# The Reactions of 5α-Allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6-one, a Potential Intermediate in the Synthesis of Friedolabdanes

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5α-Allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6-one (8) has been prepared. In connection with its potential use for the synthesis of friedolabdanes a number of reactions of this compound and its derivatives have been studied. These include epoxidation, ozonolysis, and the attempted hydration of the double bond *via* hydroboration. The products of these reactions have indicated very substantial participation of the functional group at C-6 in the reactions of the double bond. In particular a novel reaction occurred on hydroboration involving carbon–carbon bond formation between the ethylenic and carbonyl groups.

ONE of the major groups of diterpenes is that with the friedolabdane skeleton illustrated by (+)-hardwickiic acid (1).[1] Little synthetic work in this area has been reported. One approach investigated [2,3] followed a biogenetic-type pathway involving rearrangement of epoxylabdane derivatives of the type (2).


(1)   (2)

(3)   (4)
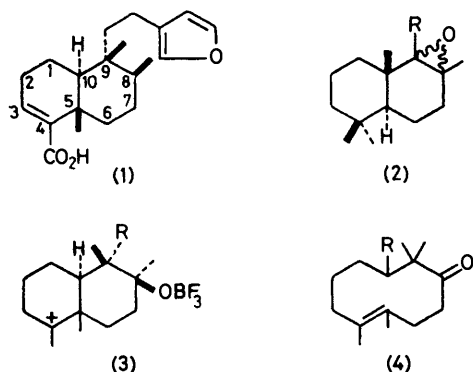
Although it was possible to bring about migration of the C-10 methyl group to C-9 and the C-5 hydrogen to C-10 the migration of the C-4 β-methyl to C-5 proved much more difficult to achieve, presumably because its migration introduces a 1,3-diaxial interaction between the methyls at C-5 and C-9. In one case migration did occur but the resulting ion (3), instead of losing a proton from C-3, underwent further rearrangement to give the cyclodecenone (4). One of the problems involving biogenetic-type carbonium rearrangements is control over which proton is lost. In nature this control is exercised by an enzyme system.

Another approach towards the synthesis of friedo-labdanes can start from the octalindione (5). This possesses functionality permitting modification at positions which correspond to C-3, C-4, C-8, C-9, and C-10 of the required diterpene skeleton [*cf.* (1)]. The initial stages of such an approach leading to the synthesis of the

intermediate (6) * are now described together with the chemistry of its precursor (8).

(5)   (6)
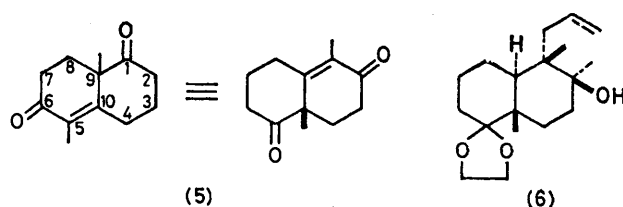
The dione (5) was selectively converted into the mono-acetal (7). Reductive-alkylation of the monoacetal with allyl bromide and the lithium–ammonia–tetra-hydrofuran system to which 1 mol. equiv. of water had been added [4] afforded in high yield the monoalkylated product (8) plus two dialkylated by-products. Analo-

(7)   (8)
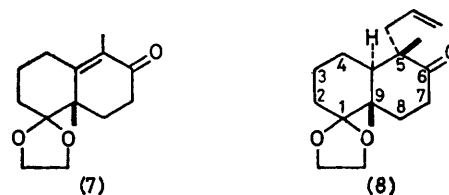
gous reductive-alkylations are known to give the *trans*-decalin structure.[5]

The reactions of (8) described below show that the allyl group is α-substituted and discussion of its chemistry is based on this stereochemistry. In order to study the potentiality of the allyl group as a precursor of the diterpene side chain, reactions of its double bond were investigated. The double bond in the structure (8) was inert to epoxidation with peracetic acid or *m*-chloroperbenzoic acid or alkaline hydrogen peroxide in benzonitrile. The keto group was therefore reduced with lithium tri-t-butoxyaluminium hydride in tetra-hydrofuran under reflux and with alkali-free sodium borohydride at 0° to give the β-alcohol (9a) as the major product and the α-alcohol as the minor product.

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* This and subsequent compounds are racemic. In each case the isomer is drawn which corresponds to the stereochemistry of the friedolabdanes. The compounds are numbered as octalin or decalin derivatives.

[1] W. Cocker, A. L. Moore, and A. C. Pratt, *Tetrahedron Letters*, 1965, 1983.

[2] M. S. Hadley and T. G. Halsall, *J. Chem. Soc. (C)*, 1974, 1334.
[3] I. J. Massey, D.Phil. Thesis 1975, University of Oxford.
[4] J. W. Apsimon, P. Baker, J. Buccini, J. W. Hooper, and S. Macaulay, *Canad. J. Chem.*, 1972, **50**, 1944.
[5] D. J. France, J. J. Hand, and M. Loss, *Tetrahedron*, 1969, **25**, 4011.

The mixture proved too difficult to separate as did the mixture of the corresponding acetates. It was treated with acid to hydrolyse the acetal group and the resulting mixture of keto-alcohols was separated by preparative layer chromatography (p.l.c.). The β-alcohol (9b) which was the major component gave an n.m.r. signal at τ 6.56 ($W_{\frac{1}{2}}$ 16.5 Hz) for an axial proton attached to

(9) a; Z =

b; Z = O
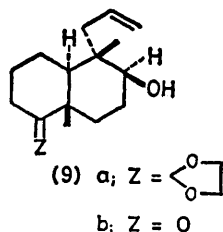
carbon carrying oxygen. The α-alcohol had a corresponding signal at τ 6.45 ($W_{\frac{1}{2}}$ 7.0 Hz). Epoxidation of the two alcohols with *m*-chloroperbenzoic acid in dichloromethane gave in each case a pair of epimeric ketols formed by reaction of the hydroxy-group with the initially formed epimeric mixture of epoxides. The β-alcohol gave rise to the crystalline keto-primary alcohols (10b) and (11b).


(10) a; Z =   (11) a; Z =

b; Z = O   b; Z = O
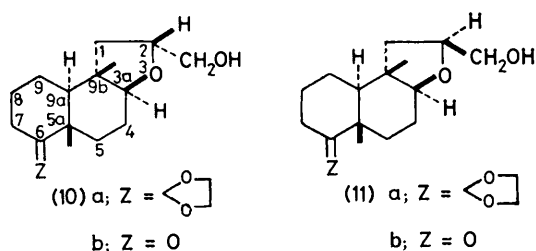
They were also obtained starting from reaction of *m*-chloroperbenzoic acid with a sample of the β-hydroxy-acetal (9a) containing about 20% of the α-isomer (12).

(12)
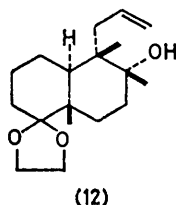
This gave rise to the two crystalline hydroxy-acetals (10a), m.p. 146—148°, and (11a), m.p. 139—142°, which on hydrolysis gave the keto-primary alcohols (10b), m.p. 146—149°, and (11b), m.p. 143—146°, respectively.

The structural assignments are consistent with the spectral data. The CH_2OH groups of the hydroxy-acetals (10a) and (11a) showed signals at τ 6.32 (complex; doublet after D_2O exchange, *J* 6.5 Hz), and τ 6.36 [d, *J* 6.5 Hz (unchanged after D_2O exchange)] respectively. The effect of the OH group on the CH_2OH signal of (10a) is associated with the degree of hydrogen bonding between the OH group and the oxygen of the heterocyclic ring. Models indicated that in structure (10a) the α-orientated hydroxymethyl group is free from

an unfavourable interaction with the 4bβ-methyl group which is found in structure (11a) and is able to hydrogen

(13)

(14) R^1 = OH; R^2 = H

(15) R^1 = H; R^2 = OH
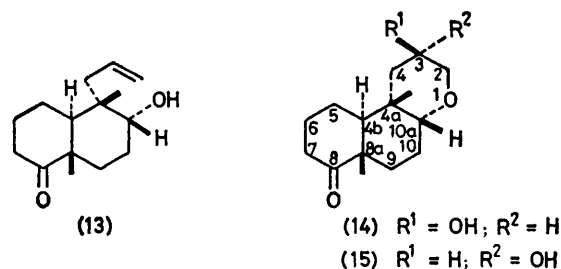
bond without hindrance to the heterocyclic oxygen atom.

The α-alcohol (13) gave two ethers. Spectral data are consistent with the ethers having the epimeric structures (14) and (15) but it is not possible to distinguish which is which with certainty. The n.m.r. signals for the protons in the $>CH(OH)$ group are at τ 6.02 and τ 5.96 respectively but the band widths do not significantly differ.

The hetero ring in these two ethers must be present as a chair since only this conformation is compatible with the equatorial conformation of H-10a, which is required by the half-band width (7 Hz) of its n.m.r. signal.

The formation of the six-membered hetero ring from the α-axial hydroxy-group is only possible if the hetero ring is *cis*-fused to the carbocyclic ring and hence that the allyl side chain in the α-alcohol (13) and in the ketone (8) is α-orientated.

The two alcohols can arise from the diastereoisomeric epoxides (16a) and (16b) (Scheme 1). Antiperiplanar

SCHEME 1
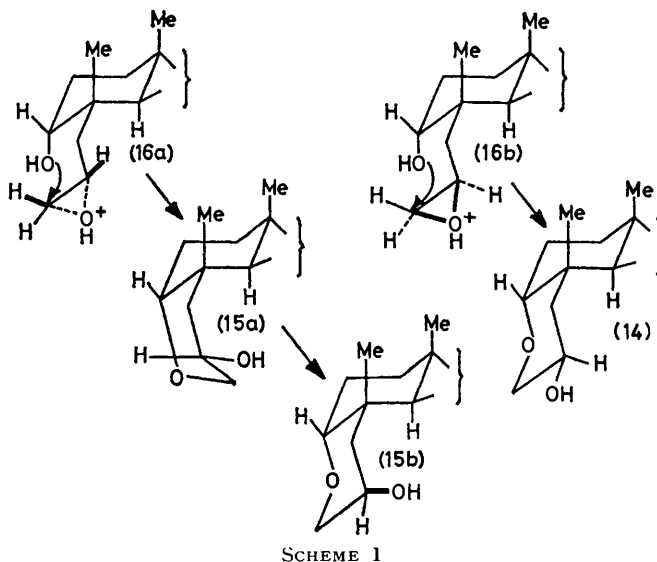
approach of the α-hydroxy-group in the epoxide (16b) can proceed smoothly leading to structure (14). The opening of the other epoxide (16a) requires that the newly formed heterocyclic ring has initially a boat conformation with the hydroxy-group equatorial. This ring can flip over to the more stable conformation with the hydroxy-group axial as in (15b).

