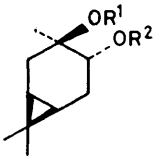
The Chemistry of Terpenes. Part 23.[1] Reaction of (+)-Carane-3β,4α-diol with Sulphuric Acid

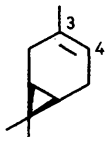
By **Wesley Cocker** * and **David H. Grayson**, Department of Chemistry, Trinity College, Dublin 2, Ireland

Reaction of (+)-car-3-ene with hydrogen peroxide in acetic acid and alkaline hydrolysis of the product gives (+)-carane-3β,4α-diol (1) and 1-acetyl-3,3-dimethylcyclohexa-1,4-diene (4). Lengthy treatment of (1) with hot, dilute sulphuric acid gives principally *p*-cymene (7) and (±)-carvenone (8). Shorter treatment of the diol (1) with acid gives (−)-2-*endo*-hydroxy-4-isopropyl-1-methyl-7-oxabicyclo[2.2.1]heptane (10), (−)-2-*exo*-hydroxy-2,6,6-trimethyl-7-oxabicyclo[3.2.1]octane (11), (−)-2-*exo*-hydroxy-1,6,6-trimethyl-7-oxabicyclo[3.2.1]octane (12), (−)-*p*-menth-4-ene-*trans*-1,2-diol (13), and (+)-*p*-menth-4(8)-ene-*trans*-1,2-diol (14).

In 1928, Pillay and Simonsen [2] prepared (+)-carane-3β,4α-diol (1) from (+)-car-3-ene (2) and investigated its



(1) $R^1 = R^2 = H$
(5) $R^1 = OAc$, $R^2 = H$
(6) $R^1 = Ac$, $R^2 = H$
(30) $R^1 = H$, $R^2 = CO \cdot C_6H_4 \cdot CO_2H(o)$



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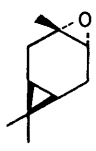

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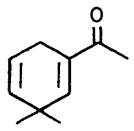

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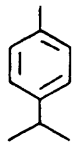

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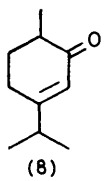

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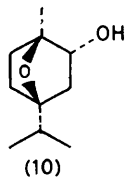

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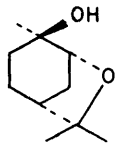

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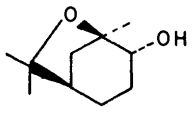

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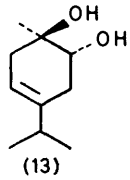

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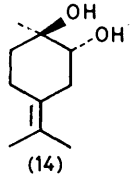
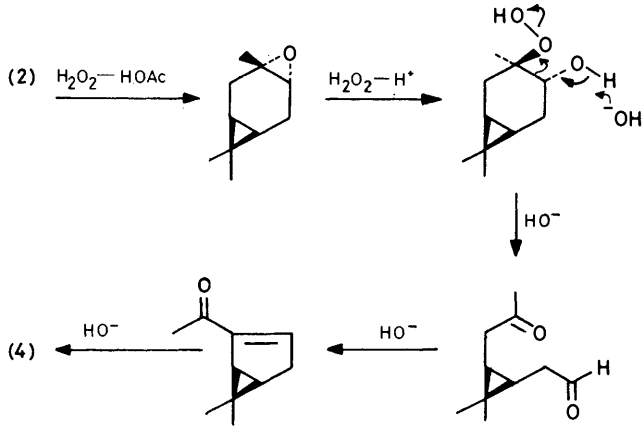


(14)

reaction with hot dilute sulphuric acid. They obtained a liquid, $C_{10}H_{16}O$, $[\alpha]_D$ −39.16°, as principal product and regarded it as an oxide of (+)-car-3-ene (2) with unspecified stereochemistry. Treatment of the product with phthalic anhydride was claimed to afford a hydrogen phthalate identical with that obtained from the diol (1).

