

The Chemistry of Terpenes. Part 24.¹ Some Oxidation Products of 1,5,5,6-Tetramethylcyclohexa-1,3-diene (α -Pyrone) †

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r-3,6-Epidioxy-3,*t*-4,5,5-tetramethylcyclohexene (2), formed by dye-sensitised photo-oxygenation of α -pyrone (1) is reduced by triphenylphosphine to *r*-3,4-epoxy-4,*t*-5,6,6-tetramethylcyclohexene (7) and by lithium aluminium hydride to 1,5,5,*t*-6-tetramethylcyclohex-2-ene-*r*-1,*c*-4-diol (11). *r*-3,4-Epoxy-1,5,5,*t*-6-tetramethylcyclohexene (6) is the major product of the reaction in ether of perbenzoic acid with α -pyrone (1). From these oxidation products a number of diols and ketols have been obtained.

α -PYRONE (1,5,5,6-tetramethylcyclohexa-1,3-diene) (1) has previously been oxidised by several reagents. For example, selenium dioxide afforded ² 1,2,3,4-tetramethylbenzene and unidentified selenium compounds, and peracetic acid gave ³ a hydroxy-acetate of undetermined

structure. The peroxide (2) was formed ⁴ by dye-sensitised photooxidation of α -pyrone, but it was not fully characterised.

In the formation of (2), attack of oxygen will take place

³ W. Zacharewicz, A. Uzarewicz, and M. Zaidlewicz, *Roczniki Chem.*, 1960, **34**, 1523 (*Chem. Abs.*, 1961, **55**, 21160b).

⁴ G. O. Schenck and K. Ziegler, Ger. Pat., 913892 (*Chem. Abs.*, 1958, **52**, 14704g); K. Gollnick and G. O. Schenck, '1,4-Cyclo-additions,' ed. J. Hamer, Academic Press, New York, 1967, p. 269.

† All compounds here described are racemic.

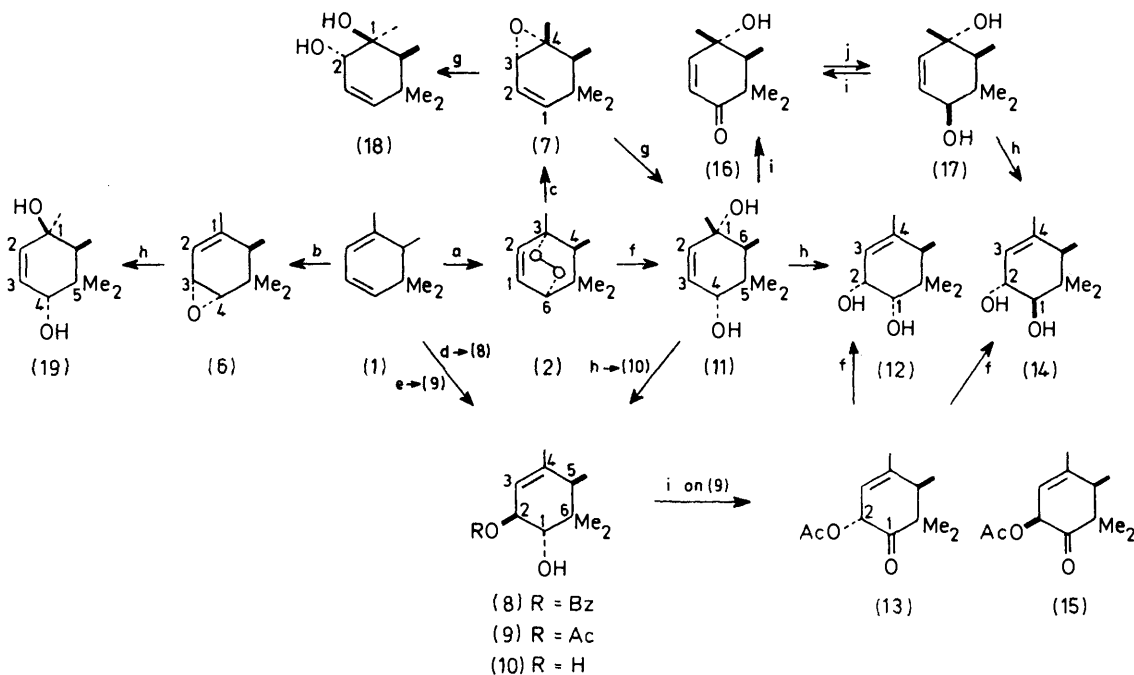
¹ Part 23, W. Cocker and D. H. Grayson, preceding paper.

