

Rearrangement of Epoxides. Part 2.¹ The Preparation and Rearrangement of Some Epoxides of 2,2-Dimethylbicyclo[4.3.0]non-1(9)-enes carrying Substituents at C(3) and C(6)

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The preparation of 3 α ,9 α -epoxy-4,4-dimethylhexahydroindan-5 β ,8 β -carbolactone (17), ethyl 3 α ,9 α -epoxy-4,4-dimethyl-5-oxahexahydroindane-8 β -carboxylate (20), ethyl 3 β ,9 β -epoxy-4,4-dimethyl-5-oxohexahydroindane-8 β -carboxylate (21), 3 β ,9 β -epoxy-8 β -hydroxymethyl-4,4-dimethylhexahydroindan-5 β -ol (19), and a mixture of the α - and β -epoxides of 4,4,8-trimethyl-1,6,7,8-tetrahydro-2*H*-inden-5(4*H*)-one (24) and (25) are described. Their rearrangements with boron trifluoride-diethyl ether complex have been carried out and the major products identified. Each rearrangement proceeds by a different pathway.

EPOXIDES play an important role in biosynthesis. Two examples are the cyclisation of squalene epoxide^{2,3} and the probable involvement of 7 α ,8 α -epoxytirucallane derivatives in the formation of meliacins and limonoids.^{4,5} In both cases the epoxide gives rise to a carbonium ion which initiates cyclisation followed by rearrangement in the first case and rearrangement in the second. In the laboratory similar processes can be initiated by treating alicyclic epoxides with boron trifluoride-diethyl ether complex or other Lewis acids but it is still difficult to predict what the fate of the initially formed ion will be. In order to obtain further information about the rearrangement of epoxides of cyclic systems with features found in polyisoprenoids, epoxides of the general formula (1) † where R¹ and R² are (HO,H), (=O), or [-O-CO-(lactonic),H], and R³ is CH₃, CH₂OH, CO₂Et, or -C-O-(lactonic) have been prepared and the rearrangement of a number of them with boron trifluoride-diethyl ether complex in benzene has been studied.

† All compounds are racemic. When necessary the isomer is drawn with the C(8) substituent β .

¹ M. S. Hadley and T. G. Halsall, *J.C.S. Perkin I*, 1974, 1334.

² E. E. van Tamelen, J. D. Willett, R. B. Clayton, and K. E. Lord, *J. Amer. Chem. Soc.*, 1966, **88**, 4572.

³ E. J. Corey, W. E. Russey, and P. R. Orriz de Montellano, *J. Amer. Chem. Soc.*, 1966, **88**, 4750.

Ethyl 4,4-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro-2*H*-indene-8-carboxylate (3) was prepared starting from ethyl 2-oxocyclopentane-1-carboxylate which was treated⁶ with methyl vinyl ketone in benzene in the presence of triethylamine to give the Michael addition product. This was cyclised by a modification of the method of Dauben *et al.*⁷ to ethyl 5-oxo-5,6,7,8-tetrahydroindane-8-carboxylate (2) which was then methylated using a 1 : 4 molar ratio of enone and methyl iodide in *t*-butyl alcohol in the presence of potassium *t*-butoxide to give the dimethyl derivative (3). Use of a higher ratio of methyl iodide gave a mixture of the dimethyl derivative (3) together with both the mono- and tri-methylated products.

Reduction of the oxo-ester (3) with a stoichiometric amount of sodium borohydride afforded a mixture which was separated by chromatography on silica gel into the carbolactone (9) (32%), m.p. 40–41 °C, and the hydroxy-

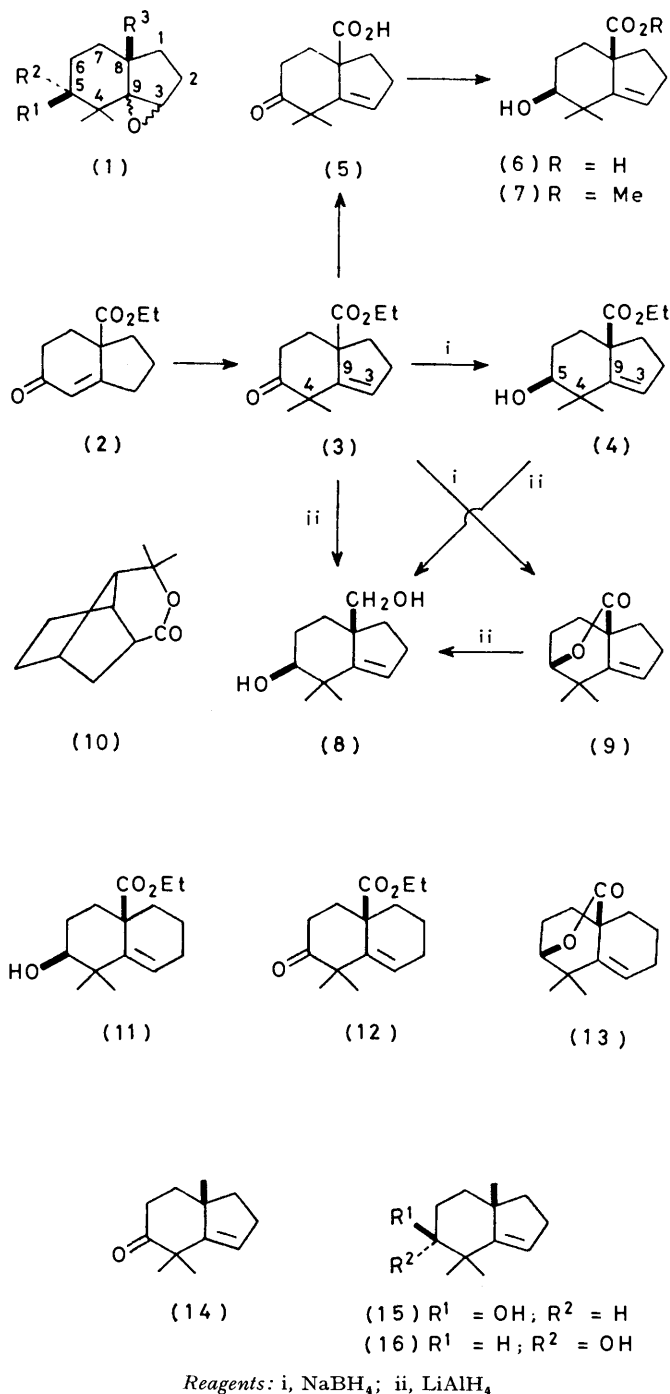
⁴ J. G. St. C. Buchanan and T. G. Halsall, *J. Chem. Soc. (C)*, 1970, 2280; G. P. Cotterrell, T. G. Halsall, and M. J. Wriglesworth, *Chem. Comm.*, 1967, 1121.

⁵ D. Lavie and E. C. Levy, *Tetrahedron Letters*, 1968, 2097.

⁶ W. G. Dauben and J. W. McFarland, *J. Amer. Chem. Soc.*, 1960, **82**, 4245.

⁷ W. G. Dauben, J. W. McFarland, and J. B. Rogan, *J. Org. Chem.*, 1961, **26**, 297.

ester (4). The carbolactone had i.r. bands at 1763 (δ -lactone) and 1665 cm^{-1} (C=C). The lactone frequency is higher than that (1740 cm^{-1}) usually observed for



δ -lactones but may be associated with strain in the lactone ring which is referred to later. Wilder and Win-

ston⁸ quote a value of 1764 cm^{-1} for the strained δ -lactone (10). The β -configuration of the hydroxy-group in the hydroxy-ester (4) is shown by the conversion of the ester into the carbolactone (9) described below. Reduction of the oxo-ester (3) with an excess of sodium borohydride afforded a higher proportion of hydroxy-ester to carbolactone. In this case chromatography did not lead to isolation of pure lactone or ester but did afford a small amount of the diol (8).

As the procedure to separate the lactone (9) was slow and tedious, lactonisation of the hydroxy-ester (4) was studied. Heating the ethyl ester (4) under reflux with concentrated hydrochloric acid was unsuccessful but treatment under similar conditions with concentrated sulphuric acid in dioxan led to the lactone which was also obtained when the mixture resulting from sodium borohydride reduction was similarly treated.

Reduction of the lactone (9), of the oxo-ester (3), and of the hydroxy-ester (4) with lithium aluminium hydride gave the diol (8). The two protons of the CH_2OH group were magnetically non-equivalent. The diol was also obtained by reduction with lithium aluminium hydride of the oxo-ester (3) and the hydroxy-ester (4).

Hydrolysis of the oxo-ester (3) afforded the corresponding acid (5), m.p. 123–124 $^\circ\text{C}$, reduction of which with sodium borohydride gave the hydroxy-acid (6), m.p. 165–166 $^\circ\text{C}$. Hydrolysis of the hydroxy-ester (4) afforded only the hydroxy-acid (6) on acidification of the alkaline solution. The lactone (9) was only formed from the hydroxy-acid (6) when it was treated with sulphuric acid in dioxan.

Comparison of the conditions required to bring about lactonisation of the hydroxy-ester (4) with those required for lactonisation of the corresponding hydroxy-ester (11) in the octalin series shows considerable differences. In the octalin system reduction of the octalone (12) with sodium borohydride afforded only the lactone (13).^{9,10} The hydroxy-ester (11) was obtained by catalytic hydrogenation of the octalone but gave the lactone (13) on chromatography on neutral alumina.⁹ Examination of models indicates that in the octalin lactone (13) the ring A can achieve a normal boat conformation, whereas in the case of the lactone (9) ring A is distorted from a normal boat conformation because of the constraints on bonding angles imposed by the five-membered ring and since the hydroxy and ester groups are farther apart.

4,4,8-Trimethyl-1,6,7,9-tetrahydro-2*H*-inden-5(4*H*)-one (14) was prepared by methylation of 8-methyl-5,6,7,8-tetrahydroindan-5-one which was obtained in a one step acid-catalysed reaction of methyl vinyl ketone and 2-methylcyclopentanone following the procedure¹¹ used for the corresponding octalone. Reduction of the ketone (14) with lithium aluminium hydride did not proceed stereospecifically but gave a mixture of the epimeric 5-alcohols (15) and (16). These were not separable by p.l.c. and the mixture showed a complex

⁸ P. Wilder and A. Winston, *J. Amer. Chem. Soc.*, 1955, **76**, 5598.

⁹ W. L. Meyer and A. S. Levinson, *J. Org. Chem.*, 1963, **28**, 2184.

¹⁰ F. J. McQuillin and R. B. Yeats, *J. Chem. Soc.*, 1965, 4273.

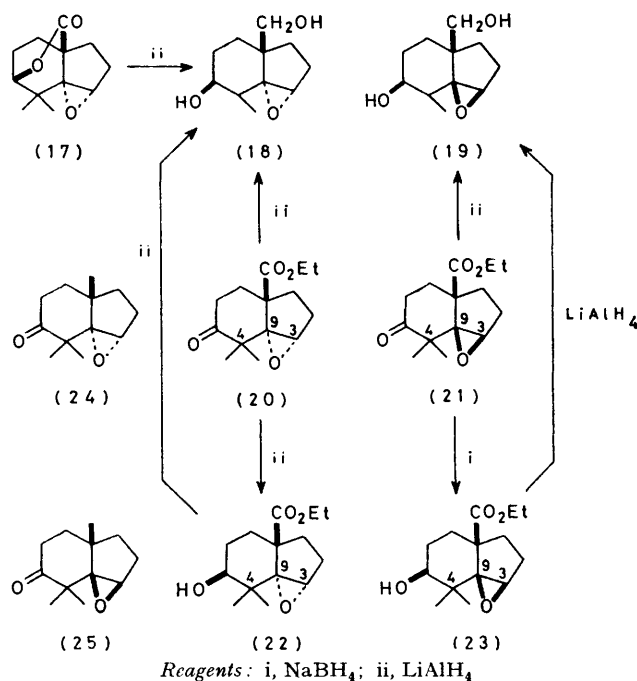
¹¹ C. H. Heathcock, M. E. Ellis, J. E. McMurray, and A. Coppoline, *Tetrahedron Letters*, 1971, 4995.

n.m.r. signal at τ 6.79 due to the two $CH(OH)$ signals overlapping.

