

Sensitised Photo-oxidation of 5-Methylene-cyclohexa- and -cyclohepta-1,3-diene Derivatives

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Sensitised photo-oxidations of 5-benzyl-1,5-dimethyl-6-methylene-3-t-butylcyclohexa-1,3-diene and 1,5,5-trimethyl-7-methylenecyclohepta-1,3-diene produce the corresponding 1,4-epidioxides. Both thermal and photochemical decompositions of these peroxides afford only the diepoxides as isolable products.

1,4-EPIDIOXIDES have become of particular interest since they are readily available from the reaction of dienes with singlet oxygen,¹ and are transformed into a number of unusual organic molecules.² A typical example is the formation of oxepin-2-ones (1) from the



unstable 1,4-epidioxides of 6-mono- and 6,6-di-substituted fulvenes produced by photo-oxidation;³ the

† Preparations of simply substituted methylenecyclohexadienes were unsuccessful because of the instability of the precursor cyclohexadienones. Attempted synthesis of the isopropylidene analogues of (2) and (3) by the Wittig process also failed.

¹ For reviews see K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, 1964, **9**, 507; '1,4-Cycloaddition Reactions,' ed. J. Harner, Academic Press, New York, 1967, pp. 255—337; A. Schönberg and G. O. Schenck, 'Preparative Organic Photochemistry,' Springer-Verlag, New York, 1968, pp. 382—397; K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

rearrangement pathway is novel and the products (1) are otherwise difficult to prepare. In view of increasing interest in the photo-oxidation of conjugated alkylidene-cycloalkadienes, we undertook the preparation and the photo-oxidation of 5-benzyl-1,5-dimethyl-6-methylene-3-t-butylcyclohexa-1,3-diene (2) and 7-methylene-1,5,5-trimethylcyclohepta-1,3-diene (3), and examined the thermal and photochemical reactivity of their 1,4-epidioxides.

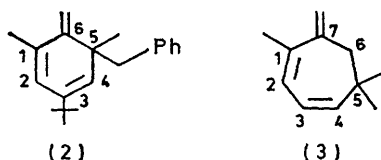
The trienes (2) and (3) were prepared from the readily available benzyl-dimethyl-t-butylcyclohexadienone and eucarvone by the Wittig reaction with methylenetriphenylphosphorane.†

Photo-oxidation of the triene (2) (visible light; Methylene Blue as sensitiser) proceeded normally to give

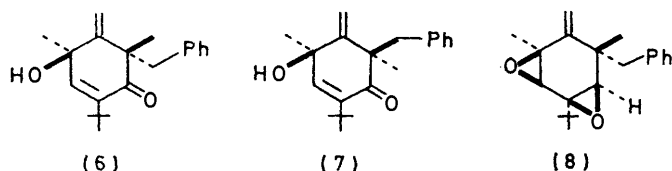
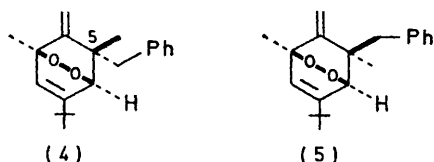
² For a review see W. Adam, *Angew. Chem. Internat. Edn.*, 1974, **13**, 619, and references therein.

³ W. Skorjanetz, K. H. Schulte-Elte, and G. Ohloff, *Helv. Chim. Acta*, 1971, **54**, 1913; N. Harada, S. Suzuki, H. Uda, and H. Ueno, *J. Amer. Chem. Soc.*, 1972, **94**, 1777; *Chem. Letters*, 1972, 805; N. Harada, H. Uda, and H. Ueno, *ibid.*, p. 663; A. Kawamoto, H. Kosugi, and H. Uda, *ibid.*, p. 807; N. Harada, H. Uda, H. Ueno, and S. Utsumi, *ibid.*, 1973, 1173.

two stable crystalline 1,4-epidioxides (4) and (5) in 44 and 7% yields, respectively. No significant solvent nor temperature dependence in the photo-oxidation was



observed. Apparently the products (4) and (5) are stereoisomeric; the major one (4) arises by preferential attack of singlet oxygen from the less hindered side (C-5 methyl side) of the starting triene (2) and the stereochemistry was rigorously established by n.m.r. spectroscopy. In the n.m.r. spectrum of the major epidioxide (4), the C-5 methyl signal was observed at lower field (δ 1.37) and the benzyl methylene signal at higher field (AB type, δ 2.25 and 2.51) than in the case of the minor isomer (5) [δ 0.90 (Me) and 2.78 and 3.37

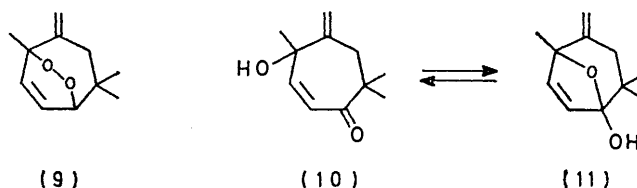


(PhCH₂) as appropriate for a *cis*- or *trans*-relation to the epidioxy-group, respectively.