Hydroxy-participation in the opening of an oxiran ring has been previously observed.[6]

Although epoxidation of the ketone (8) did not take place, reaction of the β-methoxy derivative (17) and of the bis-acetal (18) with *m*-chloroperbenzoic and of the bis-acetal with a buffered solution of peracetic acid afforded diastereoisomeric mixtures of (19) and (20a)

(17) (18)

(19) (20)
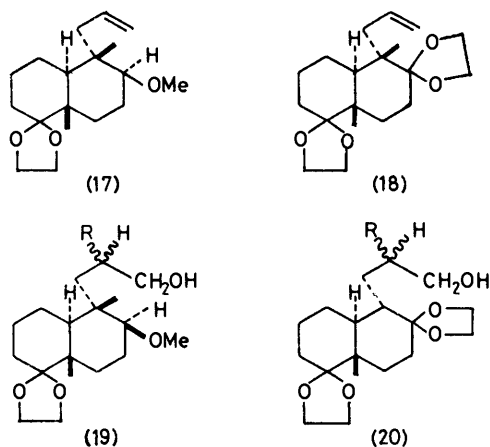
a; R = OAc
b; R = *m* - ClC₆H₄CO₂

or (20b) respectively. Nevertheless the ketone (8) proved to be unreactive when treated with the benzonitrile–hydrogen peroxide–sodium carbonate system.

Epoxidation of the deoxy-compound (21) with *m*-chloroperbenzoic acid gave a diastereoisomeric mixture of epoxides (22) in 55% yield. The deoxy compound

(21) (22)
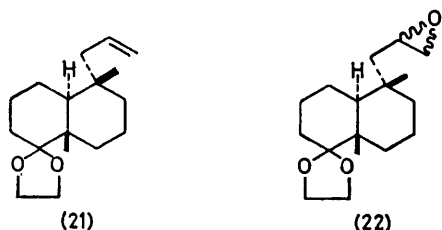
was made by Huang-Minlon reduction of the corresponding ketone. The dehydro derivative of the allyl acetal (21) was also obtained as a by-product.

An attempt to hydrate the double bond of the acetal (8) in an anti-Markownikov manner by hydroboration with 9-borabicyclo[3.3.1]nonane (9-BBN) in boiling tetrahydrofuran (THF) followed by treatment with ethanolic alkaline hydrogen peroxide afforded in 40% yield an unexpected crystalline saturated hydroxy-acetal (C₁₇H₂₈O₃). The i.r. spectrum indicated the presence of a hydroxy-group but no band due to an olefin bond. The n.m.r. spectrum had a signal at τ 6.16 (4 H,–OC*H₂*· C*H₂*O–) and two singlets at τ 8.93 and 9.08 due to two methyl groups on quaternary carbon.

There was no signal due to a proton on carbon attached

⁶ M. G. Human, M. N. Paddon, and R. N. Warrener, *Synth. Comm.*, 1975, **5**(2), 107.

to a hydroxy-group, indicating that the hydroxy-group is tertiary, no signal due to an olefinic proton, and no signal due to a methyl group at the end of a side chain. These results are only consistent with a tricarbocyclic structure and suggest that the product has structure (27). A possible mechanism involves attack by boron on the oxygen of the carbonyl group with attack by the double bond at the carbonyl carbon to give an intermediate ion which is then reduced by transfer either inter- or intramolecularly of hydride ion from boron.

Again the close involvement of the carbonyl group with the allyl double bond is emphasised.

Ozonolysis of the carbon–carbon double bond in the bis-acetal compound (18) afforded the aldehyde (24). Reduction of the aldehyde with lithium aluminium hydride in tetrahydrofuran afforded the alcohol (25a) in an overall yield of 52% from (18). A much higher yield of alcohol is obtained (*ca.* 70%) when the metal hydride reduction is performed on the crude ozonolysis product. The bis-acetal alcohol (25a) on treatment with aqueous methanolic hydrogen chloride gave the diketone (25b) and the methoxy ether (26) in a 1 : 1 ratio, while


9—BBN + (8) ⟶

(23)
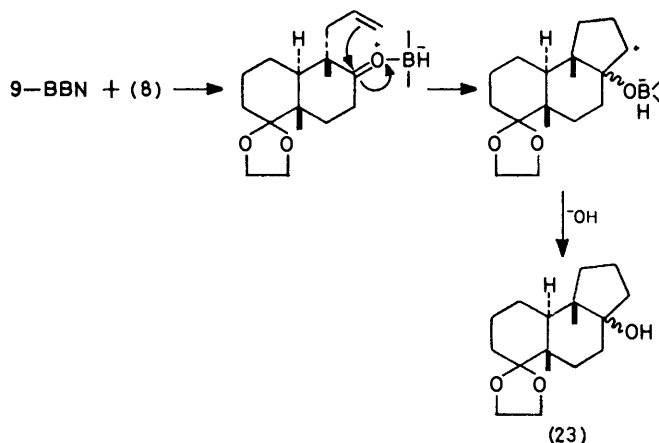
the treatment with hydrogen chloride in acetone gave, as well as the diketone (25b), the product (27) in 70% yield. In contrast the acidic hydrolysis of (25a) in the two phase hydrochloric acid–ether system under reflux afforded exclusively the diketone (25b).

The experiments so far described to modify the side chain of (8) all involve participation of the carbonyl group. The modification of the functionality at C-6 in the ketone (8) before modification of the side chain was therefore examined. Wittig reactions with (8) and (28) were unsuccessful probably owing to the clustering of the carbonyl group by the allyl side chain. However the carbonyl group of the ketone (8) reacted with methyllithium to give in high yield the tertiary alcohol (6) which is a useful intermediate for further study.

Attempts were made to introduce other functionalised side chains at C-5 in the octalone (7). Alkylation with benzyloxymethyl chloride under non-reductive conditions gave almost exclusively the O-alkylated compound (29) which is readily converted back into (7) and (5) on

acid treatment. Only a trace of the C-alkylation product (30) was formed. The dienol-ether (29), when set aside at room temperature, underwent auto-oxidation

The ketol (34) prepared by regio-selective reduction [8] of (5) on reductive alkylation with allyl bromide afforded mainly (35) plus two di-allyl derivatives. The α-
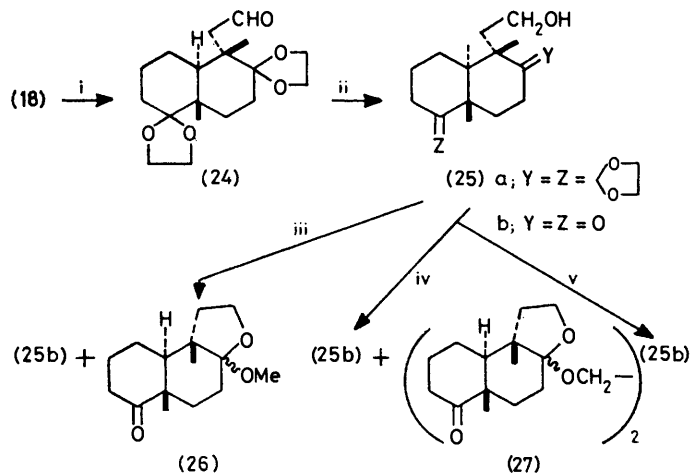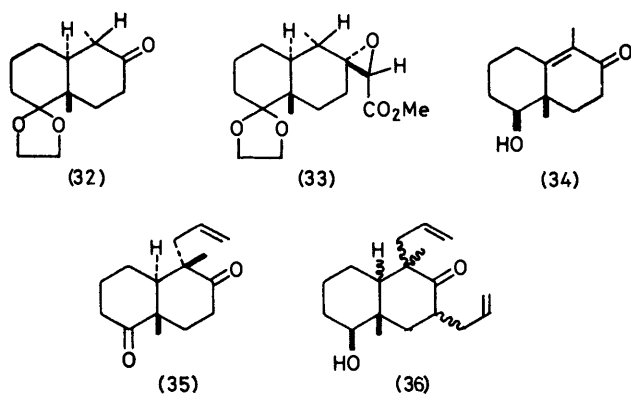

SCHEME 2   Reagents: i, O₃-pyridine, CH₂Cl₂; ii, LiAlH₄-tetrahydrofuran; iii, HCl-MeOH; iv, HCl-Me₂CO; v, HCl-Et₂O

to the ketol (31). Attempted reductive alkylation failed.
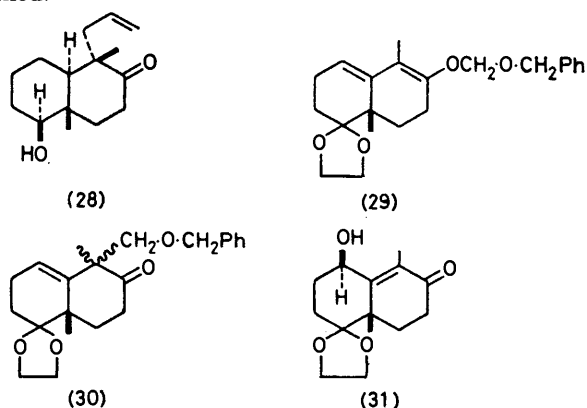
An attempt to carry out a reductive alkylation with methyl bromoacetate gave the saturated ketone (32)

plus the epoxy ester (33) with a possible stereochemistry as depicted.[7]

[7] C. C. Tung, A. J. Speziale, and H. W. Frazier, J. Org. Chem., 1963, 28, 1574.

stereochemistry of the side chain and of the ring junction in (35) was established by oxidation of the alcohol (35) to the diketone (35) which is readily obtained from (8) on acid hydrolysis.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. U.v. spectra were recorded for solutions in ethanol. I.r. spectra were determined for solutions in chloroform. ¹H N.m.r. spectra were determined at 60, 90, or 100 MHz and ¹³C n.m.r. spectra were recorded on a Brüker WH instrument for solutions in deuteriochloroform with tetramethylsilane as internal standard.