The bicyclic olefins (9), (8), (3), and (4) were epoxidised with *m*-chloroperbenzoic acid. The lactone (9) afforded only one epoxide (17), m.p. 98–99 °C, which is assigned the α -configuration on the basis of the chemistry, discussed below, of the rearrangement product formed from it by the action of boron trifluoride–diethyl ether complex in benzene. Reduction of the epoxy-lactone (17) with lithium aluminium hydride gave the α -epoxy-diol (18), m.p. 93–94 °C. Epoxidation of the unsaturated diol (8) with *m*-chloroperbenzoic acid gave the epimeric β -epoxide (19), m.p. 128–130 °C. The oxo-ester (3) on treatment with *m*-chloroperbenzoic acid gave the α -epoxide (20), m.p. 49–50 °C (62%), and the β -epoxide (21), m.p. 53.5–54.5 °C (14%). The stereochemistry of these two epoxides was established by sodium borohydride reduction of the α -epoxide (20) when the epoxide derived from lactone (9) was obtained. Reduction of the β -epoxide (21) with lithium aluminium hydride gave the β -epoxy-diol (19). Treatment of the hydroxy-ester (4) with *m*-chloroperbenzoic acid for 6 h gave a mixture which was separated into the α -epoxy-lactone (17), the α -epoxy-hydroxy-ester (22), m.p. 93–94 °C, and the β -epoxy-hydroxy-ester (23), oil, as a minor component. On oxidation for 28 h the ratio of α -epoxy-lactone (17) to α -epoxy-hydroxy-ester (22) increased suggesting that the acids present in the reaction catalyse lactone formation from the α -epoxy-hydroxy-ester. Reduction of the α -epoxy-oxo-ester (20) with lithium aluminium hydride gave a mixture of the α -epoxy-hydroxy-ester (22) and the α -epoxy-diol (18) (1 : 2 ratio). The β -epoxy-oxo-ester (21) with sodium borohydride gave the β -epoxy-hydroxy-ester (23) which was reduced with lithium aluminium hydride to the β -epoxy-diol (19). The α -epoxy-hydroxy-ester (22) similarly gave the α -epoxy-diol (18).

These results inter-relate all the epoxides with an oxygen-carrying substituent at C(8) to the α -epoxy-lactone (17). Further evidence for the stereochemistry of the epoxy-lactone (17) is provided by the following considerations. Only one epoxide has been isolated from the lactone (9). If models are made of the oxo- and hydroxy-esters (3) and (4) and of the two possible epoxides from each of them it is apparent that there is a change from concavity to convexity on the β -face of the molecules with respect to the angle made by carbon atoms C(3)–C(9)–C(4). The effect of this is a shortening of the distance between the oxygen atom at C-5 and the carbon atom of the ester carbonyl group as one goes from the β -epoxy-ester (23) to the olefinic ester (4) and finally to the α -epoxy-ester (22). It should, therefore, be possible to form a less-strained δ -lactone with the α -epoxide (22) than with the β -epoxide and the strain in the olefinic lactone should be intermediate. Comparison of the products from sodium borohydride reduction of the oxo-esters (20), (3), and (21) supports this. The α -epoxide (20) affords only the lactone (17), the olefinic oxo-ester (3) gives a mixture of hydroxy-ester (3) and lactone (9),

while the β -epoxide (21) gave only hydroxy-ester (23). Further, the results described above indicate that organic acids can catalyse the conversion of the α -epoxy-hydroxy-ester (22) into the epoxy-lactone (17) but not of the β -epoxy-hydroxy-ester (23) while concentrated sul-



phuric acid in dioxan is needed to convert the olefinic hydroxy-ester (4) into the lactone (9).

Epoxidation of the oxo-olefin (14) with *p*-nitroperbenzoic acid gave an oil which appeared to be homogeneous by t.l.c., but its n.m.r. spectrum indicated that it was a mixture of the two epoxides. Attempts to separate the two epoxides by multiple elution p.l.c. were unsuccessful.

Treatment of the epoxy-carbolactone (17) in benzene with boron trifluoride–diethyl ether complex afforded two rearranged products. The product formed in higher yield, m.p. 134–135 °C, is assigned structure (26), C₁₂H₁₆O₃. It absorbed at 3 410 cm⁻¹ indicative of a hydroxy-group and at 1 755 cm⁻¹ indicative of a γ -lactone. The possibility of the carbonyl bond being due to a five-membered ring ketone is excluded as the ¹³C n.m.r. signal of the carbonyl carbon was at δ 144.49 p.p.m., a figure too low for a ketone carbon. The ¹H n.m.r. spectrum had signals indicative of two methyl groups attached to quaternary carbon, an olefinic proton and two $CH-O$ protons. One of these must be in a $CHOH$ group and the other due to a proton or carbon attached to lactonic oxygen. These data indicate a bicarbocyclic γ -lactone with one double bond and one secondary hydroxy-group and suggest structures (26) or the related $\Delta^{1,8}$ isomer (31). Oxidation of the hydroxy-group with Jones reagent gave a ketone (27), m.p. 112–115 °C, with bands at 1 785 and 1 735 cm⁻¹ due to the γ -lactone and the five-membered ring ketone. There

were signals at τ 4.32 due to the olefinic proton, τ 5.87 (t, J 3 Hz) assigned to the proton on the carbon attached to lactone oxygen and at τ 8.60 (s) and 8.98 (s) due to the methyl groups. The signal at τ 8.60 is assigned to the β -methyl group which is deshielded by the lactonic carbonyl group.

Reduction of the ketone (27) with sodium borohydride afforded only one product (28), m.p. 65–66 °C, which was epimeric with the initial rearranged compound. In the n.m.r. spectrum of the epimer the OH signal, which collapsed in D₂O, appeared as a sharp doublet at τ 6.92 (J 14 Hz) indicating that its hydroxy-group is strongly hydrogen bonded to the lactonic carbonyl group. It must, therefore, be *cis* to it and accordingly β -orientated. It follows that in the rearrangement product the hydroxy-group and hence the epoxy-group from which it is derived must be α -orientated. The stereochemistry of structure (28) is consistent with (27) for the ketone with the lactonic carbonyl group shielding the C-3 oxo-group from attack by sodium borohydride on its β -face.

Epoxidation of the rearrangement product (26) led to one epoxide, m.p. 136–138 °C, which is assigned structure (29) on the basis of its spectral data and reactions. The stereochemistry of the epoxide group is not established, but a model of structure (26) indicates considerable steric hindrance on the α -face of the double bond from the α -methyl group which suggests that the epoxide is probably β in orientation. Rearrangement of the epoxide (29) with boron trifluoride–diethyl ether complex in benzene gave as a major component a compound, isolated as an oil, which is assigned structure (30). It had bands at 3 675 (OH), 1 780 (γ -lactone), and 1 720 cm⁻¹. The 1 720 cm⁻¹ band is too low for a cyclopentanone but would be consistent with structure (30). The n.m.r. spectrum of the hydroxy oxo-lactone (30) has signals which are assigned as follows: C(4)-*gem* methyls (singlets at τ 8.59 and 8.61); CHOH (τ 5.50, d, J 6 Hz); C(CH₃)₂-CH(O-)-CH₂-C=O (triplet at τ 5.64; J 3 Hz (1 H) coupled with a doublet at τ 7.2, J 3 Hz (2 H); -CH₂-CH(ax)-C=O (τ 6.65, dd, J 9 and 10 Hz). On decoupling of the protons with the signal at τ 7.27 the signal at 5.64 collapsed to a singlet and on decoupling the proton with the signal at τ 5.64 the signal at τ 7.27 became a singlet. These data show that the carbonyl group is situated β to the lactonic oxygen. The epoxide group of (29) and hence the double bond of the original rearrangement product (26) from the epoxy-carbolactone (17) must, therefore, be at C(7) and C(8).

The minor product from the rearrangement of the epoxy-carbolactone (17) was an oxo-lactone [bands at 1 760 (lactone) and 1 745 cm⁻¹ (five-membered ring ketone)] and is formulated as (32).

Rearrangement of the α -epoxy-oxo-ester (20) with boron trifluoride–diethyl ether complex in benzene at 10 °C for 10 min gave a reaction product containing a carboxylic acid. It was treated with ethereal diazomethane and the product was separated by p.l.c. into one major and four minor fractions. The major fraction (31%), which was the least polar and was obtained as an

oil, was a pure compound. It contained two carbonyl groups ($\nu_{C=O}$ 1 740 and 1 726 cm⁻¹) but no hydroxy-group. The n.m.r. spectrum showed the presence of =CH₂, -CH=C-, a vinylic methyl group, and methyl and ethyl ester groups. The mass spectrum had a molecular ion at m/e 266 which is 14 mass units higher than the molecular weight of the parent epoxide. The compound had an intense u.v. absorption at λ_{max} 236 nm (ϵ 13 000) indicating that the methylene group was conjugated with a trisubstituted double bond. The structure consistent with this data is (33). Reduction of this ester with lithium aluminium hydride gave a crystalline diol (34; R = H) which gave the mono *p*-nitrobenzoate (34; R = O-CO-C₆H₄-NO₂).

The second fraction (5%) was unchanged epoxide. The third fraction (12%) although apparently homogeneous to t.l.c. was not pure since its n.m.r. spectrum indicated the presence of two methyl and two ethyl ester groups. There were no signals indicative of a methylene (=CH₂) groups but signals indicative of two vinylic methyl groups and two olefinic protons. There was absorption at 244 nm. The data is consistent with the presence of the diene diester (35) together with a second component. The fourth and fifth fractions (7 and 14%) were mixtures which could not be resolved.

The β -epoxy-oxo-ester (21) on rearrangement with boron trifluoride–diethyl ether complex in benzene at 20 °C for 10 min gave a product from which unchanged epoxide (36%) and an aldehyde (22%) were isolated. The CHO group was detected by characteristic signals at ν_{max} 2 730 cm⁻¹ and τ 0.24. The i.r. spectrum showed two carbonyl bands at 1 735 and 1 718 cm⁻¹ but no hydroxy-group. The n.m.r. spectrum showed the presence of an ethyl ester group and two low-field methyl signals at τ 7.79 and 8.21. The aldehyde absorbed at 252 nm (ϵ 4 100). The data are consistent with structure (36). Oxo-groups in five-membered rings conjugated with an exocyclic double bond absorb between 1 725 and 1 708 cm⁻¹ and the band at 1 718 cm⁻¹ is consistent with this. The band at 1 735 cm⁻¹ could be due to overlapping bands due to the ester and aldehyde groups. The signals at τ 7.79 and 8.21 are in agreement with the expected chemical shifts of the two vinylic methyl groups of structure (36) and compare favourably with the signals at τ 7.84 and 8.20 shown by the corresponding vinylic methyl groups of 2-isopropylidene-cyclopentanone (37).¹² The calculated u.v. maximum for structure (36) is 254 nm, consistent with the experimental value of 252 nm.

