very appreciable change in the melting point, the various fractions differed considerably in rotatory power. It appears not improbable that the semicarbazone may have the structure (VI) and that the varying rotatory power of the different fractions is due *in part* to the fact that the semicarbazone is not stereochemically homogeneous. This would be anticipated, since isomerisation of the epoxide involves one of the asymmetric centres. It may well be that a carenone semicarbazone would be more stable than a carenone, since enolisation, which would presumably promote instability, is not possible. An attempt to confirm the suggested structure by catalytic hydrogenation to carenone semicarbazone failed, since two molecules of hydrogen were absorbed with the formation of a mixture of semicarbazones. If, however,



semicarbazone formation has been accompanied by ring fission, then, on the assumption that no molecular rearrangement has occurred, the semicarbazone must be derived from a menthadiene having an *isopropenyl* side chain as in (VII). Unfortunately it was also not found possible to determine the structure of this semicarbazone by hydrolysis to the parent ketone.

Hydrolysis with oxalic or phthalic acid gave in poor yield a mixture of ketones, which were optically active. One of these ketones, b. p. $87^\circ/15$ mm., had the formula $C_7H_{10}O$, being characterised by the preparation of a 2 : 4-dinitrophenylhydrazone, m. p. $176-177^\circ$. If (VI) correctly represented the parent semicarbazone, this ketone might well have been (IX), formed from the intermediate *m*-menthadiene (VIII) by the loss of acetone as occurs in the formation of 3-methylcyclohexanone from pulegone oxime, the observed rotatory power being due to some impurity. It was found, however, that the 2 : 4-dinitrophenylhydrazone, m. p. $176-177^\circ$, was not identical with the corresponding derivative prepared from 2-methyl- Δ^2 -cyclohexenone or with that derived from the isomeric 3-methyl- Δ^2 -cyclohexenone. It is not at present possible to suggest a structure for this simple ketone.

A further product of the hydrolysis of the semicarbazone was a ketone, b. p. $127-130^\circ/13$ mm., which consisted, in part at any rate, of $\Delta^6:4^{(8)}$ -*p*-menthadien-3-one, since it gave on ozonolysis the butene acid, m. p. $121-122^\circ$ (see p. 1499). The presence of this ketone amongst the hydrolysis products of the semicarbazone proves, as was indicated above, that the lack of homogeneity of the semicarbazone is not solely stereochemical.

Somewhat unexpected results were obtained when the epoxide itself, or the semicarbazone referred to above, was treated with an alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate. Interaction was slow, the main products being two highly crystalline 2 : 4-dinitrophenylhydrazones, one crystallising in garnet prisms, m. p. $192-193^\circ$, and the other

in orange-yellow needles, m. p. 165—166°. Analysis showed that hydrazone formation had been accompanied by the addition of ethyl alcohol, the two hydrazones having the composition $C_{18}H_{24}O_5N_4$. It is not improbable that this addition is due to fission of the cyclopropane ring and that the two hydrazones are derived respectively from the *m*- and the *p*-menthenone. Their formation, not only from the epoxide, but also from the semicarbazone may be regarded as offering indirect support to the suggestion (p. 1498) that the latter is derived, in part at any rate, from an unsaturated dicyclic ketone. In aqueous solution hydrazone formation is accompanied by hydration, a yellow 2 : 4-dinitrophenylhydrazone, m. p. 145—147°, being obtained.

