Rearrangement of Epoxides. Part I. Preparation and Rearrangement of the α- and β-Epoxides of 14,15-Bisnorlabd-8-en-13(R and S)-yl Acetates and of Related Epoxides

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The preparation and rearrangement with boron trifluoride–ether complex of a number of 8α,9α- and 8β,9β-epoxy-14,15-bisnor- and 14,15,16-trisnor-labdane derivatives have been carried out to determine whether the clerodane diterpene skeleton could be obtained. A variety of rearranged carbon skeletons has been obtained but not that of clerodane, probably because formation of this would involve the generation of a 1.3-diaxial interaction between the the methyl groups at C-5 and C-9.

In an attempt to modify the course of the rearrangements in these epoxy-decalin derivatives, the α- and β-epoxides have been prepared from 6β-hydroxy-1,2,5,5,9β-pentamethyl-Δ¹-octalin and 6β-hydroxy-1.5.5.9β-tetramethyl-Δ¹-octalin and their rearrangements studied. The results are best explained by assuming that the epoxides rearrange in a non-concerted manner even when the migrating groups are antiperiplanar and that the key factor determining the products is the nature of the steric interactions in the starting epoxide and in the products.

A novel product from the bisnorlabdane epoxide (14) is the cyclodecenone (42).

DITERPENES of the 9,4-*friedo*-labdane (clerodane) type typified by (+)-hardwickiic acid (1) [1] and kolavenol (2) [2] may arise by a biogenetic pathway involving rearrangements of the ions (3) and its enantiomer with the labdane and *enantio*-labdane skeletons. In order to study this type of rearrangement further and to attempt to open up routes to the synthesis of *friedo*-labdanes the rearrangements catalysed by boron trifluoride of epoxides of the type illustrated by (4)—(6) (R¹ = H or OH) have been investigated.

Sclareol (7) was the starting material for the synthesis of such epoxides (R¹ = H). To avoid subsequent complications its side-chain was degraded by permanganate oxidation and the resulting hydroxy-ketone (8) was dehydrated with magnesium perchlorate in boiling toluene [3] to give the ketone (9) together with a small amount of the Δ⁷-isomer. Epoxidation of the ketone (9) with perbenzoic acid in benzene gave one epoxide (6) which was later shown to have the α-configuration.

The epoxide (6) with boron trifluoride–ether complex in benzene gave as the major product the acetal (12). Its i.r. spectrum indicated the absence of hydroxy and carbonyl groups. It gave two singlet methyl signals at τ 8·57 and 8·71 due to $\text{MeC}{<}^{\text{O}}_{\text{O}}$ and

$\text{MeC}{-}\text{O}$. The acetal was also obtained from the ketone (9) by the action of osmium tetraoxide. The oxygen atoms must therefore be *cis*-oriented and α, assuming attack by the tetraoxide from the less hindered α-face. The acetal can arise by initial cleavage of the epoxide ring at either C-8 or C-9 followed by *cis*-attack of the carbonyl group on the resulting positive carbon atom. The only other significant product from the boron trifluoride reaction was the diketone (13) whose structure is discussed below.

From this result it became clear that the only func-

tional groups which could be kept in the side-chain during epoxide rearrangements to facilitate later synthesis of the complete side chains of naturally occurring *friedo*-labdanes were those which did not trap the carbonium ion initially formed by opening the epoxide. The ketone (9) was therefore reduced with lithium aluminium hydride and the resulting pair of C-13 epimeric alcohols (10) were acetylated. The mixture of the two C-13 epimeric acetates (11) could not be separated. Although not ideal, in order to obtain information about the rearrangement of 8,9-epoxides, this mixture of acetates was used for a series of reactions. In each of the pairs of C-13 epimers obtained, the n.m.r. signals of the substituents on the rings were identical or virtually identical for both epimers.
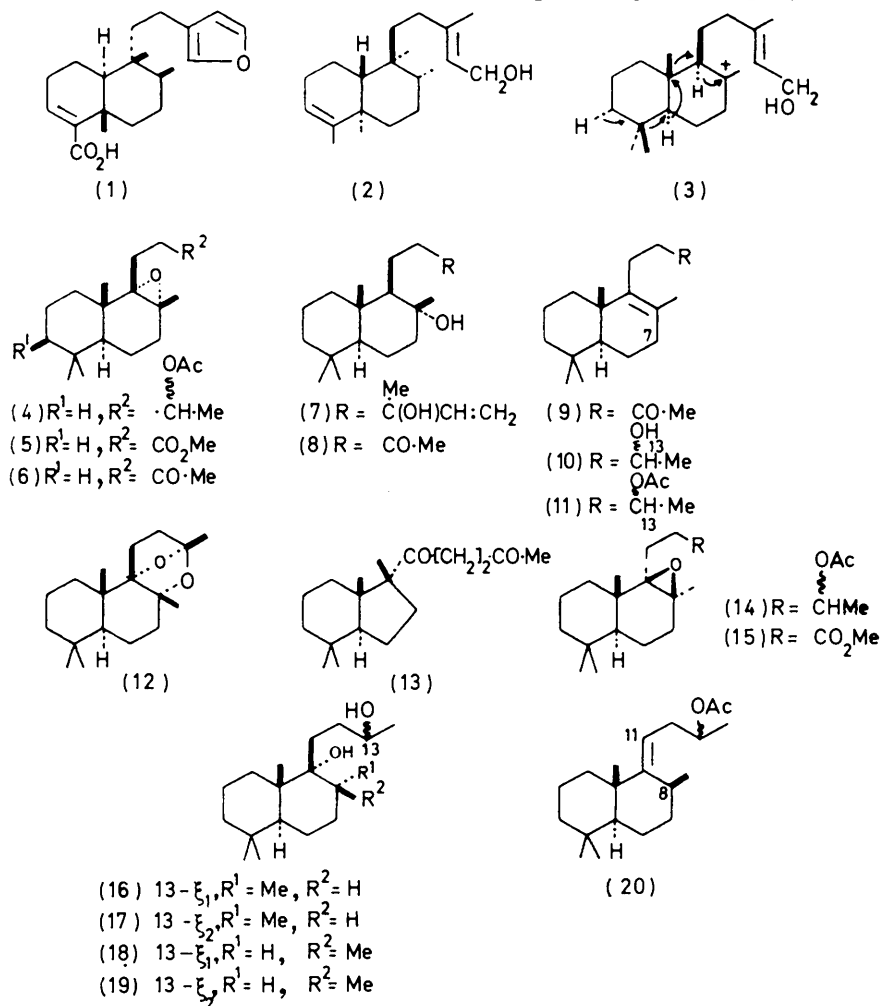
The mixture of C-13 epimeric acetates (11) was epoxidised with perbenzoic acid. In contrast to the situation with the ketone (9) both α- and β-epoxides [(4) and (14)] were obtained, in the ratio 2 : 1. The C-13 epimeric pairs of α- and β-epoxides were separated by preparative t.l.c. (p.l.c.). The pair of C-13 epimeric acetoxy-epoxides (4) was reduced with lithium in ethylamine to give a mixture of four crystalline diols (16)—(19) which were separated, with difficulty, by p.l.c. The yields of isolated diols were 23, 20, 17, and 17% respectively. All had n.m.r. spectra which had no singlet due to a $Me(\text{OH})\text{C}{<}$ group but doublets (J 6 Hz) assigned to the methyl group at C-8 at τ 9·13 (16) and (17), 8·94 (18), and 8·97 (19). This indicates that the epoxide ring in both pairs of epimers has opened exclusively in one direction to give C-9 alcohols with a secondary methyl group at C-8. The n.m.r. spectra of the diols (16) and (17) were virtually identical as were those of the diols (18) and (19). This indicated that each pair consisted of C-13 epimers and that the pairs differed in the configuration of the C-8 methyl group.

The C-13 monoacetate of one isomer of each pair (16) and (19) was dehydrated with phosphoryl chloride in pyridine. The product from the diol (16) was the acetate (11; $ξ_1$ configuration at C-13) which had i.r. and n.m.r. spectra identical with those of the mixture of the

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

[2] R. Misra, P. C. Pandey, and S. Dev, *Tetrahedron Letters,* 1964, 3751.

[3] L. Ruzicka, C. F. Seidel, and L. L. Engel, *Helv. Chim. Acta,* 1942, **25**, 621.

two C-13 epimeric acetates (11) described above. That from the diol (19) was the acetate (20). The n.m.r. spectrum of the acetate (20) had a signal at τ 4·95 (t, J 0·5 Hz) due to a single olefinic proton [C(11)H] and one at τ 8·86 (d, J 7 Hz) for the axial β-methyl group at C-8. The doublet for the methyl group in the side chain was at τ 8·81. These results indicate that in the diol

The stereochemistry of the epoxy-ketone (6) was elucidated when reduction of the ketone with sodium borohydride and acetylation of the product gave the pair of C-13 epimeric acetoxy-epoxides (4). Conversely hydrolysis of this pair of acetoxy-epoxides with 0·5% methanolic potassium hydroxide followed by oxidation of the product gave the epoxy-ketone (6).

(1) (2) (3)

(4) R¹= H, R²= ·CH·Me
(5) R¹= H, R²= CO₂Me
(6) R¹= H, R²= CO·Me

(7) R = C(OH)CH:CH₂
(8) R = CO·Me

(9) R = CO·Me
(10) R = CH·Me
(11) R = CH·Me

(12) (13)

(14) R = CHMe
(15) R = CO₂Me

(16) 13-ξ₁, R¹= Me, R²= H
(17) 13-ξ₂, R¹= Me, R²= H
(18) 13-ξ₁, R¹= H, R²= Me
(19) 13-ξ₂, R¹= H, R²= Me

(20)

ξ₁ Refers to the isomer with the lower rotation in each pair. It does *not* imply that the absolute configuration at C-13 is identical in (16) and (18).