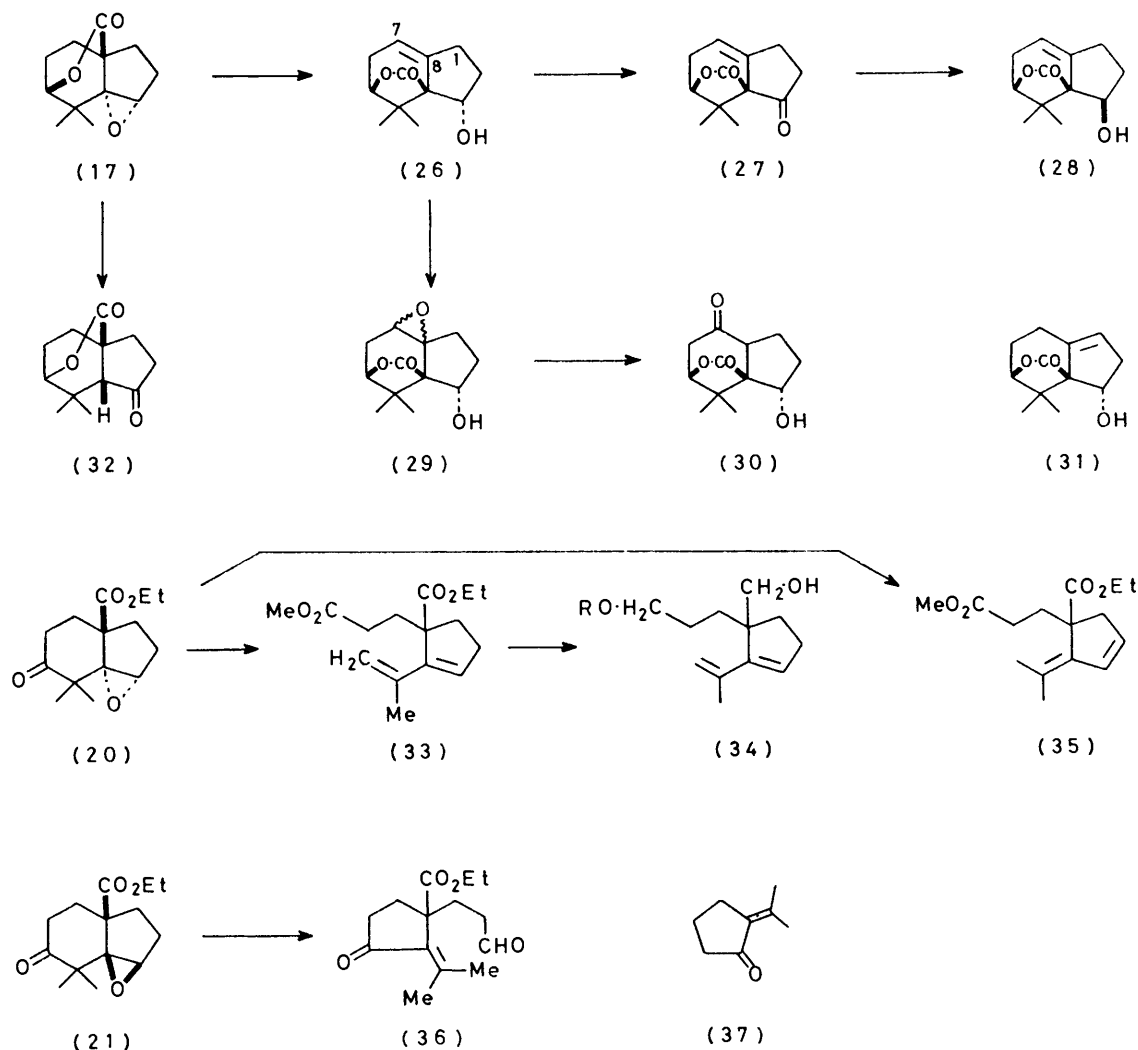
Rearrangement of the β -epoxy-diol (19) with boron trifluoride–diethyl ether complex in benzene gave one major and several minor products which were not obtained in sufficient quantity to permit characterization. The major product was obtained as a glass. Its i.r. spectrum showed no carbonyl absorption but had strong hydroxy-bands at 3 670 and 3 520 cm⁻¹. The n.m.r. spectrum indicated a symmetrical molecule. It

¹² L. M. Jackmann and S. Sternhall, 'Applications of Nuclear Magnetic Resonance Spectra in Organic Chemistry', Pergamon Press, Oxford, 2nd edn., 1969, p. 223.

had a multiplet at τ 5.91 due to two $CH(OH)$ protons, a sharp two-proton singlet at τ 6.20 indicative of CH_2-O , and a sharp six-proton singlet at τ 8.42 due to two equivalent methyl groups attached to carbon-bearing oxygen. There were two exchangeable hydroxy-protons. The diol afforded a crystalline diacetate the n.m.r. spectrum of which again indicated a symmetrical structure with only one signal for the two $CH-OAC$ protons, a singlet at τ 6.25 for CH_2-O , and a singlet at τ 8.58 for two methyl

with the β -diketone structure (39) which would be expected to cleave with base to the $\alpha\beta$ unsaturated oxo-acid (40). It is intended to carry out further work on this rearrangement and on the rearrangement of the corresponding α -epoxy-diol (18).

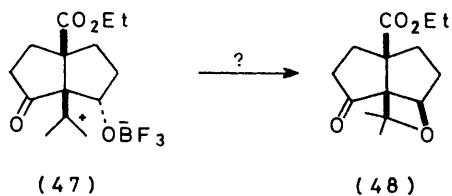
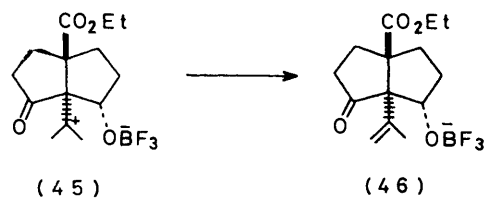
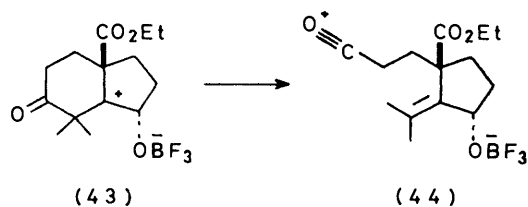
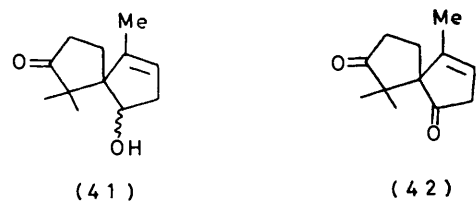
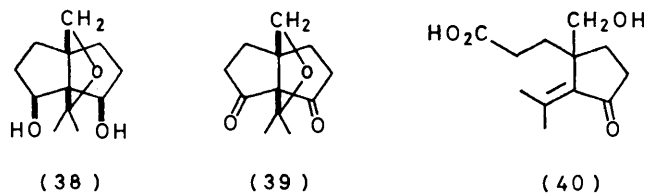
The mixture of α - and β -epoxy-ketones (24) and (25) on rearrangement afforded one major crystalline product. Its i.r. spectrum indicated a hydroxy-group, and an oxo-group in a five-membered ring (ν_{max} 3 540 and 1 730 cm^{-1}).



groups. The diol also afforded a dione with a single carbonyl band at 1 762 cm^{-1} indicative of an oxo group in a five-membered ring. The signals of the *gem*-dimethyl group and the CH_2-O group in the diol and the diacetate were extremely sharp and no splitting was observed when the recording solvent was changed from carbon tetrachloride to benzene. These data suggest that the diol has the novel heterocyclic propellane structure (38) and the dione structure (39). An ethanolic solution of the dione showed no intense u.v. absorption but on addition of ethanolic potassium hydroxide solution an intense absorption at 250 nm gradually built up accompanied by a weaker absorption. This is consistent

The n.m.r. spectrum showed an olefinic proton and a vinylic methyl group (τ 4.50 and 8.33), a proton on carbon carrying oxygen (τ 5.71), and two methyl groups on quaternary carbon. A possible structure for the product is the spiro-structure (41). The vinylic methyl signal appeared as a multiplet containing at least four lines. The nature of the coupling was elucidated by irradiating the olefinic proton signal when the vinylic methyl signal collapsed to a simple triplet with J 2.2 Hz due to coupling with a methylene group. The coupling constant with the olefinic proton was J 1.6 Hz. These values are consistent with the group $CH_3-C=CH-CH_2$ and are comparable with values for allylic and homoallylic coupling

constants obtained for this group in other molecules.¹³ The low τ value (τ 5.71) for the CH-OH proton is consistent with structure (41) as the proton lies in a de-



shielded region of space relative to the double bond. In cyclopentene the corresponding C(4) methylene protons are deshielded by τ 0.39 relative to cyclopentane.¹⁴ It is likely that the crystalline ketol has arisen from only one of the two epoxides.

Oxidation of the spiro-ketol with chromic acid gave a

* After the paper had been submitted a paper by Y. Sawaki and Y. Ogata (*J. Amer. Chem. Soc.*, 1978, **100**, 856) dealing with other examples of acyl migration became available. The authors thank one of the referees for drawing their attention to this paper.

¹³ Ref. 12, p. 317.

dione (42) with a broad carbonyl absorption at 1735 cm^{-1} . Its n.m.r. spectrum was similar to that of the ketol with the vinylic methyl group signal appearing as a multiplet containing at least six lines. The CO-CH₂-CH=C signal appeared as a discrete multiplet at τ 7.28 with at least five lines. On irradiating the olefinic signal the vinylic methyl signal collapsed to a triplet as before.

The question arises whether it is possible to explain why quite different products are formed in the rearrangements described. In turn, this partly depends upon the actual pathways leading to the products. In the case of the epoxy-carbolactone (17) the migration of the lactonic carbonyl group at first sight appears unusual in that it involves the migration of an electron-deficient carbon to a positive carbon atom. If, however, in the transition state during migration there is double-bond character between the carbon atom from which the migrating group leaves and the carbon atom to which it moves then the migrating carbon will itself become positive and in the case of a lactonic carbon atom it can be stabilised by mesomeric effects ($-\text{O}-\overset{+}{\text{C}}=\text{O} \leftrightarrow -\text{O}-\text{C}=\overset{+}{\text{O}} \leftrightarrow -\overset{+}{\text{O}}=\text{C}=\text{O}$).

* Turning to the keto epoxides (20) and (21) more than one pathway can be written to explain the products. For instance the diene acid corresponding to the ester (33) could arise *via* cleavage of the ion (43) to the acylium ion (44) followed by elimination to the diene. Alternatively the epoxide could initially rearrange to the ion (45) followed by loss of a proton and subsequent fragmentation of the resulting β -oxy-ketone (46). Both pathways involve the ability of the oxygen of the acylium ion to carry positive charge. The ion (45) is of interest in that if the corresponding ion (47) is formed from the β -epoxide an explanation is needed why it leads to the aldehyde (36) instead of to the acid. One possibility in the case is the formation of an intermediate oxetan (48). It has been reported¹⁵ that rearrangement of the epoxide (49) with boron trifluoride-diethyl ether complex gave (50), (51), and acetone. The formation of acetone may involve the oxetan (52) as an intermediate.

In the rearrangement of the epoxy-diol (38) a likely mechanism is rearrangement to the ion (53) followed by ring closure onto the oxygen of the CH₂OH group. Again the group which has migrated is the one which could occur as a stabilised carbonium ion (CH=OH⁺).

Discussion of the formation of the spiro-ketol (41) is only possible when it is known whether it has been formed from the α - or β -epoxide. An analogy for its formation is provided by the rearrangement of 5 α ,6 α -epoxy-4,4-dimethylsteroids (54) to the spiro-ketol (55).¹⁶

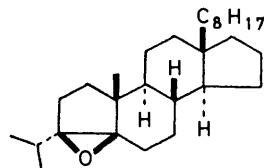
At this stage it is not possible to put forward rules which would predict the products formed but the results suggest that in some of the rearrangements there may be significant double-bond character in the transition state between the carbon from which the migrating group

¹⁴ Ref. 12, p. 85.

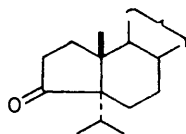
¹⁵ I. Morelli, S. Catalano, G. Moretto, and A. Marsili, *Tetrahedron Letters*, 1972, 717.

¹⁶ T. G. Halsall, E. R. H. Jones, E. L. Tan, and G. R. Chaudhry, *J. Chem. Soc. (C)*, 1966, 1374.

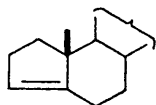
moves and the positive carbon which arises when the epoxide ring opens and that the group which migrates can carry readily positive charge.



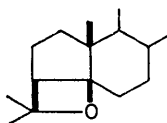
(49)



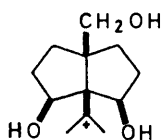
(50)



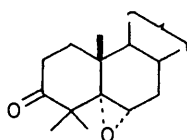
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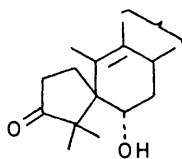
(52)



(53)



(54)



(55)

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were determined for solutions in carbon tetrachloride or chloroform or for thin films in the case of liquids, unless otherwise stated. U.v. spectra were recorded using ethanol as solvent, ^1H n.m.r. spectra were determined at 100, 90, or 60 MHz for solutions in carbon tetrachloride or deuteriochloroform as stated. ^{13}C n.m.r. spectra were recorded at 22.62 MHz using solutions in deuteriochloroform or dimethyl sulphoxide.

The alumina used for column chromatography was Laporte Industries Grade H which was deactivated by the addition of 5% of a 10% solution of acetic acid in water. Silica gel was BDH 60–120 mesh. Thin layer chromatography (t.l.c.) was carried out using 0.3-mm layers of unbaked Kieselgel HF₂₅₄₊₃₆₆ on glass plates. Preparative layer chromatography (p.l.c.) was carried out using 1-mm layers of unbaked Kieselgel HF₂₅₄₊₃₆₆ on glass plates [20 × 20 cm (small); 100 × 25 cm (large)].

Light petroleum refers to the fraction with b.p. 40–60 °C. Boron trifluoride–diethyl ether complex was purified by addition of 0.5% of diethyl ether (to remove any excess of boron trifluoride) and then distilled from calcium hydride.