For t.l.c. unbaked Merck Kieselgel PF 254 + 366 plates were used. For p.l.c. unbaked Kieselgel HF 254 + 366 plates were used in two sizes (100 cm × 20 cm × 1 mm and 20 cm × 20 cm × 1 mm). G.l.c. was carried out on a Pye 104 series chromatograph fitted with a flame ionisation detector. The column used for determining the purity of products and for following reactions was a 5 ft glass column packed with 3% silicon oil on Chromosorb W. Light petroleum refers to the fraction with b.p. 40—60°.

Preparation of 5,5-*Ethylenedioxy*-1,10-*dimethyl*-Δ¹⁽⁹⁾-*octalin-2-one* (7).—This was prepared according to Corey's method [9] for the corresponding 5,5-ethylenedioxy derivative of 9-methyl-Δ⁵⁽¹⁰⁾-octalin-1,6-dione. A mixture of dry benzene (550 ml) and dry ethylene glycol (75.9 g, 1.22 mol) was heated under reflux with vigorous stirring until all the water was removed. To this mixture was added dropwise a solution of anhydrous toluene-*p*-sulphonic acid (0.4 g, 0.002 mol) and 5,9-dimethyl-Δ⁵⁽¹⁰⁾-octalin-1,6-dione (16.8 g, 0.084 mol) in benzene (40 ml). The proportion of the monoethylenedioxy compound reached a maximum after 180 min as monitored by g.l.c. The reaction mixture was then cooled and worked up to afford an oily residue (20.0 g) whose g.l.c. analysis showed that

[8] C. B. C. Boyce and J. S. Whitehurst, J. Chem. Soc., 1960, 2680.
[9] E. J. Corey, M. Ohno, R. B. Mitra, and G. A. Vatakencherry, J. Amer. Chem. Soc., 1964, 86, 478.

the mono- and bis-ethylenedioxy derivatives were in a ratio 95 : 5. Separation and purification by a combination of crystallisation and chromatography afforded the desired 5,5-ethylenedioxy-1,10-dimethyl-$\Delta^{1(9)}$-octalin-2-one (7) (15.6 g, 89% with respect to the dione consumed). A sample crystallised from ether had m.p. 57—58° (lit.,[10] 55—56°), τ 6.07 (4 H, s, -OCH$_2$CH$_2$O-), 8.23 (3 H, s, $>$C= CMe-), and 8.69 (3 H, s, CMe-); $\nu_{max.}$ (CCl$_4$) 1 675 and 1 610 cm^{-1}; m/e 236 (M^+, 91%); $\lambda_{max.}$ (EtOH) 242 nm (ε 13 688). The bis-ethylenedioxy-compound (2.91 g) was crystallised from ether, as needles, m.p. 58—60°, τ(CCl$_4$) 4.75 (1 H, m, $>$C=CH), 6.13—6.16 (8 H, m, 2 $\times$ -OCH$_2$-CH$_2$O-), 7.52 (1 H, m, allylic), 8.81 (3 H, s, CMe), and 9.08 (3 H, d, J 8.0 Hz, CHMe); $\nu_{max.}$ (CCl$_4$) 3 050, 1 655, and 920 cm^{-1}; m/e 280 (M^+, 9%).

Reductive Alkylation of 1,1-*Ethylenedioxy*-5,9-*dimethyl*-$\Delta^{5(10)}$-*octalin*-6-*one with Lithium—Ammonia and Allyl Bromide in Tetrahydrofuran—Water.*[4,11]—A solution of the enone (7) (4.72 g, 20.0 mmol) in tetrahydrofuran (50 ml) (freshly distilled from benzophenone—sodium) and water (0.36 g, 20.0 mmol) was added dropwise to a stirred solution of lithium (0.60 g, 86.0 mmol) in ammonia (50 ml) (distilled from sodium) during 30 min. The solution was stirred for a further 30 min and then freshly distilled allyl bromide (17.6 g, 144.0 mmol) in tetrahydrofuran (20 ml) was slowly added. The ammonia was allowed to evaporate off overnight, the excess of lithium was destroyed by adding ethanol followed by water, most of the solvent was removed under reduced pressure, and the residue was treated with ether and worked up to give an oily residue (5.5 g) which t.l.c. analysis showed to be a mixture of three products. Separation by combined fractional distillation and column chromatography on silica gel (200 g), with ether—light petroleum as eluant, yielded the expected 5α-*allyl*-1,1-*ethylenedioxy*-5β,9β-*dimethyl*-trans-*decalin*-6-*one* (8) (4.8 g), 85% yield, b.p. 130—135° at 0.4 mmHg (oil-bath), τ 4.33 (1 H, m, band width 40.0 Hz, -CH$_2$CH=CH$_2$), 4.94br (1 H, s, -CH$_2$CH=CH$_2$), 5.09br (1 H, d, J 8.0 Hz, -CH$_2$CH=CH$_2$), 6.10br (4 H, s, -OCH$_2$CH$_2$O-), 8.82 (3 H, s, CMe), and 8.98 (3 H, s, CMe); $\nu_{max.}$ (film) 3 070, 1 640, and 910 cm^{-1} (terminal olefin), and 1 705 cm^{-1} ($>$C=O); m/e 278 (M^+, 4%), base peak m/e 99 (Found: C, 73.75; H, 9.55. C$_{17}$-H$_{26}$O$_3$ requires C, 73.35; H, 9.4%); 5ξ,7ξ-diallyl-1,1-ethylenedioxy-5,9β-dimethyldecalin-6-one (oil) (0.20 g); τ 4.29 (2 H, m, 2 $\times$ -CH$_2$CH=HH$_2$), 4.99 (2 H, s, slightly shouldered, 2 $\times$ -CH$_2$CH=CH$_2$), 5.11 (2 H, s, shouldered, 2 $\times$ CH$_2$CH=CH$_2$), 6.12br (4 H, s, -OCH$_2$CH$_2$O-), 7.40—7.60 (4 H, m, allylic CH$_2$), 8.70 (3 H, s, CMe), 8.96 (3 H, s, CMe); $\nu_{max.}$ 3 070, 1 640, and 912 cm^{-1} (-CH=CH$_2$), and 1 700 cm^{-1} ($>$C=O), m/e 318 (M^+, 20%), base peak m/e 99, and 86 (30), 112 (17), 41 (15), and 55 (12) (Found: C, 75.15; H, 9.4. Calc. for C$_{17}$H$_{30}$O$_3$: C, 75.45; H, 9.45%); and another stereoisomer of 5ξ,7ξ-diallyl-1,1-ethylenedioxy-5,9β-dimethyldecalin-6-one (oil) (0.30 g), τ 4.28 (2H, m, 2 $\times$ CH$_2$CH=CH$_2$), 4.80—5.16 (4 H, complex, 2 $\times$ -CH$_2$CH=CH$_2$), 6.0 (4 H, s, -OCH$_2$CH$_2$O-), 9.17 (3 H, s, CMe), and 9.19 (3 H, s, Me); $\nu_{max.}$ 3 070, 1 640, and 920 cm^{-1} (CH=CH$_2$), and 1 700 cm^{-1} ($>$C=O), m/e 318 (M^+, 7%), base peak m/e 99, and 86 (48), 41 (46), 55 (26), and 112 (29) (Found: C, 75.3; H, 9.3%).

Reduction of 5α-*Allyl*-1,1-*ethylenedioxy*-5β,9β-*dimethyl*-trans-*decalin*-6-*one* (8).—(i) Lithium tri-t-butoxyaluminium hydride (1.1 g, 4.6 mmol) was added under nitrogen to a

solution of the acetal (8) (1.0 g, 3.1 mmol) in tetrahydrofuran. The mixture was heated under reflux for 48 h, and then cooled, and water was added to decompose the metal complexes. Extraction with ether followed by the usual work-up gave an oily residue (900 mg) which was shown by t.l.c. to contain some starting material. The residue was applied on two (1 m) preparative silica gel plates which were developed three times with light petroleum—ether (3 : 1) as eluant to afford the starting material (300 mg) and the 5α-allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6β-ol (9a) (522 mg, 47% yield) admixed with about 25% of the α-epimer as indicated by g.l.c. A sample purified by fractional distillation under reduced pressure [135° at 0.2 mmHg (oil-bath)] still contained 5—10% of the 6α-ol epimer (g.l.c.), and had the following physical properties; τ 4.11 (1 H, m, -CH$_2$CH= CH$_2$), 4.84 (1 H, s, -CH$_2$CH=CH$_2$), 4.96br (1 H, s, -CH$_2$CH= CH$_2$), 6.09 (4 H, s, -OCH$_2$CH$_2$O-), 6.50 (1 H, complex, $W_{\frac{1}{2}}$ ca. 19 Hz, -CHOH), 8.92 (3 H, s, CMe), and 9.17 (3 H, s, CMe); $\nu_{max.}$ (film) 3 450, 3 035, 1 635, and 910 cm^{-1}; m/e 280 (M^+, 7%), base peak m/e 99 (Found: C, 72.6; H, 10.1. Calc. for C$_{17}$H$_{28}$O$_3$: C, 72.8; H, 10.05%).

(ii) Sodium borohydride (205 mg, 5.3 mmol) purified by crystallisation from diglyme was added in several portions to a cooled solution of the acetal (8) (1.5 g, 5.2 mmol) in anhydrous methanol. The solution was stirred for 2 h. Then water was added and work-up gave an oily residue (1 285 g, 85% yield) which was shown by g.l.c. analysis to be a mixture (*ca.* 8.5 : 1.5) of the 6β- and 6α-hydroxy compounds respectively.

Preparation of 5α-*Allyl*-6β-*hydroxy*-5β,9β-*dimethyl*-trans-*decalin*-1-*one* (9b) *and its* 6α-*Epimer*.—A mixture (80 : 20) of the 6β-hydroxy-compound (9a) and its 6α-epimer (12) (920 mg) in acetone (10 ml) was treated with 1.5% hydrochloric acid (0.5 ml) under reflux for 4 h. The reaction mixture was then treated with sodium hydrogen carbonate solution and most of the solvent removed under reduced pressure. Work-up gave an oily residue (660 mg) which was applied to two large p.l.c. plates of silica gel and developed 9 times with light petroleum—ether (1 : 3). Two bands were extracted in order of decreasing R_F values.