Although the low boiling point of the oil appeared to preclude the possibility that the epoxide was in reality an inert ketone, a determination of the absorption spectrum seemed desirable, since this would establish conclusively the presence or absence of the chromophore system $>C:\dot{C}:C:O$. Dr A. E. Gillam kindly undertook this and he reports that the oil, without purification, has λ_{max} . at 2900 Å with a molecular extinction coefficient at 1800, and the purified oil has the maximum at 2910 with a molecular extinction coefficient at 1340. These results definitely exclude the possibility of a carbonyl group with an $\alpha\beta$ -ethylenic linkage, but the band at 2900 is puzzling; the presence of an isolated carbonyl group cannot be excluded, although a trace of an absorbing impurity containing three conjugated linkages (as in β -ionone) might afford an explanation. That this absorption is due to the presence of traces of impurities would appear to be supported by the following observation. Although, as mentioned above, the oil itself reacts extremely slowly with Brady's reagent, it was noticed that the residue in the distilling flask after a distillation always reacted immediately with this reagent. When the epoxide was distilled at the ordinary pressure or heated for a short time at 160—170°, it developed a deep yellow colour; the oil formed a very sparingly soluble, purple 2 : 4-dinitrophenylhydrazone, m. p. 218—220°. With semicarbazide acetate the ketone gave a somewhat complex mixture of semicarbazones (see p. 1503), so it has not yet been obtained pure. It is hoped later to investigate its structure.

During a study of the reactions of *dl*-1 : 8-dibromo-*p*-menthan-3-one it was observed that on warming with sodium acetate in acetic acid solution it gave a ketone, $C_{10}H_{14}O$, b. p. 120—122°/14 mm., characterised by the preparation of two 2 : 4-dinitrophenylhydrazones, m. p. 187° and 125—127°. After ozonolysis the ketone gave as the main products of the degradation acetone, lævulic acid, and a crystalline acid, $C_7H_{10}O_4$, m. p. 121—122°. The first two substances are obviously degradation products of $\Delta^1:4^{(8)}$ -*p*-menthadien-3-one (X), a ketone the formation of which might be expected by the removal of hydrogen bromide



from the dibromide. The acid, m. p. 121—122°, was unstable to potassium permanganate in alkaline solution. On reduction with sodium in ethyl-alcoholic solution it gave β -methyladipic acid, and on ozonolysis in acetic acid solution lævulic acid was obtained. This acid must therefore be 2-methyl- Δ^1 -butene-1 : 4-dicarboxylic acid (XI).* Although the melting point could not be raised by crystallisation, the acid did not appear to be homogeneous and it was possibly a mixture of *cis*- and *trans*-forms. Evaporation of an aqueous solution of the ammonium salt gave a salt which was sparingly soluble in alcohol. From this salt an acid, m. p. 140—141°, was obtained. It is possible that this acid is 2-methyl- Δ^2 -butene-1 : 4-dicarboxylic acid, which melts at this temperature (Pauly and Will, *Annalen*, 1918, 416, 14). Although the structure of the menthadienone is thus rigidly proved, it seems somewhat remarkable that it should be capable of existence, since it might

* The resistance to oxidation by ozone of ketones containing an $\alpha\beta$ -ethylenic linkage has been observed by Eccott and Linstead (J., 1930, 914).

be expected that it would isomerise very readily to thymol. No evidence of the presence of a phenol was observed during the purification of the ketone, but from amongst the oxidation products a small quantity of an oil having phenolic properties was isolated. It is not unlikely that this was homocatechol, which, in its diketonic form, would be an intermediate stage in the degradation to the butene acid.

EXPERIMENTAL.

The crude epoxide, as isolated by fractional distillation, had b. p. 88—90°/17 mm., d_{25}^{25} 0.9453, n_D^{25} 1.4769, α_D ca. —52° (Found: C, 78.8; H, 9.5%). To remove traces of alcohols a cold solution of the oil (10 c.c.) in pyridine (30 c.c.) was treated with 3 : 5-dinitrobenzoyl chloride (2 g.), kept overnight, and poured on ice and dilute sulphuric acid. The oil was extracted with ether, the extract washed successively with dilute sulphuric acid, aqueous sodium carbonate, and water and dried, and the solvent removed. The reddish-brown residual oil was distilled in steam, a viscid oil (*A*) remaining in the flask. The oil volatile in steam was recovered by ether extraction in the usual manner. 1- Δ^3 -Carene-5 : 6-epoxide, which was an extremely pleasant smelling, colourless, mobile oil, had b. p. 83—85°/14 mm., d_{25}^{25} 0.9454, n_D^{25} 1.4729, $[\alpha]_{5461}^{25}$ —88°, $[R_L]_D$ 44.63 (calc., 43.63) (Found: C, 79.6; H, 9.5. $C_{10}H_{14}O$ requires C, 80.0; H, 9.3%). With the Zerewitinoff reagent it reacted apparently abnormally, showing the presence of two active hydrogen atoms. Hydrogenation of the oil (2.05 g.) in ethyl alcohol with a palladium-norit catalyst (2 g.; 10%) was slow, 530 c.c. of hydrogen being absorbed (calc. for $2H_2$, 640 c.c.).