Preparation of Ethyl 5-Oxo-5,6,7,8-tetrahydroindane-8-carboxylate (2).—The ester was prepared from ethyl 2-oxo-1-(3-oxobutyl)cyclopentane-1-carboxylate⁶ by a modification of the method of Dauben *et al.*⁷ The dione (120 g, 0.56 mol) was added to a stirred solution of aluminium t-butoxide (120 g, 0.49 mol) in benzene (900 ml) and the mixture was heated under reflux and dry nitrogen for 90 h. Work-up in the usual manner afforded ethyl 5-oxo-5,6,7,8-tetrahydro-

indene-8-carboxylate as an oil (58.5 g), b.p. 104–108 °C at 0.7 mmHg, n_D^{20} 1.503 (lit.,⁷ b.p. 135–136 °C at 2.7 mmHg, n_D^{20} 1.500), $\tau(\text{CCl}_4)$ 4.21 (1 H, s, C=CH-CO), 5.83 (2 H, q, J 7 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), and 8.72 (3 H, t, J 7 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$).

Methylation of Ethyl 5-Oxo-5,6,7,8-tetrahydroindane-8-carboxylate (2).—(i) *Using a 1 : 4 enone–methyl iodide ratio.* The enone (2) (59 g, 0.28 mol) in t-butyl alcohol (60 ml) was added with stirring under nitrogen to a solution of potassium t-butoxide in t-butyl alcohol prepared from potassium (40 g) and t-butyl alcohol (800 ml). Methyl iodide (159 g, 1.12 mol) was added immediately and the reaction mixture was heated under reflux for 1 h. Work-up in the usual manner afforded an oil which was distilled to give ethyl 4,4-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro-2H-indene-8-carboxylate (3) as a liquid (56 g, 82%), b.p. 92–96 °C at 0.5 mmHg, n_D^{22} 1.4885, $\nu_{\text{max}}(\text{CCl}_4)$ 2 980, 1 940, 1 724, 1 190, 1 160, and 1 060 cm^{-1} ; $\tau(\text{CCl}_4)$ 4.37 (1 H, t, J 2.4 Hz, CH=C), 5.84 (2 H, q, J 7 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 8.72 (3 H, t, J 7 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), and 8.77 and 8.99 (6 H, 2s, gem CH_3) (Found: C, 71.3; H, 8.7. $\text{C}_{14}\text{H}_{20}\text{O}_3$ requires C, 71.2; H, 8.5%). Its semicarbazone (prisms from aqueous ethanol) had m.p. 165–167 °C (Found: C, 61.1; H, 7.9; N, 14.5. $\text{C}_{15}\text{H}_{23}\text{N}_3\text{O}_3$ requires C, 61.4; H, 8.0; N, 14.3%).

(ii) *Using a 1 : 6 enone–methyl iodide ratio.* When the reaction was carried out on the enone (16.0 g) using a 1 : 6 enone–methyl iodide ratio work-up in the usual manner afforded an oil (17.3 g), b.p. 102–111 °C at 0.9 mmHg, the i.r. spectrum of which indicated the presence of both conjugated and unconjugated carbonyl groups [$\nu_{\text{max}}(\text{CCl}_4)$ 1 720 and 1 670 cm^{-1}]. The oil was chromatographed on alumina (500 g). Light petroleum eluted a fraction (1.8 g) with a strong aromatic odour which was impure on t.l.c. Its n.m.r. spectrum indicated the presence of a trimethylated product. Further elution with light petroleum–benzene (19 : 1) afforded the dimethylated enone (3) as a liquid (11 g, 60%) with the properties described above. Continued elution with light petroleum–benzene (1 : 1) gave ethyl 4-methyl-5-oxo-5,6,7,8-tetrahydroindane-8-carboxylate as a liquid (890 mg, 5%), homogeneous on t.l.c., $\lambda_{\text{max}}(\text{EtOH})$ 245 nm (ϵ 9 500), $\nu_{\text{max}}(\text{CCl}_4)$ 2 980, 1 730, 1 675, and 1 190 cm^{-1} ; $\tau(\text{CCl}_4)$ 5.86 (2 H, q, J 7 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 8.25 (3 H, s, C=C– CH_3), and 8.75 (3 H, t, J 7 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$). Its semicarbazone (pale yellow needles from ethyl acetate–methanol) had m.p. 180–189 °C (Found: C, 60.0; H, 7.6; N, 14.8. $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_3$ requires C, 60.2; H, 7.5; N, 15.0%).

Reduction of the Oxo-ester (3) with Sodium Borohydride.—(i) *Using a stoichiometric amount of sodium borohydride.* A solution of oxo-ester (3) (4.97 g, 0.021 mol) and sodium borohydride (0.56 g, 0.012 mol) in ethanol (100 ml) was stirred at 20 °C for 4 h. The alcohol was removed under reduced pressure, brine was added, and the solution extracted with ether to give an oil (4.06 g) which was chromatographed on silica gel (125 g). The fractions eluted with light petroleum–diethyl ether (9 : 1) afforded 4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-indene-5 β ,8 β -carbolactone (9) (1.28 g, 32%), as crystals (on standing), m.p. 40–41 °C, $\nu_{\text{max}}(\text{film})$ 3 050, 2 970, 1 763, 1 665, 1 465, 1 075, and 946 cm^{-1} ; $\tau(\text{CCl}_4)$ 4.66 (1 H, t, J 2.4 Hz, H=C=C), 5.92 (1 H, t, J 3 Hz, –CH–O), 7.25–8.60 (8 H, CH_2), 8.82 (6 H, s) (2 × CH_3); ^{13}C n.m.r. (CDCl₃) 176.19 C(10) (s), 148.83 C(9) (s), 121.42 C(3) (d), 84.72 C(5) (d), 57.74 C(8) (s), 37.72 C(4) (s), 31.94, 28.97, 27.30, 26.55, 26.11, and 23.15 p.p.m. from Me₄Si (Found: m/e 192, C, 74.85; H, 8.30. $\text{C}_{12}\text{H}_{16}\text{O}_2$ requires m/e 192, C, 74.95; H, 8.40%). Further fractions eluted with light

petroleum-diethyl ether (8 : 2) gave *ethyl 5 β -hydroxy-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-indene-8 β -carboxylate* (4) (1.10 g, 22%) as an oil, homogeneous by t.l.c., ν_{\max} (film) 3 500, 3 050, 1 730, 1 645, 1 190, 1 060, and 960 cm^{-1} ; τ (CCl_4) 4.45 (1 H, 6, J 2.5 Hz, $\text{HC}=\text{C}$ -), 5.96 (2 H, q, J 7 Hz, $-\text{CO}_2\text{CH}_2\text{CH}_3$), 6.85 (1 H, dd, $J_{\text{ax-ax}}$ 10 Hz and $J_{\text{ax-eq}}$ 5 Hz, CHOH), 7.35–9.0 (9 H, CH_2 and OH), 8.78 (3 H, t, J 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 8.82 (3 H, s), and 9.22 (3 H, s) ($2 \times \text{CH}_3$); m/e 238 (M^+ for $\text{C}_{14}\text{H}_{22}\text{O}_3$: 238).

(ii) *Using excess of sodium borohydride.* The oxo-ester (3) (4.15 g, 0.018 mol) was stirred at 25 °C for 18 h in ethanol (50 ml) with sodium borohydride (1.0 g, 0.026 mol). Work-up afforded an oil (3.97 g) containing three components (t.l.c.) which was absorbed in alumina (140 g). Elution with light petroleum-benzene mixtures gave an oil (514 mg) which was a mixture of the hydroxy-ester (4) and the lactone (9). Elution with benzene gave an oil (1.45 g) which was largely the hydroxy-ester (4) together with a small amount of the lactone (9). Elution with ether gave 8 β -hydroxymethyl-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-inden-5 β -ol (8) as platelets (from diethyl ether-acetone) (65 mg, 2%), m.p. 142–143 °C. The detailed physical constants of this compound are given below.

Treatment of the Hydroxy-ester (4) with Hydrochloric Acid in Ethanol.—Concentrated hydrochloric acid was added to a solution of the hydroxy-ester (4) (0.5 g) in ethanol and the mixture was heated under reflux and nitrogen for 7 h. Work-up as usual gave starting material (4).

Treatment of the Hydroxy-ester (4) with Sulphuric Acid in Dioxan.—A solution of hydroxy-ester (4) (3.6 g, 0.015 mol) and concentrated sulphuric acid (1 ml, 0.018 mol) in dioxan (100 ml) was heated under reflux and nitrogen for 2 h. Work-up as usual gave an oil (2.58 g) which was chromatographed on silica gel (40 g). The fractions eluted by light petroleum-diethyl ether (19 : 1) afforded the carbolactone (9) (2.01 g, 69%) as crystals (after evaporation of solvent and careful washing of the resultant crystals with diethyl ether), m.p. 40–41 °C.

Treatment of the Mixture of the Carbolactone (9) and the Hydroxy-ester (4) with Concentrated Sulphuric Acid in Dioxan.—A mixture (8.51 g) of the carbolactone (9) and the hydroxyester (4) (ca. 2 : 1 ratio by n.m.r.) was dissolved in dioxan (250 ml), treated with concentrated sulphuric acid (3 ml), and heated under reflux for 2 h. Work-up as usual gave the carbolactone (9).

Reduction of Carbolactone (9) with Lithium Aluminium Hydride.—A stirred solution of carbolactone (9) (300 mg, 0.0015 mol) in dry ether (50 ml) was treated with lithium aluminium hydride (80 mg), and the reaction left overnight at 20 °C. Work-up as usual gave 8 β -hydroxymethyl-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-inden-5 β -ol (8) (150 mg, 50%), as prisms (from diethyl ether-light petroleum), m.p. 140–142 °C, ν_{\max} (KBr) 3 410, 3 050, 1 635, 1 470, 1 330, 1 070, 1 015, and 980 cm^{-1} ; τ (CDCl_3) 4.28 (1 H, t, J 2.4 Hz, $\text{C}=\text{CH}$), 6.28 and 6.37 (2 H, AB system, J 8 Hz, CH_2OH), 6.65 (1 H, dd, $J_{\text{ax-ax}}$ 12 Hz, $J_{\text{ax-eq}}$ 6 Hz, CHOH), 7.4–8.7 (10 H, CH_2 and OH), and 8.77 (3 H, s) and 8.98 (3 H, s) ($2 \times \text{CH}_3$); ^{13}C n.m.r. (DMSO) 154.34 C(9) (s), 123.87 C(3) (d), 76.45 C(5) (d), 61.64 C(10), (t), 51.85 C(8) (s), 39.07 C(4) (s), 37.67, 32.70, 29.47, 27.96, 26.82, and 21.21 p.p.m. from Me_4Si (Found: C, 73.40; H, 10.25%; m/e 196. $\text{C}_{12}\text{H}_{20}\text{O}_2$ requires C, 73.40; H, 10.20%; M^+ 196).

Reduction of the Oxo-ester (3) with Lithium Aluminium Hydride.—Lithium aluminium hydride was added carefully to a stirred solution of the oxo-ester (3) (2.13 g, 9 mmol) in

dry ether (100 ml) and the reaction was left overnight at 20 °C. Brine was then added and the organic phase was separated. Work-up gave 8 β -hydroxymethyl-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-inden-5 β -ol (8) (1.31 g, 73%), m.p. 138–141 °C.

Reduction of the Hydroxy-ester (4) with Lithium Aluminium Hydride.—A solution of the hydroxy-ester (4) (700 mg, 2.9 mmol) in dry ether was treated with lithium aluminium hydride (200 mg). The reaction was left overnight at 20 °C. Brine was added and the organic layer was separated. Work-up afforded 8 β -hydroxymethyl-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-inden-5 β -ol (8) (350 mg, 61%), m.p. 139–142 °C.

Alkaline Hydrolysis of the Oxo-ester (3).—A solution of the oxo-ester (3) (1.60 g, 6.8 mmol) and potassium hydroxide (0.40 g, 10 mmol) in ethanol (50 ml) was heated under reflux for 2 h. Work-up as usual gave 4,4-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro-2H-indene-8-carboxylic acid (5) (800 mg, 60%) as crystals (from diethyl ether-light petroleum), m.p. 123–124 °C, ν_{\max} 3 400–2 600br, 1 720, 1 640, 1 450, 1 385, 1 270, 1 170, 1 040, and 970 cm^{-1} ; τ (CDCl_3) –0.40br (1 H, s, $W_{\frac{1}{2}}$ 15 Hz, CO_2H), 4.20 (1 H, t, J 2.5 Hz, $\text{C}=\text{CH}$), 6.9–8.50 (8 H, m, CH_2), and 8.70 (3 H, s) and 8.78 (3 H, s) ($2 \times \text{CH}_3$) (Found: C, 69.4; H, 7.8%; m/e 208. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.20; H, 7.75%; M^+ 208).