(16) the C-9 hydroxy-group and the C-8 proton are diaxial with the α- and β-configurations. The stereochemistry of the diol (19) and of the epoxide (4) follows.
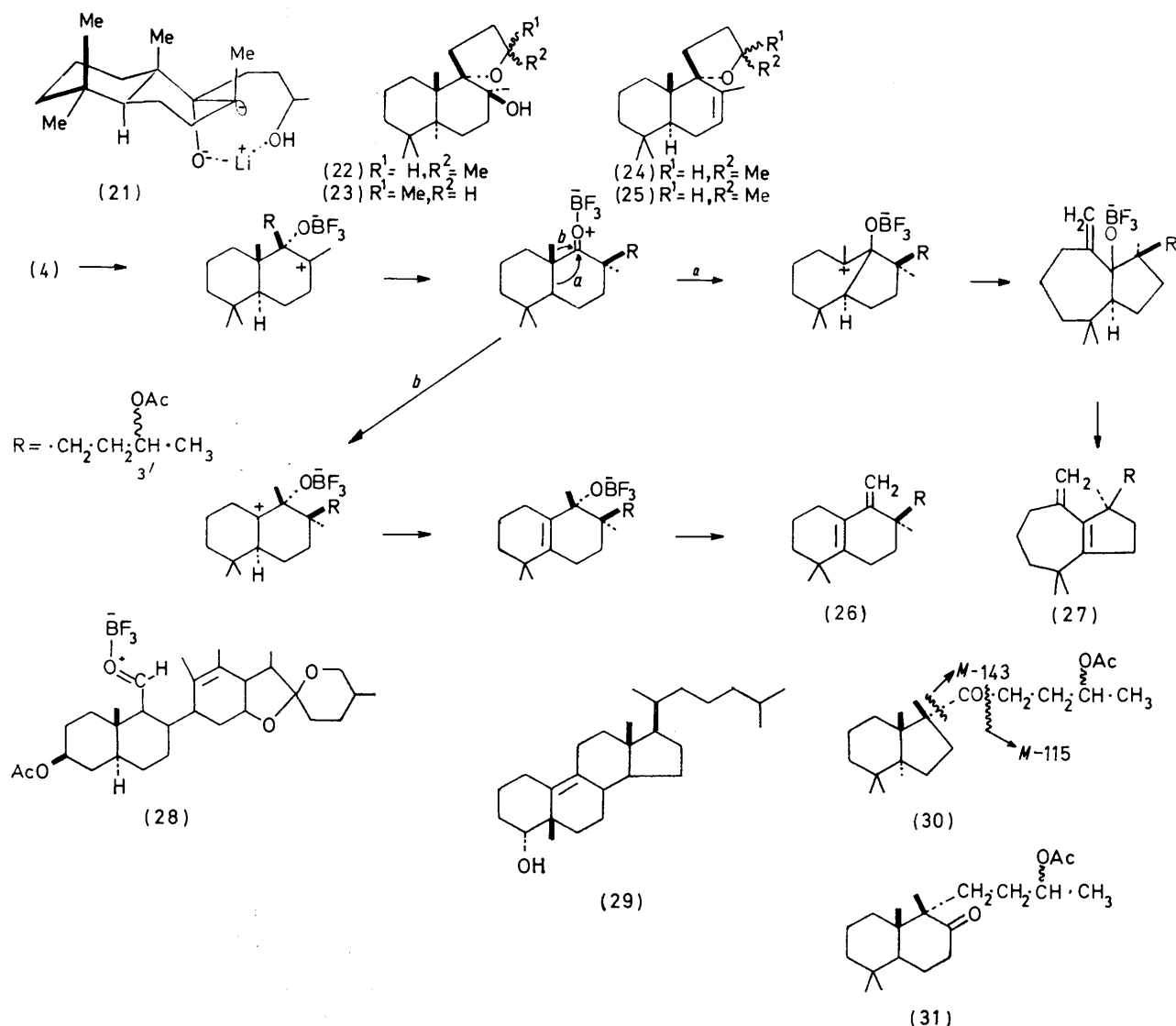
The formation of relatively large amounts of the diols (18) and (19) with an axial C-8 methyl group, involving a 1,3-diaxial interaction with the C-10 methyl group, and the cleavage of the epoxide ring in one direction are of interest. It may be that in an intermediate ion, the lithium ion is associated with two oxygens and holds the conformation of the side-chain so that the C-8 methyl group is axial as in structure (21), protonation then occurring from the α-face. Cleavage of the epoxide ring at C-9 may be disfavoured as association of the lithium ion with the two oxygens then requires an eight-membered ring.

Treatment of the C-13 epimeric pair of β-epoxy-acetates (14) with 1% methanolic potassium hydroxide gave two hydroxy-ethers assigned the structures (22) and (23) on the basis of their n.m.r. spectra which were very similar. They had methyl singlets at τ 8·96 and 8·92 for Me(OH)C<, methyl doublets (J 6 Hz) at 8·79 and 8·78 for –O·CH·CH_3, and complex one-proton multiplets at 5·96 and 5·93 for –O·CH(CH₃)CH₂–. Their mass spectra were identical. On dehydration with phosphoryl chloride in pyridine they afforded the olefins (24) and (25) whose n.m.r. spectra showed a signal due to an olefinic methyl group and a broad single olefinic proton signal. The ethers (22) and (23) can arise by attack on the epoxide group by the alkoxide ion formed

by hydrolysis of the acetate group, with diaxial opening. With the α-epoxides (4) attack would have to occur at C-8 from the β-face when hindrance from the C-10 methyl group would arise.

Treatment of the C-13 epimeric pair of α-epoxy-acetates (4) with boron trifluoride–ether complex gave four significant products. The least polar, obtained in a variable yield of 10—25%, was a *transoid* conjugated diene [$\lambda_{max.}$ 242 nm (ε 17,000)]. An exocyclic methylene

further olefinic proton signal indicated that the second double bond was tetra-substituted and in the group

$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=CH_2,$$ the calculated $\lambda_{max.}$ of which is 242 nm assuming an exocyclic methylene group. A broad four-proton signal at τ 7·92 indicated the presence of four allylic protons. The mass spectrum gave a parent ion with *m/e* 304 corresponding to $C_{20}H_{32}O_2$. With two double bonds present this indicates the presence of two

(21)

(22) $R^1 = H, R^2 = Me$
(23) $R^1 = Me, R^2 = H$

(24) $R^1 = H, R^2 = Me$
(25) $R^1 = H, R^2 = Me$

$R = \cdot CH_2 \cdot CH_2 \cdot \overset{OAc}{\underset{|}{CH}} \cdot CH_3$

(4) —→

(26)

(27)

(28)

(29)

(30)

(31)

group was indicated by a strong band at 895 cm⁻¹ and by the n.m.r. spectrum which showed two one-proton singlets at τ 5·08 and 5·26, the latter being superimposed on the multiplet due to the proton $>CH\cdot OAc$. In addition to the acetate methyl at τ 8·05 and the side chain methyl doublet at 8·85 (*J* 6·5 Hz) there were only *three* methyl singlets 8·95 (2 Me) and 8·98 (1 Me). Thus of the original methyl groups one had been transformed, presumably to the methylene group. The absence of any

rings. Two possible structures are (26) and (27) which can arise by the mechanism indicated. No distinction was made between these two structures because of lack of material. A similar intermediate ion (28) also involving mesomerism between an oxycarbonium ion ($\overset{+}{C}-O\cdot\overset{-}{B}F_3$) and a co-ordinated carbonyl group ($>C=\overset{+}{O}-\overset{-}{B}F_3$) has recently been proposed to explain the formation of an 11β-alcohol from an 11α,12α-epoxide in the tigogenin

series.[4] The formation of the 4α-alcohol (29) from 4β,5β-epoxycholestane [5] also involves this type of ion.

The second product was a keto-acetate (20—35% yield) which absorbed at 1695 and 1735 cm⁻¹ (CS₂). The keto-group was not conjugated (no intense u.v. absorption) despite its low stretching frequency. The n.m.r. spectrum with a two-proton multiplet at τ 7·65 indicated a -CH₂·CO- group. There was a doublet at τ 8·79 due to the side chain methyl group and a nine-proton singlet at 9·12 due to three methyl groups. A singlet at τ 8·83 was assigned to a methyl group located on a carbon α to the keto-group. Of the four possible ketones which could arise from epoxide cleavage followed by a 1,2-alkyl shift only two (30) and (31) are consistent with the data. Structure (30) arises from axial cleavage of the epoxide followed by ring contraction whereas structure (31) results from equatorial cleavage followed by methyl migration. The mass spectrum favours structure (30) since it shows strong peaks at $M - 115$ and $M - 143$ corresponding to fission α to the keto-group.

Rearrangement of the structurally similar epoxide (67) described below gave the ring contracted compound (77) as the sole ketonic product with also a low carbonyl stretching frequency at 1695 cm⁻¹ (CS₂). Confirmation of structure (30) was thwarted by the lack of reactivity of the keto-group, no reaction being observed with trifluoroperacetic acid or acetic anhydride in the presence of toluene-p-sulphonic acid. Sodium borohydride slowly (48 h) reduced the keto-group to give a secondary alcohol which had a methyl signal within the region τ 9·11—9·18, replacing the one originally at 8·83. Hydrolysis followed by oxidation gave the diketone (13) identical with that obtained directly from the rearrangement of the epoxy-ketone (6). The diketone was characterised as its mono-semicarbazone.

The third product had no hydroxy-band and only an acetate carbonyl band in its i.r. spectrum. In the n.m.r. spectrum the only lowfield signal was that of the proton $>$CH·OAc. The mass spectrum corresponded to C₂₀H₃₄O₃ indicating an ethereal oxygen atom attached to two fully substituted carbon atoms. There was only one three-proton signal due to a Me$\overset{|}{\underset{|}{C}}$-O- group (τ 8·81) so the ether oxygen is also bonded to a carbon at a ring junction. Structure (33) is consistent with these data. It can be formed by two anti-periplanar migrations leading to the ion (32) followed by bonding of the C-8 oxygen (formally cis-attack) at C-10. The ether was hydrolysed and oxidised to give a ketone which formed a crystalline semicarbazone.

The fourth product was a hydroxy-acetate with bands at 1735 and 3600 cm⁻¹. A methyl singlet at τ 8·92 was assigned to a MeC(OH)- group. The mass spectrum indicated a formula C₂₀H₃₄O₃. This is consistent with two rings and a tetra-substituted double bond, there being no n.m.r. signal due to an olefinic proton. There

was also no signal due to a methyl group on a double bond, and this must therefore be between rings A and B. Structure (35) fits the data. It can arise from the ion (32) by loss of a proton from C-10, or from structure (4) by antiperiplanar rearrangement of the C-10 methyl group to C-9 followed by elimination of the trans-proton at C-5.