Both epidioxides (4) and (5) afforded, through the Kornblum-de la Mare fragmentation,⁴ the stereoisomeric 1,4-hydroxy-ketones (6) and (7) in quantitative yields on treatment with methanolic potassium hydroxide at room temperature. Decomposition of the major epidioxide (4), either by heating in bis-(2-methoxyethyl) ether or by u.v. irradiation, gave a 10 or 61% yield, respectively, of the diepoxide (8) as the only isolable product; there was no indication of the presence of any other rearrangement product. Thus, the exocyclic methylene group in structure (2) or (4) does not participate in either the photo-oxidation or the O-O bond cleavage.

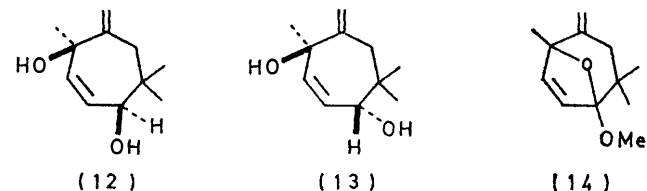
Similar photo-oxidation of the triene (3) gave a mixture of four products, separated by preparative t.l.c. The compound which moved most rapidly was isolated in 36% yield and identified as the 1,4-epidioxide (9) from its spectral and chemical (see below) properties. The second and third components (3.5 and 1.0%) possessed an $\alpha\beta$ -unsaturated ketone function but no exocyclic methylene group. It was found that these two compounds were formed by the attack of more than one molecule of singlet oxygen (see Experimental section) and that the epidioxide (9) was not the intermediate leading

to them. However, these compounds were not identified because of lack of material. The most polar compound, isolated in 12% yield, was a 1 : 1 tautomeric mixture of the 1,4-hydroxy-ketone (10) and the acetal (11) on the basis of the following spectral and chemical evidence. The n.m.r. spectrum in deuteriochloroform at room temperature exhibits two sets of peaks of equal intensity corresponding to structures (10) and (11). However in [²H₆]dimethyl sulphoxide the hydroxy-ketone form (10) is favoured (by 1 : 0.66 at room temperature), and at 70 °C the peaks of the acetal (11) do



not appear. Reduction of the mixture with lithium aluminium hydride gave the *cis*- (12) and the *trans*-1,4-diol (13) in roughly equal amounts, which were oxidised back to the mixture of tautomers (10) and (11) with active manganese dioxide. The *cis*-diol (12) was identical with a specimen obtained directly from the epidioxide (9) by reduction with lithium aluminium hydride. Furthermore, methylation of the mixture with sodium hydride-methyl iodide afforded the methyl ether (14) in high yield as the sole product. The hydroxy-ketone (10) is presumably produced from the epidioxide (9) during work-up or t.l.c. separation; in fact treatment of (9) with methanolic potassium hydroxide yielded quantitatively the mixture of (10) and (11).

On pyrolysis in bis-(2-methoxyethyl) ether or photolysis in ether, the epidioxide (9) gave the diepoxide (15), in 43 and 17% yields, respectively. Again, no evidence

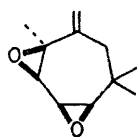


was obtained for any products of rearrangement involving the exocyclic methylene group. When the photolysis was carried out in methanol, two methanol addition products were obtained in 26 and 10% yields, respectively. These compounds presumably arise from the initially formed diepoxide (15), since photolysis of (15) in methanol also gave them, in similar yields (30 and 9%). The addition products were assigned structures (16) and (17) from analytical and spectral data of the products and the *p*-chlorobenzoyl (18) and the acetyl (19) derivatives.

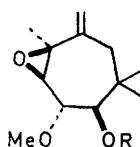
Treatment of the epidioxide (9) with triphenylphosphine in benzene gave the epoxy-diene (20),

⁴ M. Kornblum and H. E. de la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880.

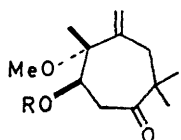
identical with material produced by an alternative synthesis from eucarvone.