Reduction of the Oxo-acid (5) with Sodium Borohydride.—Sodium borohydride (50 mg) was added to a stirred solution of the oxo-acid (5) (100 mg, 0.5 mmol) in ethanol (20 ml) and the reaction was left at 20 °C for 15 h. Work-up as usual gave 5 β -hydroxy-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-indene-8 β -carboxylic acid (6), as prisms (from diethyl ether), m.p. 165–166 °C; ν_{\max} (KBr) 3 480, 3 010–2 500br, 1 718, 1 645, 1 385, 1 060, and 1 012 cm^{-1} ; τ (CDCl_3) 4.28 (1 H, t, J 2.5 Hz, $\text{C}=\text{CH}$), 6.65 [1 H, dd, $J_{\text{ax-ax}}$ 12 Hz, $J_{\text{ax-eq}}$ 6 Hz, $\text{CH}(\text{OH})$], and 8.76 (3 H, s) and 9.06 (3 H, s) ($2 \times \text{CH}_3$) (Found: C, 68.6; H, 8.35%; m/e 210. $\text{C}_{12}\text{H}_{18}\text{O}_3$ requires C, 68.55; H, 8.65%; M^+ 210). The acid was also obtained by alkaline hydrolysis of the ethyl ester (4). Methylation of the hydroxy-acid (6) with ethereal diazomethane afforded methyl 5 β -hydroxy-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-indene-8 β -carboxylate (7), as an oil, homogeneous on t.l.c.; ν_{\max} (film) 3 380, 2 950, 1 728, 1 240, 1 170, and 1 070 cm^{-1} ; τ (CDCl_3) 4.30 (1 H, t, J 2.5 Hz), 6.30 (3 H, s, OCH_3), 6.57 (1 H, dd, $J_{\text{ax-ax}}$ 9 Hz, $J_{\text{ax-eq}}$ 5 Hz, CHOH), and 8.75 (3 H, s) and 9.14 (3 H, s) ($2 \times \text{CH}_3$) (m/e 224. $\text{C}_{13}\text{H}_{20}\text{O}_3$ requires M^+ 224). Heating of the hydroxy-acid (6) (100 mg) in dioxan (20 ml) containing three drops of concentrated sulphuric acid under reflux for 2 h afforded the lactone (9) (60 mg).

Preparation of 8-Methyl-5,6,7,8-tetrahydroindan-5-one.—A mixture of 2-methylcyclopentanone (5.46 g), freshly distilled methyl vinyl ketone (4.88 g), and three drops of concentrated sulphuric acid was heated under reflux for 16 h. The mixture was cooled, diluted with hexane (20 ml), washed with 5% aqueous sodium hydroxide solution, and dried over magnesium sulphate. Removal of the solvent gave a red liquid (7.12 g) which was distilled to give a pale yellow liquid (3.42 g), b.p. 72–80 °C at 0.4 mmHg, ν_{\max} (CCl_4) 2 950, 1 730, 1 710, and 1 670 cm^{-1} . This liquid was adsorbed onto alumina (400 g). Elution with light petroleum-diethyl ether mixtures yielded crude 2-methyl-2-(3-oxobutyl)-cyclopentanone as a pale yellow liquid (244 mg), ν_{\max} (CCl_4) 2 950, 1 746, 1 710, 1 460, 1 380, and 1 095 cm^{-1} . Further elution gave 8-methyl-5,6,7,8-tetrahydroindan-5-one (1.64 g, 20%) as a pale yellow liquid, b.p. 90–92 °C at 0.15 mmHg,

n_D^{14} 1.5146, λ_{\max} (EtOH) 241 nm (ϵ 10 300) (lit.,¹⁷ b.p. 112 °C at 4 mmHg), n_D^{22} 1.4989. Further elution gave a pale yellow oil (182 mg), thought to be crude 9-hydroxy-8-methylhexahydroindan-5-one, ν_{\max} (CCl₄) 3 500, 2 950, 1 725, 1 460, 1 410, 1 370, and 1 160 cm⁻¹.

Preparation of 4,4,8-Trimethyl-1,6,7,8-tetrahydro-2H-inden-5(4H)-one (14).—Potassium t-butoxide solution prepared by dissolving potassium (5.5 g, 0.14 g-atom) in t-butyl alcohol (120 ml) with stirring and warming under dry nitrogen was added to a stirred solution of 8-methyl-5,6,7,8-tetrahydroindan-5-one (7.1 g, 0.047 mol) in dry t-butyl alcohol at 50 °C to give a clear orange solution. After 1 min, a solution of methyl iodide (40.3 g, 0.28 mol) in dry t-butyl alcohol (20 ml) was added and the resulting milky white suspension was stirred and heated under reflux for 1 h. Work-up in the usual way gave an orange liquid (7.45 g) which was adsorbed onto alumina (600 g). Elution with light petroleum–diethyl ether mixtures gave a liquid (580 mg) whose n.m.r. and mass spectra indicated that it contained tri- and tetra-methylated products (*m/e* 192, 206). Further elution gave 4,4,8-trimethyl-1,6,7,8-tetrahydro-2H-inden-5(4H)-one (14) (2.53 g, 30%) as a sweet smelling liquid, n_D^{15} 1.4935, ν_{\max} (CCl₄) 2 960, 1 715, 1 460, 1 380, and 1 150 cm⁻¹; τ (CCl₄) 4.58 (1 H, t, *J* 2.2 Hz, CH=C), 7.0–9.0 (8 H, CH₂), and 8.78br (9 H, s, 3 CH₃-C). The *semicarbazone* (plates from ethyl acetate–methanol) had m.p. 177–183 °C (Found: C, 66.4; H, 8.9; N, 17.6. C₁₃H₂₁N₃O requires C, 66.4; H, 8.9; N, 17.9%). Further elution gave 4,8-dimethyl-5,6,7,8-tetrahydroindan-5-one (2.35 g, 30%) as a sweet smelling liquid, b.p. 111 °C at 6 mmHg, n_D^{15} 1.5128, λ_{\max} (EtOH) 250 nm (ϵ 10 500); ν_{\max} (CCl₄) 2 970, 1 666, 1 460, 1 378, 1 350, 1 328, and 1 295 cm⁻¹; τ (CCl₄) 7.0–9.0 (10 H, CH₂), 8.32br (3 H, s, CH₃-C=), and 8.89 (3 H, s, CH₃-C) (lit.,¹⁸ b.p. 87 °C at 0.85 mmHg). The *semicarbazone* (needles from aqueous ethanol) had m.p. 208 °C (Found: C, 64.9; H, 8.5; N, 18.75. Calc. for C₁₂H₁₉N₃O: C, 65.2; H, 8.6; N, 19.0%).

Reduction of 4,4,8-Trimethyl-1,6,7,8-tetrahydro-2H-inden-5(4H)-one (14).—The ketone (14) (966 mg, 0.005 mol) in ether (10 ml) was added to a stirred slurry of lithium aluminium hydride (105 mg, 0.0027 mol) in ether (10 ml) during 0.25 h. The stirred mixture was heated under reflux for 2 h, and the excess of hydride was destroyed by addition of ethyl acetate to the cooled solution. The usual work-up afforded an oil (922 mg) which was purified on p.l.c. [2 large plates, 1 elution with benzene–ether (1 : 1)]. The main band yielded a mixture of the epimers of 4,4,8-trimethyl-1,4,5,6,7,8-hexahydro-2H-inden-5-ol as an oil (648 mg, 67%), homogeneous to t.l.c., τ (CCl₄) 4.61 (1 H, t, *J* 2.5 Hz, CH=C), 6.79 [1 H, complex m, CH(OH), α and β], 7.30 (1 H, s, exchangeable OH), 7.4–9.2 (8 H, CH₂), and 8.86br and 9.00 (9 H, s, s, 3 CH₃C) (Found: C, 79.8; H, 11.1. C₁₂H₂₀O requires C, 80.0; H, 11.1%).

Epoxidation of the Lactone (9).—The lactone (9) (3.384 g, 0.018 mol) and *m*-chloroperbenzoic acid (3.440 g, 0.020 mol) in chloroform (234 ml) were stirred for 6 h at 20 °C. A saturated solution of sodium hydrogen carbonate was added and the organic phase was separated. Work-up as usual gave 3 α ,9 α -epoxy-4,4-dimethylhexahydroindane-5 β ,8 β -carbolactone (17) (1.725 g, 47%) as prisms (from ether), m.p. 98–99 °C, ν_{\max} (KBr) 2 980, 2 950, 1 755, 1 460, 1 360, 1 160, 1 065, and 980 cm⁻¹; τ (CDCl₃) 5.70br (1 H, s,

$W_{\frac{1}{2}}$ 3 Hz, HC-O), 6.50 (1 H, s, C-CH-O), 7.6–8.5 (8 H, m, CH₂), and 8.90 (3 H, s) and 8.97 (3 H, s) (2 \times CH₃); ¹³C n.m.r. (CDCl₃) 175.09 C(10) (s), 83.39 C(5) (d), 73.03 C(9) (s), 61.11 C(3) (d), 49.03 C(8) (s), 35.11 C(4) (s), 27.18, 24.65, 24.00, 22.60, 21.79, and 21.46, p.p.m. from Me₄Si (Found: C, 69.3; H, 7.75%; *m/e* 208. C₁₂H₁₆O₃ requires C, 69.40; H, 7.70%; *M*⁺ 208).

Treatment of the Epoxy-lactone (17) with Lithium Aluminium Hydride.—Lithium aluminium hydride (100 mg) was added carefully to a stirred solution of epoxide (17) (300 mg, 1.5 mmol) in diethyl ether (75 ml) and the reaction was left for 6 h at 20 °C. Work-up as usual afforded 3 α ,9 α -epoxy-8 β -hydroxymethyl-4,4-dimethylhexahydroindan-5 β -ol (18) (150 mg, 50%) as crystals (from diethyl ether–light petroleum), m.p. 93–94 °C, ν_{\max} (KBr) 3 340, 2 980, 1 460, 1 362, 1 065, 1 045, 992, 921, and 829 cm⁻¹; τ (CDCl₃) 6.14 and 6.46 (2 H, AB system, *J* 11.7 Hz, CH₂OH), 6.31 [1 H, dd, *J*_{ax-ax} 8 Hz, *J*_{ax-eq} 4 Hz, (OH)CH_{ax}], 6.58br (1 H, s, $W_{\frac{1}{2}}$ 4.5 Hz, C-CH-O), 7.95–8.45 (10 H, m, CH₂ and 2-OH), and 8.93 (3 H, s) and 9.10 (3 H, s) (2 \times CH₃); ¹³C n.m.r. (DMSO) 74.99 C(5) (d), 72.39 C(9) (s), 61.54 C(10) (t), 56.96 C(3) (d), 46.37 C(8) (s), 38.05 C(4) (s), 28.88, 28.07, 26.35, 23.16, and 18.58 p.p.m. from Me₄Si (Found: C, 67.10; H, 9.60%; *m/e* 212. C₁₂H₂₀O₃ requires C, 67.80; H, 9.50%; *M*⁺ 212).

Epoxidation of 8 β -Hydroxymethyl-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-inden-5 β -ol (8).—The diol (8) (750 mg, 3.8 mmol) was treated with *m*-chloroperbenzoic acid (800 mg, 4.5 mmol) in chloroform (50 ml) and stirred for 6 h at 20 °C. Work up as usual afforded 3 β ,9 β -epoxy-8 β -hydroxymethyl-4,4-dimethylhexahydroindan-5 β -ol (19) (510 mg, 59%), as crystals (from diethyl ether), m.p. 128–130 °C, ν_{\max} (KBr) 3 500, 2 940, 1 455, 1 362, 1 035, 980, and 900 cm⁻¹; τ (CDCl₃) 6.05 and 6.36 (2 H, AB system, *J* 11 Hz, CH₂OH), 6.50 [1 H, dd, *J*_{ax-ax} 7.5 Hz, *J*_{ax-eq} 3 Hz, (OH)CH_{ax}], 6.62br (1 H, s, $W_{\frac{1}{2}}$ 9 Hz, C-CH-O), 7.90–8.85 (10 H, CH₂ and 2-OH), and 8.89 (3 H, s) and 9.08 (3 H, s) (2 \times CH₃); ¹³C n.m.r. (DMSO) 76.05 C(5) (d), 72.12 C(9) (s), 63.16 C(10) (t), 61.33 C(3) (d), 45.90 C(8) (s), 37.97 C(4) (s), 31.93, 27.18, 26.37, 23.68, 23.51, and 17.47 p.p.m. from Me₄Si (Found: C, 68.2; H, 9.35%; *m/e* 212. C₁₂H₂₀O₃ requires C, 67.90; H, 9.40%; *M*⁺ 212).