² W. Zacharewicz and A. Uzarewicz, *Roczniki Chem.*, 1960, **34**, 413 (*Chem. Abs.*, 1961, **55**, 420f).

on the less hindered side of the α -pyronene molecule, which for the conformer (1a) is opposite to that of the secondary methyl group. This has been confirmed by benzene-induced solvent shifts in the n.m.r. spectrum of (2). Benzene will complex with the olefinic centre of (2) on the side away from the oxide bridge and be close to the secondary methyl group. As expected this is revealed by a significant benzene-induced upfield shift (τ 9.24 \rightarrow 9.51; see Supplementary Publication).

Analogously, the corresponding acetate (9) results from the treatment of α -pyronene with peracetic acid. Both esters show n.m.r. signals characteristic of the MeC=CH group, and on alkaline hydrolysis both yield the diol (10).

We obtained the more highly substituted epoxide (7) of α -pyronene (1) as the sole product of the reduction of the peroxide (2) with triphenylphosphine,⁶ a result which establishes the configuration of (7). Reductive cleavage of (2) with lithium aluminium hydride yields the diol



Reagents: a, O₂, *hν*, sensitiser; b, PhCO₃H in Et₂O; c, (Ph)₃P; d, PhCO₃H in CHCl₃; e, MeCO₃H; f, LiAlH₄; g, H₂O; h, H₃O⁺; i, CrO₃ in Et₂O; j, NaBH₄

Earlier⁵ we identified the peroxide (3) derived from β -pyronene (4) and also reported that oxidation of the latter with perbenzoic acid in ether gives the tetrasubstituted epoxide (5). We now report that similar oxidation of α -pyronene (1) gives the disubstituted epoxide (6) as the major product. Electronic factors favour attack of peroxy-acid on the trisubstituted double bond of (1) but sterically its disubstituted double bond is the more open to attack in the half-chair conformer (1a). This appears to be the preferred conformer since the 220 MHz n.m.r. spectrum of α -pyronene shows no long-range coupling of the near planar MeCH-CMe=CH system which is present in the only reasonable alternative conformer (1b).

Oxidation of α -pyronene (1) with perbenzoic acid in chloroform affords the hydroxy-benzoate (8) (cf. ref. 5).

⁵ W. Cocker, K. J. Crowley, and K. Srinivasan, *J.C.S. Perkin I*, 1973, 2485.

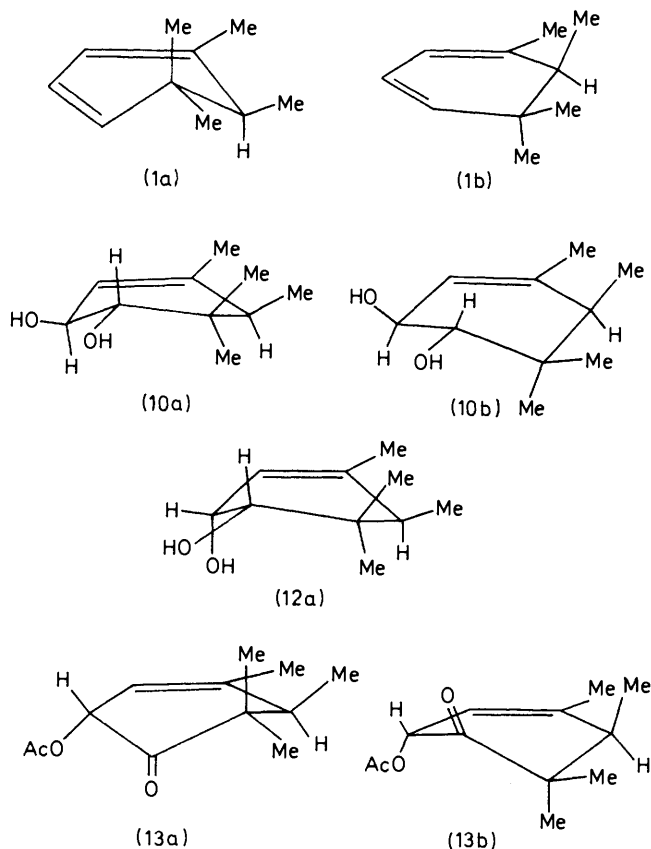
(11) whose hydroxy-groups must consequently have the *cis*-relationship and be *trans* to the secondary methyl group. The diol (11) is also obtained by aqueous hydrolysis of the epoxide (7).