The red gum (*A*), which was not volatile in steam, was dissolved in ether, and the extract dried and evaporated, giving a gum (1.5 g.), which partly crystallised on trituration with methyl alcohol. The solid 3 : 5-dinitrobenzoate was collected; it crystallised from methyl alcohol in colourless leaflets, m. p. 119° (Found: C, 59.1; H, 5.4. $C_{17}H_{18}O_6N_2$ requires C, 59.0; H, 5.2%).

The presence of a small percentage of linalool in the oil was established by heating a fraction of the oil (1.1 g.), b. p. 95—96°/20 mm., which had been recovered from the treatment of the crude epoxide with semicarbazide acetate (see p. 1503), with xenylcarbimide at 100° for 1 hour. The urethane, isolated in the usual manner, gave a crystalline solid (0.1 g.), which, after recrystallisation from ligroin (b. p. 60—80°), had m. p. 83—85°, both alone and in admixture with *linalool xenylurethane*, which is very suitable for the characterisation of this alcohol (Found: N, 4.4. $C_{23}H_{27}O_2N$ requires N, 4.0%).

Ozonolysis of 1- Δ^3 -Carene-5 : 6-epoxide.—The pure epoxide (5 c.c.) in methyl acetate (50 c.c.) was ozonised at 0°, the issuing gases being passed through water (*A*). After completion of the ozonolysis the solvent was removed under diminished pressure, and the ozonide decomposed by heating with water (10 c.c.) on the water-bath under conditions permitting the trapping of any readily volatile carbonyl derivative in an aqueous solution of *p*-nitrophenylhydrazine acetate (*B*). The aqueous solution (*A*) contained a trace of formaldehyde (warming with dimedone). From (*B*) a small quantity of a yellow *p*-nitrophenylhydrazone separated, which crystallised from alcohol in needles, m. p. 147°, both alone and in admixture with acetone-*p*-nitrophenylhydrazone.

The clear aqueous solution from two such experiments was evaporated on the water-bath and the residual gum, after drying in a vacuum over sulphuric acid, was triturated with benzene, the solid (*C*) (0.2 g.) which separated being collected. After removal of the benzene the liquid acid was dissolved in aqueous sodium carbonate and oxidised with aqueous potassium permanganate at 0° (mechanical stirring) until the colour was permanent (2.5%; 150 c.c.). The alkaline solution, after filtration, was concentrated, acidified, and repeatedly extracted with ether. Evaporation of the ether from the dried extract gave a partly crystalline acid (9 g.). The acid was esterified with methyl alcohol (50 c.c.) and sulphuric acid (5 c.c.), and the resulting ester, isolated in the usual manner, distilled under diminished pressure, yielding as the main fraction an oil (5.5 g.), b. p. 122—137°/16 mm., together with a considerable high-boiling residue. Hydrolysis of the methyl ester with methyl-alcoholic potassium hydroxide solution gave a crystalline acid. After trituration with benzene the acid was collected and crystallised from hot water, from which it separated in rosettes of needles, m. p. 135—136° after sintering at 120°, both alone and in admixture with a synthetic specimen of *cis*-homocaronic acid (Found: C, 55.6; H, 6.9. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 7.0%). The identity of the two acids was confirmed by the preparation of the *di-p*-phenylphenacyl esters, which crystallised from acetone-alcohol in soft prisms, m. p. 147—149°, both alone and in admixture (Found: C, 76.9; H, 5.8. $C_{36}H_{32}O_8$ requires C, 77.1; H, 5.7%).