Epoxidation of Ethyl 4,4-Dimethyl-5-oxo-1,4,5,6,7,8-hexahydro-2H-indene-8-carboxylate (3).—*m*-Chloroperbenzoic acid (1.8 g, 10 mmol) in chloroform (25 ml) was added to a stirred solution of the oxo-ester (3) (1.87 g, 8 mmol) in chloroform (25 ml) at 20 °C, and the mixture was left for 5 h. Work-up in the usual way gave an oil (1.87 g) containing two components (t.l.c.), which was applied to four large p.l.c. plates and eluted twice with light petroleum–diethyl ether (3 : 1). Extraction of the upper band gave ethyl 3 α ,9 α -epoxy-4,4-dimethyl-5-oxohexahydroindane-8 β -carboxylate (20) (1.24 g, 62%) as an oil which crystallised when set aside to give needles (from aqueous methanol), m.p. 49–50 °C, ν_{\max} (CCl₄) 2 960, 1 725, 1 460, 1 385, 1 368, 1 190, 1 160, and 947 cm⁻¹; τ (CCl₄) (2 H, ABC₃m centred on 5.84 CO₂CH₂CH₃), 6.51 (1 H, s, C-CH-O), 7.0–9.0 (8 H, m, CH₂), 8.70 (3 H, t, *J* 7.2 Hz, CO₂CH₂CH₃), and 8.90 and 9.10 (6 H, s, CH₃-C-CH₃) (Found: C, 66.6; H, 7.8%; *m/e* 252. C₁₄H₂₀O₄ requires C, 66.7; H, 7.9%; *M*⁺ 252). The lower band gave ethyl 3 β ,9 β -epoxy-4,4-dimethyl-5-oxohexahydro-

¹⁷ E. C. du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 1937, 53.

¹⁸ D. Caine, A. M. Alejande, K. Mung, and W. J. Powers, III, *J. Org. Chem.*, 1972, 37, 706.

indane-8 β -carboxylate (21) (272 mg, 14%) as an oil which crystallised when set aside to give bulky prisms (from hexane), m.p. 53.5–54.5 °C, ν_{\max} (CCl₄) 2 960, 1 725, 1 460, 1 385, 1 368, 1 190, 1 160, and 945 cm⁻¹; τ (CCl₄) 5.78 (2 H, q, J 6.9 Hz, CO₂CH₂CH₃), 6.71br (1 H, s, $W_{\frac{1}{2}}$ 2.7 Hz, $\overline{\text{C-CH-O}}$), 7.0–9.0 (8 H, m, CH₂), 8.68 (3 H, t, J 7.1 Hz, CO₂CH₂CH₃), and 8.82 and 9.07 (6 H, 2 s, CH₃-C-CH₃) (Found: C, 66.9; H, 7.8%; m/e 252. C₁₄H₂₀O₄ requires C, 66.7; H, 7.9%, M^+ 252).

Epoxidation of Ethyl 5 β -Hydroxy-4,4-dimethyl-1,4,5,6,7,8-hexahydro-2H-indene-8 β -carboxylate (4).—(i) For 6 h. A solution of the hydroxy-ester (4) (3.21 g, 11 mmol) and *m*-chloroperbenzoic acid (2.70 g, 15 mmol) in chloroform (100 ml) was stirred for 6 h at 20 °C. Work-up as usual afforded a mixture (2.82 g) which, when chromatographed on silica gel (60 g) gave, in the fractions eluted with light petroleum–diethyl ether (9 : 1), 3 α ,9 α -epoxy-4,4-dimethylhexahydroindane-5 β ,8 β -carbolactone (17) (528 mg, 15%) (i.r. and n.m.r. spectra superimposable on the spectra of an authentic sample). Fractions eluted with light petroleum–diethyl ether (8 : 2) gave ethyl 3 α ,9 α -epoxy-5 β -hydroxy-4,4-dimethylhexahydroindane-8 β -carboxylate (22) (954 mg, 30%) as an oil which crystallized when set aside, m.p. 93–94 °C; ν_{\max} (film) 3 480, 2 980, 1 720, 1 460, 1 365, 1 245, 1 030, and 940 cm⁻¹; τ (CCl₄) (2 H, ABC₃m centred on 5.89, CO-O-CH₂-CH₃) 6.46 (1 H, m, CHOH), 6.53br (1 H, s, $\overline{\text{C-CH-O}}$), 7.83 (1 H, s, CHOH, collapses when D₂O is added), 8.71 (3 H, t, J 7.2 Hz, CO-O-CH₂-CH₃), and 9.13 (6 H, s) (2 \times CH₃) (Found: C, 66.2; H, 8.7%; m/e 254. C₁₄H₂₂O₄ requires C, 66.2; H, 8.65%; M^+ 254). Further fractions eluted with light petroleum–diethyl ether (1 : 1) gave an oil (450 mg), heterogeneous on t.l.c., which was applied to three small p.l.c. plates and eluted with light petroleum–diethyl ether (3 : 7). Extraction of the more intense band gave an oil (120 mg). This oil was again applied to one small p.l.c. plate and developed five times with light petroleum–diethyl ether (1 : 1). This afforded ethyl 3 β ,9 β -epoxy-5 β -hydroxy-4,4-dimethylhexahydroindane-8 β -carboxylate (23) (40 mg) as an oil, ν_{\max} 3 480, 2 975, 1 720, 1 370, 1 260, 1 190, 1 060, 1 000, and 920 cm⁻¹; τ (CCl₄) (2 H, ABC₃ m centred on, CO-O-CH₂-CH₃), 6.53 (1 H, m, CHOH) 6.65br (1 H, s, $W_{\frac{1}{2}}$ 2 Hz, $\overline{\text{C-CH-O}}$), 8.70 (3 H, t, J 7 Hz, CO-O-CH₂-CH₃), and 9.06 (3 H, s) and 9.09 (3 H, s) (2 \times CH₃) (Found: m/e 254. C₁₄H₂₂O₄ requires M^+ 254).

(ii) For 18 h. A solution of the hydroxy-ester (4) (4.12 g, 16 mmol) and *m*-chloroperbenzoic acid (3.90 g, 22 mmol) in chloroform (100 ml) was stirred for 18 h at 20 °C. Work-up as usual afforded a mixture (3.75 g) which was chromatographed on silica gel (60 g) and gave in the fractions eluted with light petroleum–diethyl ether (9 : 1) the epoxy-lactone (17) (1.30 g, 38%). The fractions eluted with more polar solvents afforded a mixture (0.690 g); t.l.c. indicated the presence of the hydroxy-epoxides (22) and (23). No further separation of the components of this mixture was attempted.

Epoxidation of 4,4,8-Trimethyl-1,6,7,8-tetrahydro-2H-inden-5(4H)-one (14).—Treatment of the oxo-olefin (1.08 g) with *p*-nitroperbenzoic acid (1.22 g) in the usual way gave a mixture of 3 α ,9 α -epoxy-(24) and 3 β ,9 β -epoxy-4,4,8 β -trimethylhexahydroindan-5-one (25) (983 mg) as an oil, apparently homogeneous to t.l.c., ν_{\max} (CCl₄) 2 980, 1 714, 1 465, 1 380, 1 115, and 870 cm⁻¹; τ (CCl₄) 6.67br, 6.71br (1 H, 2 overlapping s, oxiran-H, α and β), 7.0–9.0 (8 H,

CH₂), 8.72, 8.76, and 8.78 (6 H, 3 s overlapping, CH₃-C-CH₃ in α - and β -epoxides), and 9.15 and 9.15 (3 H, 2 s, CH₃-C in α - and β -epoxides) (Found: C, 73.9; H, 9.3%; m/e 194. C₁₂H₁₈O₂ requires C, 74.2; H, 9.3%; M^+ 194). Attempts to separate the two epoxides by multiple elution p.l.c. were not successful.

Reduction of Ethyl 3 α ,9 α -Epoxy-4,4-dimethyl-5-oxohexahydroindane-8 β -carboxylate (20) with Sodium Borohydride.—A stirred solution of the epoxy-ester (20) (80 mg, 0.36 mmol) in ethanol (20 ml) was treated with sodium borohydride (35 mg), and the reaction was left for 6 h at 20 °C. Work-up as usual gave the epoxy-lactone (17) (45 mg, 67%) (m.p. 95–98 °C) (i.r. and n.m.r. spectra superimposable on the spectra of an authentic sample).

Reduction of the β -Epoxy-ketoester (21) with Lithium Aluminium Hydride.—Lithium aluminium hydride (150 mg) was added carefully to a stirred solution of the epoxy oxo-ester (21) (450 mg, 1.8 mmol) in diethyl ether (50 ml) and the reaction left overnight at 20 °C. Work-up as usual yielded the β -epoxy-diol (19) (250 mg, 67%) (m.p. 128–131 °C) (i.r. and n.m.r. spectra superimposable on the spectra of an authentic sample).

Treatment of the α -Epoxy-oxo-ester (20) with Lithium Aluminium Hydride.—Lithium aluminium hydride (70 mg) was added carefully to a stirred solution of the α -epoxy-oxo-ester (20) (160 mg, 0.63 mmol) in diethyl ether (25 ml) and the reaction left overnight at 20 °C. Work-up as usual afforded a mixture (110 mg), whose main components have R_F values identical with the α -epoxy-hydroxy-ester (22) and the α -epoxy-diol (18) (ratio 1 : 2 on n.m.r. spectrum). The mixture was applied to a small p.l.c. plate and eluted with ether. The upper band afforded the α -epoxy-hydroxy-ester (22) and the lower band gave the α -epoxy diol (18).

Treatment of the α -Epoxy-hydroxy-ester (22) with Lithium Aluminium Hydride.—Lithium aluminium hydride (70 mg) was added carefully to a stirred solution of the hydroxy-ester (22) (180 mg, 0.65 mmol) in diethyl ether (35 ml) and the reaction was left overnight at 20 °C. Work-up as usual gave an oil (100 mg). This was applied to a small p.l.c. plate and eluted with diethyl ether to afford the α -epoxy-diol (18).

Treatment of the β -Epoxy-oxo-ester (21) with Sodium Borohydride.—A solution of the epoxy-oxo-ester (21) (600 mg, 2.35 mmol) and sodium borohydride (150 mg) in ethanol was stirred for 6 h at 20 °C. Work-up as usual gave an oil (450 mg), homogeneous on t.l.c., which was identified as the β -epoxy-hydroxy-ester (19).

Treatment of the β -Epoxy-hydroxy-ester (23) with Lithium Aluminium Hydride.—Lithium aluminium hydride (80 mg) was added carefully to a stirred solution of the hydroxy-ester (23) (300 mg, 1.2 mmol) in dry ether (50 ml) and the reaction was left overnight at 20 °C. Work-up as usual afforded the β -epoxy-diol (19).

Rearrangement of 3 α ,9 α -Epoxy-4,4-dimethylhexahydroindane-5 β ,8 β -carbolactone (17).—Boron trifluoride–diethyl ether complex (2 ml) was added to a stirred solution of the carbolactone (17) (1.050 g) in benzene (100 ml) under dry nitrogen at 20 °C. After 20 min, when the solution turned pink, a saturated solution of sodium hydrogen carbonate was added. Work-up as usual gave an oil (0.916 g), t.l.c. of which indicated mainly two compounds. The oil was dissolved in the minimum amount of diethyl ether and light petroleum added. This afforded 3 α -hydroxy-4,4-dimethyl-2,3,4,5,6,9-hexahydroindene-5 β ,9 β -carbolactone (26) (0.378 g, 36%), the major product, as prisms (from light petroleum), m.p. 134–135 °C, ν_{\max} (KBr) 3 410, 3 020, 2 960, 1 755,

1 350, 1 205, 1 170, 992, 920, and 900 cm^{-1} ; $\tau(\text{CDCl}_3)$, 4.42br (1 H, s, $W_{\frac{1}{2}}$ 7.5 Hz, $\text{CH}=\text{C}$), 5.35br (1 H, s, $W_{\frac{1}{2}}$ 8 Hz, CHO), 5.98br (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, $\text{CH}-\text{O}$), 7.4—8.65 (7 H, CH_2 and CHOH), and 8.70 (3 H, s) and 8.88 (3 H, s) ($2 \times \text{CH}_3$); ^{13}C n.m.r. (CDCl_3) 177.49 C(10) (s), 62.00 C(9) (s), 74.90 C(3) (d), 83.16 C(5) (d), 141.87 C(8) (s), 42.36 C(4) (s), 116.88 C(7) (d), 34.21, 29.35, 28.06, 22.55, and 18.51 p.p.m. from Me_4Si (Found: C, 69.3; H, 6.70%; m/e 208. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.20; H, 7.70%; M^+ 208).