Acid-catalysed rearrangement of the diol (11) affords two other diols (10) and (12) both of which possess the MeC=CH group (n.m.r.). Since the secondary hydroxy-group of (11) is not involved in the rearrangement, the diols (10) and (12) differ in configuration only at the centre of the newly formed secondary alcohol. It also follows that the secondary hydroxy-group of the esters (8) and (9) must be oriented as in (11) and the epoxide (6), from which the esters are presumably derived, must have the configuration shown.

N.m.r. evidence supports the configuration assigned to

⁶ G. O. Pierson and O. A. Runquist, *J. Org. Chem.*, 1969, **34**, 3654; K. H. Schulte-Elte, M. Gadola, and G. Ohloff, *Helv. Chim. Acta*, 1973, **56**, 2028.

(10) and (12).^{*} Both have two boat and two half-chair conformers but models show that only (10a), (10b), and (12a) need be considered. Europium-induced shift values of (10) gave linear plots of $\delta\Delta$ against $[\text{Eu}(\text{fod})_3]/[\text{diol}]$ values up to 0.7, with $\text{HC}=\text{C} > \text{Me}^t > \text{Me}^e > \text{Me}^s > \text{Me}^c$. Assuming no large effect by co-ordination with the complex, the values are consistent⁷ with structures (10a) and (12a). The HO-CH-CH-OH



torsion angles of (10a) and (12a) are approximately 170 and 45°, respectively, in accord with the observed coupling constants of 8 Hz for (10) and 4 Hz for (12).

Two-phase oxidation by chromic acid⁸ of the hydroxy-acetate (9) gave the oxo-acetate (13) with concurrent epimerisation at the acetoxyated centre. This is the first occasion on which we have experienced any inversion of configuration on using this reagent. The assignment of configuration of (13) follows from its reduction with lithium aluminium hydride to (12); the *trans*-diol (14) is also formed in this reduction. Models show that both conformers (13a and b) are less sterically hindered than any of the conformers of the alternative oxo-acetate (15).

Oxidation of the diol (11) gave the hydroxy-ketone

^{*} However the interchanging of assignments of structures (10) and (12) cannot be rigorously excluded. Such change would involve the reversing of configurations at C-2 in (8), (9), (13), and (14).

† Details of Supplementary Publications are given in Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue.

(16), which was reduced by borohydride to the diol (17) and reconverted into (16) with Brown's reagent. The diol (17) must therefore differ from (11) in the orientation of the secondary hydroxy-group, *i.e.* in (17) the hydroxy-groups must be *trans* to each other. This is to be expected if the borohydride is complexed to the tertiary alcohol group of the hydroxy-ketone (16).

Treatment of the diol (17) with 1% sulphuric acid in chloroform gave the diol (14) which has (n.m.r.) the MeC=CH system. Since this diol is also formed by reduction of (13), it must have the configuration shown. Two other, unidentified products are formed in the acid-catalysed isomerisation of (17).

Finally, hydrolysis of the epoxide (7) with water gives the diols (11) and (18). The structure of the latter follows from its mode of formation, its n.m.r. spectrum, and its retro-Diels-Alder mass spectral fragmentation pattern, giving a base peak at *m/e* 98. Similar hydrolysis of the epoxide (6) gives the diol (19) as sole product.

EXPERIMENTAL

For general experimental conditions see ref. 5. With the exception of peaks of particular diagnostic value, i.r. and mass spectra are given in Supplementary Publication No. SUP 22171 (12 pp.),[†] which also includes ¹H n.m.r. data for the peroxides (2) and (3) in CDCl₃ and in C₆D₆.