Remarkably, the oxide was stable to bromine in chloroform solution and to cold dilute sulphuric acid. Suspecting this stability, Arbuzov and Mikhailov [3] prepared authentic (+)-3α,4α-epoxycarane (3) by oxidation of (+)-car-3-ene (2) with perbenzoic acid. The epoxide, which had $[\alpha]_D$ +13°, and readily afforded the diol (1) with dilute sulphuric acid, was clearly not identical with Simonsen's 'oxide.' We have now re-examined the earlier work.[2]

The diol (1) was prepared as previously described,[2] (+)-car-3-ene (2) being treated with hydrogen peroxide–acetic acid and the diol monoacetates so formed hydrolysed with sodium hydroxide. A good yield of (1) was obtained together with a substantial amount of 1-acetyl-3,3-dimethylcyclohexa-1,4-diene (4).[4] The formation of this unexpected side-product may be rationalised as shown in Scheme 1. Here, the initially formed α-epoxide (3) undergoes reaction with acidic hydrogen



SCHEME 1

peroxide giving a hydroxy-hydroperoxide which, on treatment with base, loses water to yield a keto-aldehyde. The latter then suffers base-catalysed cyclisation and subsequent rearrangement [4] to the cyclohexadienone (4).

[1] Part XXII, D. A. Baines, W. Cocker, D. H. Grayson, P. H. Ladwa, and N. W. A. Geraghty, *Proc. Roy. Irish Acad.*, in the press.

[2] P. P. Pillay and J. L. Simonsen, *J. Chem. Soc.*, 1928, 359.

[3] B. A. Arbuzov and B. M. Mikhailov, *J. Russ. Phys. Chem. Soc.*, 1930. **62**, 607 (*Chem. Abs.*, 1930, **24**, 4775).

[4] P. H. Boyle, W. Cocker, R. L. Gordon, and P. V. R. Shannon, *J. Chem. Soc.* (*C*), 1971, 2127.

The alternative intermediacy of the hydroxy-peroxy-ester (5) is unlikely since treatment of (+)-3α,4α-epoxycarane (3) with peracetic acid in acetic acid gave only the diol monoacetate (6).[5] On the other hand, reaction of the epoxide (3) with 70% hydrogen peroxide in the presence of a catalytic amount of sulphuric acid followed by treatment of the reaction mixture with ethanolic sodium hydroxide afforded the dienone (4) in 20% yield. Attempts to trap the intermediate hydroperoxide as its methyl ether were unsuccessful.

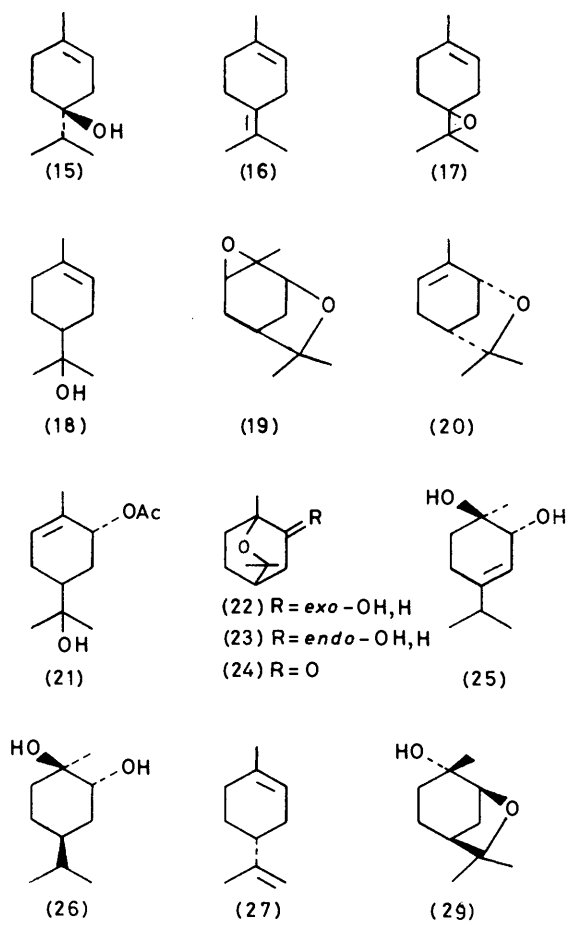
When the diol (1) was treated with hot dilute sulphuric acid as previously described [2] the product obtained consisted (g.l.c.) of *p*-cymene (7) (35%) and carvenone (8) (40%). Eight minor products made up the remaining 25% of the mixture. Not surprisingly, the carvenone was racemic. The presence of (+)-3α,4α-epoxycarane (3) was not detected and neither was that of the epimeric (−)-β-epoxide (9).