(15)

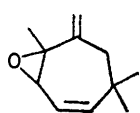


(16) R = H

(18) R = *p*-ClC₆H₄CO

(17) R = H

(19) R = Ac



(20)

EXPERIMENTAL

Distillation of liquid products was usually carried out evaporatively in a modified sublimation apparatus; oil-bath temperatures are recorded. I.r. spectra were obtained with a Hitachi EPI-S2 or -G2 and u.v. spectra with a Hitachi EPS-3T spectrophotometer. N.m.r. spectra of solutions in carbon tetrachloride (unless otherwise indicated) were recorded with a JEOL C-60HL (60 MHz) or PS-100 (100 MHz) instrument, with tetramethylsilane as internal standard; coupling constants are given in Hz. Microanalyses were carried out in the microanalytical laboratory of this Institute.

5-Benzyl-1,5-dimethyl-6-methylene-5-*t*-butylcyclohexa-1,3-diene (2).—6-Benzyl-2,6-dimethyl-4-*t*-butylcyclohexa-2,4-dienone was prepared from commercially available 2,6-dimethyl-4-*t*-butylphenol according to the procedure of Curtin and Dybvig,⁵ except for the use of sodium hydride instead of sodium metal. To a solution of methylenetriphenylphosphorane [from methyltriphenylphosphonium bromide (9.18 g, 25.7 mmol) and freshly prepared *n*-butyllithium (15.2 ml of ethereal solution, 22 mmol) in ether (30 ml)] the dienone (10 g) was added dropwise; the mixture was stirred for 5 h at room temperature and then poured into ice-water. The product was extracted with petroleum. The combined extracts were washed with water and brine, dried (Na₂SO₄), and evaporated. The resulting oil (9.0 g) was chromatographed on a short column of silica gel. Petroleum eluted rapidly the triene (2) (3.12 g), ν_{\max} (CCl₄) 3 030, 1 580, 875, and 695 cm⁻¹, δ 1.00 (9 H, s), 1.19 (3 H, s), 1.85 (3 H, d, *J* 0.75), 2.45 (1 H, d, *J* 12.0), 2.72 (1 H, d, *J* 12.0), 5.03 (1 H, d, *J* 2.2), 5.22 (1 H, d, *J* 0.75), 5.30br (1 H, s), 5.73br (1 H, s), and 6.82—7.30 (5 H, m) [in addition to unchanged dienone (3.7 g)]. This compound decomposes gradually at room temperature.

Photo-oxidation of the Triene (2).—A solution of the triene (2) (300 mg) and Methylene Blue (5—6 mg) in chloroform (100 ml) saturated with oxygen was irradiated with a 200 W tungsten lamp at room temperature. The reaction was complete within 70 min. The mixture was concentrated *in vacuo* and the dye was removed by passing through a short column of silica gel. The crude product

thus obtained was separated by preparative t.l.c. on silica gel [petroleum-ether (10 : 1)] to give *t*-5-benzyl-*r*-3,6-epidioxo-3,5-dimethyl-4-methylene-1-*t*-butylcyclohexene (4) (148 mg, 44%), m.p. 117.0—117.5° (from petroleum), ν_{\max} (CHCl₃) 2 950, 1 095, and 910 cm⁻¹, δ (CDCl₃) 1.21 (9 H, s), 1.37 (3 H, s), 1.43 (3 H, s), 2.25 (1 H, d, *J* 12.5), 2.51 (1 H, d, *J* 12.5), 3.98 (1 H, s), 4.33 (1 H, d, *J* 2.5), 4.92 (1 H, s), 5.95 (1 H, d, *J* 2.5), and 6.90—7.25 (5 H, m) (Found: C, 80.3; H, 9.1. C₂₀H₂₆O₂ requires C, 80.5; H, 8.8%), and the *C*-5-benzyl isomer (5) (22 mg, 7%), m.p. 74.5—76.0° (from petroleum), ν_{\max} (CHCl₃) 2 940, 1 080, and 900 cm⁻¹, δ (CDCl₃) 0.90 (3 H, s), 1.03 (9 H, s), 1.52 (3 H, s), 2.78 (1 H, d, *J* 13.0), 3.37 (1 H, d, *J* 13.0), 4.33 (1 H, d, *J* 2.5), 4.81 (1 H, s), 5.06 (1 H, s), 5.95 (1 H, d, *J* 2.5), and 7.20—7.40 (5 H, m) (Found: C, 80.3; H, 8.9%).

Almost identical results were obtained when the photo-oxidation was carried out at -50 °C, or in methanol at room temperature or -50 °C.