Band A gave 5α-*allyl*-6α-*hydroxy*-5β,9β-*dimethyl*-trans-*decalin*-1-*one* (13) (72 mg, 46% yield), m.p. 82—85° (from ether); τ 4.03 (1 H, m, CH$_2$CH=CH$_2$), 4.82br (1 H, d, J 2.0 Hz, -CH$_2$CH=CH$_2$), 4.98br (1 H, s, -CH$_2$CH=CH$_2$), 6.45br [1 H, s, shouldered, $W_{\frac{1}{2}}$ 7.0 Hz, -CH(OH)CH$_2$-], 8.28 (1 H, s, exchangeable with D$_2$O, OH), 8.83 (3 H, s, CMe), and 9.06 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 610, 3 520, 3 060, 1 700, 1 645, and 920 cm^{-1}; m/e 236 (M^+; 1%), m/e 218 (M^+ − H$_2$O, 10%), 196 (10), 195 (72), 177 (37), 159 (48), 149 (28), 135 (66), 111 (25), 93 (44), and 81 (38) (Found: C, 75.85; H, 10.05. C$_{15}$H$_{24}$O$_2$ requires C, 76.2; H, 10.2%).

Band B gave the 6β-*hydroxy-stereoisomer* (9b) (410 mg, 66% yield), m.p. 63—65° (from ether); τ 4.23 (1 H, m, -CH$_2$CH=CH$_2$), 4.88br (1 H, b, -CH$_2$CH=CH$_2$), 5.01vbr (1 H, s, -CH$_2$CH=CH$_2$), 6.56 [1 H, complex, $W_{\frac{1}{2}}$ 16.5 Hz -CH(OH)CH$_2$-], 8.22br (1 H, s, exchangeable with D$_2$O, OH), 8.83 (3 H, s, CMe), and 9.07 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 450, 3 060, 1 700, 1 635, and 915 cm^{-1}; m/e 236 (M^+, 1%), 196 (11), 195 (77), 177 (32), 159 (38), 149 (25), 135 (38), 111 (27), 93 (32), and 81 (30) (Found: C, 76.4; H, 10.3%).

[10] Y. Kitihara, A. Yoshikoshi, and S. Oida, *Tetrahedron Letters*, 1964, 1763.

[11] G. Stork, S. Uyeo, T. Wakamatsu, P. Grieco, and J. Labovitz, *J. Amer. Chem. Soc.*, 1971, **93**, 4947.

Reaction of 5α-*Allyl*-6α-*hydroxy*-5β,9β-*dimethyl*-trans-*decalin*-1-*one* (13) *with* m-*Chloroperbenzoic Acid.*—m-Chloroperbenzoic acid (45 mg, 0.26 mmol) and the decalone (13) (60 mg, 0.21 mmol) in dichloromethane (4 ml) were stirred at room temperature for 18 h. A catalytic amount of palladium was then added [12] to decompose any excess of m-chloroperbenzoic acid and after 30 min of stirring the reaction mixture was worked up to give a solid residue (55 mg) which t.l.c. analysis showed to contain two products apart from the starting material. The mixture was applied to one small plate (20 cm × 20 cm × 1 mm) of silica gel to give, after continuous elution with light petroleum–ether (3 : 1), 3ξ-hydroxy-4aβ,8aβ-dimethyl-(4bαH,-10aαH)-1-oxaperhydrophenanthren-8-one (14 or 15) (16 mg), m.p. 108—111° (from ether), τ 5.96 (1 H, complex, $W_{\frac{1}{2}}$ ca. 20 Hz, -OCH$_2$CHOHCH$_2$-), 6.34 (1 H, complex, $W_{\frac{1}{2}}$ ca. 7 Hz, -OCHCH$_2$-), 6.48 (2 H, complex, -OCH$_2$CHOH-CH$_2$-), 8.83 (3 H, s, CMe), and 8.92 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 3 450 and 1 700 cm^{-1}; m/e 252 (M^+, 13%), base peak m/e 221, and m/e 234 (M^+ − H$_2$O, 3%), 203 (19), 177 (51), 159 (54), 135 (45), 95 (20), 81 (20), 69 (19), and 41 (60) (Found: C, 71.6; H, 9.3. Calc. for C$_{15}$H$_{24}$O$_3$: C, 71.4; H, 9.5%), and a compound of higher R_F considered to be the stereoisomer (15) or (14) (6 mg), m.p. 82—87° (from ether); τ 6.02 (1 H, m, $W_{\frac{1}{2}}$ ca. 21 Hz, -OCH$_2$CHOHCH$_2$-), 6.32 (1 H, complex, $W_{\frac{1}{2}}$ ca. 7 Hz, OCHCH$_2$-), 6.48 (2 H, complex, -OCH$_2$CHOHCH$_2$-), 8.85 (3 H, s, CMe), and 8.90 (3 H, s, CMe), $\nu_{max.}$ (CHCl$_3$) 3 450 and 1 700 cm^{-1}; m/e 252 (M^+, 11%), base peak m/e 221, and m/e 234 (M^+ − H$_2$O, 7%), 203 (22), 117 (54), 159 (81), 135 (70), 95 (32), 81 (35), 69 (29), and 41 (81) (Found: C, 71.4; H, 9.6%).

Reaction of 5α-*Allyl*-6β-*hydroxy*-5β,9β-*dimethyl*-trans-*decalin*-1-*one* (9b) *with* m-*Chloroperbenzoic Acid.*—m-Chloroperbenzoic acid (180 mg, 1.04 mmol) and the decalone (9b) (250 mg, 0.86 mmol) in dichloromethane were stirred for 14 h. The normal work-up as described before afforded two compounds which were separated by preparative silica gel chromatography by continuous elution with light petroleum–ether (3 : 1). The compound with lower R_F value, in major amount (93 mg), was identified as 2α-*hydroxymethyl*-9bβ,5aβ-*dimethyl*-(9aαH,3aαH)-*perhydro*-*naphtho*[2,1-b]*furan*-6-*one* (10b), m.p. 146—149° (from ether); τ 5.94 [1 H, m, $W_{\frac{1}{2}}$ ca. 20 Hz, -OCH(CH$_2$OH)CH$_2$-], 6.32 [2 H, complex, $W_{\frac{1}{2}}$ ca. 13 Hz, becoming basically a doublet, J 6.0 Hz, on deuterium exchange, -OCH(CH$_2$OH)-CH$_2$-], 6.94 (1 H, complex, $W_{\frac{1}{2}}$ ca. 15 Hz, -OCHCH$_2$-), 7.86br (1 H, s, exchangeable with D$_2$O, OH), 8.81 (3 H, s, CMe), and 9.07 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 3 450 and 1 700 cm^{-1}; m/e 252 (M^+, 7%), base peak m/e 41, and m/e 221 (56), 203 (33), 177 (23), 159 (32), 135 (12), 95 (29), 81 (38), 79 (32), and 69 (54) (Found: C, 71.6; H, 9.3. C$_{15}$H$_{24}$O$_3$ requires C, 71.4; H, 9.5%). The compound of higher R_F value was considered to be the 2β-*hydroxymethyl stereoisomer* (11b), m.p. 143—146° (from ether); τ 5.93 [1 H, m, $W_{\frac{1}{2}}$ ca. 21 Hz, -OCH(CH$_2$OH)CH$_2$-], 6.34 [2 H, d, J 6.0 Hz, -OCH(CH$_2$-OH)CH$_2$-], 6.94 (1 H, complex, $W_{\frac{1}{2}}$ ca. 14 Hz, -OCHR·CH$_2$-), 7.90br (1 H, s, exchangeable with D$_2$O, OH), 8.83 (3 H, s, CMe), and 9.08 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 1 450 and 1 700 cm^{-1}; m/e 252 (M^+, 4%), base peak m/e 41, and m/e (48), 202 (22), 177 (22), 159 (29), 135 (22), 95 (24), 81 (36), 79 (26), 69 (36), and 55 (55) (Found: C, 71.45; H, 9.45%).

Reaction of 5α-*Allyl*-1,1-*ethylenedioxy*-5β,9β-*dimethyl*-trans-*decalin*-6β-*ol* (9a) *containing ca. 10% of the* 6α-*Epimer with* m-*Chloroperbenzoic Acid.*—m-Chloroperbenzoic acid (600 mg, 3.4 mmol) was added to a solution of the decalinol

(9a) [(910 mg, 2.92 mmol), admixed with ca. 10% of the 6α-epimer (12)] in dichloromethane (10 ml) and sodium hydrogen carbonate (336 mg, 4 mmol); the mixture was stirred at room temperature. The reaction, monitored by t.l.c., was complete after 16 h. A catalytic amount of palladium [12] was then added to decompose any excess of m-chloroperbenzoic acid present. The mixture was stirred for 30 min and then worked up to give an oily residue (660 mg) which by t.l.c. analysis was shown to be a complex mixture of at least three products. Separation by silica gel chromatography using the continuous elution technique with light petroleum–ether as eluant afforded two compounds in a weight ratio ca. 3 : 1. The one with lower R_F value, being in a greater amount (150 mg), was 6,6-*ethylenedioxy*-2α-*hydroxymethyl*-5aβ,9bβ-*dimethyl*-(9aαH,3aαH)-*perhydro*-*naphtho*[2,1-b]*furan*-6-*one* (10a) and gave needles, m.p. 146—148° (from ether); τ 6.10br (4 H, s, -OCH$_2$CH$_2$O-), 5.70 [1 H, m, partially overlapped by signal at 6.10, -OCH-(CH$_2$OH)·CH$_2$-], 6.32 [2 H, complex, simplified on exchange with deuterium to a doublet, J 6.5 Hz, -OCH(CH$_2$OH)-CH$_2$-] 6.82 (1 H, complex, $W_{\frac{1}{2}}$ ca. 18 Hz, -OCHCH$_2$-), 7.65 (1 H, t, J 6.0 and 6.0 Hz, exchangeable with D$_2$O, OH), 8.90 (3 H, s, CMe), and 9.15 (3 H, s, CMe); $\nu_{max.}$ (Nujol) 3 420 cm^{-1}; m/e 296 (M^+, 9%), base peak m/e 99, and m/e 281 (4), 265 (6), 224 (7), and 181 (13) (Found: C, 68.5; H, 9.25. C$_{17}$H$_{28}$O$_4$ requires C, 68.85; H, 9.5%). The other compound was the 2β-*hydroxymethyl stereoisomer* (11a) (40 mg), m.p. 139—142° (from ether); τ 6.08br (4 H, s, -OCH$_2$CH$_2$-), 5.75 [1 H, m, partially overlapped by signal at 6.10, -OCH-(CH$_2$OH)CH$_2$-], 6.36 [2 H, d, J 6.5 Hz, unchanged on deuterium exchange, -OCH(CH$_2$OH)CH$_2$-], 6.83 (1 H, complex, $W_{\frac{1}{2}}$ ca. 18 Hz, -OCHCH$_2$-), 6.8 (1 H, s, exchangeable with D$_2$O, OH), 8.87 (3 H, s, CMe), and 9.13 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 3 450 cm^{-1}; m/e 296 (M^+, 11%), base peak m/e 99, and m/e 281 (4), 265 (7), 224 (6), 193 (35), 181 (26), and 128 (18) (Found: C, 68.7; H, 9.4%).