r-3,6-Epidioxy-3,4,5,5-tetramethylcyclohexene (2).—A solution of α -pyronene (1) (2.7 g) and Methylene Blue (0.1 g) in propan-2-ol (81 ml) was stirred in oxygen below 15 °C, and irradiated with light from four 100 W tungsten filament lamps.⁹ After 12 h, when oxygen uptake had ceased, solvent was removed under reduced pressure and the residue (3.2 g) was eluted from a silica column with light petroleum-ether (9 : 1). The peroxide (2) (1.25 g), pure by g.l.c., was obtained as a pale yellow liquid, b.p. 65–67° at 1 mmHg, $n_D^{22.5}$ 1.472 8 (lit.,⁴ b.p. 41–48° at 0.001 mmHg, n_D^{20} 1.477), Raman shifts (L) 866 (O–O), and 892 and 1 618 (C=C) cm⁻¹, τ 9.24 (3 H, d, *J* 7.5 Hz, MeCH), 9.26 and 8.74 (6 H, 2s, Me₂C), 8.72 (3 H, s, MeC–O), 8.23 (1 H, q, *J* 7.5 Hz, MeCH), 6.05 (1 H, dd, *J* 6 and 1 Hz, HC–O), 3.81 (1 H, dd, *J* 6 and 1 Hz, HC=C), and 3.39 (1 H, dd, *J* 8 and 6 Hz, C=CH), *m/e* 168 (*M*⁺) (Found: C, 71.2; H, 9.5. C₁₀H₁₆O₂ requires C, 71.4; H, 9.6%).

r-3,4-Epoxy-1,5,5,6-tetramethylcyclohexene (6).— α -Pyronene (3.25 g) in ether (20 ml) was stirred, first at 0 °C for 3 h and then at 15 °C for 48 h, with perbenzoic acid [from benzoyl peroxide (8.33 g)] in ether (60 ml). Basification with 10% sodium carbonate followed by usual work-up gave a liquid (3.5 g), which was eluted from a column of Merck basic alumina (activity III; 100 g) with light petroleum-ether (19 : 1). The product, a mixture of epoxides (i.r., g.l.c.), b.p. 58–60° at 15 mmHg, was repeatedly chromatographed then distilled, giving the epoxide (6), ν_{max} (L) 1 654, 849 (epoxide), and 817 cm⁻¹, τ 9.1 and 8.73 (6 H, 2s, Me₂C), 8.98 (3 H, d, *J* 4 Hz, MeCH), 8.22 (3 H, d, *J* 1.5 Hz, MeC=C), and 4.22 (1 H, m, HC=C) (Found: C, 78.6; H, 10.5. C₁₀H₁₆O requires C, 78.9; H, 10.6%).

⁷ A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.

⁸ H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.

⁹ P. Wieland and V. Prelog, *Helv. Chim. Acta*, 1947, **30**, 1028; D. H. R. Barton, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J.C.S. Chem. Comm.*, 1972, 447.

r-3,4-Epoxy-4,t-5,6,6-tetramethylcyclohexene (7).—Triphenylphosphine (1.7 g) was added in small portions to a stirred solution of α -pyronene peroxide (2) (1 g) in toluene (20 ml) and the mixture heated on the water-bath for 8 h. The epoxide (7) (50 mg) (g.l.c. pure) was an oil, b.p. 58–60° at 15 mmHg, $\nu_{\max}(\text{L})$ 1 635 and 838 cm^{-1} , τ 9.1 (3 H, d, J 7 Hz, MeCH), 9.07 and 8.84 (6 H, 2s, Me₂C), 8.59 (3 H, s, MeCO), 8.19 (1 H, q, J 7 Hz, MeCH), 7.07 (1 H, d, J 3.5 Hz, HC=O), 4.5 (1 H, d, J 9 Hz, HC=C), and 4.2 (1 H, dd, J 9 and 3 Hz, Me₂CCH=C) (Found: C, 79.2; H, 10.7. C₁₀H₁₆O requires C, 78.9; H, 10.6%).