The acid (*C*) (above) crystallised from water in fine needles, m. p. 171—172°, and consisted

probably of impure *trans*-caronic acid, m. p. 190° (Found: C, 55.7; H, 6.9; *M*, 175. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 7.0%; *M*, 172).

Conversion of 1- Δ^3 -Carene-5:6-epoxide into Geranic Acid.—(i) *With alkali.* The epoxide (5 c.c.) was digested with aqueous potassium hydroxide (100 c.c.; KOH 2.8 g.) for 24 hours. After distillation in steam to remove a small quantity of volatile oil, the alkaline solution was acidified and extracted with ether, and the extract dried and evaporated. Two distinct preparations gave geranic acid, (i) b. p. 151—154°/23 mm., d_{15}^{15} 0.9610, n_D^{20} 1.4758, $[\alpha]_D -1^\circ$ (Found: C, 71.5; H, 9.9. Calc. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5%); (ii) b. p. 153—156°/23 mm., d_{15}^{15} 0.9636, n_D^{20} 1.4754, $[\alpha]_D -1^\circ$ (Found: C, 70.9; H, 9.7%). On ozonolysis the acid gave acetone and lævulic acid as the main products of the oxidation. On hydrogenation in alcohol with a palladium–norit catalyst the acids (1 g.) absorbed respectively 259 c.c. and 261 c.c. of hydrogen (calc., 267 c.c.). The reduced acid was identified as *dl*-tetrahydrogeranic acid by conversion into the amide, m. p. 103—104°, and the *p*-toluidide, m. p. 81°, both alone and in admixture with authentic specimens. From neither specimen of geranic acid could a crystalline *p*-phenylphenacyl ester be prepared. (ii) *With water.* The epoxide (4.7 g.) was heated with water (10 c.c.) at 150° for 3 hours. A somewhat impure geranic acid (3 g.), b. p. 148—150°/12 mm., n_D^{15} 1.4787, was obtained; the acid (2.5 g.) absorbed 725 c.c. of hydrogen (calc., 670 c.c.). A neutral oil (1.3 g.) was obtained also, from which a fraction, b. p. 90—120°/15 mm., was separated which yielded a 2:4-dinitrophenylhydrazone, m. p. 218°, identical with that described on p. 1503.

Conversion of 1- Δ^3 -Carene-5:6-epoxide into cycloGeranic Acid.—The epoxide (30 c.c.) was mixed with ethyl-alcoholic potassium hydroxide solution (500 c.c.; KOH 15 g.) and kept at room temperature (24°) for 14 days. After the addition of water (3 l.) the neutral oil (15.5 c.c.) was removed by ether, and the alkaline solution concentrated to 250 c.c. On acidification a viscid oil separated, which solidified in the ice-box after 1 hour. The solid was collected and drained on porous porcelain, and the residue (14.7 g.) repeatedly crystallised from ligroin (b. p. 30—40°). Ultimately a homogeneous acid crystallising in needles, m. p. 83°, was obtained in very small yield (Found: C, 71.6; H, 9.5. Calc. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5%). On catalytic hydrogenation it absorbed hydrogen corresponding to one ethylenic linkage, but the hydrogenated acid was not homogeneous.

dl-1:8-Dichloro-p-menthan-3-one.—The epoxide (1 c.c.) in acetic acid (3 c.c.) was saturated with hydrogen chloride at 0°. After being kept overnight, the deep red solution was poured on ice, and the solid *dichloride* collected, drained on porous porcelain, and recrystallised from methyl alcohol, from which it separated in leaflets, decomp. 72° (Found: C, 54.2; H, 7.2; Cl, 31.7. $C_{10}H_{16}OCl_2$ requires C, 53.8; H, 7.2; Cl, 31.8%). The chloride was optically inactive and decomposed on keeping.

dl-1:8-Dibromo-p-menthan-3-one.—The epoxide (0.8 g.) was dissolved in acetic–hydrobromic acid (50% w. v.; 5 c.c.) cooled in salt–ice. The red solution, on keeping overnight in the ice-box, set to a magma of crystals. After the addition of ice the solid was collected and crystallised from methyl alcohol, the *dibromide* separating in leaflets, decomp. 74° (Found: Br, 51.4. $C_{10}H_{16}OBr_2$ requires Br, 51.3%). It was extremely unstable.