Treatment of the diol (1) with sulphuric acid for a shorter time gave several products which were separated by chromatography to yield (−)-2-*endo*-hydroxy-4-isopropyl-1-methyl-7-oxabicyclo[2.2.1]heptane (10) (7%), (−)-2-*exo*-hydroxy-2,6,6-trimethyl-7-oxabicyclo-[3.2.1]octane (11) (31%), (−)-2-*exo*-hydroxy-1,6,6-trimethyl-7-oxabicyclo[3.2.1]octane (12) (27%), (−)-*p*-menth-4-ene-*trans*-1,2-diol (13) (17%), (+)-carane-3β,4α-diol (1) (8%), and (+)-*p*-menth-4(8)-ene-*trans*-1,2-diol (14) (10%). The epoxycaranes (3) and (9) were not present, and carvenone (8) was detected only in trace amounts.

The (−)-*endo*-hydroxy-1,4-cineole (10), obtained in 95% purity, was identical (i.r., t.l.c., g.l.c.) with an authentic racemic specimen prepared from (±)-*p*-menth-1-en-4-ol [racemate of (15)] by treatment with *m*-chloroperbenzoic acid followed by reaction of the product with sulphuric acid (*cf.* ref. 6). The (±)-menthenol (15) used in our work was prepared by epoxidation of terpinolene (16) followed by reduction of the epoxide (17) [7] with lithium triethylhydridoborate. The product was a mixture of the required alcohol (15) (86%) and (±)-α-terpineol (18) (14%). Attempted reduction of the epoxide (17) with lithium aluminium hydride was unsuccessful. We expected the alcohol (10) formed from (+)-car-3-ene (2) and from (+)-*p*-menth-1-en-4-ol (15) to have the same absolute configuration; in fact the (+)-modification was apparently obtained [6] from (+)-*p*-menth-1-en-4-ol (15).

The pinol derivative (11) was identified by comparison with racemic material prepared by reduction of pinol oxide (19) with lithium aluminium hydride.[8] The (±)-pinol [racemate of (20)] used in this sequence was obtained in high yield and purity by brief treatment of sobreryl acetate (21) with toluene-*p*-sulphonic acid in benzene. The absolute configuration of (11) is discussed below.

(−)-2-*exo*-Hydroxy-1,6,6-trimethyl-7-oxabicyclo-[3.2.1]octane (12) exhibited strong hydroxy i.r. absorption at 3 350 cm^{-1}. Its n.m.r. spectrum showed clear signals at τ($CDCl_3$) 6.34 (1 H, m, C*H*OH), 8.13 (1 H, s, exch. D_2O, OH), and 8.66, 8.70, and 8.78 (each s, Me). It readily formed an acetate. The m.p. of (12) was close to that reported [9] for 2-*exo*-hydroxy-1,8-cineole (22), which would be expected to show similar n.m.r. signals. For comparative purposes, this compound (22) and 2-*endo*-hydroxy-1,8-cineole (23) were prepared as follows. (±)-α-Terpineol (18) when treated with *m*-chloroperbenzoic acid gave the *endo*-alcohol (23) directly.

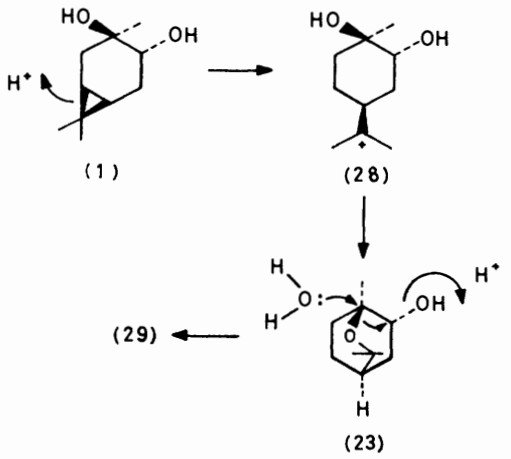


Oxidation of this to 2-oxo-1,8-cineole (24) followed by reduction with lithium hydridotri-t-butoxyaluminate afforded the *exo*-alcohol (22) (80%) which clearly differed from (12).