(32)

(4)

→ (33)

OAc
(33) R=CHMe
(34) R=CO₂Me

(35)   (36)   (37)

(38)   (39)   (40)
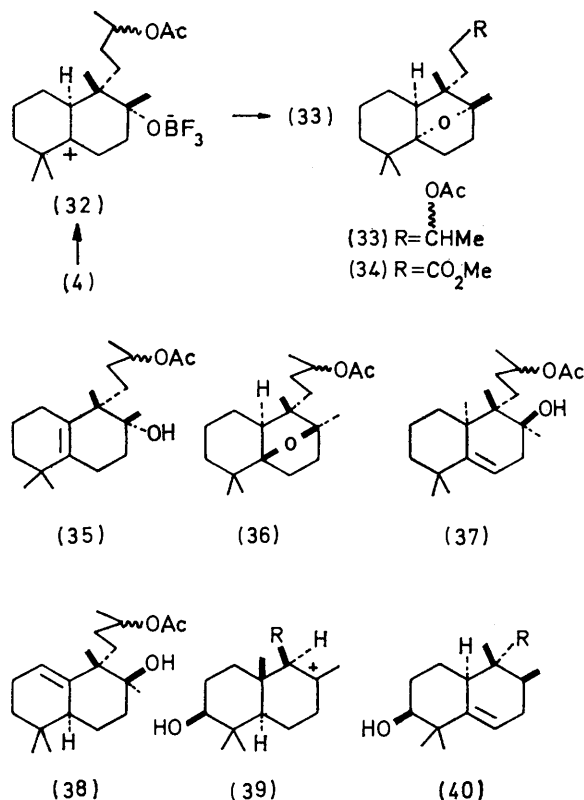
The C-13 epimeric pair of β-epoxy-acetates (14) on treatment with boron trifluoride–ether complex gave one major product (60%) which had i.r. and n.m.r. spectra similar to, but not identical with, the spectra of the ether (33) from the α-epoxy-acetates (4). Structure (36) is proposed for this product. It can arise by a cis-shift of the C-10 methyl group followed by trans migration of the C-5 hydrogen atom, and then ether formation by bonding of the C-8 oxygen to C-5. Hydrolysis of the C-13 epimeric acetates (36) gave the corresponding alcohols which were separated by p.l.c. Oxidation of the mixture of epimeric alcohols gave a ketone, characterised as its semicarbazone, m.p. 187—189°.

Two minor products were also obtained from the pair of β-epoxy-acetates (14). The first was a hydroxy-acetate with bands at 1735 and 3600 cm⁻¹. It gave a one-proton triplet at τ 4·55 (J 3·5 Hz) indicative of an olefinic proton on a ring and a signal at 8·96 assigned to a Me·C(OH)- group, but no signal due to an olefinic methyl group. Structures (37) and (38) fit the data. In favour of structure (37) is the isolation by Sharpless and van

[4] J. M. Coxon, M. P. Hartshorn, and D. N. Kirk, Tetrahedron, 1969, 25, 2603.

[5] B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, Tetrahedron, 1969, 25, 4999.

Tamelen[6] of the bicyclic alcohol (40) in 20—25% yield from the treatment of 2,3-epoxysqualene with stannic chloride in benzene. They propose[6] the formation of an intermediate ion (39) which rearranges to (40).

The other minor product was a keto-acetate with bands at 1710 and 1735 cm⁻¹. It was not simply a ketone arising from a 1,2-alkyl shift, as the n.m.r. spectrum showed a six-proton singlet at τ 8·40. This indicates two methyl groups on a double bond which must be tetrasubstituted, there being no olefinic proton signal. The molecular weight (M^+ 322) corresponded to the formula $C_{20}H_{34}O_3$. Since this has only 8 hydrogen atoms less than that of a saturated open chain C_{20} compound there can only be *one* ring present, and ring opening must have occurred. The other two methyl groups not in the side chain gave singlets at τ 8·96 and 9·26. A two-proton multiplet at τ 7·80 indicated two protons α to the keto-group. A possible structure is (42) which could arise by the mechanism indicated. In this

(14) ⟶

(41)

(43)   (42)

(15) ⟶

(44)   (45)

(46)
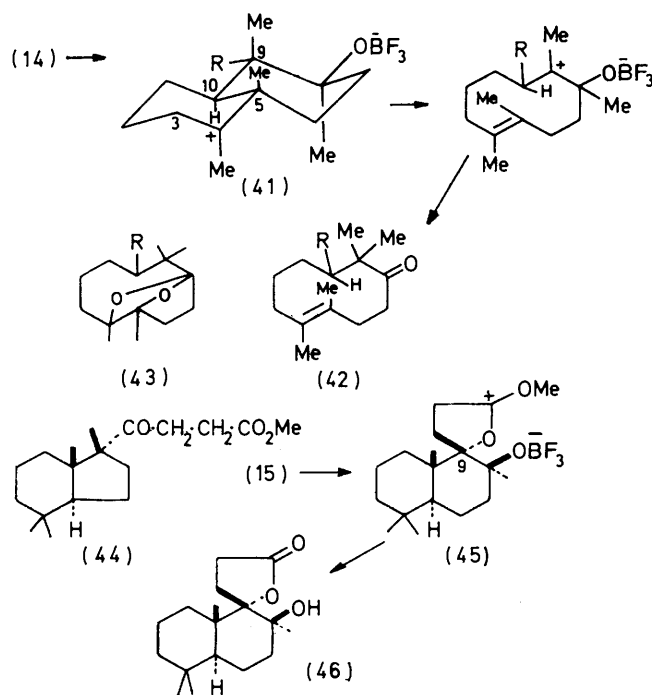
proposed mechanism the ion (41) has the desired *friedo*-labdane skeleton which was an aim of the current investigation, but instead of losing a proton from C-3 it further rearranges in a non-concerted manner with the C-5–C-10 bond and the side-chain (R) migrating in anti-periplanar fashion to give the indicated ion which then undergoes further rearrangement to (42). One factor which would favour rearrangement of the ion (41) in this manner is the relief of the 1,3-diaxial interaction between the methyl groups at C-5 and C-9.

An inspection of a model of structure (42) shows that one of the *gem*-methyl groups lies above the plane of the olefinic double bond. This will result in considerable shielding of this group in agreement with the high value of τ 9·26 found for one of the methyl signals. The

double bond in the keto-acetate was hydrolysed using osmium tetraoxide. A diol was obtained, as indicated by the i.r. spectrum and by its polarity shown by t.l.c., but attempted purification of the diol by p.l.c. afforded a new product which was very much less polar, had the molecular formula $C_{20}H_{34}O_4$ (mass spectrum), and had no i.r. band indicative of either a hydroxy-group or a carbonyl group other than that in the acetate group. The internal acetal structure (43) explains the properties of the less polar product. Its n.m.r. spectrum (c.a.t.) indicated that the six-proton singlet at τ 8·40 in the ketone (42) had moved upfield to 8·93 which is consistent with two MeĊ-O- groups. The signals between τ 9·10—9·19 corresponded to six protons of the *gem*-dimethyl group but their complexity suggested that more than one stereoisomer was present. The diol can occur as two *cis*-stereoisomers and models indicate that both can form acetals.

The rearrangements of the epoxy-esters (5) and (15) were also studied, partly to assist the interpretation of the n.m.r. spectra of the products from the C-13 epimeric pairs of the α- and β-epoxy-acetates (4) and (14). The epoxy-esters were obtained from the corresponding unsaturated ester, itself obtained from the acid produced in low yield by treatment of the unsaturated ketone (9) with an alkaline solution of iodine.

The epoxide formed in greater yield was assumed to be the α-isomer (5). This was justified by treatment of the epoxide with boron trifluoride–ether complex in benzene when a keto-ester (44) and a cyclic ether-ester (34) were obtained, analogous to those resulting from the α-epoxy-acetates (4). Some material corresponding to the diene fraction was also obtained but in insufficient quantity for characterisation.

When the β-epoxy-ester, however, was treated with boron trifluoride–ether complex in benzene a gel was immediately formed. After addition of water a crystalline compound ($C_{17}H_{28}O_3$), m.p. 168—169°, was obtained with bands at 1770 and 3600 cm⁻¹ indicative of a hydroxy-γ-lactone. The structure proposed is (46) and a mechanism for its formation is indicated. When the epoxide ring opens the ester carbonyl group can attack C-9 in an antiperiplanar manner to give the zwitterion (45) which could account for the gel formation. Addition of water followed by loss of methanol then gives the lactone (46). Reduction of the lactone with lithium aluminium hydride gave the corresponding triol.

The results described above showed that although rearrangement could occur leading to the ion (47) further migration of the C-4 β-methyl group was difficult, probably because it led to a 1,3-diaxial interaction between the C-5 and C-9 β-methyl groups in the ion (48). One possibility of promoting the migration of the C-4 β-methyl group was the introduction of a β-hydroxy-group at C-3 which could provide a source of electrons and give

[6] K. B. Sharpless and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1969, **91**, 1848.

rise to a 3-oxoclerodane (50) [*cf.* (49) —► (50)]. An example of such a rearrangement is the conversion of 5α,6α-epoxy-4,4-dimethylcholestan-3β-ol (51) with boron trifluoride–ether complex into 6α-hydroxy-4β,5β-dimethylcholestan-3-one (52).[7] Recently the decalin epoxide (53) has been shown with boron trifluoride–ether complex in benzene to give, as one of the products,

group was first introduced α to the carbonyl group in the keto-benzoate (56) using the method of Sondheimer and Elad.[11] The resulting keto-alcohol (57) was treated with methyl-lithium in ether and the product was acetylated to give the two hydroxy-acetates (58) and (59). The major one (58) (51% yield) on dehydration with phosphoryl chloride in pyridine gave the acetate (62), the
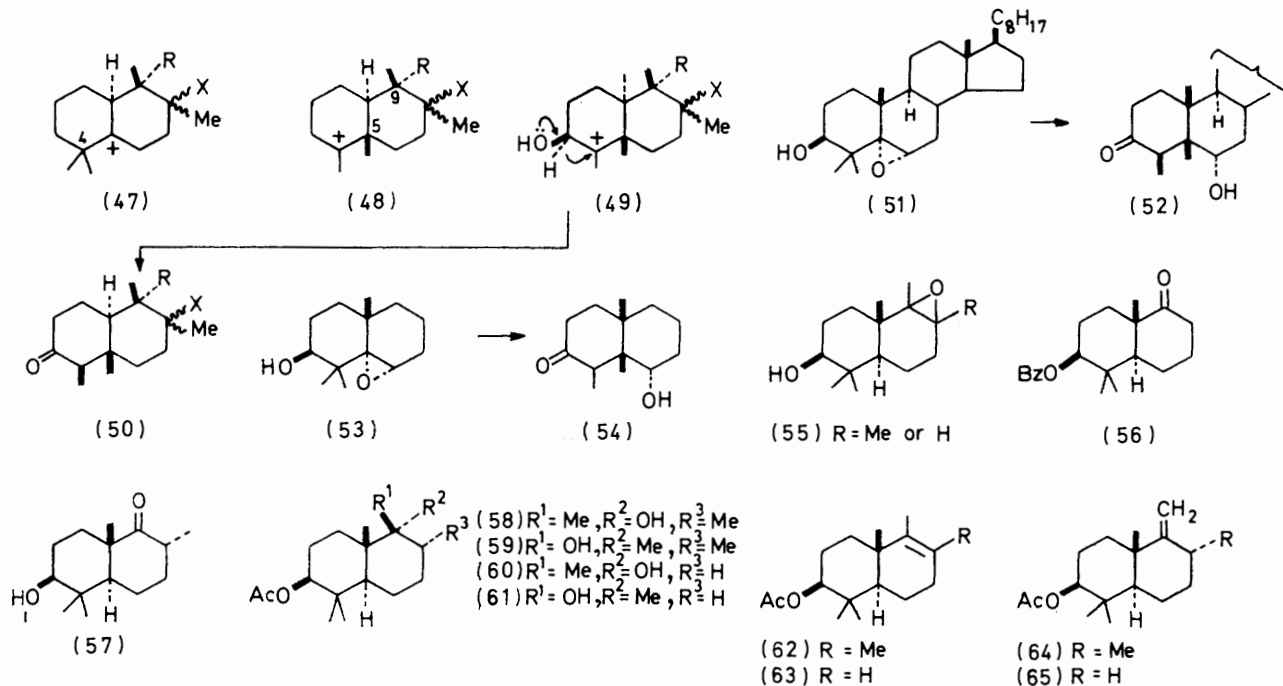
the ketone (54).[8] In both these cases, however, the resulting ring junction is *cis*-fused and a 1,3-diaxial interaction does not result.