Benzoate (8) of 4,t-5,6,6-Tetramethylcyclohex-3-ene-*r*-1,t-2-diol.—A solution of α -pyronene (3.75 g) in chloroform (60 ml) was added dropwise to a well stirred, ice-cold, solution of perbenzoic acid [from benzoyl peroxide (8.33 g)]. After 3 h at 0 °C, stirring was continued for 15 h at 15 °C and the mixture was then treated with an excess of 10% sodium carbonate. The organic layer, washed with water (3 \times 20 ml), gave a gum (3.94 g) which was eluted from silica (250 g) with light petroleum-ether (4 : 1) giving the hydroxy-benzoate (8) (1.55 g) as a gum, b.p. 120–125° (bath temp.) at 1 mmHg, τ 9.01 and 8.97 (6 H, 2s, Me₂C), *ca.* 8.97 (3 H, partly masked d, J *ca.* 7 Hz, MeCH), 8.27br (3 H, s, MeC=C), 6.21 (1 H, d, J 7.5 Hz, CHOH), 4.72 (2 H, m, CHOBz and HC=C), and 2.8–2.45 and 2.1–1.82 (5 H, both m, Ph) (Found: C, 74.1; H, 7.9. C₁₇H₂₂O₃ requires C, 74.4; H, 8.1%). The benzoate (71 mg) kept overnight with aqueous methanolic 10% potassium hydroxide (2 ml) gave the diol (10) (32 mg) (see below).

Acetate (9) of 4,t-5,6,6-Tetramethylcyclohex-3-ene-*r*-1,t-2-diol (9).—A stirred mixture of α -pyronene (6.8 g) and sodium acetate (6 g) in methylene chloride (50 ml) was treated dropwise during 15 min at 0 to –5 °C with peracetic acid, prepared by adding hydrogen peroxide (30%; 7.5 ml) to acetic anhydride (5 ml) at 0 to –5 °C. After 24 h the mixture was filtered and the filtrate stirred at 0 °C with an excess of solid sodium carbonate. Water was added and the organic layer was separated, washed with water, and dried, yielding an oil (7.23 g) which was chromatographed on silica (600 g). Elution with light petroleum containing increasing amounts of ether gave α -pyronene (1.49 g) first, then 1,2,3,4-tetramethylbenzene (0.154 g), and finally the hydroxy-acetate (9) (2.2 g) which on short-path distillation at 1 mmHg (bath temp. 95–100°) was obtained as a viscous oil, ν_{\max} 3 400, 1 730, and 1 709 cm^{-1} , τ 9.05, 8.95, and 8.94 (9 H, m, Me₂C and MeCH), 8.29br (3 H, s, MeC=C), 7.93 (3 H, s, Ac), 6.36 (1 H, d, J 7 Hz, CHOH), and 4.98–4.5 (2 H, m, AcOCH–CH=C) (Found: C, 67.2; H, 9.3. C₁₂H₂₀O₃ requires C, 67.9; H, 9.5%). Hydrolysis as for (8) gave the diol (10).

1,5,5,t-6-Tetramethylcyclohex-2-ene-*r*-1,c-4-diol (11).—A solution of the peroxide (2) (0.4 g) in ether (10 ml) was added dropwise to a stirred, ice-cold suspension of lithium aluminium hydride (0.4 g) in ether (10 ml). Stirring was continued for 18 h at 15 °C, water (5 ml) and ethyl acetate (50 ml) were carefully added, and the mixture was again stirred for 4 h. The organic layer, washed with water, gave the diol (11) (0.26 g), which formed needles (from ethyl acetate), m.p. 112°, $\nu_{\max}(\text{N})$ 3 200 cm^{-1} , τ 9.22 and 9.03 (6 H, 2s, Me₂C), 9.03 (3 H, d, J 7.5 Hz, MeCH), 8.89 (3 H, s, MeCOH), 8.03 (1 H, q, J 7.5 Hz, CHMe), 7.25 (2 H, s, *exch.* D₂O, OH), 6.52 (1 H, d, J 5 Hz, CHOH), and 4.29 (2 H, m, HC=CH) (Found: C, 69.8; H, 10.5. C₁₀H₁₆O₂ requires C, 70.5; H, 10.7%).

Isomerisation of the Diol (11). 4,t-5,6,6-Tetramethyl-

cyclohex-3-ene-*r*-1,t-2-diol (10) and 4,t-5,6,6-Tetramethylcyclohex-3-ene-*r*-1,c-2-diol (12).—A solution of the diol (11) (0.4 g) in chloroform (10 ml) was stirred for 10 min with sulphuric acid (1*N*; 10 ml). Neutralisation with 10% sodium hydrogen carbonate gave a thick gum (0.36 g) which was eluted from silica (40 g) with light petroleum-ether (1 : 1) giving the diol (12) (0.1 g) as a gum which was purified by cold-finger distillation at 1 mmHg (bath temp. 120–125°), $\nu_{\max}(\text{L})$ 3 340 and 1 655 cm^{-1} , τ 9.22 and 8.95 (6 H, 2s, Me₂C), 9.06 (3 H, d, J 7.5 Hz, MeCH), 8.31br (3 H, s, MeC=C), 6.57 (1 H, d, J 4 Hz, 1-H), 5.85 (1 H, m, 2-H), and 4.77 (1 H, m, HC=C) (Found: C, 70.9; H, 10.5. C₁₀H₁₆O₂ requires C, 70.5; H, 10.7%).