The unsaturated diol (13) was never obtained entirely free from a minor ketonic contaminant, but its n.m.r. spectrum had signals at τ($CDCl_3$) 4.85br (1 H, m, 5-H), 6.37 (1 H, dd, *J* 10.0 and 6.5 Hz, 2-H), 7.08 (2 H, s, exch. D_2O, OH), 9.01 (3 H, s, 1-Me), and 9.17 (6 H, d, *J* 6.6 Hz, Me_2CH) confirmatory of this structure. It is

[5] W. Cocker and D. H. Grayson, *J.C.S. Perkin I*, 1975, 1217.
[6] P. Garside, T. G. Halsall, and G. M. Hornby, *J. Chem. Soc.* (*C*), 1969, 716.
[7] J. C. Leffingwell, Fr. Demande, 2,003,498 (*Chem. Abs.*, 1970, **72**, 100934n).
[8] K. Piatkowski and H. Kuczynski, *Roczniki Chem.*, 1961, **35**, 1579 (*Chem. Abs.*, 1962, **57**, 2259c).
[9] A. Gandini, *Gazzetta*, 1937, **67**, 113 (*Chem. Abs.*, 1937, **31**, 6644).

easily distinguished from its double-bond isomer (25) by the position of the 2-H signal, which appears further downfield at τ 5.8 for the latter substance.[10] Supporting



SCHEME 2

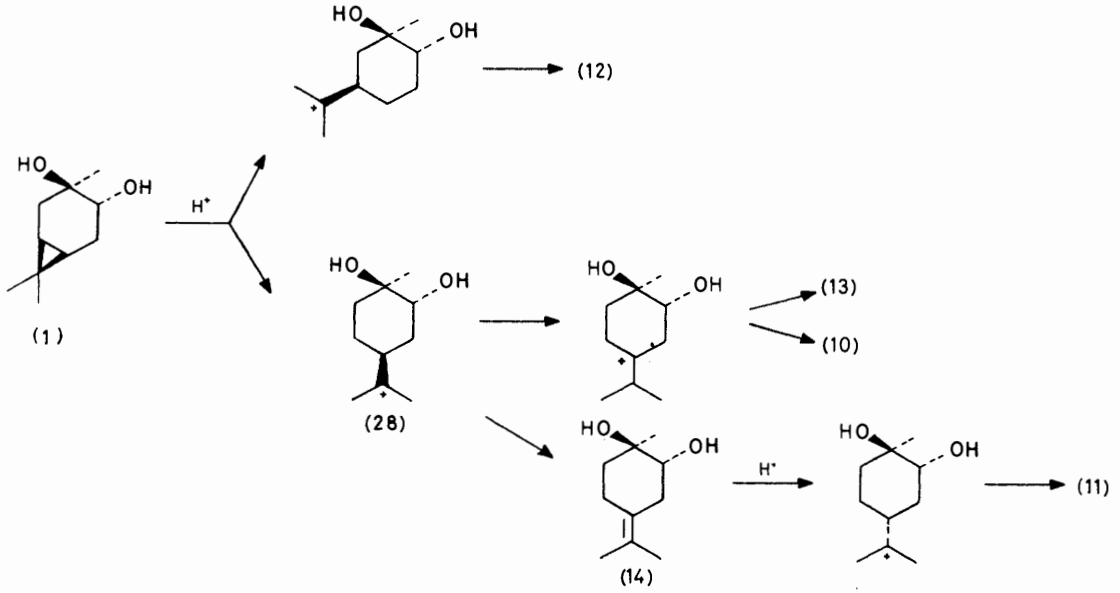
chemical evidence for the structure of (13) was obtained from its catalytic hydrogenation to (—)-*trans*-*p*-menthane-*trans*-1,2-diol (26), spectroscopically identical with an authentic specimen of its enantiomorph prepared from (+)-limonene (27).[11]

(+)-*p*-Menth-4(8)-ene-*trans*-1,2-diol (14) was isolated partially hydrated, m.p. 76°, τ($CDCl_3$) 6.36 (1 H, dd, *J* 10.0 and 5.5 Hz, 2-H), 6.93 (2 H, exch. D_2O, OH), 8.32 (6 H, s, Me_2C), and 8.90 (3 H, s, 1-Me). This compound proved resistant to catalytic hydrogenation at atmospheric pressure.