When acetone solutions of these two acetals (10a) and (11a) were separately treated with dilute hydrochloric acid the corresponding ketones [(10b and (11b)] were obtained and were identical in all respects to those already described.

Preparation of 5α-*Allyl*-1,1-*ethylenedioxy*-6β-*methoxy*-5β,-9β-*dimethyl*-trans-*decalin* (17).—An 80% oil suspension of sodium hydride (297 mg, 9.6 mmol), washed twice with light petroleum, was added in portions under a slow stream of nitrogen to a cooled and stirred solution of 5α-allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6β-ol (9a) admixed with ca. 20% of the 6α-epimer (920 mg, 3.3 mmol) and methyl iodide (936 mg, 6.5 mmol) in anhydrous 1,2-dimethoxyethane–dimethylformamide (1 : 1; 10 ml). The mixture was then stirred under nitrogen for 24 h. Further methyl iodide (936 mg, 6.5 mmol) was added and stirring continued for 8 h. After the methyl iodide had been removed by warming, water was carefully added to the mixture to destroy any excess of sodium hydride followed by addition of hydrochloric acid and extraction with ether. The ether extracts gave a residue (820 mg) which by t.l.c. analysis was shown to contain starting material. Combined preparative silica gel chromatography and crystallisation afforded 5α-*allyl*-1,1-*ethylenedioxy*-6β-*methoxy*-5β,9β-*dimethyl*-trans-*decalin* (17) (390 mg, 61%), m.p. 52—54° (from ether); τ (CCl$_4$) 4.17 (1 H, m, -CH$_2$CH=CH$_2$), 4.88br (1 H, s, -CH$_2$CH=CH$_2$), 5.04 (1 H, dd, further coupled, J 4.0 and 9.0 Hz, -CH$_2$CH=CH$_2$), 6.11 (4 H, s, -OCH$_2$CH$_2$O-), 6.68 (3 H, s, OMe), 7.09 (1 H, complex, CHOMe), 7.64 (2 H, dd,

[12] G. H. Whitham, personal communication.

J 8.0 and 14.0 Hz, $-CH_2CH=CH_2$), 8.93 (3 H, s, CMe), and 9.19 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 3 030, 1 635, and 910 cm^{-1}; m/e 294 (M^+, 15%), base peak m/e 99 (Found: C, 73.4; H, 10.35. $C_{18}H_{30}O_3$ requires C, 73.45; H, 10.2%). Starting material (320 mg) was recovered unchanged (i.r. spectroscopy).

Reaction of 5α-Allyl-1,1-ethylenedioxy-6β-methoxy-5β,9β-dimethyl-trans-decalin (17) with m-*Chloroperbenzoic Acid.*—A mixture of m-chloroperbenzoic acid (95 mg, 0.55 mmol), the methoxy-compound (17) (125 mg, 0.43 mmol), and sodium hydrogen carbonate (100 mg) in dichloromethane (5 ml) was stirred for 11 h. The usual work-up afforded a residue which appeared to be a mixture of the glycol monoesters (19). A sample purified by preparative silica gel chromatography had the following physical characteristics: τ 1.90—2.10 and 2.40—2.70 (2 H, each, complex, ArH), 4.70vbr [1 H, t, $-CH_2CH(OCOC_6H_4Cl$-$m)CH_2OH$], 6.00—6.50 [6 H, complex, $-OCH_2CH_2O-$ and $-CH(OCOC_6H_4Cl$-$m)CH_2OH$], 6.71 and 6.87 (3 H, s, 1.3 : 1 ratio, OMe), 6.95—7.20 [1 H, complex, $-CH(OMe)CH_2-$], 7.75vbr (1 H, s, exchangeable with D$_2$O, OH), and 8.99, 9.01 (3 H, s, each, CCH$_3$), and 9.22 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 450 and 1 720 cm^{-1}. No molecular ion was observed in the mass spectrum ($C_{25}H_{35}O_6Cl$ requires m/e 466) and the highest recorded peak had m/e 451 (M^+ — Me, 1%), base peak m/e 99, and m/e 436 (1), 311 (7), 295 (6), 282 (3), 265 (3), 253 (20), 221 (5), 209 (4), 159 (7), and 139 (17) (Found: C, 64.05; H, 7.75; Cl, 7.35. $C_{25}H_{35}ClO_6$ requires C, 64.3; H, 7.5; Cl, 7.6%).

Preparation of 5α-Allyl-1,1:6,6-bisethylenedioxy-5β,9β-dimethyl-trans-decalin (18).—A mixture of 5α-allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6-one (1.30 g, 4.67 mmol), dry benzene (200 ml), and freshly distilled ethylene glycol (5.0 g, 80.6 mmol) was heated under reflux for 2 h while water was azeotropically removed using a Dean–Stark apparatus. Then anhydrous toluene-p-sulphonic acid (160 mg) was added and the mixture was left under reflux with vigorous stirring for 18 h. After cooling the mixture was worked up to give an oily residue (1.5 g). Quick elution from silica gel (30 g) with light petroleum–ether (3 : 1) afforded the desired *5α-allyl-1,1:6,6-bisethylenedioxy-5β,9β-dimethyl-trans-decalin-6-one* (18) (1.1 g, 71% yield) which, when kept at room temperature, gave crystals, m.p. 63—65°; τ(CCl$_4$) 3.99 (1 H, m, band width 42.0 Hz, $-CH_2CH=CH_2$), 5.12br (1 H, s, $-CH_2CH=CH_2$), 5.27vbr (1 H, s, $-CH_2CH=CH_2$), 6.14br (8 H, s, 2 × $-OCH_2$-CH_2O-), 8.96 (3 H, s, CMe), and 9.11 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 035, 1 635, and 910 cm^{-1} ($>C=CH_2$); m/e 368 (M^+, 8%), base peak m/e 99, and m/e 86 (24) and 253 (5) (Found: C, 70.45; H, 9.45. $C_{19}H_{30}O_4$ requires C, 70.75; H, 9.35%).

Reaction of 5α-Allyl-1,1:6,6-bisethylenedioxy-5β,9β-dimethyl-trans-decalin (18) with Peracetic Acid.—The same procedure as described for the attempted epoxidation of the monoethylenedioxy compound (8) was followed. To a stirred mixture of compound (18) (180 mg, 0.55 mmol), dichloromethane (5 ml), and sodium hydrogen carbonate (340 mg, 3.2 mmol) was added a solution of sodium acetate trihydrate (25 mg, 0.18 mmol) in 40% peracetic acid (172 mg, 0.90 mmol). The reaction mixture was first stirred at room temperature during 7 h, but since no change was observed on analysis by t.l.c., it was heated under reflux for 3 h, cooled, and worked up to afford a residue (160 mg) which t.l.c. showed to contain very little starting material. The n.m.r. spectrum of this crude product indicated form-

ation of the glycol monoacetate. The residue was chromatographed on preparative silica gel and eluted four times with light petroleum–ether (4 : 1) yielding the starting material (9 mg) and a mixture of diastereoisomers (80 mg) of 5α-(2-acetoxy-3-hydroxypropyl)-1,1:6,6-bisethylenedioxy-5β,9β-dimethyl-*trans*-decalin (20a), τ (100 MHz) 5.75—6.40 [11 H, complex, 2 × $-OCH_2CH_2O-$ and $CH_2CH(OAc)$-CH_2OH], 7.95 (3 H, s, AcO), and methyl resonances at 8.90, 8.95, 8.96, and 9.02; $\nu_{max.}$ (CHCl$_3$) 3 500, 1 725, and 1 240 cm^{-1}. No further attempt to separate the mixture was made.

Reaction of 5α-Allyl-1,1:6,6-bisethylenedioxy-5β,9β-dimethyl-trans-decalin-6-one (18) with m-*Chloroperbenzoic Acid.*—m-Chloroperbenzoic acid (79 mg, 0.45 mmol) was added to a solution of the 5α-allyl-bis-acetal compound (18) (125 mg, 0.38 mmol) in dichloromethane (5 ml) and sodium hydrogen carbonate (84 mg, 1 mmol). The mixture was kept for *ca.* 18 h at room temperature and was then washed with saturated sodium hydrogen carbonate solution and water, dried (MgSO$_4$), and evaporated. The residue (185 mg) was chromatographed on silica gel (10 g) and eluted with light petroleum–ether (1 : 1) to give an oily residue which by n.m.r. spectroscopy appeared to be a mixture of diastereoisomers of 5α-(2-m-chlorobenzoyloxy-3-hydroxypropyl)-1, 1:6,6-bisethylenedioxy-5β,9β-dimethyl-*trans*-decalin (20b); τ 1.90—2.20 and 2.40—2.75 (4 H, m, each, ArH), 5.55 [1 H, t, J 5.0 and 5.0 Hz, m-ClC$_6$M$_4$CO$_2$CH(CH$_2-$)CH$_2$OH], 6.00—6.15 (8 H, 2 br s, 2 × $-OCH_2CH_2O-$), 6.32 (2 H, complex partially overlapped by the signal centred at 6.12, $-CHCH_2$OH), 7.56br (1 H, s, exchangeable with D$_2$O), and 8.90 (s), 8.91 (s), 8.96 (s, shouldered), and 9.03 (s, shouldered, total intensity 6 H, $>$CMe); $\nu_{max.}$ (CHCl$_3$) 3 450 and 1 720 cm^{-1}; m/e 494 (M^+, <1%).