The mother liquors (0.538 g) were absorbed on silica gel (60 g) and chromatographed. The fractions eluted with light petroleum–diethyl ether (8:2) gave the hydroxy-lactone (26) (0.030 g, 3%). Further fractions eluted with light petroleum–diethyl ether (1:1) yielded 4,4-dimethyl-3-oxohexahydroindane-5 β ,9 β -carbolactone (32) (0.102 g, 10%), m.p. 97–98 °C (from diethyl ether–light petroleum), ν_{max} (KBr) 2 980, 1 760, 1 745, 1 369, 1 160, 1 065, 1 045, 990, and 938 cm^{-1} ; $\tau(\text{CDCl}_3)$ 5.83 (1 H, t, J 3 Hz, $\text{CH}-\text{O}$), 7.50–8.40 (H, CH_2), and 8.80 (6 H, s) ($2 \times \text{CH}_3$); ^{13}C n.m.r. (CDCl_3) 221.86 C(3) (s), 176.31 C(10) (s), 85.39 C(5) (d), 59.33 C(9) (d), 46.01 C(8) (s), 39.31 C(4) (s), 36.65, 34.63, 30.02, 24.76, 23.39, and 21.90 p.p.m. from Me_4Si (Found: C, 69.3; H, 7.7%; m/e 208. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.20; H, 7.70%; M^+ 208).

Oxidation of 3 α -Hydroxy-4,4-dimethyl-2,3,4,5,6,9-hexahydroindene-5 β ,9 β -carbolactone (26).—Jones reagent (40 ml H_2O , 5.29 g CrO_3 , 4 ml H_2SO_4) was added to a solution of the hydroxy-lactone (26) (521 mg, 2.5 mmol) in acetone (130 ml) at 0 °C, and the mixture was stirred for 8 h. A saturated solution of sodium bisulphite was added. Extraction with ether afforded 4,4-dimethyl-3-oxo-2,3,4,5,6,9-hexahydroindene-5 β ,9 β -carbolactone (27) (178 mg, 34%), as prisms (from diethyl ether), m.p. 112–115 °C; ν_{max} (KBr) 2 990, 1 785, 1 735, 1 332, 1 268, 1 140, 990, and 920 cm^{-1} ; $\tau(\text{CDCl}_3)$ 4.32br (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, $\text{CH}=\text{C}$), 5.87 (1 H, t, J 2 Hz, $\text{CH}-\text{O}$), 7.10–7.80 (6 H, CH_2), and 8.60 (3 H, s) and 8.98 (3 H, s) ($2 \times \text{CH}_3$) (Found: C, 69.8; H, 6.6%; m/e 206. $\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C, 69.90; H, 6.80%; M^+ 206).

Reduction of 4,4-Dimethyl-3-oxo-2,3,4,5,6,9-hexahydroindene-5 β ,9 β -carbolactone (27) with Sodium Borohydride.—A solution of the oxo-lactone (27) (178 mg, 0.86 mmol) and sodium borohydride (100 mg, 2 mmol) in ethanol (50 ml) was stirred at room temperature for 4 h. Work-up as usual afforded 3 β -hydroxy-4,4-dimethyl-2,3,4,5,6,9-hexahydroindene-5 β ,9 β -carbolactone (28) (90 mg, 50%), as prisms from light petroleum, m.p. 65–66 °C, ν_{max} (KBr) 3 380, 2 980, 1 770, 1 335, 1 262, 1 140, 1 075, 990, and 927 cm^{-1} ; $\tau(\text{CDCl}_3)$ 4.47br (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, $\text{C}=\text{CH}$), 5.87br (1 H, s, $W_{\frac{1}{2}}$ 5 Hz, $\text{CH}-\text{O}$), 5.90 (1 H, m, over 22 Hz, CHOH), 6.92 (1 H, d, J 14 Hz, CHOH , exchanged with D_2O), 7.40–8.15 (6 H, CH_2), 8.73 (3 H, s), and 9.03 (3 H, s) ($2 \times \text{CH}_3$); ^{13}C n.m.r. (CDCl_3) 183.10 C(10) (s), 59.60 C(9) (s), 72.17 C(3) (d), 83.12 C(5) (d), 140.10 C(8) (s), 41.48 C(4) (s), 117.97 C(7) (d), 33.06, 29.18, 27.07, 22.70, and 16.50 p.p.m. from Me_4Si (Found: C, 69.1; H, 7.6%; m/e 208. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.20; H, 7.70%; M^+ 208).

Epoxidation of the 3 α -Hydroxy-lactone (26).—A solution of the 3 α -hydroxy-lactone (26) (300 mg, 1.4 mmol) and *m*-chloroperbenzoic acid (290 mg, 1.7 mmol) in chloroform (50 ml) was stirred for 6 h. Work-up as usual gave 7 ξ ,8 ξ -epoxy-3 α -hydroxy-4,4-dimethyl-hexahydroindane-6 β ,9 β -carbolactone (29) (110 mg, 33%), as needles (from diethyl ether), m.p. 136–138 °C, ν_{max} (KBr) 3 450, 2 982, 1 765, 1 348, 1 180, 1 040, 1 005, and 910 cm^{-1} ; $\tau(\text{CDCl}_3)$ 5.10 (1 H, t, J 4 Hz, CHOH), 6.02br (1 H, s, $W_{\frac{1}{2}}$ 5 Hz, $\text{CH}-\text{O}$),

6.51 (1 H, d, J 4 Hz, $\overline{\text{C}-\text{CH}-\text{O}}$), 7.40–8.50 (7 H, CH_2 and CHOH), and 8.64 (3 H, s) and 8.72 (3 H, s) ($2 \times \text{CH}_3$) (Found: C, 65.4; H, 7.5%; m/e 224. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires C, 64.30; H, 7.90%; M^+ 224).

Rearrangement of 7 ξ ,8 ξ -Epoxy-3 α -hydroxy-4,4-dimethyl-hexahydroindane-5 β ,9 β -carbolactone (29) with Boron Trifluoride–Diethyl Ether Complex.—Boron trifluoride–diethyl ether complex (0.5 ml) was added to a stirred solution of the epoxy-lactone (29) (120 mg, 0.6 mmol) in benzene under dry nitrogen at 20 °C and allowed to react for 20 min. A saturated solution of sodium hydrogen carbonate was then added. Work-up as usual gave an oil (60 mg), t.l.c. indicated one major and two minor components. This oil was applied to a medium p.l.c. plate and eluted with light petroleum–diethyl ether (1:1). Extraction of the most intense band gave 3 α -hydroxy-4,4-dimethyl-7-oxohexahydroindane-5 β ,9 β -carbolactone (30) (20 mg, 17%) as an oil, homogeneous by t.l.c., ν_{max} (CS_2) 3 675, 1 780, 1 720, 1 325, 1 175, 1 030, and 967 cm^{-1} ; $\tau(\text{CDCl}_3)$ 5.50 (1 H, d, J 6 Hz, CHOH), 5.64 (1 H, t, J 2.5 Hz, $\text{CH}-\text{O}$) (collapsed on irradiation of proton at τ 7.27), 6.65 (1 H, dd, J_1 9 Hz and J_2 10 Hz, $\text{CH}_2-\text{CH}_{\text{ax}}-\text{C}=\text{O}$), 7.27 (2 H, d, J 2.5 Hz, $\text{O}-\text{CH}-\text{CH}_2-\text{C}=\text{O}$) (collapsed on irradiation of proton at τ 5.64), and 8.59 (3 H, s) and 8.61 (3 H, s) ($2 \times \text{CH}_3$) (m/e 224. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires M^+ 224).

Rearrangement of Ethyl 3 α ,9 α -Epoxy-4,4-dimethyl-5-oxohexahydroindane-8 β -carboxylate (20).—Freshly distilled boron trifluoride–diethyl ether complex (0.75 ml) was added to a stirred solution of the oxo-ester α -epoxide (20) (1.30 g) in dry benzene (40 ml) under dry nitrogen at 10 °C; after being stirred for 10 min the solution was deep orange. Sodium hydrogen carbonate solution (5%; 50 ml) was added, and work-up in the usual way gave a pale yellow oil (1.28 g) whose t.l.c. and i.r. suggested the presence of carboxylic acid. The mixture was methylated using ethereal diazomethane to give an oil (1.22 g) containing one major and four minor products (t.l.c.), which was applied to four large p.l.c. plates and eluted once with light petroleum–diethyl ether (1:1). Five bands in order of decreasing R_F were extracted.

Band A gave ethyl 2-isopropenyl-1-(2-methoxycarbonyl-ethyl)cyclopent-2-enecarboxylate (33) (405 mg) as an oil, homogeneous to t.l.c., λ_{max} (EtOH) 236 nm (ϵ 13 000); ν_{max} (CCl_4) 2 950, 1 740, 1 726, 1 440, 1 378, 1 170, 1 080, 1 031, and 894 cm^{-1} ; $\tau(\text{CCl}_4)$ 4.12 (1 H, t, J 2.6 Hz, $\text{CH}=\text{C}$), 5.14br (2 H, s, $W_{\frac{1}{2}}$ 3.2 Hz, $\text{CH}_2=\text{C}$), 5.93 (2 H, q, J 7.1 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 6.41 (3 H, s, CH_2CH_3), 7.3–8.4 (8 H, CH_2), 8.12 (3 H, m, $W_{\frac{1}{2}}$ 2.5 Hz, $\text{CH}_3-\text{C}=\text{CH}_2$), and 8.81 (3 H, t, J 7.1 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$) (m/e 266. $\text{C}_{15}\text{H}_{22}\text{O}_4$ requires M^+ 266).

Band B gave unchanged epoxide (63 mg) as an oil with t.l.c., and i.r. and n.m.r. spectra identical with an authentic sample.

Band C gave an oil (150 mg) whose t.l.c. indicated that it contained one major and several minor components. This oil was applied to two small p.l.c. plates and eluted seven times with light petroleum–diethyl ether (2:1), and extraction of the main band gave an oil (54 mg), homogeneous to t.l.c., λ_{max} (EtOH) 244 nm (ϵ 4 500); ν_{max} (CCl_4) 2 960, 1 751, 1 733, 1 440, 1 370, 1 180, 1 124, 1 031, and 864 cm^{-1} ; $\tau(\text{CCl}_4)$ 4.28 (1 H, m, $W_{\frac{1}{2}}$ 6.0 Hz, $\text{CH}=\text{C}$), 4.62 (1 H, d, J 9.9 Hz, $\text{CH}=\text{C}$), 5.89 (2 H, 2 q, J 7.3 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 6.40 (3 H, 2 s, $2 \times \text{CH}_3\text{O}$), 7.3–9.0 (6 H, CH_2), 8.15 (3 H, m, $W_{\frac{1}{2}}$ 3.3 Hz, $\text{CH}_3-\text{C}=\text{C}$), 8.44 (3 H, m, $W_{\frac{1}{2}}$ 2.9 Hz, $\text{CH}_3=\text{C}$), and 8.73 and 8.81 (3 H, 2 t, J 7.3 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$) (m/e 266. $\text{C}_{15}\text{H}_{24}\text{O}_4$ requires M^+ 266).

Band D (86 mg) and E (188 mg) were mixtures which could not be separated into pure components.