The dibromide (from the epoxide, 10 c.c.) in alcohol (100 c.c.) and palladium–norit (3 g.; 10%) was shaken with hydrogen. Hydrogenation was slow at atmospheric pressure and room temperature, but was complete in 10 hours at 3 atms. and 60°. The resulting ketone (4.5 g.), isolated in the usual manner, had b. p. 97°/23 mm. (Found: C, 78.2; H, 12.1. Calc. for $C_{10}H_{18}O$: C, 77.9; H, 11.7%). It was identified as *dl*-menthone by the preparation of the oxime, m. p. 80—81°, and the 2:4-dinitrophenylhydrazone, which was dimorphic, crystallising from alcohol either in yellow leaflets, seen under the microscope to be small plates, or in needles, m. p. 141—142°, both alone or in admixture with an authentic specimen kindly prepared for us by Dr. A. G. Short in Professor Read's laboratory (Found: C, 57.6; H, 6.7. $C_{16}H_{22}O_4N_4$ requires C, 57.5; H, 6.6%).

Action of Sodium Acetate on dl-1:8-Dibromo-p-menthan-3-one: $\Delta^{1:4(8)}$ -*p-Menthadien-3-one.*—A solution of the dibromide (20 g.) in acetic acid (100 c.c.) was heated with anhydrous sodium acetate (20 g.) at 140° for 2 hours. The cooled solution was added to aqueous sodium carbonate (Na_2CO_3 , 80 g.), the oil extracted with ether, the ether evaporated, and the residual oil, which contained bromine, digested with methyl-alcoholic potassium hydroxide solution (KOH, 3 g.) for 1 hour. The resulting ketone (6 g.), isolated by distillation in steam and extraction with ether, had b. p. 120—130°/16 mm., and on redistillation had b. p. 120—122°/14 mm., d_{25}^{25} 0.9683, n_D^{25} 1.5190, $[\alpha]_{5461} -0.1^\circ$, $[R_L]_D$ 46.66 (calc., 45.26) (Found: C, 79.5; H, 9.3. $C_{10}H_{14}O$ requires C, 80.0; H, 9.3%). The ketone was a colourless mobile oil, becoming yellow on keeping; its odour was somewhat unpleasant but on dilution with alcohol was reminiscent of

peppermint. The 2 : 4-dinitrophenylhydrazone separated as a somewhat gummy solid, becoming crystalline on scratching; the α -form crystallised from ethyl acetate-alcohol in red feathery needles, m. p. 187° (Found : C, 58.7; H, 5.4. $C_{16}H_{18}O_4N_4$ requires C, 58.2; H, 5.5%). The more soluble β -form crystallised from methyl alcohol in red leaflets, seen under the microscope to be long lathes, m. p. 125—127° (Found : C, 58.2; H, 5.7%). The ketone reacted rapidly with hydrobromic-acetic acid (w. v. 50%), yielding *dl*-1 : 8-dibromo-*p*-menthan-3-one, decomp. 74° both alone and in admixture.

*Ozonolysis of $\Delta^{1,4(8)}$ -*p*-Menthadien-3-one.*—The ketone (6.5 g.) in methyl acetate (50 c.c.) was ozonised at 0° until ozone passed freely through the solution. After removal of the solvent under diminished pressure, water (10 c.c.) was added, and the ozonide decomposed by passing steam through the mixture. The steam distillate was extracted once with ether to remove some oil in suspension, and a portion of the aqueous solution was mixed with aqueous 2 : 4-dinitrophenylhydrazine sulphate, a yellow hydrazone being deposited. This, after crystallisation from ligroin (b. p. 60—80°), had m. p. 123—125°, raised to 125—126° in admixture with acetone-2 : 4-dinitrophenylhydrazone. The main portion of the steam distillate was saturated with ammonium sulphate and repeatedly extracted with ether. The combined ethereal extracts, including the first (see above), left on evaporation a small quantity of an oil, from which a *semicarbazone* was prepared. This crystallised from methyl alcohol in leaflets, decomp. 232—233°; it was not identified (Found : C, 52.3, 52.8; H, 4.4, 4.6; N, 20.3. $C_9H_9O_3N_3$ requires C, 52.2; H, 4.3; N, 20.3%).