Preparation of 5α-Allyl-1,1-ethylenedioxy-5β,9β-dimethyl-trans-decalin (21) using Huang–Minlon's Method.—A mixture of 5α-allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6-one (8) (2.78 g, 10 mmol) and hydrazine hydrate (1.37 g, 30 mmol) in diethylene glycol (15 ml) was heated at *ca.* 110° for 3 h. The mixture was then cooled to *ca.* 40°, potassium hydroxide (1.2 g, 30 mmol) was added in small pieces, and the mixture was slowly heated to allow the water and hydrazine to distil off (*ca.* 120°) and then heated at *ca.* 195—200° for 6 h. The mixture yielded an oily residue (2.60 g) which was shown by t.l.c. analysis to be a complex mixture of several compounds. Separation on a silica gel column with light petroleum–ether (1 : 1) as eluant gave (i) the desired 5α-*allyl-1,1-ethylenedioxy-5β,9β-dimethyl-trans-decalin* (21) (750 mg, 27% yield), b.p. 115° at 0.1 mmHg (oil-bath), τ(CCl$_4$) 4.26 (1 H, m, $-CH_2-$$CH=CH_2$), 5.00vbr (1 H, s, $-CH_2CH=CH_2$), 5.18vbr (1 H, d, J 9.0 Hz, $-CH_2CH=CH_2$), 6.19br (4 H, s, $-OCH_2CH_2O-$), 8.09br (2 H, s, $-CH_2CH=CH_2$), 9.0 (3 H, s, CMe), and 9.20 (3 H, s, CMe); $\nu_{max.}$ (film) 3 060, 1 630, and 910 cm^{-1}; m/e 264 (M^+, 13%), base peak m/e 99, and m/e 223 (38), 161 (18), 125 (17), 86 (41), and 55 (19) (Found: C, 77.45; H, 10.7. $C_{17}H_{28}O_2$ requires C, 77.3; H, 10.6%); (ii) *1,1-ethylenedioxy-5β,9β-dimethyl-5α-propyl-trans-decalin* (320 mg), b.p. 118° at 0.1 mmHg (oil-bath); τ(CCl$_4$) 6.10 (4 H, s, $-OCH_2CH_2O-$,), 8.99 (3 H, s, CMe), 9.22 (3 H, s, CMe), and 9.12 (3 H, t, J 7.0 Hz, CH$_2$Me); m/e 266 (M^+, 17%), base peak m/e 99, and m/e 223 (32), 161 (13), 113 (13), 86 (43), and 55 (17) (Found: C, 76.6; H, 11.1. $C_{17}H_{30}O_2$ requires C, 76.7; H, 11.25%), and (iii) a mixture of the 6α- and 6β-alcohols from the corresponding ketone (8) already reported.

Epoxidation of 5α-*Allyl*-1,1-*ethylenedioxy*-5β,9β-*dimethyl*-trans-*decalin* (21) *with* m-*Chloroperbenzoic Acid.*—A solution of m-chloroperbenzoic acid (691 mg, 4.0 mmol) and the acetal (21) (700 mg, 2.65 mmol) in dichloromethane (10 ml) was stirred at room temperature. T.l.c. analysis of the reaction mixture indicated the complete disappearance of the starting olefin after 14 h. Work-up afforded 660 mg of the products which were purified by alumina column chromatography yielding an 8 : 2 mixture (n.m.r. analysis) of the two 2'-epimeric 5α-(2,3-epoxypropyl)-1,1-ethylene-dioxy-5β,9β-dimethyl-*trans*-decalins (22) (410 mg, 55% yield). The mixture had b.p. 140° at 0.1 mmHg (oil-bath); τ(CCl$_4$) 6.15 (4 H, s, shouldered), 7.20 and 7.42 (each

1 H, complex, $W_{\frac{1}{2}}$ ca. 13 Hz, -CH$_2$CHCH$_2$O), 7.78 (1 H, dd,

d, *J* 3.0, *J* 8.0 Hz, -CH$_2$CHCH$_2$O), 8.95 (3 H, s, slightly shouldered, CMe), and 9.10 (3 H, s, shouldered, CMe); *m/e* 280 (M^+, 1%), base peak *m/e* 99, and 266 *m/e* (6), 223 (18), 162 (8), 139 (10), 113 (8), 86 (26), and 55 (10) (Found: C, 72.6; H, 10.15. C$_{17}$H$_{28}$O$_3$ requires C, 72.85; C, 10.0%).

Attempted Hydration of 5α-*Allyl*-1,1-*ethylenedioxy*-5β,9β-*dimethyl*-trans-*decalin*-6-*one* (8).[13]—A solution of 9-bora-bicyclo[4.4.0]nonane (935 mg, 7.6 mmol) in freshly distilled tetrahydrofuran (10 ml), all contained in an equalising pressure dropping funnel, was added dropwise at room temperature to a solution of the decalone (8) (2.0 g, 7.5 mmol) in tetrahydrofuran (10 ml). The whole experiment was carried out under a nitrogen atmosphere. The reaction mixture was heated under reflux for 8 h then brought to room temperature. To the reaction mixture was then added in this order: ethanol (3 ml), 1.5N aqueous sodium hydr-oxide solution (1.5 ml), and 30% hydrogen peroxide (3 ml). The mixture was heated under reflux for 3 h and then worked up by adding sodium hydrogen carbonate to saturate the mixture followed by filtration and evaporation of the solvent. The residue (2.059 g) was analysed by t.l.c. which showed that there was still some starting material present. Separation by column chromatography on alumina with light petroleum–ether (1 : 3) as eluant yielded starting material (900 mg) and an oily compound considered to be 6,6-ethylenedioxy-5aβ,9bβ-dimethyl-(9aαH)-perhydro-benz[e]inden-3aξ-ol (23) which afforded flakes, m.p. 49—58°, from light petroleum–ether at 0°, τ(CCl$_4$) 6.16 (4 H, split s, -OCH$_2$CH$_2$O-), 8.93 (3 H, s, Me), and 9.08 (3 H, s, CMe); ν$_{max.}$ (CCl$_4$) 3 600, 1 450, 1 460, and 1 380 cm^{-1}, *m/e* 280 (M^+, 40%), base peak *m/e* 99, and *m/e* 262 (21), 247 (11), 200 (21), 185 (29), 174 (29), 113 (52), 86 (50), and 55 (40) (Found: C, 72.05; H, 9.05. Calc. for C$_{17}$H$_{28}$O$_3$: C, 72.85; H, 8.7%).

Ozonolysis of 5α-*Allyl*-1,1:6,6-*bisethylenedioxy*-5β,9β-*dimethyl*-trans-*decalin* (18) *in Pyridine–Methylene Chloride as Solvent.*[14]—A solution of 5α-allyl compound (18) (1.60 g, 4.9 mmol) in anhydrous pyridine–dichloromethane (1 : 1; 40 ml) was cooled to *ca.* −70° and ozone was bubbled through at a rate of 18 l h^{-1} during 90 min. Residual ozone was removed by flushing the system with nitrogen. The reaction mixture was worked up to afford an oil (1.5 g) which consisted of mainly one component as shown by t.l.c. A sample (100 mg) was purified by preparative silica gel chromatography yielding 1,1:6,6-*bisethylenedioxy*-5β,9β-*dimethyl*-5α-(2-*oxoethyl*)-trans-*decalin* (24) (52 mg) which gave crystals when kept at room temperature, m.p. 93—95°; τ(CCl$_4$) 0.37 (1 H, t, *J* 4.0 and 4.0 Hz, CH$_2$C*H*O), 6.12

and 6.18 (8 H, s each, 2 × -OCH$_2$CH$_2$O-), 7.80—7.92 (2 H, complex, $W_{\frac{1}{2}}$ 11.0 Hz, C*H*$_2$CHO), 8.91 (3 H, s, CMe), and 8.93 (3 H, s, CMe); ν$_{max.}$ (CHCl$_3$) 1 700 cm^{-1}; *m/e* 324 (M^+, 2%), base peak *m/e* 99, and *m/e* 296 (22) and 253 (10) (Found: C, 66.5; H, 8.7. C$_{18}$H$_{28}$O$_5$ requires C, 66.6; H, 8.7%) and a mixture (22 mg) presumably containing the acid corresponding to (18) as shown by the i.r. analysis. The yield was 55% of crystallised material.

Reduction of 1.1:6,6-*Bisethylenedioxy*-5β,9β-*dimethyl*-5a-(2-*oxoethyl*)-trans-*decalin* (24) *with Lithium Aluminium Hydride.*—A solution of the crude 2'-oxoethyl compound (24) (1.40 g) in anhydrous tetrahydrofuran (10 ml) was added under nitrogen and with stirring to a slurry of lithium aluminium hydride (300 mg, 7.8 mmol) in tetra-hydrofuran (5 ml). The mixture was stirred at 20° over-night. It was worked up by adding water (0.30 ml), 15% sodium hydroxide solution (0.30 ml), and water (1.8 ml) and then filtered. Evaporation of filtrate afforded a residue (1.2 g) which on purification by alumina column chromato-graphy (20 g) with ether as eluant yielded 1,1:6,6-*bis-ethylenedioxy*-5α-(2-*hydroxyethyl*)-5β,9β-*dimethyl*-trans-*decalin* (25a) (730 mg) as an oil. A sample distilled under reduced pressure had b.p. 155° at 0.10 mmHg (oil-bath), τ 5.95—6.20 (8 H, split lines, 2 × -OCH$_2$CH$_2$O-), 6.45 (2 H, sextet with some lines overlapped, CH$_2$C*H$_2$*OH), 5.23vbr (1 H, exchangeable with D$_2$O, OH), 8.77 (3 H, s, CMe), and 8.99 (3 H, s, CMe); ν$_{max.}$ (film) 3 400 cm^{-1}; *m/e* 326 (M^+, 2%), base peak *m/e* 99, and *m/e* 296 (7), 253 (11), 86 (22), and 55 (12) (Found: C, 66.45; H, 9.2. C$_{18}$H$_{30}$O$_5$ requires C, 66.25; H, 9.2%).