Further elution with the same solvent mixture gave the diol (10) (0.16 g) as silky needles, m.p. 65–66°, $\nu_{\max}(\text{N})$ 3 280, 3 200, and 1 666 cm^{-1} , τ 9.13 and 9.02 (6 H, 2s, Me₂C), 9.0 (3 H, d, J 7 Hz, MeCH), 8.31 (3 H, m, MeC=C), 6.5 (1 H, d, J 8 Hz, 1-H), 6.07 (1 H, m, 2-H), and 4.8 (1 H, m, HC=C), *m/e* 170 (M^+) (Found: C, 70.3; H, 10.6. C₁₀H₁₆O₂ requires C, 70.5; H, 10.7%).

2-*r*-Acetoxy-4,t-5,6,6-tetramethylcyclohex-3-enone (13).—A solution of the hydroxy-acetate (9) (0.13 g) in ether (5 ml) was stirred for 48 h at 15–20 °C with Brown's reagent⁸ (1 ml). Usual work-up gave a gum which was eluted from silica (15 g) with light petroleum-ether (9 : 1) giving the acetoxy-ketone (13) (82 mg) as a gum, b.p. 75–80° at 1 mmHg, $\nu_{\max}(\text{L})$ 1 738 and 1 720 cm^{-1} , τ 9.03 (1 H, d, J 4 Hz, MeCH), 8.91 and 8.71 (6 H, 2s, Me₂C), 8.26br (3 H, s, MeC=C), 7.89 (3 H, s, Ac), 4.7br (1 H, s, HC=C), and 4.3 (1 H, m, HC–OAc).

4,c-5,6,6-Tetramethylcyclohex-3-ene-*r*-1,t-2-diol (14) and 4,t-5,6,6-Tetramethylcyclohex-3-ene-*r*-1,c-2-diol (12).—A solution of the acetoxy-ketone (13) (0.27 g) in ether (10 ml) was added slowly to a cold, stirred suspension of lithium aluminium hydride (0.12 g) in ether (10 ml) and stirring was continued for 15 h at 15 °C. Work-up without the use of mineral acid and extraction of the product with ethyl acetate gave a gum (0.21 g) which was eluted from silica (20 g) with light petroleum-ether (6 : 4). The diol (14) (76 mg) was eluted first as needles (light petroleum), m.p. 58–59°, $\nu_{\max}(\text{N})$ 3 370 and 1 661 cm^{-1} , τ 9.08 and 9.02 (6 H, 2s, Me₂C), 8.92 (3 H, d, J 7 Hz, MeCH), 8.28br (3 H, s, MeC=C), 6.59 (1 H, d, J 5 Hz, 1-H), 5.86 (1 H, m, 2-H), and 4.62br (1 H, s, HC=C), *m/e* 170 (M^+) (Found: C, 70.2; H, 10.9. C₁₀H₁₆O₂ requires C, 70.5; H, 10.7%). Further elution gave (n.m.r.) the diol (12) (70 mg) (see above).

Oxidation of the Diol (11). *r*-4-Hydroxy-4,t-5,6,6-tetramethylcyclohex-2-enone (16).—A solution of the diol (11) (70 mg) in ether (10 ml) was stirred for 15 h with Brown's reagent⁸ (0.5 ml), the temperature rising from 0 to 20 °C. The product was eluted from silica (15 g) with light petroleum-ether (1 : 1) giving the hydroxy-ketone (16) as an oil, b.p. 95° at 0.2 mmHg, λ_{\max} 217 nm ($\log \epsilon$ 3.9), $\nu_{\max}(\text{L})$ 3 360 and 1 662 cm^{-1} , τ 8.98 and 8.86 (6 H, 2s, Me₂C), 8.77 (3 H, d, J 7.5 Hz, MeCH), 7.92 (1 H, q, J 6.5 Hz, CHMe), 4.21 (1 H, d, J 10.8 Hz, HC=C), and 3.32 (1 H, d, J 10.8 Hz, HC=C), *m/e* 168 (M^+) (Found: C, 71.0; H, 9.5. C₁₀H₁₆O₂ requires C, 71.4; H, 9.6%).