The aqueous residue from the steam distillation was evaporated, finally in a vacuum over sulphuric acid, and the brown semicrystalline residue triturated with chloroform, which left undissolved a solid (2.2 g.). The chloroform was evaporated, the brown gum dissolved in ether, and the ethereal solution washed with aqueous sodium carbonate (*A*), dried, and evaporated. The residual oil (0.2 g.), which was soluble in aqueous sodium hydroxide, yielding a solution which rapidly oxidised, gave an intense green colour with ferric chloride. It did not crystallise and no derivatives could be prepared.

The sodium carbonate solution (*A*) was acidified; the acid (3.2 g.) recovered by ether was a brown oil, which partly crystallised on trituration with chloroform. After removal of the solid (0.4 g.) the filtrate was evaporated, the residue dissolved in cold water and filtered from a little tar, and the filtrate treated with aqueous 2 : 4-dinitrophenylhydrazine sulphate. The 2 : 4-dinitrophenylhydrazone, after crystallisation from chloroform-methyl alcohol, had m. p. 205—206°, both alone and in admixture with lævulic acid 2 : 4-dinitrophenylhydrazone (Found : N, 18.9. Calc. for $C_{11}H_{12}O_6N_4$: N, 18.9%).

The solid acid (2.6 g.), m. p. *ca.* 110°, was repeatedly crystallised from benzene, from which it separated in nodules, m. p. 121—122° but not clearing till 125° (Found : C, 52.8; H, 6.3; *M*, 157. $C_7H_{10}O_4$ requires C, 53.2; H, 6.3%; *M*, 158). On ozonolysis in acetic acid solution the acid gave in quantitative yield lævulic acid, identified by the preparation of the 2 : 4-dinitrophenylhydrazone, m. p. 205—206° both alone and in admixture. On evaporation of an aqueous solution of the ammonium salt of the unsaturated acid a solid separated which was sparingly soluble in alcohol. This was collected, the salt decomposed with dilute sulphuric acid, and the acid recovered by ether. The *acid* now crystallised from water or benzene-acetone in rosettes of small prisms, m. p. 140—141° (Found : C, 53.6; H, 6.3%). This acid (0.2 g.) was reduced with sodium (4 g.) in alcohol; the reduced acid, isolated by ether in the usual manner, had m. p. 88—90°, raised to 92—93° by crystallisation from benzene; in admixture with β -methyladipic acid, m. p. 93—94° (Found : C, 52.8; H, 7.3. Calc. for $C_7H_{12}O_4$: C, 52.5; H, 7.5%). The identity was confirmed by the preparation of the *di-p-phenylphenacyl* ester from both acids. This crystallised from ethyl acetate in needles, m. p. 124—125° (Found : C, 76.0; H, 5.9. $C_{35}H_{32}O_8$ requires C, 76.6; H, 5.8%).

The acid regenerated from the soluble ammonium salt from which the sparingly soluble salt of the acid, m. p. 140—141°, had been separated, was a somewhat mobile oil containing only traces of a crystalline solid. Catalytic hydrogenation and titration showed it to contain approximately 60% of a lactone, presumably the lactone of β -hydroxy- β -methylbutane- $\alpha\delta$ -dicarboxylic acid.