Initially, we assumed that the absolute configuration of the hydroxydihydropinol (11) was the opposite of that shown, *i.e.* as in (29) where the stereochemistry at C-6 of the diol (1) is preserved, but with inversion of its configuration at C-3. This would result from the reaction sequence shown in Scheme 2. Here, protonation of the cyclopropane ring of (+)-carane-3β,4α-diol (1) gives the ion (28) which cyclises to the 2-*endo*-hydroxy-1,8-cineole (23). Acid-catalysed rearrangement of the latter then gives (29), the enantiomorph of (11). Alternatively, protonation of the relatively basic[12] ether function of (23) followed by pinacolic rearrangement might be expected. In the event, 2-*endo*-hydroxy-1,8-cineole (23) was unchanged after boiling with 5% v/v sulphuric acid, thus eliminating these mechanistic pathways.

Both the sign and magnitude of rotation of (11) corresponded with that of material obtained by Kuczynski[8] from (+)-pinol (20). Inversion of configuration at C-6 of the diol (1) must therefore have occurred prior to ether formation. Scheme 3 rationalises the formation of (11) and the other products obtained from (+)-carane-3β,4α-diol (1).

With the exception of the hydroxy-ether (12), all the products of this reaction are potential precursors of *p*-cymene (7) and carvenone (8). None corresponds to Simonsen's 'oxide',[2] and none would be expected to yield the hydrogen phthalate of diol (1). We have confirmed that (1) does afford the ester (30) on heating with phthalic anhydride at 110 °C. This has the spectral and other characteristics expected of it and it is readily hydrolysed to its precursor (1).



SCHEME 3

[10] G. O. Pierson and O. A. Runquist, *J. Org. Chem.*, 1969, **34**, 3654.

[11] H. Schmidt, P. Richter, and M. Mühlstädt, *Chem. Ber.*, 1963, **96**, 2636.

[12] J. L. Simonsen and L. N. Owen, 'The Terpenes,' vol. 1, 2nd edn., Cambridge University Press, 1953, p. 426.

EXPERIMENTAL

The general conditions used have been described previously.[1] Optical rotations were measured for ethanolic solutions. I.r. data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 22170 (10 pp.).*

Oxidation of (+)-Car-3-ene with Hydrogen Peroxide–Acetic Acid. (+)-*Carane*-3β-4α-*diol* (1).—(+)-Car-3-ene {$[\alpha]_D^{21}$ +15° (*c* 0.2); 136 g} was stirred during 120 h at 35 °C with acetic acid (300 ml) and hydrogen peroxide (30%; 224 ml). Usual work-up gave a neutral oil (173 g), which was hydrolysed at room temperature for 3 h with sodium hydroxide (60 g) in methanol (500 ml) and water (150 ml). Extraction with ether gave an oily solid (120 g) which consisted (g.l.c.) of the diol (1) (86%) together with a substance (14%) of much shorter retention time. Crystallisation of the crude product from ether–light petroleum gave (+)-carane-3β,4α-diol (1) as its monohydrate, m.p. 72—73°. Chromatography of the concentrated mother liquors on silica gel afforded 1-acetyl-3,3-dimethylcyclohexa-1,4-diene (4) as an oil, identical with authentic material.[4]

Reaction of (+)-3α,4α-Epoxycarane with Peracetic Acid in Acetic Acid.—Hydrogen peroxide (75%; 2 ml) was added to acetic anhydride (10 ml) and the mixture was kept at 20 °C during 0.5 h. The epoxide (3) (2 g) was then added and the solution was set aside for 96 h. Usual work-up afforded only (−)-3β-acetoxy-4α-hydroxycarane (6) (1.6 g),[5] identical with material previously prepared.