6-Benzyl-4-hydroxy-4,6-dimethyl-5-methylene-2-*t*-butylcyclohex-2-enones (6) and (7).—A few drops of methanolic potassium hydroxide (2 mg in 1 ml) were added to a solution of the epidioxide (4) (23 mg) and the mixture was stirred for 21 h at room temperature. Water was added, and the product was extracted with ether. The extracts were combined, washed with water and brine, dried, and evaporated to leave the *hydroxy-ketone* (6) (22 mg, 96%), b.p. 160—165° at 15 mmHg, ν_{\max} (CCl₄) 3 580, 3 530—3 100, 3 010, 1 675, 910, and 695 cm⁻¹, δ 1.06 (3 H, s), 1.13 (3 H, s), 1.20 (9 H, s), 1.75br (1 H, s), 2.69 (1 H, d, *J* 13.0), 3.16 (1 H, d, *J* 13.0), 4.84 (1 H, s), 5.58 (1 H, s), 6.30 (1 H, s), and 6.90—7.20 (5 H, m) (Found: C, 80.8; H, 8.5. C₂₀H₂₆O₂ requires C, 80.5; H, 8.8%).

In the same manner the epidioxide (5) gave quantitatively the isomeric *hydroxy-ketone* (7), b.p. 100—160° at 15 mmHg, ν_{\max} (CCl₄) 3 580, 3 530—3 100, 3 010, 1 680, 910, and 695 cm⁻¹, δ 0.84 (3 H, s), 1.15 (9 H, s), 1.45 (3 H, s), 1.60br (1 H, s), 2.72 (1 H, d, *J* 13.5), 3.28 (1 H, d, *J* 13.5), 4.85 (1 H, s), 5.48 (1 H, s), 6.28 (1 H, s), and 6.82—7.25 (5 H, m).

Photolysis of the Epidioxide (4).—A solution of the epidioxide (4) (78 mg) in ether (40 ml) was placed in a Pyrex tube and irradiated with a 500 W high-pressure mercury arc for 55 min at room temperature. The ether was evaporated off and the oily residue (96 mg) upon preparative t.l.c. on silica gel [petroleum-ether (10 : 1)] gave 1-benzyl-2,3:4,5-diepoxy-1,5-dimethyl-6-methylene-3-*t*-butylcyclohexane (8) (47 mg, 61%), b.p. 95—105° at 15 mmHg, ν_{\max} (CCl₄) 2 950, 2 910, 910, and 700 cm⁻¹, δ 1.04 (9 H, s), 1.13 (3 H, s), 1.48 (3 H, s), 2.60br (2 H, s), 2.66 (1 H, s), 3.10 (1 H, s), 5.10 (1 H, s), 5.44 (1 H, s), and 6.90—7.26 (5 H, m) (Found: C, 80.2; H, 8.8. C₂₀H₂₆O₂ requires C, 80.5; H, 8.8%).

Pyrolysis of the Epidioxide (4).—A solution of the epidioxide (4) (83 mg) in bis-(2-methoxyethyl) ether (5 ml) was heated under reflux for 1.5 h under nitrogen, poured into water, and extracted with ether. The combined extracts were washed with water and brine, dried, and evaporated. The oily residue upon preparative t.l.c. as above, gave the diepoxide (8) (8 mg, 10%).

7-Methylene-1,5,5-trimethylcyclohepta-1,3-diene (3).—To a solution of methylenetriphenylphosphorane [from methyltriphenylphosphonium bromide (17.35 g, 50 mmol) and

⁵ D. Y. Curtin and D. H. Dybvig, *J. Amer. Chem. Soc.*, 1962, **84**, 225.

sodium hydride (1.08 g) in dimethyl sulphoxide (100 ml)]⁶ freshly distilled eucarvone⁷ (6.0 g, 40 mmol) was added dropwise. The mixture was stirred for 19 h at room temperature under nitrogen, poured into ice-water, and extracted with petroleum. The combined extracts were washed with water and brine, dried, and concentrated *in vacuo*. The concentrate was passed through a short column of silica gel and the eluate was evaporated *in vacuo* and distilled at 95 °C and 25 mmHg to yield the *triene* (3) (5.22 g, 88%), ν_{\max} (CCl₄) 3 080, 1 570, and 890 cm⁻¹, δ 1.00 (6 H, s), 2.05 (3 H, s), 2.30 (2 H, s), 4.95br (1 H, s), 5.18 (1 H, d, *J* 1.3), and 5.52–5.85 (3 H, m) (Found: C, 88.9; H, 10.8. C₁₁H₁₆ requires C, 89.1; H, 10.9%).