Isomerisation of 1- Δ^3 -Carene-5 : 6-epoxide.—The epoxide (3 g.) was kept in a preheated bath at 160—165° for 10 minutes and the product from two such experiments, which was deep yellow, was dissolved in ether, a trace of acid removed by aqueous sodium hydroxide, and the oil remaining after removal of the ether from the dried extract distilled at 13 mm. Two fractions, (i) b. p. —95° (0.8 g.) and (ii) 95—140° (3 g.), were obtained. Fraction (ii) was a yellow oil which became sage-green on exposure to air. With Brady's reagent it reacted immediately to give a

deep red solid, m. p. 203° (0.5 g. from 0.5 g. of oil). The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate or cyclohexyl acetate in purple needles, m. p. 218—220° (Found : C, 58.4; H, 5.4. $C_{16}H_{18}O_4N_4$ requires C, 58.2; H, 5.4%). Evidence of the presence of a second dinitrophenylhydrazone was obtained, but this could not be purified. The semicarbazone, which formed rapidly when the ketone was treated with semicarbazide acetate in alcoholic solution, had m. p. ca. 150°. By fractional crystallisation from methyl and ethyl alcohols two apparently homogeneous semicarbazones were obtained. The more sparingly soluble α -semicarbazone (0.2 g. from 3 g. of semicarbazone) crystallised from acetic acid in prisms, decomp. 221—222° after sintering at 212° (Found : C, 64.4; H, 8.5. $C_{11}H_{17}ON_3$ requires C, 63.8; H, 8.2%). The β -semicarbazone crystallised from methyl alcohol, in which it was very readily soluble, in needles, decomp. 183—185° (Found : C, 64.1; H, 8.5%). The bulk of the semicarbazone was an inseparable mixture, m. p. 150—170°, which became reddish-brown on exposure to air. All the fractions of the semicarbazone were strongly phototropic.

Action of Aqueous 2 : 4-Dinitrophenylhydrazine Sulphate on the Epoxide.—The epoxide (0.7 g.) was mixed with aqueous 2 : 4-dinitrophenylhydrazine sulphate (60 c.c.; 6.7 c.c. = 1 g. of the hydrazine) and kept in the cold with occasional shaking for 5 days. The supernatant liquid was decanted from the gummy solid, and the latter triturated with ligroin (b. p. 40—60°). The gum was dissolved in hot alcohol, and the alcohol decanted from the oil which separated on cooling and kept for some days, a yellow crystalline solid being slowly deposited. After crystallisation first from methyl alcohol and finally from ligroin (b. p. 60—80°) the 2 : 4-dinitrophenylhydrazone of the hydroxy-ketone was obtained in light yellow needles, m. p. 145—147° (Found : C, 55.2; H, 5.5. $C_{16}H_{20}O_5N_4$ requires C, 55.2; H, 5.7%).

Action of Alcoholic 2 : 4-Dinitrophenylhydrazine Sulphate on the Epoxide.—The epoxide (0.9 g.) was mixed with an alcoholic solution (50 c.c.) of 2 : 4-dinitrophenylhydrazine (1.5 g.) and sulphuric acid (3 c.c.), the solution, which gradually became red, being kept for 8 days. The red solid (A) (0.8 g.), m. p. 140—148°, which had separated was collected; the filtrate, after the addition of a little dilute sulphuric acid, deposited yellow needles (B), m. p. 145—147°. Crystallisation of (A) from ethyl acetate gave a sparingly soluble α -2 : 4-dinitrophenylhydrazone in well-formed garnet prisms, m. p. 192—193° (Found : C, 57.7; H, 6.3; N, 15.2. $C_{18}H_{24}O_5N_4$ requires C, 57.4; H, 6.4; N, 14.9%). From the ethyl acetate mother-liquor a β -2 : 4-dinitrophenylhydrazone, orange-coloured prismatic needles, m. p. 165—166° after sintering at 163°, was obtained by prolonged fractional crystallisation first from alcohol and finally from ligroin (b. p. 60—80°) (Found : C, 57.5; H, 6.1; N, 15.2%). The 2 : 4-dinitrophenylhydrazone (B) was not obtained quite pure, but it appeared to be identical with that derived from the hydroxy-ketone referred to above.