To determine whether a 3β-hydroxy-group would affect the course of the rearrangement the action of boron trifluoride–ether complex on epoxides of the type (55) * was studied. As no suitable diterpene was available as a precursor for this type of compound the required compounds were synthesised.

The synthesis of the keto-benzoate (56), a key intermediate for the synthesis of an epoxide of the type (55), had been previously reported by two groups.[9,10] The route adopted starting from resorcinol was a combination of the two routes used previously and involved 13 steps. In addition to the tetrasubstituted epoxides (67) and (71) the trisubstituted epoxides (69) and (73) were also prepared. With the latter it was hoped that cleavage would occur preferentially at C-5 to give the desired tertiary carbonium ion. If rearrangement then occurred to give a *friedo*-labdane skeleton the necessary methyl group at C-6 could be introduced later.

To obtain the tetrasubstituted epoxides a methyl

n.m.r. spectrum of which had no olefinic proton signals but a six-proton singlet at τ 8·48 due to two olefinic methyl groups. This confirmed the axial nature of the hydroxy-group in compound (58) and showed that
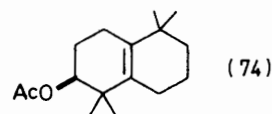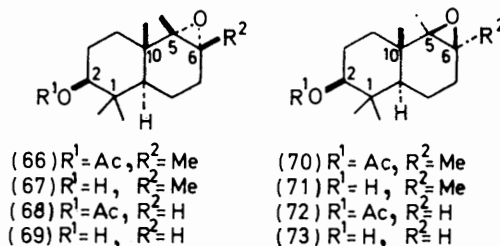
methyl-lithium had a slight preference for equatorial attack. The minor hydroxy-acetate (59) (33% yield)

* This compound and compounds (53)—(87) are racemic. In each case the isomer is drawn which corresponds to the stereochemistry of labdane or the related *friedo*-labdanes. Compounds (55)—(86) are numbered as octalin or decalin derivatives.

[7] T. G. Halsall, Sir Ewart R. H. Jones, E. L. Tan, and G. R. Chaudhry, *J. Chem. Soc. (C)*, 1966, 1374.

[8] H. W. Whitlock, jun., and A. H. Olson, *J. Amer. Chem. Soc.*, 1970, **92**, 5383.

[9] J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 1957, 684.

[10] F. Sondheimer and D. Elad, *J. Amer. Chem. Soc.*, 1957, **79**, 5542.

[11] F. Sondheimer and D. Elad, *J. Amer. Chem. Soc.*, 1958, **80**, 1967.

on similar dehydration gave the expected *exo*-methylene compound (64) which gave two one-proton singlets at τ 5·73 and 5·50 (=CH₂) and a three-proton doublet at 9·00 (*J* 6 Hz; -CH-C*H₃*).

Epoxidation of the acetate (62) gave two epoxides in the ratio 2 : 1. The major product was assumed to be the α-epoxide (66) and the minor product the β-epoxide (70) as α-attack should take place preferentially. A comparison made below of the chemical shifts of the methyl groups with those of the methyl groups of the trisubstituted epoxides supports the assignment. Hydrolysis of the epoxy-acetates gave the epoxy-alcohols (67) and (71).

The trisubstituted epoxides were obtained similarly. The keto-benzoate (56) with methyl-lithium gave a mixture of alcohols which on acetylation gave the hydroxy-acetates (60) and (61). Dehydration of the major isomer (45% yield) with phosphoryl chloride in pyridine gave a mixture of (63) (85%) and (65) (15%), the trisubstituted olefin being the expected product from the hydroxy-acetate (60) with the hydroxy-group axial. The olefin (63) had a signal at τ 4·85 (1H, *W₁* 3·5 Hz, C=C*H*-) and a signal at 8·44 for the olefinic methyl group. The minor isomer (61) on dehydration gave a mixture of the olefins (63) (20%) and (65) (80%). The *exo*-methylene derivative (65) had a singlet (2H) at τ 5·53 superimposed on the multiplet due to the -C*H*(OAc) proton.

The *exo*-methylene compound (65) on treatment with methanolic sulphuric acid in benzene followed by re-acetylation of the product gave the trisubstituted olefin (63) in 75% yield and an olefin (15% yield) whose n.m.r. spectrum showed no signal due to an olefinic proton or olefinic methyl group. Its four methyl groups gave rise to two six-proton singlets at τ 9·02 and 9·04. It is formulated as (74).

The acetate (63) gave two epoxides (68) and (72) in the ratio 3 : 2. The major product was the α-epoxide, since reduction with lithium in ethylamine followed by acetylation gave only the hydroxy-acetate (60). Hydrolysis of the epoxy-acetates gave the corresponding epoxy-alcohols (69) and (73).

The chemical shifts of the methyl signals in the epoxy-decalins are listed in the Table. Comparison of

Chemical shifts (τ) of the methyl signals in the n.m.r. spectra * of the epoxides listed

Epoxide	Methyl groups at			
	C-1	C-5	C-6	C-10
(66)	9·17, 9·19	8·86	8·81	8·99
(67)	9·04, 9·21	8·79	8·75	8·98
(70)	9·18, 9·20	8·89	8·79	8·98
(71)	9·04, 9·25	8·83	8·74	8·96
(68)	9·16, 9·18	8·86		8·94
(69)	9·03, 9·20	8·80		8·93
(72)	9·17, 9·20	8·89		8·96
(73)	9·03, 9·25	8·83		8·94

* Acetates in CCl₄, alcohols in CDCl₃.

the values for the trisubstituted epoxides of proven stereochemistry with those of the tetrasubstituted epoxides supports the stereochemical assignments con-

cerning the tetrasubstituted group made above. For the epoxy-alcohols the C-1 methyl signals are at τ 9·03/ 9·20 for the trisubstituted α-epoxide (69) and 9·03/9·25 for the corresponding β-isomer (73). For the tetra-substituted epoxy-alcohols there is an analogous change τ 9·04/9·21 to 9·04/9·25. Again in the case of the C-5 methyl groups the signals are at higher τ values for the β-isomers. With the C-10 methyl group in the tri-substituted epoxides the signals in the β-epoxides are slightly higher (0·01—0·02 p.p.m.) whereas in the tetra-substituted series the C-10 methyl signals of the β-epoxides are slightly lower (0·01—0·02 p.p.m.). In these cases the C-6 β-methyl group in the α-epoxides should exert some shielding effect on the methyl group, which will be absent in the β-epoxides with the C-6 methyl in the α-configuration.

All four epoxy-alcohols were treated with boron tri-fluoride–ether complex in benzene. The tetrasub-stituted α-epoxide (67) gave a mixture which after

(i) Rearrangement followed by acetylation
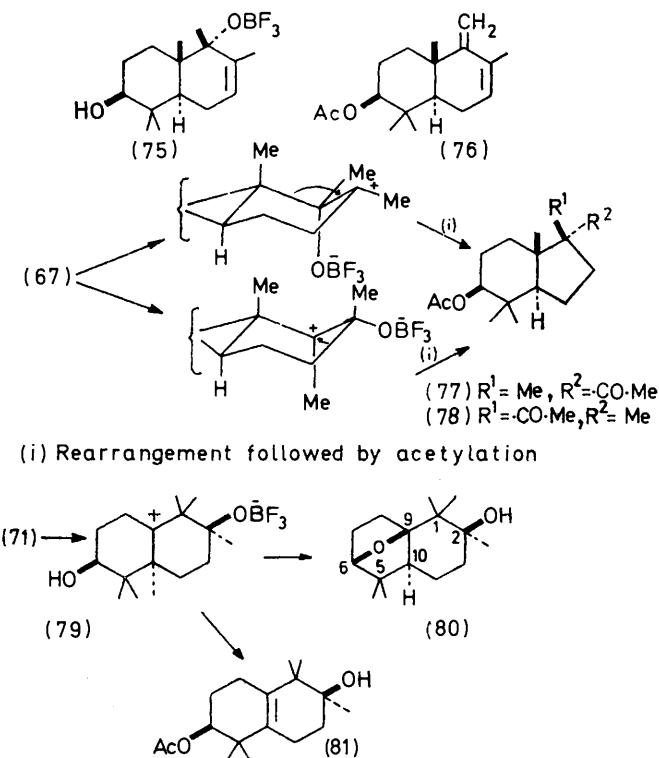
acetylation gave two products accounting for 85—90% of the possible yield. One was a conjugated diene (20%) which is formulated as (76). It had λ_max 235 nm (ε 16,000) indicative of a *transoid* system. It gave a broad (*W₁* 4 Hz) one-proton signal at τ 4·40 (-C=C*H*-CH₂-) and a singlet (2H) at 5·22 (-C=CH₂). A doublet (*J* 1·5 Hz) at τ 8·24 was assigned to an olefinic methyl group, the splitting being due to allylic coupling to an olefinic proton. The diene can arise *via* the intermediate (75) formed when the epoxide ring is opened. This result is in contrast with that from the epoxide (4) when the C-9 alkyl group migrates.