Photo-oxidation of the Triene (3).—A solution of the triene (3) (1.0 g) and Methylene Blue (5–6 mg) in chloroform (80 ml) saturated with oxygen was irradiated with a 200 W tungsten lamp at room temperature for 18 h. A finely dispersed stream of oxygen was bubbled through the solution during irradiation. The mixture was concentrated *in vacuo* and the dye was removed by passing the concentrate through a short column of alumina and silica gel. Concentration of the eluate *in vacuo* left an oily mixture of four products, which were separated by preparative t.l.c. on silica gel [petroleum-ether (3:1)] to yield 3,7-epidioxo-3,6,6-trimethyl-4-methylenecycloheptene (9) (350 mg, 36%), the 1:1 tautomeric mixture of 4-hydroxy-4,7,7-trimethyl-5-methylenecyclohept-2-enone (10) and the acetal (11) (131 mg, 12%), and two minor products A (15 mg) and B (17 mg). The epidioxide (9) had m.p. 27.0–27.2° (from petroleum), b.p. 75° at 5 mmHg, ν_{\max} (CCl₄) 3 060, 1 640, 1 120, 1 080, 975, and 905 cm⁻¹, λ_{\max} (EtOH) 300 nm (ϵ 110), δ 0.85 (3 H, s), 1.05 (3 H, s), 1.35 (3 H, s), 2.00 (1 H, d, *J* 13.5), 2.45 (1 H, d, *J* 13.5), 4.03 (1 H, dd, *J* 1.1 and 6.8), 4.83 (1 H, m), 4.92br (1 H, s), 6.10 (1 H, dd, *J* 1.1 and 9.0), and 6.43 (1 H, dd, *J* 6.8 and 9.0) (Found: C, 73.1; H, 9.0. C₁₁H₁₆O₂ requires C, 73.3; H, 8.95%).

The tautomeric mixture [(10) and (11)] had b.p. 80° at 1 mmHg, ν_{\max} (CCl₄) 3 580, 3 550–3 100, 3 060, 1 660, 1 100, and 900 cm⁻¹, λ_{\max} (EtOH) 220 nm (ϵ 4 100), δ [ketol form (10)] 1.07 (3 H, s), 1.10 (3 H, s), 1.45 (3 H, s), 2.18 (1 H, d, *J* 13.8), 2.46 (1 H, d, *J* 13.8), 2.82br (1 H, s), 4.88br (1 H, s), 5.40 (1 H, d, *J* 1.0), 5.60 (1 H, d, *J* 13.0), and 6.02 (1 H, d, *J* 13.0), δ [acetal form (11)] 0.90 (3 H, s), 0.97 (3 H, s), 1.40 (3 H, s), 1.83 (1 H, d, *J* 15.0), 2.17 (1 H, d, *J* 15.0), 4.08br (1 H, s), 4.67br (1 H, s), 4.82br (1 H, s), 5.92 (1 H, d, *J* 5.8), and 6.05 (1 H, d, *J* 5.8) (Found: C, 73.1; H, 8.75. C₁₁H₁₆O₂ requires C, 73.3; H, 8.95%).

The minor product A had b.p. 110–120° at 2–3 mmHg, ν_{\max} (CCl₄) 2 950, 1 665, 1 635, 1 610, 1 055, and 1 015 cm⁻¹, λ_{\max} (EtOH) 240 nm (ϵ 5 700), δ 1.20 (6 H, s), 2.38br (2 H, s), 4.45br (2 H, s), 4.71 (2 H, m), 5.90 (1 H, d, *J* 12.8), and 6.34 (1 H, d, *J* 12.8) (Found: C, 69.4; H, 7.5. C₁₁H₁₄O₃ requires C, 68.0; H, 7.3%).

The minor product B had m.p. 135–136° (from petroleum-ether), ν_{\max} (CHCl₃) 3 050 and 1 665 cm⁻¹, λ_{\max} (EtOH) 225 (ϵ 7 500) and 240 nm (ϵ 7 300), δ (CDCl₃) 1.09 (3 H, s), 1.33 (3 H, s), 1.75 (1 H, d, *J* 15.8), 2.30 (1 H, d, *J* 15.8), 4.20 (2 H, s), 4.30 (1 H, d, *J* 14.3), 5.19 (1 H, d, *J* 14.3), 5.70 (1 H, d, *J* 12.8), and 6.18 (1 H, d, *J* 12.8) (Found: C, 62.6; H, 6.8. C₁₁H₁₄O₄ requires C, 62.8; H, 6.7%).