Reaction of (+)-3α,4α-Epoxycarane with Acidic Hydrogen Peroxide and Treatment of the Product with Base. 1-*Acetyl*-3,3-*dimethylcyclohexa*-1,4-*diene* (4).—A mixture of the epoxide (3) (5 g) and hydrogen peroxide (70%; 2.5 ml) in 1,4-dioxan (25 ml), cooled to 0 °C, was treated with concentrated sulphuric acid (0.1 ml) and the mixture was kept at 20 °C for 2 h. Usual work-up afforded an oily product (5.3 g). This (1 g), in ethanol (25 ml) containing sodium hydroxide solution (30%; 2 ml), was kept at 50 °C for 15 min. Extraction with ether gave a yellow oil (0.9 g), which (g.l.c.) consisted of (−)-*cis*-caran-4-one [13] (5%), 1-acetyl-3,3-dimethylcyclohexa-1,4-diene (4) (20%),[4] and (+)-carane-3β,4α-diol (1) (75%).

Reaction of (+)-Carane-3β,4α-*diol with Hot Dilute Sulphuric Acid.*—(*a*) A mixture of the diol (1) (6 g) and sulphuric acid (5% v/v; 20 ml) was stirred and heated at 90 °C for 48 h. Extraction with ether gave an oily product (5.3 g) which (g.l.c.) contained *p*-cymene (7) (35%) and carvenone (8) (40%). Eight minor products of intermediate retention time were also present. *p*-Cymene and carvenone were isolated by preparative g.l.c. and identified by comparison with authentic specimens. The carvenone had $[\alpha]_D^{20}$ 0° (*c* 0.2).

(*b*) The diol (1) (6 g) was heated with sulphuric acid as in (*a*) for 1.5 h. Extraction with ether gave a neutral oil (5.5 g) consisting (g.l.c.) of compounds (11) (31%), (12) (27%), (10) (7%), (13) (17%), (1) (8%), and (14) (10%) in this order of elution. The mixture was chromatographed on silica gel (200 g) with an ether–light petroleum gradient as eluant.

(−)-2-*endo*-Hydroxy-1-methyl-4-isopropyl-7-oxabicyclo-[2,2,1]heptane (10) * was an oil, $[\alpha]_D^{20}$ −27° (*c* 0.1) (lit.,[6] +5°), $\nu_{max.}$ (L) 3 370 cm^{-1}, τ($CDCl_3$) 6.03 (1 H, dd, *J* 10.0 and 4.0 Hz, 2-H), 7.60br (1 H, s, exch. D_2O, O*H*), 8.58 (3 H, s, 1-Me), and 9.05 (6 H, d, *J* 7.5 Hz, Me_2CH). It was identical with an authentic specimen prepared as follows: terpinolene (16) (6.8 g), in chloroform (20 ml), was treated at 0 °C with *m*-chloroperbenzoic acid (9 g). After 6 h, usual work-up followed by distillation gave the epoxide (17),[7] b.p. 87—88° at 18 mmHg. This (5 g), in dry THF (10 ml), was treated with a solution of lithium triethylhydridoborate in THF (1M; 50 ml). After 6 h at 20 °C work-up gave a product (4.4 g) consisting (g.l.c.) of (±)-*p*-menth-1-en-4-ol (15) (86%) * and (±)-α-terpineol (18) (14%), which were separated by preparative g.l.c. *p*-Menth-1-en-4-ol had $\nu_{max.}$ (L) 3 400 cm^{-1}, τ($CDCl_3$) 4.66 (1 H, m, 2-H), 8.00 (1 H, s, exch. D_2O, OH), 8.30 (1 H, s, 1-Me), and 8.75 and 8.71 (6 H, 2d, each *J* 6.5 Hz, Me_2CH). The menthenol (15) (1 g), in chloroform (20 ml), was treated with *m*-chloroperbenzoic acid (1.4 g). After 12 h at 20 °C, work-up afforded a neutral oil (0.9 g) which, in THF (20 ml), was treated with sulphuric acid (0.1M; 10 ml). The mixture was heated to 60 °C for 4 h and extracted with ether. The resulting oil (0.6 g) contained (g.l.c.) two substantial volatile components in the ratio 40 : 60. The major of these, isolated by column chromatography on silica gel, was shown by i.r., t.l.c., and g.l.c. comparison to be identical with the 1,4-cineole derivative (10).

(−)-2-*exo*-Hydroxy-2,6,6-trimethyl-7-oxabicyclo[3.2.1]-octane (11) and (−)-2-*exo*-hydroxy-1,6,6-trimethyl-7-oxabicyclo[3.2.1]octane (12) were co-eluted from the silica gel column but were separated by preparative g.l.c.