Reduction of Ethyl 2-Isopropenyl-1-(2-methoxycarbonyl-ethyl)cyclopent-2-enecarboxylate (33).—A solution of the diester (33) (120 mg) in dry diethyl ether (25 ml) was added slowly to a stirred slurry of lithium aluminium hydride (35 mg) in diethyl ether (25 ml) at 25 °C, and the stirred mixture was heated under reflux for 2 h. The mixture was cooled to 0 °C and ethyl acetate was added cautiously to destroy the excess of lithium aluminium hydride, and dilute hydrochloric acid (5 ml) was added to dissolve the inorganic precipitate. Ethyl acetate was added, and work-up in the usual way gave a glass (87 mg) which was applied to one small p.l.c. plate and eluted once with light petroleum–diethyl ether (1 : 5). Extraction of the major band with ethyl acetate gave 1-(3-hydroxypropyl)-2-isopropenylcyclopent-2-en-1-ylmethanol (34; R = H) (56 mg) as microcrystals (from hexane–diethyl ether), m.p. 68–72 °C, λ_{\max} (EtOH) 238 nm (ϵ 5 600) ν_{\max} (CCl₄) 3 650sh, 3 610sh, 4 40br, 1 452, 1 376, 1 050, and 866 cm⁻¹; τ (CHCl₃) 4.04 (1 H, t, *J* 2.0 Hz, CH=C), 4.94 (1 H, m, *W*_{1/2} 3.4 Hz, =CH–H), 5.13 (1 H, m, *W*_{1/2} 5.0 Hz, =CH–H), 6.41 (2 H, m, *W*_{1/2} 4.6 Hz, CH₂OH), 6.46 (2 H, m, *W*_{1/2} 8.6 Hz, CH₂OH), 6.92br (2 H, s, *W*_{1/2} 9.0 Hz, 2-OH), 7.3–8.7 (8 H, CH₂), and 8.44 (3 H, m, *W*_{1/2} 8.3 Hz, CH₃–C=CH₂) (Found: C, 73.8; H, 10.0%; *m/e* 196. C₁₂H₂₀O₂ requires C, 73.5; H, 10.2%; *M*⁺ 196). Treatment of a solution of the diol (15) (55 mg) in dry pyridine (10 ml) with *p*-nitrobenzoyl chloride (105 mg) at 110 °C for 0.5 h gave after the usual work-up a light brown gum (54 mg) which was applied to one small p.l.c. plate and eluted once with chloroform. Extraction of the major band gave the *mono-p*-nitrobenzoate (34; R = COC₆H₄NO₂) (12 mg) as a gum, homogeneous to t.l.c., ν_{\max} (CCl₄) 3 640, 2 990, 1 732, 1 358, 1 292, 1 128, and 900 cm⁻¹; τ 1.81 (4 H, m, aromatic H), 4.04 (1 H, m, *W*_{1/2} 5.4 Hz, CH=C), 4.93, 5.13 (2 H, 2 m, *W*_{1/2} 3.7, 5.1 Hz, C=CH₂), 5.71 (2 H, t, *J* 10.3 Hz, CH₂–CH₂–OCO), 6.42 (2 H, AB_q, *J*_{AB} 10.3 Hz, CH₂OH), 7.4–8.4 (9 H, CH₂ and OH), and 8.31 (3 H, m, CH₃–C=CH₂) (*m/e* 345. C₁₉H₂₃NO₅ requires *M*⁺ 345).

Rearrangement of Ethyl 3 β ,9 β -Epoxy-4,4-dimethyl-5-oxohexahydroindane-8 β -carboxylate (21).—Freshly distilled boron trifluoride–diethyl ether complex (0.2 ml) was added to a stirred solution of the oxo-ester β -epoxide (21) (343 mg) in dry benzene under dry nitrogen at 20 °C and the mixture was stirred for 10 min to give a yellow solution. Addition of sodium hydrogen carbonate solution (5%, 40 ml) followed by work-up in the usual way gave a pale yellow oil (287 mg) containing two major components (t.l.c.). The oil was applied to three small p.l.c. plates and eluted once with light petroleum–diethyl ether (1 : 2). Extraction of the upper band gave unchanged epoxide (12 mg, 36%) and extraction of the lower band gave a glass (77 mg), ν_{\max} (CCl₄) 3 620, 3 540, 3 440, 2 980, 2 730, 1 733, 1 718, 1 625, 1 457, 1 368, 1 155, 1 095, and 1 030 cm⁻¹; τ (CCl₄) 0.25 (1 H, m, *W*_{1/2} 2.0 Hz, CHO), 5.02 (<1 H, complex), 5.85 (3 H, 2 overlapping q, *J* 6.5 Hz, CO₂CH₂CH₃), 7.3–9 (12 H, CH₂), 7.80 (3 H, s, CH₃–C=), 8.18 (3 H, s, CH₃–C=), and 8.72 (5 H, 2 overlapping t, *J* 7.3 Hz, CO₂CH₂CH₃). This glass was applied to one small p.l.c. plate and eluted six times with light petroleum–diethyl ether (2 : 3). Extraction of the main band gave ethyl 2-isopropylidene-3-oxo-1-(3-oxopropyl)cyclopentane-carboxylate (36), as a glass (37 mg), λ_{\max} (EtOH) 252 nm (ϵ 4 100); ν_{\max} (CCl₄) 2 980, 2 730, 1 735, 1 718, 1 630, 1 450, 1 372, 1 160, 1 096, and 1 034 cm⁻¹; τ (CCl₄) 0.24 (1 H, m, *W*_{1/2} 2.0 Hz, CHO), 5.85 (2 H, q, *J* 7.2 Hz, CO₂–

CH₂CH₃), 7.2–9 (8 H, CH₂), 7.79 (3 H, s, CH₃–C=), 8.21 (3 H, s, CH₃–C=), and 8.75 (3 H, t, *J* 7.2 Hz, CO₂CH₂CH₃) (*m/e* 252. C₁₄H₂₀O₄ requires *M*⁺ 252).

Rearrangement of 3 β ,9 β -Epoxy-8 β -hydroxymethyl-4,4-dimethylhexahydroindane-5 β -ol (19).—Freshly distilled boron trifluoride–diethyl ether (0.25 ml) was added to a stirred solution of the diol epoxide (19) (445 mg) in dry benzene (50 ml) under dry nitrogen at 25 °C, and the mixture was stirred for 10 min. After addition of sodium hydrogen carbonate solution (5%; 40 ml) work-up using ethyl acetate gave a pale yellow gum (360 mg), containing one major component (t.l.c.). The gum was applied to one large p.l.c. plate and eluted once with benzene–diethyl ether (1 : 4). Extraction of the most intense band with ethyl acetate gave 2,2-dimethyl-3-oxatricyclo[3.3.3.0]undecane-8 β ,9 β -diol (38) (86 mg) as a glass, homogeneous to t.l.c., ν_{\max} (CCl₄) 3 670, 3 520, 2 970, 1 470, 1 455, 1 386, 1 370, 1 160, 1 120, 1 062, and 1 032 cm⁻¹; τ (CHCl₃) 5.91 (2 H, merged m, *W*_{1/2} 9.9 Hz, 2 CHO), 6.20 (2 H, s, CH₂–O), 7.13br (2 H, s, disappears with D₂O, 2-OH), 7.5–8.5 (8 H, CH₂), and 8.42 [6 H, s, (CH₃)₂C–O] (*m/e* 212. C₁₂H₂₀O₃ requires *M*⁺ 212). Treatment of the diol (58) (29 mg) with acetic anhydride (1.0 ml) in pyridine (5 ml) at 100 °C for 2.5 h gave a pale yellow gum (36 mg) which was applied to one small p.l.c. plate and eluted once with light petroleum–diethyl ether (1 : 2). Extraction of the main band gave 2,2-dimethyl-3-oxatricyclo[3.3.3.0]undecane-8 β ,9 β -diyl diacetate (20 mg) as an oil which crystallised when set aside to give prisms (from hexane–diethyl ether), m.p. 75–79 °C, ν_{\max} (CCl₄) 2 980, 1 750, 1 360, 1 250, 1 055, and 1 024 cm⁻¹; τ (CCl₄) 5.10 (2 H, m, 2 CH–OCOCH₃), 6.25 (2 H, s, CH₂–O), 7.5–8.5 (8 H, CH₂), 7.94 (6 H, s, 2 CH₃COO), and 8.58 [6 H, s, (CH₃)₂C–O]; τ (C₆H₆) 5.12 (2 H, t, *J* 6.4 Hz, 2 CHOAc), 6.68 (2 H, s, CH₂–O), 8.1–9.2 (8 H, CH₂), 8.61 (6 H, s, 2 CH₃CO₂), and 8.78 [6 H, s, (CH₃)₂C–O] [Found: C, 64.6; H, 8.2%; *m/e* 281 (= *M* – 15). C₁₆H₂₄O₅ requires C, 64.9; H, 8.1%; *M*, 296].

Oxidation of 2,2-Dimethyl-3-oxatricyclo[3.3.3.0]undecane-8 β ,9 β -diol (38).—A solution of the diol (35 mg) in acetone was treated with Jones reagent in the usual way to give a solid (25 mg) which was applied to one small p.l.c. plate and eluted twice with benzene–diethyl ether (1 : 4). Extraction of the main band gave 2,2-dimethyl-3-oxatricyclo[3.3.3.0]undecane-8,9-dione (39) (12 mg) as an amorphous solid, m.p. 149–152 °C, ν_{\max} (CCl₄) 2 960, 1 762, 1 460, 1 410, 1 387, 1 372, 1 262, and 1 112 cm⁻¹; τ (CHCl₃) 6.10 (2 H, s, CH₂–O), 7.3–8.3 (8 H, CH₂), and 8.83 [6 H, s, (CH₃)₂C–O] (Found: C, 69.1; H, 7.9%; *m/e* 208. C₁₂H₁₆O₃ requires C, 69.2; H, 7.7%; *M*⁺ 208). A solution of a small sample of the dione in ethanol showed no characteristic u.v. absorption, but on addition of a solution of potassium hydroxide in ethanol, an intense absorption at 250 nm appeared, accompanied by a weaker absorption at 305 nm.

Rearrangement of the Mixture of 3 α ,9 α - (24) and 3 β ,9 β -Epoxy-4,4,8 β -trimethylhexahydroindane-5-one (25).—Freshly distilled boron trifluoride–diethyl ether complex (0.57 ml) was added to a stirred solution of the oxo-epoxides (440 mg) in dry benzene (20 ml) under dry nitrogen at 25 °C to give an orange solution which became deep red after 10 min. 5% Sodium hydrogen carbonate solution (50 ml) was added to give a bright yellow organic phase which was worked up in the usual way to give a yellow crystalline solid (383 mg) containing one major and several minor components (t.l.c.). Trituration of the solid with cold diethyl ether left 9-hydroxy-1,1,6-trimethylspiro[4.4]non-6-en-2-one (41) (97 mg, 22%) as

bulky plates (from light petroleum–diethyl ether), m.p. 123–124 °C, $\nu_{\max}(\text{CCl}_4)$ 3 450, 2 960, 1 732, 1 380, 1 080, and 870 cm^{-1} ; $\tau(\text{CDCl}_3)$ 4.50br (1 H, s, $W_{\frac{1}{2}}$ 5.0 Hz, $\text{CH}=\text{C}$), 5.71 (1 H, t, J 5.3 Hz, CHOH), 7.2–8.2 (6 H, CH_2), 8.22 (1 H, s, disappears with D_2O , CHOH), 8.33 (3 H, m, collapses to t, J 2.2 Hz, on irradiation at τ 4.50; $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2$), and 8.79 and 8.91 (6 H, s, $\text{CH}_3-\text{C}-\text{CH}_3$) (Found: C, 74.4; H, 9.5%; m/e 194. $\text{C}_{12}\text{H}_{18}\text{O}_2$ requires C, 74.2; H, 9.3%; M^+ 194). Evaporation of the ether washings from the trituration gave a yellow oil (211 mg) which was applied to two small p.l.c. plates and eluted twice with light petroleum–diethyl ether (1 : 1). Although at least six bands separated on extraction, none afforded significant amounts of material.

Oxidation of 9-Hydroxy-1,1,6-trimethylspiro[4.4]non-6-ene-2-one (41).—Jones reagent was added dropwise to a stirred solution of the spiro-oxo-alcohol (170) (49 mg) in acetone (10 ml) until a permanent orange-brown colouration was ob-

tained. Excess of chromic acid was destroyed by addition of a few drops of sodium metabisulphite solution, and working up in the usual way gave 1,1,6-trimethylspiro[4.4]non-6-ene-2,9-dione (42) (48 mg) as a gum, homogeneous to t.l.c., $\nu_{\max}(\text{CCl}_4)$ 2 960, 1 735, 1 465, 1 390, 1 360, and 1 080 cm^{-1} ; $\tau(\text{CCl}_4)$ 4.15 (1 H, m, $W_{\frac{1}{2}}$ 5.2 Hz, $\text{CH}=\text{C}$), 7.28 (2 H, quintet, J 2.4 Hz, $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2-\text{CO}$), 7.4–8.2 (4 H, CH_2), 8.28 (3 H, m, collapses to t, J 2.4 Hz, on irradiation at τ 4.15; $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2$), and 9.07 and 9.09 (6 H, 2 s, $\text{CH}_3-\text{C}-\text{CH}_3$) (Found: m/e 192. $\text{C}_{12}\text{H}_{16}\text{O}_2$ requires M^+ 192).

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