Reduction of the Hydroxy-Ketone (16). 1,5,5,t-6-Tetramethylcyclohex-2-ene-*r*-1,t-4-diol (17).—A solution of the hydroxy-ketone (16) (0.38 g) and sodium borohydride (0.12 g) in methanol (10 ml) was kept overnight at 15 °C and the product extracted with ethyl acetate. The diol (17) was obtained (0.28 g) as needles, m.p. 119–121° (light petroleum), $\nu_{\max}(\text{N})$ 3 320 cm^{-1} , τ 9.24 and 8.99 (6 H, 2s,

Me₂C), 8.9 (3 H, d, *J* 5.5 Hz, MeCH), 8.84 (3 H, s, MeCOH), 6.04 (1 H, d, *J* 7 Hz, CHOH), and 4.43 (2 H, s, HC=CH), *m/e* 155 (*M*⁺ - Me) (Found: C, 70.0; H, 11.1. C₁₀H₁₈O₂ requires C, 70.5; H, 10.7%). The diol (70 mg) was re-oxidised by Brown's reagent⁸ to its precursor (16) (44 mg).

Acid-catalysed Rearrangement of the Diol (17).—The diol (17) (0.2 g) in chloroform (5 ml) and sulphuric acid (1%; 5 ml) was stirred for 10 min, then neutralised with 10% sodium hydrogen carbonate, and the product was extracted with ethyl acetate. The resulting gum (0.18 g) was eluted from silica (20 g) with light petroleum-ether (1 : 1) giving the diol (14) (44 mg), identical (i.r., n.m.r.) with the product obtained from the acetoxy-ketone (13). Further elution gave unidentified products.

Hydrolysis of the Epoxide (7). 1,5,5,c-6-Tetramethylcyclohex-3-ene-r-1-t-2-diol (18).—Freshly distilled epoxide (7) [from the peroxide (2) (1 g)] was stirred for 12 h at room temperature with water (5 ml). The resulting solid (0.2 g) was chromatographed on silica (20 g) and eluted with light petroleum-ether (1 : 1) giving the diol (18) (77 mg), m.p. 137° (light petroleum), $\nu_{\max.}(\text{N})$ 3 360 and 3 250 cm⁻¹, τ 9.09, 8.96, and 8.89 (9 H, 3s MeCOH and Me₂C), 8.97 (3 H, d,

J 6.6 Hz, MeCH), 8.16 (1 H, q, *J* 6.6 Hz, HCMe), 7.79 (1 H, d, *J* 6 Hz, OH), 7.49 (1 H, s, OH), 6.31 (1 H, t, *J* 5.5 Hz, HCOH), and 4.33 (2 H, m, HC=CH), *m/e* 153 (*M*⁺ - OH) (Found: C, 71.2; H, 10.7. C₁₀H₁₈O₂ requires C, 70.5; H, 10.7%). Further elution afforded (i.r., n.m.r.) the diol (11) (125 mg).

Hydrolysis of the Epoxide (6). 1,5,5,c-6-Tetramethylcyclohex-2-ene-r-1,t-4-diol (19).—The epoxide (6) (0.6 g) was stirred for 12 h with water (3 ml) and the product extracted with ether. The resulting gum (0.5 g), eluted from silica (100 g) with light petroleum-ether (2 : 3), gave the diol (19) (0.3 g) as a gum, b.p. 145–150° (bath temp.) at 15 mmHg, $\nu_{\max.}$ 3 320 and 1 653 cm⁻¹, τ 9.1 and 8.99 (6 H, 2s, Me₂CO), 8.99 (3 H, d, *J* 7.5 Hz, MeCH), 8.74 (3 H, s, MeCOH), 6.42 (1 H, d, *J* ca. 5 Hz, HCOH), and 4.26 (2 H, m, HC=CH) (Found: C, 70.1; H, 10.5. C₁₀H₁₈O₂ requires C, 70.5; H, 10.7%).

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