The pinol derivative (11) * had m.p. 75—76° (pentane), $[\alpha]_D^{20}$ −92° (*c* 0.2) (lit.,[8] m.p. 79.5°, $[\alpha]_D^{20}$ −92.3°), $\nu_{max.}$ (N) 3 320 cm^{-1}, τ($CDCl_3$) 6.14 (1 H, m, 1-H), 8.37 (1 H, s, exch. D_2O, OH), 8.60 (3 H, s, Me) and 8.75 (6 H, s, 2 Me) (Found: C, 70.7; H, 10.5. Calc. for $C_{10}H_{18}O_2$: C, 70.5; H, 10.7%). An authentic racemic specimen was prepared as follows. Sobrerol treated with acetic anhydride in pyridine gave its monoacetate (21),* $\nu_{max.}$(L) 1 724 cm^{-1}, which (4 g) was refluxed in benzene (20 ml) with toluene-*p*-sulphonic acid (40 mg) for 15 min. Usual work-up gave (±)-pinol [racemate of (20); 2.7 g] in a high state of purity. This, in chloroform (30 ml) containing anhydrous sodium acetate (3 g), was treated at 0 °C with *m*-chloroperbenzoic acid (3.5 g). After 12 h work-up yielded pinol epoxide (19) * (2.3 g), $\nu_{max.}$(L) 1 040 cm^{-1}. This (2 g), in dry ether (50 ml), was stirred with an excess of lithium aluminium hydride (1 g) during 48 h. Work-up afforded an oil (1.7 g) consisting of unchanged epoxide (19) and the hydroxy-ether (11). Chromatography on silica gel gave a pure specimen of (±)-(11) identical with the material obtained as described above.

(−)-2-exo-*Hydroxy*-1,6,6-*trimethyl*-7-*oxabicyclo*[3.2.1]-*octane* (12) * crystallised from pentane as *needles*, m.p. 75—76°, $[\alpha]_D^{20}$ −79° (*c* 0.1), $\nu_{max.}$(N) 3 350 cm^{-1} (Found: C, 71.0; H, 10.2. $C_{10}H_{18}O_2$ requires C, 70.5; H, 10.7%). Treatment with acetic anhydride in pyridine afforded an oily acetate,* $\nu_{max.}$(L) 1 728 cm^{-1}, τ($CDCl_3$) 5.25 (1 H, m, 2-H), 7.96 (3 H, s, OAc), 8.66 (3 H, s, Me), and 8.75 (6 H, s, 2 Me).

Preparation of 2-exo-*Hydroxy*-1,8-*cineole* (22).—A stirred solution of (±)-α-terpineol (18) (11 g), in chloroform (100 ml), was treated dropwise at 0 °C with a solution of *m*-chloroperbenzoic acid (16 g) in chloroform (100 ml). After 12 h at 0 °C, the mixture was worked up in the usual way

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1976, Index issue.

[13] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc.* (*C*), 1967, 485.

giving an oil [14] (13 g). This contained (g.l.c.) two main components in the ratio 30 : 70 which were separated by column chromatography on silica gel. The minor, solid product, eluted first, was 2-*endo*-hydroxy-1,8-cineole (23),* m.p. 103—104° (from hexane) (lit.,[14] 108°), $\nu_{max.}$(N) 3 360 cm^{-1}. This (1 g), in ether (15 ml), was stirred with standard oxidant [15] (10 ml) for 6 h at 20 °C. Usual work-up gave an oily ketonic (i.r., g.l.c.) product (24) (0.8 g). Lithium aluminium hydride (0.38 g), in dry THF (30 ml), was treated dropwise with a solution of dry t-butyl alcohol (2.2 g) in THF (5 ml). After stirring for 10 min, a solution of the oxo-cineole (24) (0.8 g), in THF (1 ml), was added. After 1 h at 20 °C, usual work-up gave a solid (0.7 g) consisting (g.l.c.) of the alcohols (22) (80%) and (23) (20%). A pure sample of 2-*exo*-hydroxy-1,8-cineole (22) * was obtained by preparative g.l.c. and, after sublimation, had m.p. 79—80° (lit.,[9] 80°), $\nu_{max.}$(N) 3 370 cm^{-1}.