Action of Semicarbazide Acetate on the Epoxide.—The epoxide (38 g.) in methyl alcohol (200 c.c.) was kept with aqueous semicarbazide acetate for 5 days, and for a further 3 days in the ice-box after dilution with water; the precipitated gummy solid was collected and washed with ligroin to remove oil (16 g.). The semicarbazone (21.7 g.), after crystallisation from methyl alcohol, had m. p. 192°, $[\alpha]_{5461} -95^\circ$ in pyridine (c, 4.55) (Found : C, 63.8; H, 8.0. $C_{11}H_{17}ON_3$ requires C, 63.8; H, 8.2%). Repeated fractional crystallisation gave one fraction in feathery needles, m. p. 192—194°, $[\alpha]_{5461} -70^\circ$ in pyridine (c, 3.46) (Found : C, 64.0; H, 8.2%), and another in well-formed prisms, m. p. 199° (Found : C, 64.2; H, 8.2%).

The semicarbazone (2 g.) was hydrogenated in ethyl-alcoholic solution, a palladium-norit catalyst being used; absorption of hydrogen corresponding to two molecules was complete in 10 hours. The product, m. p. 183—187°, was a mixture, from which by crystallisation from alcohol an apparently homogeneous semicarbazone, m. p. 212°, separating in prisms, was obtained (Found : C, 62.8; H, 10.1. $C_{11}H_{21}ON_3$ requires C, 62.6; H, 9.9%).

When the semicarbazone (0.5 g.), m. p. 192°, was kept in an alcoholic solution (20 c.c.) of 2 : 4-dinitrophenylhydrazine (0.7 g.) and sulphuric acid (1.4 c.c.) for 10 days, a red crystalline 2 : 4-dinitrophenylhydrazone (0.1 g.) separated, and after dilution with dilute sulphuric acid a further quantity (0.65 g.) was deposited in a week. By crystallisation the α -2 : 4-dinitrophenylhydrazone, m. p. 192° (Found : C, 57.7; H, 6.1%), and β -hydrazone, m. p. 165—166° (Found : C, 57.7; H, 6.4%), identical with those described above were obtained.

Hydrolysis of the Semicarbazone.—The semicarbazone (15 g.) was distilled in steam in the presence of phthalic acid and the volatile oil, after isolation in the usual manner, was fractionated at 15 mm., yielding two fractions, (i) b. p. —120° (3 g.) and (ii) b. p. 120—135° (4 g.). Redistillation gave two main fractions, (a) 87°/15 mm., $d_{20}^{25} 0.9385$, $n_D^{24} 1.4712$, $[\alpha]_{5461} + 26.3^\circ$ (Found : C, 77.8; H, 9.7. $C_7H_{10}O$ requires C, 76.4; H, 9.1%), and (b) 127—130°/13 mm., $d_{20}^{25} 0.9851$, $n_D^{24} 1.5029$, $[\alpha]_{5461} + 6.52^\circ$ (Found : C, 75.2; H, 9.2%). From fraction (a) a 2 : 4-dinitrophenyl-

hydrazone was prepared which crystallised from ethyl acetate in long, brick-red needles, m. p. 176—177° (Found: C, 53·6; H, 4·7. $C_{13}H_{14}O_4N_4$ requires C, 53·8; H, 4·8%). Direct comparison showed this 2:4-dinitrophenylhydrazone not to be identical with the corresponding *derivative* of 2-methyl- Δ^2 -cyclohexenone, which formed red prisms from ethyl acetate, m. p. 202—203° (Found: N, 19·0. $C_{13}H_{14}O_4N_4$ requires N, 19·3%), or with that of 3-methyl- Δ^2 -cyclohexenone, which formed red prismatic needles from ethyl acetate, m. p. 160° (Found: N, 19·5%).

From fraction (b) no crystalline derivatives could be prepared. The oil, however, contained a quantity of $\Delta^{1:4(8)}$ -*p*-menthadien-3-one (see p. 1501), since, on ozonolysis, it gave acetone together with the *butene* acid (p. 1502), which after crystallisation from benzene had m. p. 121—122° (Found: C, 52·8; H, 6·1. $C_7H_{10}O_4$ requires C, 53·2; H, 6·3%).

We are greatly indebted to Dr. A. E. Gillam of the University of Manchester for the determination of the absorption spectrum of the epoxide. We desire also to acknowledge grants from the Government Grants Committee of the Royal Society and Imperial Chemical Industries Limited.

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[Received, August 4th, 1939.]