The 1,1:6,6-bisethylenedioxy compound (25a) (326 mg, 1.0 mmol) was dissolved in methanol (9 ml) and 2N hydro-chloric acid (1 ml) was added. The mixture was heated under reflux for several hours until t.l.c. analysis showed complete disappearance of the starting material. Then water was added and most of the solvent was removed under reduced pressure. The residue was taken into ether and worked up as usual to give a solid residue (205 mg) which t.l.c. analysis showed to contain two components. Separ-ation by preparative silica gel chromatography with light petroleum–ether (1 : 1) as eluant afforded 5α-(2-*hydroxy-ethyl*-5β,9β-*dimethyl*-trans-*decalin*-1,6-*dione* (25b) (40 mg), m.p. 130—134° (from ether), τ 6.14 (2 H, equally spaced sextet showing further coupling, *J* 8.0 Hz, CH$_2$C*H$_2$*OH), 7.58br (1 H, s, exchangeable with D$_2$O, OH), 8.82 (3 H, s, CMe), and 8.86 (3 H, s, CMe); ν$_{max.}$ (CHCl$_3$) 3 580, 3 410, and 1 770 cm^{-1}; *m/e* 238 (M^+, 42%), base peak *m/e* 94, and *m/e* 220 (M^+ − H$_2$O, 4%), 209 (1), 194 (17), 111 (73), and 41 (79) (Found: C, 70.6; H, 9.3. C$_{14}$H$_{22}$O$_3$ requires C, 70.55; H, 9.3%) and 3aξ-methoxy-5aβ,9bβ-dimethyl-(9aαH)-perhydronaphtho[2,1-*b*]furan-6-one (26) (21 mg), m.p. 111—115° (from ether); τ 6.15 (1 H, d, *J* 6.5 Hz, -OCH$_2$CH$_2$-), 6.25 (1 H, d, *J* 6.5 Hz, -OC*H$_2$*CH$_2$-), 6.80 (3 H, s, OMe), 8.83 (3 H, s, CMe), and 8.92 (3 H, s, CMe); ν$_{max.}$ (Nujol) 1 700 cm^{-1}; *m/e* 252 (M^+, 24%), base peak *m/e* 114, and *m/e* 221 (M^+ − OMe, 49%), 237 (M^+ − Me, 95%), 95 (50), 111 (34), 55 (34), and 67 (33) (Found: C, 71.65; H, 9.75. Calc. for C$_{15}$H$_{24}$O$_3$: C, 71.4; H, 9.6%).

When the bis-ethylenedioxy compound (25a) was hydro-lysed in a mixture (9 : 1) of acetone–2N-hydrochloric acid under reflux, a mixture of two products was obtained. Separation by preparative silica gel chromatography with three elutions with light petroleum–ether (3 : 1) yielded,

[13] C. G. Scouten and H. C. Brown, *J. Org. Chem.*, 1973, **38**, 4092.

[14] R. Hayward, Ph.D. Thesis, Auckland University, New Zealand, 1973.

apart from the already reported diketone (25b), a compound, >70% of the total product, which is considered to be 1,2-bis-{5β,9bβ-dimethyl-6-oxo-(9aαH)-perhydronaphtho[2,1-b]furan-3a-yloxy}ethane (27); a sample recrystallised from ether had m.p. 121—125°; τ 6.10—6.65 (4 H, complex, -OCH$_2$CH$_2$O-) and 8.91 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 1 700 cm^{-1}; the highest recorded mass spectral peak was at m/e 266 (29%), base peak m/e 128, and m/e 238 (3), 221 (92), 165 (19), 151 (10), 137 (18), 111 (30), and 95 (40) (Found: C, 71.55; H, 9.3. C$_{30}$H$_{46}$O$_6$ requires C, 71.7; H, 9.2%).

When the hydrolysis was performed in the two-phase system ether–2N-hydrochloric acid (9 : 1) under reflux for 13 h the only product obtained was the diketone (25b).

Attempted Wittig Olefin Formation with 5α-Allyl-1,1-ethylenedioxy-5β,9β-dimethyl-trans-decalin-6-one (8) and with 5α-Allyl-1β-hydroxy-5β,9β-dimethyl-trans-decalin-6-one (28) in Dimethyl Sulphoxide (DMSO).—The procedure described here was typical for both substrates. Anhydrous dimethyl sulphoxide (8 ml) was added dropwise under nitrogen to sodium hydride (66 mg, 2.2 mmol as an 80% dispersion in mineral oil which had been washed with pentane) and the mixture heated to 80° for ca. 30 min, until the evolution of hydrogen ceased. The solution was cooled to 0° and methyltriphenylphosphonium bromide prepared according to the Wittig and Schoellkopf method [15] (714 mg, 2.0 mmol) in DMSO (4 ml) was slowly added. The resulting red solution of the ylide was stirred at room temperature for 30 min and then the decalone (8) (556 mg, 2.0 mmol) in dimethyl sulphoxide (3 ml) was added dropwise with stirring and heating. The reaction mixture was heated at 80° for 4 h and then brought to room temperature. Work-up by adding water and extracting with ether followed by further washing of the ether extract with water and drying (MgSO$_4$) gave after evaporation a residue whose t.l.c. analysis indicated it to be the starting ketone. This was confirmed by i.r. analysis.

Attempted olefin formation with the 5α-allyl-1β-hydroxy-5β,9β-dimethyl-trans-decalin compound (28), using the same conditions as described for the 1,1-ethylenedioxy derivative (8), was also unsuccessful.

Preparation of 5α-Allyl-1,1-ethylenedioxy-5β,6α,9β-trimethyl-trans-decalin-6β-ol (6).—A solution of the decalone (8) (710 mg, 3 mmol) in dry ether (10 ml) was added dropwise under nitrogen to a cooled (ca. 0°) and stirred solution of methyl-lithium prepared in situ (ca. 12 mmol) in ether (ca. 20 ml). The mixture was stirred and heated under reflux and the progress of the reaction was monitored by t.l.c. which showed it to be nearly complete after 36 h. Saturated aqueous ammonium chloride solution was then added. The ethereal layer afforded a crude product. Purification by silica column chromatography (20 g) with light petroleum–ether (2 : 1) as eluant afforded 5α-allyl-1,1-ethylenedioxy-6β-hydroxy-5β,6α,9β-trimethyl-trans-decalin (6) (530 mg) 69% yield) as an oil, which by g.l.c. analysis was homogeneous, τ(CCl$_4$) 3.95 (1 H, m, -CH$_2$CH=CH$_2$), 4.96br (1 H, s, -CH$_2$CH=CH$_2$), 5.11br (1 H, s, -CH$_2$CH=CH$_2$), 6.12 (4 H, split s, -OCH$_2$CH$_2$O-), 8.90 [3 H, s, -C(OH)MeCH$_2$-], 9.01 (3 H, s, CMe), and 9.23 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$), 3 600, 3 065, 1 630, and 915 cm^{-1}: m/e 294 (M^+, 9%), base peak m/e 99, and m/e 253 (8), 149 (16), 93 (23), and 86 (37) (Found: C, 73.1; H, 10.15. C$_{18}$H$_{30}$O$_3$ requires C, 73.5; H, 10.2%).

Attempted C-Alkylation of 1,1-Ethylenedioxy-5,9-dimethyl-Δ$^{5(10)}$-octalin-6-one (7) with Benzyloxymethyl Chloride.—A

number of attempts were made at this alkylation in a variety of solvents. A typical experiment is as follows: to a stirred warm suspension of sodium hydride (80% oil suspension, washed with light petroleum; 0.084 g, 28 mmol) in dimethylformamide–1,2-dimethoxyethane (4 : 1; 10 ml) was added a solution of the acetal (7) (2.0 g, 8.4 mmol) in dimethyl formamide–1,2-dimethoxyethane (4 : 1; 10 ml) during 30 min. The stirring was continued for 8 h and the temperature kept at 65°. The mixture was then cooled to about 10° and a solution of benzyloxymethyl chloride (1.53 g, 9 mmol) in 1,2-dimethoxyethane (3 ml) was slowly added. The solution was stirred for 30 min, the excess of sodium hydride was destroyed by addition of methanol and then dilute hydrochloric acid, and most of the solvents were evaporated off under reduced pressure. The residue was treated with ether and worked up. The oily residue was purified by chromatoghraphy on alumina. Elution with ether–light petroleum yielded 2-benzyloxymethoxy-5,5-ethylenedioxy-1,10-dimethyl-3,4,5,6,7,10-hexahydronaphthalene (29) (1.93 g, 65%), b.p. 145° at 0.2 mmHg (oil-bath), τ 2.67 (s, 5 H, ArH), 4.51 (t, 1 H, J 4.0 Hz, >C=CH), 4.99 (2 H, s, PhCH$_2$O-), 5.33 (2 H, s, -OCH$_2$O-), 6.02br (4 H, s, -OCH$_2$-CH$_2$O-), 7.64 (4 H, m, allylic H), 8.22 (3 H, s, >C=CMe), and 8.85 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 1 650 and 1 625 cm^{-1}; $\lambda_{max.}$ (EtOH) 244 nm (ε 13 475), m/e 356 (M^+, <1) (Found: C, 74.4; H, 7.95. C$_{22}$H$_{28}$O$_4$ requires C, 74.15; H, 7.85%). A minor product of lower R_F value than that of (33) was separated by preparative silica gel, and identified as 5ξ-benzyloxymethyl-1,1-ethylenedioxy-5ξ,9β-dimethyl-Δ$^{4(10)}$-octalin-6-one (30); τ 2.75 (5 H, s, ArH), 4.54 (1 H, t, J 4.0 Hz, vinylic), 5.58 (2 H, s, PhCH$_2$O-), 6.07br (4 H, s, -OCH$_2$CH$_2$O-), 6.36 [1 H, d, J 9.0 Hz, -C(5)CH$_2$O-], 6.70 [1 H, d, J 9.0 Hz, -C(5)CH$_2$O-], 8.77 (3 H, s, CMe), and 8.96 (3 H, s, CMe); $\nu_{max.}$ (CS$_2$) 1 710 and 1 645 cm^{-1}, m/e 356 (M^+ <1%).

The dienol (29) was slightly unstable when kept at room temperature giving the starting material (7) as the main product and a minor product, 5,5-ethylenedioxy-8α-hydroxy-1,10-dimethyl-Δ$^{1(9)}$-octalin-2-one (31), which crystallised from ether as prisms, m.p. 168—170°; τ 5.08 (1 H, t, J 3.0 Hz, CHOH), 6.06 (4 H, s, -OCH$_2$CH$_2$O-), 8.14 (3 H, s, CMe), 8.42 (1 H, s, exchangeable with D$_2$O, OH), and 8.49 (3 H, s, CMe); $\nu_{max.}$ (Nujol) 3 350, 1 645, and 1 610 cm^{-1}; $\lambda_{max.}$ (EtOH) 247 nm (ε 11 735), m/e 252 (M^+, 2%) (Found: C, 66.4; H, 8.1. C$_{14}$H$_{20}$O$_4$ requires C, 66.75; H, 8.0%).

Treatment of 2-Benzyloxymethoxy-5,5-ethylenedioxy-1,10-dimethyl-3,4,5,6,7,10-hexahydronaphthalene (29) with Toluene-p-sulphonic Acid in Methanol–Water at Low Temperature.—Toluene-p-sulphonic acid (0.012 g, 0.06 mmol) was added to a solution of the dienol ether (29) (0.137 g, 3.8 mmol) in methanol–water (90 : 10; 5 ml) cooled to −5°. The mixture was stirred for 6 h. The methanol was removed and the residue, after treatment with ether–aqueous sodium hydrogen carbonate, was worked up to give an oily residue (0.092 g) from which two products were separated by preparative silica gel chromatography. They were identified as the diketone (5) (0.032 g) and its corresponding monoacetal (7) (0.050 g).