(−)-p-*Menth*-4-*ene*-trans-1,2-*diol* (13) * was obtained as an oil of *ca.* 95% purity, $[\alpha]_D^{19}$ −25° (*c* 0.2), $\nu_{max.}$(L) 3 400 cm^{-1}. A sample sufficiently pure for analysis could not be obtained.

Catalytic Hydrogenation of the Diol (13). (−)-trans-p-*Menthane*-trans-1,2-*diol* (26).*—The diol (13) (150 mg), in ethyl acetate (30 ml), was reduced at 1 atm of hydrogen over palladised charcoal (10%; 50 mg). One mol. equiv. of hydrogen was absorbed. Work-up afforded an oily solid which, after recrystallisation from hexane, had m.p. 64—65°, $[\alpha]_D^{20}$ −2° (*c* 0.2), $\nu_{max.}$(N) 3 250 cm^{-1}, τ($CDCl_3$) 6.45 (1 H, m, 2-H), 7.44br (2 H, s, exch. D_2O, 2 OH groups), 8.83 (3 H, s, 1-Me), and 9.13 (6 H, d, *J* 6.5 Hz, Me_2CH). It was spectroscopically identical with its enantiomorph prepared from (+)-limonene (27) as follows. The mixture (3 g) of α- and β-epoxides obtained by oxidation of (+)-limonene {$[\alpha]_D^{20}$ +62° (*c* 0.2)} with *m*-chloroperbenzoic acid was stirred with sulphuric acid (1%; 30 ml) for 10 h at 0 °C. Extraction with ether afforded an oil (2.6 g) which was hydrogenated at 1 atm in ethyl acetate (30 ml) over palladised charcoal (5%; 0.2 g). One mol. equiv. of hydrogen was absorbed. The product was chromatographed on silica gel to yield the diol [enantiomorph of (26)] (0.8 g), m.p. 63—64°, $[\alpha]_D^{20}$ *ca.* 0° (*c* 0.1). Azeotropic distillation with benzene followed by vacuum sublimation raised the m.p. to 88° (lit.,[11] 89°).

(+)-p-*Menth*-4(8)-*ene*-trans-1,2-*diol* (14) * had m.p. 76—77° (benzene), $[\alpha]_D^{19}$ +17° (*c* 0.1), $\nu_{max.}$(N) 3 260 cm^{-1} (Found: C, 65.5; H, 10.3. $C_{10}H_{18}O_2,\frac{2}{3}H_2O$ requires C, 65.9; H, 10.6%).

Reaction of 2-endo-*Hydroxy*-1,8-*cineole* (23) *with Sulphuric Acid*.—The alcohol (23) (1 g) was refluxed with sulphuric acid (5% v/v; 5 ml) for 1 h. Extraction with ether gave a solid (0.8 g), m.p. 102°, which was identified with unchanged starting material.

4-*Hydrogen Phthalate of* (+)-*Carane*-3β,4α-*diol* (1).—An intimate mixture of the diol (1) (3.4 g) and phthalic anhydride (7 g) was heated, without solvent, at 110 °C for 5 h. The resulting solid mass was taken up in cold chloroform (75 ml), phthalic acid (1.3 g) was filtered off, and the soluble material was separated into neutral and acidic fractions. The former consisted largely of unchanged diol (1 g); the latter (4 g), crystallised from aqueous methanol, gave the hydrogen phthalate (30) * (3.7 g), m.p. 199—200° (lit.,[2] 191—192°), $[\alpha]_D^{21}$ +5.5° (*c* 0.1), $\nu_{max.}$(N) 3 370, 1 728, and 1 700 cm^{-1}, τ[$(CD_3)_2SO$] 2.26br (4 H, s, ArH), 8.79 (3 H, s, 3-Me), 8.98 and 9.04 (each 3 H, 2s, Me_2C), and 9.30br (2 H, m, H-1 and -6).

Hydrolysis of the Hydrogen Phthalate (30).—The ester (0.5 g) was refluxed with potassium hydroxide (0.5 g) in methanol (10 ml) and water (2 ml) for 2 h. Usual work-up gave the diol (1) as needles (0.2 g).

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