The second product (*ca.* 65%) was an acetoxy methyl

ketone ($v_{max.}$ 1735 and 1695 cm^{-1}) [singlets at τ 7·94 (–COMe) and 8·04 (–O·COMe)]. Two structures (77) and (78) are possible depending upon the direction of initial cleavage of the epoxide ring. With the corresponding epoxide (4) the major product was the ketone (30) arising from axial opening and generation of charge at C-8. If axial opening applies with (67) then structure (77) follows for the methyl ketone. In support of this, both ketones have a low carbonyl absorption (1695 cm^{-1}) and have a signal at τ 8·83 assigned to the angular methyl group β to the acetyl group.

The β-epoxy-alcohol (71) gave a complex mixture which was acetylated. At least eight components were present, and by use of column chromatography and p.l.c. two of these (40% of the mixture) were isolated in crystalline form. The small scale of the reaction (100 mg) did not allow separation and characterisation of the remaining components which were present in about equal amounts. The first product ($C_{15}H_{26}O_2$) is formulated as (80). It had one hydroxy-group but no carbonyl group indicating that the original hydroxy-group has been involved in cyclic ether formation. This was confirmed by a one proton doublet at τ 6·17 (J 4 Hz), as expected for the $\rangle$CH–O– group of structure (80). This value is too high for a 6,10-epoxy-structure (4-membered ring). The C-3β proton in 3α,5α-epoxycholestane gives a signal at τ 5·47. Examination of a model shows that the torsion angles between the C(6)–H bond and the C(7)–Hα and C(7)–Hβ bonds are about 80 and 45° respectively. Very little coupling would be expected with the 7α-proton and the coupling with the 7β-proton should therefore give a simple doublet with J ca. 4 Hz. This ether must have arisen by a completely non-concerted process. It involves a cis-migration of the methyl group followed by cis attack of the hydroxy-group on the resulting angular carbonium ion (79).

The second product ($C_{17}H_{28}O_3$) is a hydroxy-acetate ($v_{max.}$ 1735 and 3600 cm^{-1}) and is assigned the structure (81). If there are two rings, then there must be one double bond which is tetrasubstituted as there is no n.m.r. signal due to an olefinic proton. There is a signal at τ 8·90 assigned to CH_3·C(OH)– but no olefinic methyl signal. Structure (81) involves again cis-migration of a methyl group and involves loss of a proton from the same ion (79) as gives rise to the ether (80).

As the α-epoxy-alcohol (67) gave only products arising from axial cleavage of the epoxide, the α-epoxy-alcohol (69) was next examined in the hope that it would undergo equatorial cleavage to give the more stable tertiary carbonium ion followed by concerted rearrangement. The epoxy-alcohol was treated in benzene with the minimum amount of boron trifluoride–ether complex necessary for the reaction to ensure that co-ordination of the hydroxy-group with boron trifluoride, which would decrease the electron density on the oxygen and prevent it participating in the rearrangement, was reduced to a minimum. Examination of the product by t.l.c. indicated almost exclusive formation of one compound. The product was acetylated to give a crystalline diacetate

(82). The assigned structure was confirmed by n.m.r. spectroscopy when a very simple spectrum was obtained owing to the molecular symmetry. It showed a two-proton ABX quartet for the protons on the carbons carrying –OAc with J 4 and 7 Hz. The four methyl groups gave two sharp six-proton singlets at τ 8·98 and 9·01. The two acetate methyl groups showed a six-proton singlet at τ 7·99 superimposed on the multiplet due to the four allylic protons. The remaining four protons appeared as a multiplet at τ 8·23.

The β-epoxy-alcohol (73) on similar treatment gave a mixture which afforded two products. The less polar one $C_{14}H_{24}O_3$ (15% yield) is formulated as (84). It contained a hydroxy-group ($v_{max.}$ 3500 cm^{-1}) and the large number of bands in the 900—1000 cm^{-1} region indicated an ether group in agreement with a doublet (1H) at τ 6·15 (J 4·5 Hz) assigned to a proton on a carbon atom attached to ethereal oxygen. The splitting is as expected for structure (84). The ether must arise by an initial cis-migration of the angular methyl group to give the ion (83). Attack by the hydroxy-group of ring A on the carbonium ion can then give rise to (84). Alternatively further migration of the angular hydrogen may occur. This leads to the same ion (83) but attack of the original ring B hydroxy-group occurs. It is not possible
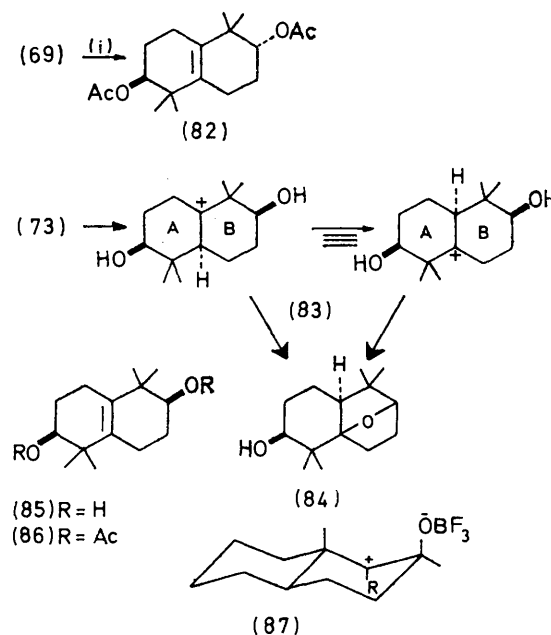
(i) Rearrangement followed by acetylation

to distinguish between these alternatives without labelling of the hydroxy-groups.

The more polar product was the diol (85). It gave a diacetate (86) whose n.m.r. spectrum was virtually identical with that of the diacetate (82) which differs from (86) only in the configuration of one of the acetoxy-groups. The only significant difference was in the chemical shift and splitting of the signals due to the protons on carbon carrying –OAc. These appeared as triplets (J 10 and 4 Hz) at τ 5·38, as opposed to τ 5·28

in the case of (82). Again a cis-migration of a methyl group is involved.

The initial aim of the work was an attempt to form the *friedo*-labdane skeleton. With the tetrasubstituted α-epoxide of the type (4) the required rearrangement necessitated equatorial cleavage of the epoxide. Previous work by Hartshorn and Kirk [12] had indicated that axial cleavage was preferred but that the energetic preference for such cleavage was not so great that it could not be overcome by steric, conformational, or electrostatic effects. It was considered originally that in the epoxides of type (4) concerted methyl and hydride shifts might be sufficiently energetically favourable, especially when $R^1 = OH$, to overcome the preference for axial cleavage. The results, which in a number of cases involve cis-migration, are in fact best explained by assuming that the rearrangements arising from the reactions of epoxides with boron trifluoride are *not* concerted. This conclusion agrees with that of Whitlock and Olson [8] who have showed that the rearrangement of the hydroxy-epoxide (53) to the hydroxy-ketone (54) with boron trifluoride is not concerted although the groups involved are antiperiplanar but instead involves a set of rapidly interconverting carbonium ions. With the α-epoxide (4) equatorial cleavage does occur but rearrangement ceases when the charge reaches C-5. The migration of the 4α-methyl group presumably does not occur because it would give rise to a 1,3-diaxial interaction with the α-substituent at C-9. The α-epoxide (67) with a methyl group instead of the group $-CH_2 \cdot CH_2 \cdot CH-$(OAc)Me on the epoxide ring gave products arising entirely from axial cleavage. The inductive effect of a methyl group will be less than that of $-CH_2 \cdot CH_2 \cdot CH-$(OAc)Me and so less favourable to charge development in equatorial cleavage.

The tetrasubstituted β-epoxides cleaved axially to give the ion (87). However, instead of ring contraction of ring B by a trans-shift, cis-migration of the angular methyl group occurred. The driving force could be the relief of the 1,3-diaxial interaction between the angular methyl group and the β-geminal methyl group.

The trisubstituted epoxides present a simpler overall picture. Cleavage occurs to give the more stable ion and this is followed by migration of the angular methyl group which relieves a 1,3-diaxial interaction. However no migration of the β-geminal methyl group occurred, presumably because this would reintroduce such an interaction.

The importance of removal of formation of a 1,3-diaxial interaction suggests that in the boron trifluoride induced rearrangement of the 7α,8α-epoxide (88) to the apotirucall-14-ene (89) [13] rather than to an isotirucall-13(17)-ene derivative (90), in contrast to the acid-catalysed conversion of tirucallenyl acetate (91) into isotirucallenyl acetate (92) (cf. ref. 14), the important factor is the unfavourable 1,3-diaxial interaction between the 7α-

hydroxy-group and the 14α-methyl group in the isotirucall-13(17)-ene derivative. In isotirucallenyl acetate (92) only a hydrogen–methyl interaction is involved. If the epoxide rearrangements are non-concerted then our initial suggestion [13] that the epoxide (88) gave the apotirucallane (89) because of a concerted process involving the C(15)α-proton and the epoxide oxygen is not valid.

The difficulty of inducing the C-4β methyl group to migrate in the epoxides studied raises the question of how this arises in the biogenesis of the *friedo*-labdanes.

(88)   (89)

(90)   (91)

(92)   (93)
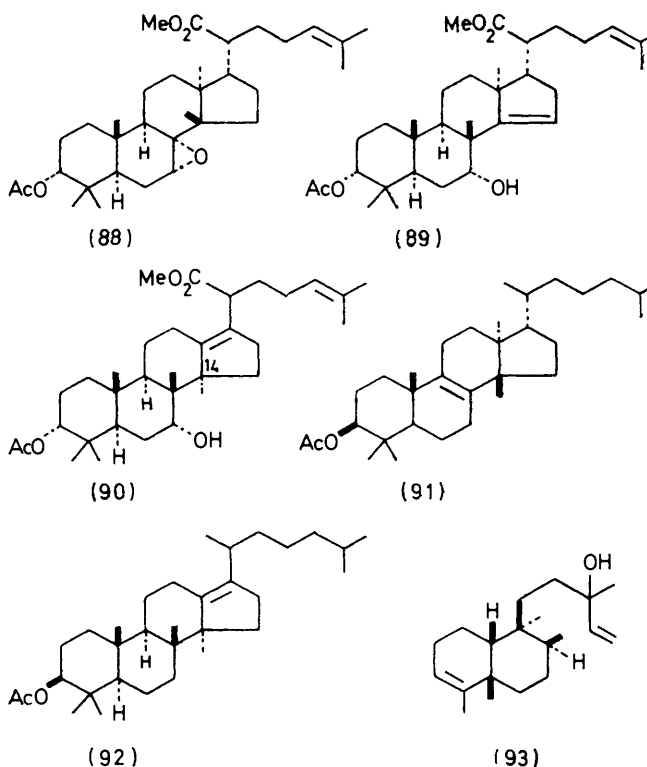
It is possible that the pathway is more complex than a simple set of methyl and hydride shifts. A more complex pathway may also explain the formation of compounds such as plathyterpol (93) [15] in which two of the four centres of asymmetry in the ring are of opposite configurations to those expected from a concerted migration of groups from an ion of type (3).