Almost identical results were obtained when the photo-

oxidation was carried out at –50 °C, or in methanol at –50 °C or room temperature.

Conversion of the Epidioxide (9) into the Mixture of Compounds (10) and (11).—To a solution of the epidioxide (9) (58 mg) in methanol (20 ml) were added a few drops of methanolic potassium hydroxide (10 mg in 10 ml). After being stirred at room temperature for 3 h, the mixture was poured into ice-water and extracted with ether. The extracts were washed with water and brine, and dried. Evaporation gave a mixture of the ketol (10) and the acetal (11) (55 mg, 95%).

1,5,5-Trimethyl-7-methylenecyclohept-2-ene-cis-1,4-diol (12).—To a slurry of lithium aluminium hydride (38 mg, 1 mmol) in anhydrous ether (2 ml) cooled in ice was added dropwise within 10 min a solution of the epidioxide (9) (180 mg, 1 mmol) in anhydrous ether (2 ml). The mixture was stirred for 1 h and poured into ice-water containing a trace of potassium hydroxide, and the water layer was extracted with ether. The combined ether layers were washed with water and brine, dried, and evaporated. The residual oil (193 mg) was subjected to preparative t.l.c. on silica gel [petroleum-ether (3:2)] to give the viscous *cis*-diol (12) (107 mg, 60%), b.p. 95–100° at 2 mmHg, ν_{\max} (CCl₄) 3 560–3 050, 1 640, 1 050, 1 010, and 905 cm⁻¹, δ 0.86 (3 H, s), 1.00 (3 H, s), 1.42 (3 H, s), 1.80 (1 H, d, *J* 13.5), 2.82 (1 H, d, *J* 13.5), 3.63 (1 H, d, *J* 4.0), 4.57br (2 H, s), 4.70 (1 H, s), 4.87 (1 H, d, *J* 1.0), 5.60 (1 H, d, *J* 12.0), and 5.74 (1 H, dd, *J* 4.0 and 12.0) (Found: C, 72.6; H, 10.2. C₁₁H₁₈O₂ requires C, 72.5; H, 10.0%).

Reduction of the Tautomeric Mixture of Compounds (10) and (11).—Lithium aluminium hydride (30 mg, 0.5 mmol) was added to a solution of the mixture of (10) and (11) (60 mg, 0.33 mmol) in anhydrous ether cooled in ice, and the mixture was stirred at room temperature for 66 h. A minimal amount of water was added to decompose the excess of reagent, and the ether layer was washed with water and brine, dried, and evaporated. Chromatography of the residue [preparative t.l.c. on silica gel; petroleum-ether (3:7)] gave the *cis*-diol (12) (17 mg, 28%) and the *trans*-diol (13) (13 mg, 21%), ν_{\max} (CHCl₃) 3 580–3 100, 1 640, 1 050, and 915 cm⁻¹, δ (CDCl₃) 0.91 (3 H, s), 1.09 (3 H, s), 1.38 (3 H, s), 1.95 (1 H, d, *J* 13.0), 2.18 (1 H, d, *J* 13.0), 1.88br (2 H, s), 4.24 (1 H, d, *J* 2.5), 4.87 (1 H, s), 5.30 (1 H, s), 5.42 (1 H, d, *J* 11.0), and 5.54 (1 H, dd, *J* 11.0 and 2.5).

1-Methoxy-2,2,5-trimethyl-4-methylene-8-oxabicyclo[3.2.1]-oct-6-ene (14).—To a stirred suspension of sodium hydride (7.2 mg, 0.3 mmol) in anhydrous tetrahydrofuran (1 ml) was added a solution of a mixture of (10) and (11) (36 mg, 0.2 mmol) in anhydrous tetrahydrofuran (0.5 ml). After stirring for 5 min, methyl iodide (114 mg, 0.8 mmol) in anhydrous tetrahydrofuran (0.5 ml) was added and the mixture was stirred at room temperature for 2 days. It was then concentrated *in vacuo*, and water and ether were added to the residue. The water layer was extracted with ether. The combined ether layers were washed with water and brine, and dried. Evaporation gave the *methyl ether* (14) (36 mg, 93%), which was homogeneous on t.l.c.; b.p. 70° at 6 mmHg, ν_{\max} (CCl₄) 1 650, 1 120, 1 090, and 910 cm⁻¹, δ 0.82 (3 H, s), 0.97 (3 H, s), 1.45 (3 H, s), 1.78 (1 H, d, *J* 15.0), 2.20 (1 H, dt, *J* 15.0 and 2.4), 3.24 (3 H, s), 4.62 (1 H, q, *J* 1.2 and 2.4), 4.82

⁶ R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128.