Attempted Reductive Alkylation of 5,5-Ethylenedioxy-1,10-dimethyl-Δ$^{1(9)}$-octalin-2-one (7) with Lithium–Ammonia in Tetrahydrofuran and Methyl Bromoacetate.—A mixture of the αβ-unsaturated ketone (7) (1 390 g, 5.8 mmol) and isopropyl alcohol (348 mg, 5.8 mmol) in freshly distilled tetrahydrofuran (10 ml) was added dropwise under nitrogen

[15] G. Wittig and U. Schoellkopf, *Org. Synthesis*, 1960, **40**, 66.

to a stirred solution of lithium (105 mg, 15.1 mmol) in liquid ammonia (20 ml) (distilled from sodium) and tetrahydrofuran (10 ml). After the mixture had been stirred for 1 h, the ammonia was removed completely by a stream of nitrogen, at room temperature. The mixture was cooled to about $-40°$ and freshly distilled methyl bromoacetate (1 520 g, 28 mmol) in tetrahydrofuran (10 ml) was slowly added. The mixture was stirred for 30 min, the excess of lithium destroyed by adding saturated aqueous ammonium chloride, the solvent removed, and the residue taken into ether and worked up to give a solid residue (1.7 g). Purification by a combination of crystallisation and preparative silica gel chromatography afforded the ξ-epoxide of 5,5-ethylenedioxy-2-methoxycarbonylmethylene-1α,10β-dimethyl-*trans*-decalin (33) (820 mg, 45%), as prisms (from ether), m.p. 112—115°, τ 6.07 (4 H, s, $^-OCH_2CH_2O^-$), 6.22 (3 H, 2, CO_2Me), 6.39 (1 H, s, $CHCO_2Me$), 8.92 (3 H, s, CMe), and 9.28 (3 H, d, J 6.0 Hz, $-CHMe$); $\nu_{max.}$ (CCl$_4$) 1 750 cm^{-1}, m/e 310 (M^+, 2%), base peak m/e 99 (Found: C, 65.9; H, 8.55. Calc. for $C_{19}H_{28}O_5$: C, 66.0; H, 8.45%). A second product isolated was the known [5] 5,5-ethylenedioxy-1α,10β-dimethyl-*trans*-octalin-2-one (32) (300 mg).

Stereoselective Reduction of 5,9-Dimethyl-Δ$^{5(10)}$-octalin-1,6-dione (5) with Alkali-free Sodium Borohydride.—A solution of sodium borohydride (100 mg, 2.6 mmol) (crystallised from diglyme) in dry ethanol (3 ml) was added dropwise during 60 min to a stirred solution of the dione (5) (1.94 g, 10.0 mmol) in ethanol which had been cooled to 0°. The solution was stirred for about 90 min and worked up as usual to give an oily residue (1.85 g). Separation by a combination of crystallisation and preparative silica gel chromatography afforded 1β-hydroxy-5,9β-dimethyl-Δ$^{5(10)}$-octalin-6-one (38) (1.64 g, yield 85%), m.p. 73—75° (from ether at 0°); τ 6.60 (1 H, dd, J 6.0 and 10.0 Hz, $-CHOH\cdot CH_2^-$), 8.22 (3 H, s, $>C=CMe-$), and 8.82 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 610, 3 490, 1 670, and 1 610 cm^{-1}; $\lambda_{max.}$ 248 nm (ε 19 600); m/e 194 (M^+, 53%), base peak m/e 138, and m/e 123 (48), 110 (28), 91 (26), and 79 (26) (Found: C, 74.05; H, 9.5. $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.3%).

Reductive Alkylation of 1β-Hydroxy-5,9β-dimethyl-Δ$^{5(10)}$-octalin-6-one (34) with Lithium–Ammonia and Allyl Bromide in Tetrahydrofuran–Water.—A solution of the enone (34) (1.84 g, 10.0 mmol) in freshly distilled tetrahydrofuran (10 ml) containing added water (180 mg, 10.0 mmol) was added dropwise to a stirred solution of lithium (280 mg, 40 mmol) in ammonia (ca. 10 ml) (distilled from sodium) and tetrahydrofuran (5 ml). The solution was stirred vigorously for a further 30 min and then allyl bromide (4.80 g, 40.0 mmol) (freshly distilled) in tetrahydrofuran (5 ml) was slowly added. Ammonia was completely removed by flushing out with nitrogen and warming followed by treatment with ethanol. Work-up as in previous experiments gave an oily material (1.95 g). T.l.c. analysis showed three products which were separated by a combination of distillation under reduced pressure and preparative silica gel chromatography affording in increasing order of R_F value 5α-allyl-1β-hydroxy-5β,9β-dimethyl-*trans*-decalin-6-one (28) (1.22 g, 51% yield), b.p. 120° at 0.2 mmHg (oil-bath), τ(CCl$_4$) 4.43 (1 H, m, band width 44 Hz, $-CH_2CH=CH_2$),

[16] E. J. Corey and G. W. J. Fleet, *Tetrahedron Letters*, 1973, 4499.

5.0br (1 H, s, $-CH_2CH=CH_2$), 5.10br (1 H, d, J 8.0 Hz, $-CH_2CH=CH_2$), 6.88 (1 H, m, $W_{\frac{1}{2}}$ ca. 16 Hz, $-CHOH\cdot CH_2^-$), 8.06br (1 H, s, exchangeable with D$_2$O, OH), and 8.97 and 8.99 (3 H each, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 610, 3 460, 3 070, 1 700, 1 635, and 920 cm^{-1}; m/e 236 (M^+, 9%), base peak m/e 41, and m/e 221 (66), 135 (32), 123 (30), 110 (46), 95 (58), 67 (61), and 55 (73) (Found: C, 76.15; H, 10.1. $C_{15}H_{25}O_2$ requires C, 76.3; H, 10.15%); isomer I of 5ξ,7ξ-diallyl-1β-hydroxy-5ξ,9β-dimethyl-(10ξH)-decalin-6-one (36) (180 mg), b.p. 120—122° at 0.2 mmHg (oil-bath), τ(CCl$_4$) 4.05—4.73 (2 H, m, $W_{\frac{1}{2}}$ 44.0 Hz, 2 × $-CH_2CH=CH_2$), 4.90—5.26 (4 H, complex, $W_{\frac{1}{2}}$ 24.0 Hz, 2 × $-CH_2CH=CH_2$), 6.82 (1 H, complex, $W_{\frac{1}{2}}$ ca. 18 Hz, $-CHOH\cdot CH_2^-$), 8.65br (1 H, s, exchangeable with D$_2$O, OH), 9.04 (3 H, s, CMe), and 9.26 (3 H, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 610, 3 500, 3 070, 1 705, 1 635, and 920 cm^{-1}; m/e 276 (M^+, 16%), base peak m/e 41, and m/e 235 (16), 147 (13), 135 (20), 123 (20), 109 (31), and 95 (61) (Found: C, 78.4; H, 10.25. Calc. for $C_{18}H_{28}O_2$: C, 78.25; H, 10.15%) and isomer II of the same compound (36) (500 mg), b.p. 125° at 0.2 mmHg (oil-bath), τ(CCl$_4$) 3.90—4.70 (2 H, m, band width 45.0 Hz, 2 × $-CH_2CH=CH_2$), 4.80—5.20 (4 H, complex, $W_{\frac{1}{2}}$ 22.5 Hz, 2 × $-CH_2CH=CH_2$), 6.85 (1 H, complex, $W_{\frac{1}{2}}$ ca. 1 Hz, $-CHOH\cdot CH_2^-$), 7.20—7.60 (4 H, complex, $W_{\frac{1}{2}}$ 23.0 Hz, 2 × $-CH_2CH=CH_2$), and 8.88 and 8.96 (3 H each, s, CMe); $\nu_{max.}$ (CCl$_4$) 3 615, 3 070, 1 700, 1 635, and 920 cm^{-1}; m/e 276 (M^+, 6%), base peak m/e 41, and m/e 261 (60), 235 (11), 147 (12), 135 (20), 123 (14), 109 (43), and 95 (54) (Found: C, 78.45; H, 10.3%).

Oxidation of 5α-Allyl-1β-hydroxy-5β,9β-dimethyl-trans-decalin-6-one (28).—A solution of the ketol (28) (236 mg, 0.1 mmol) in dichloromethane was added at room temperature to the red complex of chromium trioxide and 3,5-dimethylpyrazole prepared *in situ* by mixing chromium trioxide (120 mg, 1.2 mmol) and 3,5-dimethylpyrazole [16] (115.2 mg, 1.2 mmol) in dichloromethane (5 ml). The mixture was stirred for 4 h and then the solvent was removed under reduced pressure. An ethereal solution of the residue was washed with water, dried (MgSO$_4$), and evaporated. The residue was applied to one large plate of silica gel to give after two elutions with light petroleum–ether (1 : 1) starting material (50 mg) and the corresponding diketone (110 mg) which was identical in all aspects to the one prepared by hydrolysis of the already reported 5α-allyl-1,1-ethylenedioxy-5β,9β-dimethyl-*trans*-decalin-6-one (8).

Hydrolysis of 5α-Allyl-1,1-ethylenedioxy-5β,9β-dimethyl-trans-decalin-6-one (8).—The acetal (8) (278 mg, 1.0 mmol) was dissolved in methanol (5 ml) and dilute sulphuric acid (1 ml) was added. The mixture was heated to 60° for 1 h, then cooled, treated with sodium hydrogen carbonate solution and extracted with water. Work-up and purification by preparative silica gel chromatography afforded 5α-allyl-5β,9β-dimethyl-*trans*-decalin-1,6-dione (35) (170 mg, 71%), which crystallised from ether as needles, m.p. 71—72°, τ 4.41 (1 H, m, band width 42.5 Hz, $-CH_2CH=CH_2$), 4.97br (1 H, s, vinylic H), 5.09br (1 H, d, J 7.0 Hz, vinylic H), 8.70 (3 H, s, CMe), and 8.86 (3 H, s, CMe); $\nu_{max.}$ (CHCl$_3$) 3 035, 1 705, 1 690, and 910 cm^{-1}; m/e 234 (M^+, 44%), base peak m/e 110 (Found: C, 76.15; H, 9.3. $C_{15}H_{22}O_2$ requires C, 76.05; H, 9.4%).