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were determined for solutions in carbon disulphide or for thin films in the case of liquids, unless otherwise stated. U.v. spectra were recorded using ethanol as solvent. N.m.r. spectra were determined at 100 or 60 MHz for solutions in carbon tetrachloride unless stated otherwise.

The alumina used for column chromatography was Laporte Industries Grade H. ' 5 and 10% deactivated ' refer to deactivation with, respectively, 5 and 10% of a

[12] M. P. Hartshorn and D. N. Kirk, *Tetrahedron*, 1965, **21**, 1547.

[13] G. P. Cotterrell, T. G. Halsall, and M. J. Wriglesworth, *J. Chem. Soc.* (*C*), 1970, 1503.

[14] D. Arigoni, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 222.

[15] T. J. King, S. Rodrigo, and S. C. Wallwork, *Chem. Comm.*, 1969, 683.

10% solution of acetic acid in water. ' Neutral alumina ' was Camag, and water was used for deactivation. ' Silica gel ' was Harringtons M.60. Silica gel impregnated with silver nitrate was prepared by adding a 25% aqueous silver nitrate solution (100 ml) to silica gel (100 g), shaking the mixture for 10 min, removing the solvent on a rotary evaporator, and finally baking at 110° for 12 h. For p.l.c., Kieselgel PF$_{254 + 366}$ plates were used in two sizes (100 cm × 20 cm × 1 mm and 20 cm × 20 cm × 1 mm), referred to as ' large ' and ' small ' respectively. After elution, the bands were removed and the silica placed in a sintered glass funnel and washed with ether (for very polar compounds, the silica was extracted in a Soxhlet apparatus). ' Silver nitrate plates ' refer to Kieselgel H plates impregnated with 20% silver nitrate. Light petroleum refers to the fraction with b.p. 40—60°.

Boron trifluoride–ether complex was purified by addition of 0·5% of ether (to remove any excess of boron trifluoride) and then distilled from calcium hydride to remove acidic impurities.

8-Hydroxy-14,15-*bisnorlabdan*-13-*one* (8).—This was obtained from the oxidation of sclareol (7) by the literature procedure [3] as needles (from light petroleum), m.p. 92—93° (lit.,[3] 91—92°) or, on one occasion, as plates, m.p. 123—125°.

Dehydration of 8-*Hydroxy*-14,15-*bisnorlabdan*-13-*one* (8) *with Magnesium Perchlorate in Toluene.*—The ketone (8) (12 g) and powdered magnesium perchlorate (36 g) in toluene (75 ml) were heated under reflux with stirring for 5 h. Toluene was then removed under reduced pressure and the residue extracted with light petroleum. Evaporation of the extract gave an oil which was adsorbed from light petroleum on silica gel (250 g). Light petroleum–ether (10 : 1) eluted 14,15-bisnorlabd-8-en-13-one (9) (10·5 g, 90%) as an oil, ν_{max} 1160, 1365, and 1710 cm^{-1}, τ 7·67 (2H, m, –CH$_2$CO–), 7·97 (3H, s, COMe), 8·48 (3H, s, –C=CMe), 9·05 (3H, s, Me at C-10), and 9·10 (3H, s) and 9·17 (3H, s) (*gem*-dimethyl), *m/e* 262. The n.m.r. spectrum showed an olefinic impurity (–C=C–*H* at τ 4·60) to the extent of 3%—probably 14,15-bisnorlabd-7-en-13-one.

Epoxidation of 14,15-*Bisnorlabd*-8-*en*-13-*one* (9).—Perbenzoic acid in benzene (1·05M; 5·2 ml) was added dropwise to the olefin (9) (1·5 g) in benzene (15 ml) with stirring. After 15 min, calcium hydroxide was added to remove the excess of peracid; the solution was then filtered and evaporated. The residue obtained was applied to 2 large preparative plates and these were eluted 4 times with light petroleum–ether (20 : 1). The major band afforded 8α,9α-*epoxy*-14,15-*bisnorlabdan*-13-*one* (6) (1·2 g, 80%) as an oil, homogeneous to t.l.c., ν_{max} 710, 840, 900, 990, 1075, 1160, 1365, and 1710 cm^{-1}, τ 7·64 (2H, m, –CH$_2$CO–), 7·95 (3H, s, COMe), 8·89 (3H, s, –C–C–Me), 9·00 (3H, s, Me at C-10),

and 9·17 (3H, s) and 9·21 (3H, s) (*gem*-dimethyl), *m/e* 278 (Found: C, 77·3; H, 10·7. C$_{18}$H$_{30}$O$_2$ requires C, 77·6; H, 10·9%).

A minor band afforded an epoxide (50 mg, 3%) which showed epoxide protons in the n.m.r. spectrum and arose from the olefinic impurity.

Treatment of 8α,9α-*Epoxy*-14,15-*bisnorlabdan*-13-*one* (6) *with Boron Trifluoride–Ether Complex.*—Boron trifluoride–ether complex (3 drops) was added with swirling to 8α,9α-epoxy-14,15-bisnorlabdan-13-one (200 mg) in dry benzene (2 ml). The solution was kept for 15 min and then potassium carbonate was added followed by a drop of water.

The product was applied to 2 small preparative plates which were eluted 4 times with light petroleum–ether (20 : 1). The band with higher R_F afforded 8α,13:9α,13-*diepoxy*-14,15-*bisnorlabdane* (12) (120 mg, 60%) as needles (from light petroleum), m.p. 66—68°, ν_{max} 830, 875, 940, 970, 1020, 1050, 1150, 1170, 1210, 1330, and 1390 cm^{-1}, τ 8·57 [3H, s, –O–C(Me)–O–], 8·71 [3H, s, –O–C(Me)–], 9·05 (3H, s) and 9·07 (3H, s) (*gem*-dimethyl), and 9·17 (3H, s, Me at C-10), *m/e* 278 (Found: C, 77·1; H, 10·4. C$_{18}$H$_{30}$O$_2$ requires C, 77·6; H, 10·9%).

The band with lower R_F afforded 14,15-*bisnor*-10(9 → 8)*abeo-labdane*-9,13-*dione* (13) (20 mg, 10%) as an oil, homogeneous to t.l.c., ν_{max} 1010, 1160, 1370, 1390, 1695, and 1710 cm^{-1}, τ 7·88 (3H, s, COMe), 7·45 (4H, m, –CO·CH$_2$·CH$_2$·CO–), 8·82 [3H, s, –CO–C(Me)–], and 9·14 (9H, s, Me's at C-4 and C-10), *m/e* 278. The 13-*semicarbazone* was obtained as needles (from aqueous ethanol), m.p. 212—214° (Found: C, 68·0; H, 9·7; N, 12·25. C$_{19}$H$_{33}$N$_3$O$_2$ requires C, 68·0; H, 9·9; N, 12·55%).

Reaction of 14,15-*Bisnorlabd*-8-*en*-13-*one* (9) *with Osmium Tetraoxide.*—The olefin (9) (100 mg) and osmium tetraoxide (100 mg) in pyridine (5 ml) were stirred for 24 h at 20°. Sodium hydrogen sulphite (250 mg) in water (4 ml) and pyridine (2 ml) was added and stirring continued for a further 30 min. The mixture was extracted with dichloromethane and the extract was evaporated. The residue was applied to one small preparative plate and this was eluted 3 times with light petroleum–ether (20 : 1). The major band afforded 8α,13:9α,13-diepoxy-14,15-bisnorlabdane (12) (60 mg, 55%) as needles (from light petroleum), m.p. 65—67°, identical by i.r., n.m.r., and mixed m.p. with the major product from the reaction of 8α,9α-epoxy-14,15-bisnorlabdan-13-one with boron trifluoride–ether complex.

14,15-*Bisnorlabd*-8-*en*-13(R *and* S)-*yl Acetates* (11).—14,15-Bisnorlabd-8-en-13-one (9) (600 mg) in ether (10 ml) was added dropwise to lithium aluminium hydride (100 mg) in ether (10 ml) with stirring. Water was then added cautiously; isolation through ether afforded the mixture of 14,15-bisnorlabd-8-en-13(R and S)-ols (10) (570 mg, 95%) as an oil, ν_{max} 860, 940, 960, 1005, 1080, 1130, 1380, and 3350 cm^{-1}, τ 6·32 [1H, sextet, *J* 6 Hz, –CH$_2$·C*H*(OH)Me], 8·44 (3H, s, –C=CMe), 8·64 (1H, s, –OH), 8·85 [3H, d, *J* 6 Hz, –CH(OH)*Me*], and 9·06 (3H, s), 9·11 (3H, s), and 9·16 (3H, s), (Me's at C-4 and C-10).

This mixture was acetylated and, after chromatographing the product on silica gel (10 g), the 14,15-*bisnorlabd*-8-*en*-13(R and S)-*yl acetates* (11) were obtained as an inseparable mixture (t.l.c.) (oil), ν_{max} (film), 860, 965, 1035, 1075, 1135, 1255, 1385, and 1735 cm^{-1}, τ 5·22 [1H, sextet, *J* 6 Hz, –CH$_2$C*H*(OAc)Me], 8·04 (3H, s, OAc), 8·45 (3H, s, –C=CMe), 8·81 [3H, d, *J* 6 Hz, –CH(OAc)*Me*], 9·07 (3H, s, Me at C-10), and 9·12 (3H, s) and 9·17 (3H, s) (Me's at C-4), *m/e* 306 (Found: C, 78·25; H, 11·0. C$_{20}$H$_{34}$O$_2$ requires C, 78·4; H, 11·2%).

Epoxidation of 14,15-*Bisnorlabd*-8-*en*-13(R *and* S)-*yl Acetates* (11).—Perbenzoic acid in benzene (1M; 2 ml) was added to the acetates (11) (550 mg) in benzene (5 ml). After 30 min, the mixture was worked up in the usual way to give an oil which was applied to one large preparative plate. This was eluted 8 times with light petroleum–ether (50 : 1). The band of higher R_F afforded 8α,9α-*epoxy*-14,15-*bisnorlabdan*-13(R and S)-*yl acetates* (4) (250 mg, 46%) as an oil, homogeneous to t.l.c., ν_{max} 720, 855, 965, 1045, 1065, 1130, 1250, 1380, 1735 cm^{-1}, τ 5·27 [1H, m, –CH$_2$CH-(OAc)Me], 8·05 and 8·07 (3H in total, 2s caused by *R* and *S*

configurations at C-13, OAc), 8·82 [3H, d, J 6 Hz, -CH(OAc)-Me], 8·87 (3H, s, -C-C-Me), 9·03 (3H, s, Me at C-10), and
$$\underset{O}{\diagup\!\!\!\!\diagdown}$$
9·17 (3H, s) and 9·21 (3H, s) (Me's at C-4), m/e 322 (Found: C, 74·6; H, 10·7. $C_{20}H_{34}O_3$ requires C, 74·5; H, 10·6%).