⁷ E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, 1956, **78**, 174.

(1 H, q, J 1.2 and 2.4), 5.94 (1 H, d, J 5.5), and 6.04 (1 H, d, J 5.5) (Found: C, 72.8; H, 9.8. $C_{12}H_{18}O_2$ requires C, 72.5; H, 10.0%).

Pyrolysis of the Epidioxide (9).—A solution of the epidioxide (9) (171 mg) in anhydrous bis-(2-methoxyethyl) ether (5 ml) was heated at 165 °C for 2 h under nitrogen. After cooling, the mixture was poured into water and extracted with ether. The combined extracts were washed with water and brine, dried, and evaporated. The residue was chromatographed [preparative t.l.c. on silica gel; petroleum-ether (3 : 1)] to give the crude product (94 mg) which was further purified by preparative t.l.c. on alumina [petroleum-ether (5 : 1)] to yield oily *cis*-2,3,4,5-diepoxy-1,1,5-trimethyl-6-methylenecycloheptane (15) (74 mg, 43%), b.p. 80° at 2 mmHg, ν_{\max} (CCl_4) 3 090, 2 950, 1 635, 1 190, 1 080, 1 040, 945, and 915 cm^{-1} , δ 0.93 (3 H, s), 1.08 (3 H, s), 1.43 (3 H, s), 1.44 (1 H, d, J 13.5), 2.42 (1 H, d, J 13.5), 2.58 (1 H, dd, J 1.5 and 3.5), 3.10 (1 H, dd, J 3.5 and 4.5), 3.24 (1 H, d, J 4.5), 5.00 (1 H, s), and 5.25 (1 H, s) (Found: C, 73.7; H, 8.7. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.95%).

Photolysis of the Epidioxide (9).—(a) *In ether.* A solution of the epidioxide (9) (286 mg) in anhydrous ether (80 ml) was irradiated through a Pyrex filter with a 500 W high-pressure mercury lamp at room temperature for 2 h. The solvent was removed and the residue (82 mg) was subjected to preparative t.l.c. on silica gel and then on alumina as in the preceding experiment to give the diepoxide (15) (40 mg, 17%).

(b) *In methanol.* A solution of the epidioxide (9) (200 mg) in methanol (8 ml) was irradiated for 3 h under the same conditions as in (a). Preparative t.l.c. on silica gel [petroleum-ether (3 : 2)] gave crystalline *c*-5,6-epoxy-*t*-7-methoxy-2,2,5-trimethyl-4-methylenecycloheptan-*r*-1-ol (16) (61 mg, 26%) and 6-hydroxy-5-methoxy-2,2,5-trimethyl-4-methylenecycloheptanone (17) (24 mg, 10%). The epoxide (16) had m.p. 70.0–70.5° (from petroleum), ν_{\max} ($CHCl_3$) 3 580, 3 080, 1 635, 1 165, 1 085, 1 040, and 920 cm^{-1} , δ ($CDCl_3$) 0.95 (3 H, s), 1.15 (3 H, s), 1.48 (3 H, s), 1.78 (1 H, d, J 12.5), 2.18 (1 H, d, J 12.5), 2.75 (1 H, d, J 6.0), 2.98 (1 H, s), 3.22 (3 H, s), 3.28 (1 H, d, J 6.0), 3.82 (1 H, s), 4.92 (1 H, s), and 5.22 (1 H, s) (Found: C, 68.1; H, 10.0. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.5%). The hydroxy-ketone (17) had m.p. 120.0–121.0° (from benzene-petroleum), ν_{\max} ($CHCl_3$) 3 700–3 200, 3 100, 1 695, 1 150, 1 100, 1 085, and 920 cm^{-1} , δ ($CDCl_3$) 1.12 (3 H, s), 1.15 (3 H, s), 1.42 (3 H, s), 1.96 (1 H, d, J 13.5), 1.60–2.20br (1 H), 2.40 (1 H, dd, J 6.7 and 13.0), 2.75 (1 H, d, J 13.5), 3.18 (3 H, s), 3.63 (1 H, d, J 13.0), 3.74 (1 H, d, J 6.7), and 5.18 (2 H, s) (Found: C, 66.9; H, 9.8. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.5%).

These compounds were also obtained by photolysis of the diepoxide (15) in methanol, and compound (16) was detected in the product obtained from the reaction of (15) with silica gel-methanol (40–110 °C; 72 h).

***p*-Chlorobenzoate of Compound (16).**—A solution of compound (16) (21 mg) and *p*-chlorobenzoyl chloride (53 mg) in pyridine (1 ml) was left at room temperature for 1 day. The mixture was worked up by addition of water followed

by extraction with ether and purified by preparative t.l.c. on silica gel to give the *p*-chlorobenzoate (18) (11 mg, 32%), δ 1.08 (3 H, s), 1.20 (3 H, s), 1.60 (3 H, s), 1.87 (1 H, d, J 14.0), 2.15 (1 H, d, J 14.0), 2.67 (1 H, d, J 5.0), 3.07 (4 H, m), 4.92br (1 H, d, J 2.0), 5.26 (2 H, s), 7.40 (2 H, d, J 9.0), and 8.04 (2 H, d, J 9.0).

Acetate of Compound (17).—A solution of compound (17) (26 mg) and acetic anhydride (185 mg) in pyridine (1 ml) was left at room temperature for 2 days. The mixture was worked up as above to give the acetate (19) (11 mg, 35%), δ 1.06 (6 H, s), 1.29 (3 H, s), 1.86 (1 H, d, J 13.0), 1.92 (3 H, s), 2.42 (1 H, dd, J 7.5 and 12.0), 2.76 (1 H, d, J 13.0), 3.12 (3 H, s), 3.41 (1 H, d, J 12.0), 4.74 (1 H, d, J 7.5), and 5.08 (2 H, s).

6,7-Epoxy-3,3,6-trimethyl-5-methylenecycloheptene (20).—*From the epidioxide (9).* Into a solution of the epidioxide (9) (60 mg, 0.33 mmol) in benzene (5 ml) was injected a solution of triphenylphosphine (92 mg, 0.35 mmol) in benzene (2 ml) at room temperature under nitrogen, and the mixture was heated under reflux for 130 min. The solvent was removed by distillation through a short Vigreux column *in vacuo*. The residue was purified by preparative t.l.c. on silica gel [petroleum-ether (8 : 1)] to give the epoxy-diene (20) (28 mg, 51%), b.p. 60–65° at 1 mmHg, ν_{\max} (CCl_4) 3 080, 1 180, 1 090, 1 060, 905, and 870 cm^{-1} , δ 0.93 (3 H, s), 1.04 (3 H, s), 1.49 (3 H, s), 1.78 (1 H, d, J 13.5), 2.72 (1 H, d, J 13.5), 3.06 (1 H, t, J 3.3), 5.09 (1 H, s), 5.30 (1 H, s), and 5.52 (2 H, d, J 3.3) (Found: C, 80.25; H, 9.8. $C_{11}H_{16}O$ requires C, 80.4; H, 9.8%).

From eucarvone. To a solution of eucarvone (314 mg, 2.09 mmol) and sodium hydroxide (40 mg) in methanol (2 ml) at room temperature, 28% hydrogen peroxide (382 mg, 3.14 mmol) was added dropwise. The mixture was stirred for 2 h, then poured into ice-water and extracted with ethyl acetate. The combined extracts were washed with water, dried, and evaporated. The residual oil (253 mg) was chromatographed [preparative t.l.c. on silica gel; ethyl acetate-hexane (1 : 5)] to give the $\alpha\beta$ -epoxy-ketone (133 mg, 38%), ν_{\max} (neat) 2 960, 2 920, 1 700, 1 650, 850, and 780 cm^{-1} , δ 0.95 (3 H, s), 1.12 (3 H, s), 1.43 (3 H, s), 1.82 and 3.32 (1 H, each, AB-type q, J 11.3), 3.14 (1 H, t, J 3.8), and 5.58 (2 H, d, J 3.8). A nuclear Overhauser enhancement (14%) of the β -epoxy-proton signal (δ 3.14) was observed upon irradiation at the frequency of the α -epoxy-methyl signal (δ 1.42).

To a solution of methylenetriphenylphosphorane in ether [from methyltriphenylphosphonium bromide (347 mg, 1.0 mmol) and *n*-butyl-lithium (0.95 mmol)] cooled in ice under nitrogen was added dropwise a solution of the epoxy-ketone (54 mg, 0.33 mmol) in ether (2 ml). The mixture was stirred at 0 °C for 5 h and poured into ice-water. The water layer was extracted with petroleum. The combined organic layers were washed with water, dried, and evaporated. The residual oil (71 mg) was chromatographed [preparative t.l.c. on silica gel; ethyl acetate-hexane (1 : 19)] to give the epoxy-diene (20), identical with the sample obtained from the epidioxide (9).

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