The band of lower R_F afforded 8β,9β-*epoxy*-14,15-*bisnorlabdan*-13(R and S)-*yl acetates* (14) (200 mg, 36%) as an oil, homogeneous to t.l.c., ν_{max} 855, 965, 1035, 1070, 1130, 1250, 1380, and 1735 cm⁻¹, τ 5·27 [1H, m, -CH₂CH(OAc)Me], 8·05 (3H, s, OAc), 8·78 and 8·80 (3H in total, 2s caused by R and S configurations at C-13, -C-CMe), 8·82 [3H, d, J
$$\underset{O}{\diagup\!\!\!\!\diagdown}$$
6 Hz, -CH(OAc)Me], 8·99 (3H, s, Me at C-10), and 9·18 (3H, s) and 9·22 (3H, s) (Me's at C-4), m/e 322 (Found: C, 75·0; H, 11·0. $C_{20}H_{34}O_3$ requires C, 74·5; H, 10·6%).

Reduction of the Acetates (4) *with Lithium in Ethylamine.*—The epoxy-acetates (4) (600 mg) were dissolved in freshly distilled anhydrous ethylamine (30 ml) and finely divided lithium was added (100 mg). The solution was stirred for 30 min after a permanent blue colour had developed. Ethanol was then added to discharge the blue colour; evaporation and isolation through ether gave an oil which was applied to 2 large preparative plates. These were eluted 15 times with light petroleum-ether (7 : 1). Examination of the plate at 366 nm showed two bands (A and B) close together followed by a further two bands (C and D) which were incompletely separated. Band A afforded 14,15-*bisnor*-8α-*labdane*-9α,13ξ₁-*diol* (16) (140 mg, 23%) as needles (from light petroleum), m.p. 106—107°, $[\alpha]_D$ +7° (c 0·5), ν_{max} 960, 1000, 1030, 1065, 1110, 3450, and 3600 cm⁻¹, τ (CDCl₃) 6·27 [1H, sextet, J 6 Hz, -CH₂CH(OH)Me], 7·79br (2H, s, -OH), 8·81 [3H, d, J 6 Hz, -CH(OH)Me], 9·07 (3H, s, Me at C-10), 9·13 (3H, d, J 6 Hz, -CHMe), and 9·12 (3H, s) and 9·16 (3H, s) (Me's at C-4) (Found: C, 76·6; H, 11·9. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

Band B afforded 14,15-*bisnor*-8α-*labdane*-9α,13ξ₂-*diol* (17) (120 mg, 20%) as needles (from light petroleum), m.p. 84—86°, $[\alpha]_D$ +11° (c 0·3), ν_{max} 1000, 1030, 1060, 1105, 3450, and 3600 cm⁻¹, τ (CDCl₃) 6·23 [1H, sextet, J 6 Hz, -CH₂CH(OH)·Me], 8·23br (2H, s, -OH), 8·81 [3H, d, J 6 Hz, -CH(OH)·Me], 9·06 (3H, s, Me at C-10), 9·13 (3H, d, J 6 Hz, -CHMe), and 9·12 (3H, s) and 9·16 (3H, s) (Me's at C-4) (Found: C, 77·0; H, 12·3. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

Bands C and D were removed together and reapplied to one large preparative plate; this was eluted 20 times with light petroleum-ether (4 : 1). Band C afforded 14,15-*bisnorlabdane*-9α,13ξ₂-*diol* (19) (100 mg, 17%) as plates (from light petroleum), m.p. 108—110°, $[\alpha]_D$ +14° (c 0·3), ν_{max} 930, 960, 1010, 1035, 1085, 3450, and 3600 cm⁻¹, τ (CDCl₃) 6·15 [1H, sextet, J 6 Hz, -CH₂CH(OH)Me], 8·79 [3H, d, J 6 Hz, -CH(OH)Me], 8·94 (3H, d, J 6 Hz, -CHMe), 8·97 (3H, s, Me at C-10), and 9·10 (3H, s) and 9·15 (3H, s) (Me's at C-4) (Found: C, 76·1; H, 11·6. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

Band D afforded 14,15-*bisnorlabdane*-9α,13ξ₁-*diol* (18) (100 mg, 17%) as needles (from light petroleum), m.p. 145—146°, $[\alpha]_D$ -5° (c 0·1), ν_{max} 930, 960, 1010, 1035, 1085, 3450, and 3600 cm⁻¹, τ (CDCl₃) 6·24 [1H, sextet, J 6 Hz, -CH₂CH(OH)Me], 8·79 [3H, d, J 6 Hz, -CH(OH)Me], 8·97 (3H, d, J 6 Hz, -CHMe), 8·99 (3H, s, Me at C-10), and 9·10 (3H, s) and 9·15 (3H, s) (Me's at C-4) (Found: C, 76·4; H, 11·8. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%).

Dehydration of 13ξ₁-*Acetoxy*-14,15-*bisnor*-8α-*labdan*-9α-*ol*

(16).—14,15-Bisnor-8α-labdane-9α,13ξ₁-diol (50 mg) was acetylated. The crude 13ξ₁-acetoxy-14,15-bisnor-8α-labdan-9α-ol (50 mg) was dissolved in pyridine (0·5 ml), phosphoryl chloride (0·1 ml) was added, and the solution was kept at 50° for 8 h. It was then poured into ice-cold water; isolation through ether gave an oil which was applied to one small preparative plate. This was eluted 4 times with light petroleum-ether (30 : 1). The major band afforded 14,15-bisnorlabd-8-en-13ξ₁-yl acetate (40 mg, 84%) as an oil, homogeneous to t.l.c., with i.r. and n.m.r. spectra identical with those of the mixture of 13(R and S)-yl acetates (11) obtained previously.

Dehydration of 13ξ₂-*Acetoxy*-14,15-*bisnorlabdan*-9α-*ol* (19). —14,15-Bisnorlabdane-9α,13ξ₂-diol (19) was converted into the 13ξ₂-monoacetate which was then dehydrated with phosphoryl chloride as described in the previous experiment. After p.l.c., 14,15-*bisnorlabd*-9(11)-*en*-13ξ₂-*yl acetate* (20) (40 mg, 84%) was obtained as an oil, homogeneous to t.l.c., ν_{max} 850, 960, 1065, 1140, 1245, 1380, and 1730 cm⁻¹, τ 4·95 (1H, t, J 6·5 Hz, -C=CH·CH₂-), 5·20 [1H, sextet, J 6·5 Hz, -CH₂CH(OAc)Me], 7·81 [1H, sextet, J 7 Hz, -C=C·CH(Me)·CH₂-], 8·05 (3H, s, OAc), 8·81 [3H, d, J 6·5 Hz, -CH₂CH(OAc)Me], 8·86 [3H, d, J 7 Hz, -C=C·CH(*Me*)-], 8·92 (3H, s, Me at C-10), and 9·13 (6H, s, Me's at C-4) (Found: C, 78·3; H, 11·0. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%).

Correlation of 8α,9α-*Epoxy*-14,15-*bisnorlabdan*-13-*one* (6) *and* 8α,9α-*Epoxy*-14,15-*bisnorlabdan*-13(R and S)-*yl Acetates* (4).—Sodium borohydride (20 mg) was added to 8α,9α-epoxy-14,15-bisnorlabdan-13-one (120 mg) in ethanol-water (9 : 1) and the mixture was stirred for 30 min. Isolation through ether gave 8α,9α-epoxy-14,15-bisnorlabdan-13(R and S)-ols (115 mg) as an oil, ν_{max} 900, 1000, 1040, 1065, 1130, 1180, 1380, and 3450 cm⁻¹, τ 6·40 [1H, sextet, J 7 Hz, -CH₂CH(OH)Me], 8·84 and 8·86 (3H in total, 2s caused by R and S configurations at C-13, -C-CMe), 8·90 [3H, d, J
$$\underset{O}{\diagup\!\!\!\!\diagdown}$$
7 Hz, -CH(OH)]Me], 9·01 (3H, s, Me at C-10), and 9·17 (3H, s) and 9·21 (3H, s) (Me's at C-4). Acetylation gave, after chromatography on silica gel, 8α,9α-epoxy-14,15-bisnorlabdan-13(R and S)-yl acetates (4) (90 mg), i.r., n.m.r., and t.l.c. identical with those of the less polar (α) epoxide acetates obtained by epoxidation of 14,15-bisnorlabd-8-en-13(R and S)-yl acetates.

Hydrolysis of 8β,9β-*Epoxy*-14,15-*bisnorlabdan*-13(R and S)-*yl Acetates* (14).—The acetates (14) (100 mg) in methanolic potassium hydroxide (1%; 20 ml) were kept at 20° for 24 h. After neutralisation, solvent was removed under reduced pressure and the residue extracted with ether to give an oil which was applied to 2 small preparative plates. These were eluted 10 times with light petroleum-ether (10 : 1). The band with higher R_F afforded 9α,13ξ₁-*epoxy*-14,15-*bisnor*-8α-*labdan*-8β-*ol* (22) (30 mg, 35%) as a gum, homogeneous to t.l.c., but which could not be induced to crystallise, ν_{max} 810, 890, 930, 1005, 1020, 1095, 1370, 1390, and 3500 cm⁻¹, τ 5·96 [1H, m, $W_{\frac{1}{2}}$ 23 Hz, -O·CH(Me)·CH₂], 8·79 (3H, d, J 6 Hz, -CHMe), 8·96 [3H, s, C(OH)Me], 9·02 (3H, s, Me at C-10), and 9·10 (3H, s) and 9·18 (3H, s) (Me's at C-4), m/e 280 ($C_{18}H_{32}O_2$ requires M, 280).

The band with lower R_F afforded 9α,13ξ₂-*epoxy*-14,15-*bisnor*-8α-*labdan*-8β-*ol* (23) (30 mg, 35%) as a gum, homogeneous to t.l.c., but which could not be induced to crystallise, ν_{max} 840, 890, 930, 995, 1020, 1100, 1370, 1390, and 3500 cm⁻¹, τ 5·93 [1H, m, $W_{\frac{1}{2}}$ 22 Hz, -O·CH(Me)·CH₂-],

8·78 (3H, d, *J* 6 Hz, -C*H*Me), 8·92 [6H, s, -C(OH)*Me* and Me at C-10], and 9·12 (3H, s) and 9·17 (3H, s) (Me's at C-4), *m/e* 280 ($C_{18}H_{32}O_2$ requires *M*, 280).

Dehydration of 9α,13ξ₁-*Epoxy*-14,15-*bisnor*-8α-*labdan*-8β-*ol* (22).—The alcohol (22) (25 mg) was dehydrated with phosphoryl chloride in pyridine as described above. The product was applied to one small preparative plate which was eluted 3 times with light petroleum–ether (30 : 1). The major band afforded 9α,13ξ₁-*epoxy*-14,15-*bisnorlabd*-7-*ene* (24) (20 mg) as an oil, homogeneous to t.l.c., τ 4·62br (1H, s, $W_{\frac{1}{2}}$ 8 Hz, -C=C*H*·CH₂-), 6·08 [1H, m, $W_{\frac{1}{2}}$ 20 Hz, -O·C*H*(Me)·CH₂], 8·37 (3H, s, -C=CMe), 8·80 [3H, d, *J* 6 Hz, -CH(OR)*Me*], 9·10 (6H, s, Me's at C-4), and 9·22 (3H, s, Me at C-10).

Dehydration of 9α,13ξ₂-*Epoxy*-14,15-*bisnor*-8α-*labdan*-8β-*ol*.—In a similar manner to that described above, the alcohol (22) afforded 9α,13ξ₂-*epoxy*-14,15-*bisnorlabd*-7-*ene* (25) as an oil, homogeneous to t.l.c., τ 4·57br (1H, s, $W_{\frac{1}{2}}$ 8 Hz, -C=C*H*·CH₂-), 5·85 [1H, m, $W_{\frac{1}{2}}$ 22 Hz, -O·C*H*(Me)·CH₂], 8·31 (3H, s, -C=C-*Me*), 8·82 [3H, d, *J* 6 Hz, -CH(OR)*Me*], 9·11 (6H, s, Me's at C-4), and 9·18 (3H, s, Me at C-10).

Treatment of 8α,9α-*Epoxy*-14,15-*bisnorlabd*-13(R *and* S)-*yl Acetates* (4) *with Boron Trifluoride–Ether Complex*.—The acetates (4) (150 mg) in dry benzene (2 ml) were treated with boron trifluoride–ether complex (3 drops) in the manner described earlier. The oil obtained was applied to 2 small preparative plates and these were eluted 6 times with light petroleum–ether (20 : 1). The band with highest R_F afforded the dienes (26; two epimers at 3') or (27; two epimers at 3') as an oil, homogeneous to t.l.c., ν_{max}. 895, 970, 1040, 1065, 1135, 1255, 1385, 1625, and 1735 cm⁻¹, λ_{max}. 242 nm (ε 17,000), τ 5·08 (1H, s, -C=C*H*H), 5·26 [2H, s for -C=CH*H* superimposed on m for -CH₂·C*H*(OAc)Me], 7·92 (4H, m, -C*H*₂·C=C·C*H*₂-), 8·05 (3H, s, OAc), 8·85 [3H, d, *J* 6·5 Hz, -CH(OAc)*Me*], 8·95 (6H, s, 2 × Me), 8·98 (3H, s, Me) (Found: C, 78·45; H, 10·3%; *m/e*, 304. Calc. for $C_{20}H_{32}O_2$: C, 78·9; H, 10·6%; *M*, 304).

The second band afforded 13(R *and* S)-*acetoxy*-14,15-*bisnor*-10(9 ⟶ 8)abeo-*labdan*-9-*ones* (30) as an oil, homogeneous to t.l.c., ν_{max}. 1065, 1250, 1380, 1695, and 1735 cm⁻¹, τ 5·22 [1H, sextet, *J* 6·5 Hz, -CH₂C*H*(OAc)Me], 7·65 (2H, m, $W_{\frac{1}{2}}$ 25 Hz, -CH₂C*H*₂CO-), 8·04 and 8·05 (3H in total, 2s for OAc caused by *R* and *S* orientations at C-13), 8·79 [3H, d, *J* 6·5 Hz, -CH(OAc)*Me*], 8·83 (3H, s, MeC-CO-), and 9·12 (9H, s, Me's at C-4 and C-10), *m/e* 322 ($C_{20}H_{34}O_3$ requires *M*, 322). The two C-13 epimeric acetoxy-ketones were hydrolysed with methanolic potassium hydroxide (2%) and the resulting hydroxy-ketones oxidised with chromium trioxide in aqueous pyridine to give 14,15-bisnor-10(9 ⟶ 8)abeo-labdane-9,13-dione (13) which was characterised as the 13-semicarbazone (needles from aqueous ethanol), m.p. and mixed m.p. 212—214°.

Reduction of 13(*R* and *S*)-acetoxy-14,15-bisnor-10(9 ⟶ 8)abeo-labdan-9-ones with sodium borohydride in 95% ethanol for 48 h, afforded an oily product which was purified by p.l.c. [4 elutions with light petroleum–ether (6 : 1)]. The major band afforded 13(*R* and *S*)-acetoxy-14,15-bisnor-10(9 ⟶ 8)abeo-labdan-9-ols as a gum, ν_{max}. 1250, 1735, and 3600 cm⁻¹, τ 5·10 [1H, m, $W_{\frac{1}{2}}$ 25 Hz, -CH₂C*H*(OAc)Me], 6·42 [1H, m, $W_{\frac{1}{2}}$ 18 Hz, -C*H*(OH)·CH₂-], 8·03 (3H, s, OAc), 8·79 [3H, d, *J* 6·5 Hz, -CH(OAc)*Me*], and 9·11 (6H, s), 9·14 (3H, s), and 9·18 (3H, s) (Me's at C-4, C-8 and C-10).

The third band afforded 5α,8α-*epoxy*-14,15-*bisnor*-9,5-friedo-*labdan*-13(R *and* S)-*yl acetates* (33) as an oil, homogeneous to t.l.c., ν_{max}. 860, 960, 1040, 1135, 1245, 1380, and

1735 cm⁻¹, τ 5·25 [1H, sextet, *J* 6·5 Hz, -CH₂C*H*(OAc)Me], 8·04 (3H, s, OAc), 8·81 [3H, d, *J* 6·5 Hz, -CH(OAc)*Me*], 8·81 (3H, s, -O·CR₂*Me*), 8·93 and 8·95 (total 3H, *R*- and *S*-at C-13, Me at C-9), and 9·01 (3H, s) and 9·30 (3H, s) (Me's at C-4), *m/e* 322 ($C_{20}H_{34}O_3$ requires *M*, 322). Hydrolysis of the acetoxy-group in the side-chain followed by oxidation gave 5α,8α-*epoxy*-14,15-*bisnor*-9,5-friedo-*labdan*-13-*one* which was characterised as the 13-*semicarbazone* (needles from aqueous ethanol), m.p. 191—192° (Found: C, 67·8; H, 9·7; N, 12·75. $C_{19}H_{33}N_3O_2$ requires C, 68·0; H, 9·9; N, 12·55%).

The fourth band afforded 13(R *and* S)-*acetoxy*-14,15-*bisnor*-9,5-friedo-*labd*-5(10)-*en*-8α-*ols* (35) as a gum, homogeneous to t.l.c., ν_{max}. (CS₂) 930, 970, 1065, 1145, 1250, 1380, 1730, and 3600 cm⁻¹, τ 5·35 [1H, m, $W_{\frac{1}{2}}$ 18 Hz, -CH₂C*H*(OAc)Me], 8·04 (3H, s, OAc), 8·83 [3H, d, *J* 6·5 Hz, -CH(OAc)*Me*], 8·92 [3H, s, -C(OH)*Me*], 8·98 (3H, s, Me at C-9), and 9·03 (3H, s) and 9·07 (3H, s) (Me's at C-4) (Found: C, 74·1; H, 10·3%; *m/e*, 322. $C_{20}H_{34}O_3$ requires C, 74·5; H, 10·6%; *M*, 322).

The ratios of the four products were variable even when the experiment was repeated using apparently identical conditions. The yields were within the following limits: compound [(26) or (27)] 10—25%; compound (30) 20—35%; compound (33) 10%; and compound (35) 10—20%.

Treatment of 8β,9β-*Epoxy*-14,15-*bisnorlabd*-13(R *and* S)-*yl Acetates* (14) *with Boron Trifluoride–Ether Complex*.—Similar treatment of the acetates (14) (150 mg) with boron trifluoride–ether complex in benzene gave an oil which was applied to 2 small preparative plates and these were eluted 6 times with light petroleum–ether (20 : 1). The major band afforded 5β,8β-*epoxy*-14,15-*bisnor*-8,5-friedo-*labdan*-13(R *and* S)-*yl acetates* (36) (90 mg, 60%) as an oil, homogeneous to t.l.c., ν_{max}. 780, 870, 910, 950, 1040, 1130, 1250, 1385, and 1735 cm⁻¹, τ 5·25 [1H, sextet, *J* 6 Hz, -CH₂C*H*(OAc)Me] 8·03 (3H, s, OAc), 8·81 [3H, d, *J* 6 Hz, -CH(OAc)*Me*], 8·84 (3H, s, -O·CR₂*Me*), and 9·08 (3H, s), 9·10 (3H, s), and 9·22 (3H, s) (Me's at C-4 and C-10).

The more polar bands were removed together and the mixture obtained was reapplied to one small preparative plate which was then eluted 10 times with light petroleum–ether (10 : 1). The band of highest R_F afforded (E)-9-(3-*acetoxybutyl*)-4,5,10,10-*tetramethylcyclodec*-4-*enone* (42) (8 mg, 5%) as an oil, homogeneous to t.l.c., ν_{max}. 860, 965, 1035, 1060, 1080, 1140, 1250, 1380, 1710, and 1735 cm⁻¹, τ 5·25 [1H, sextet, *J* 5 Hz, -CH₂C*H*(OAc)Me], 7·77 (2H, m, $W_{\frac{1}{2}}$ 15 Hz, -CH₂CH₂·CO-), 8·04 (3H, s, OAc), 8·40 (6H, s, MeC=CMe), 8·86 [3H, d, *J* 6 Hz, -CH(OAc)*Me*], and 8·96 (3H, s) and 9·26 (3H, s) (CMe₂), *m/e* 322 ($C_{20}H_{34}O_3$ requires *M*, 322).

The next band afforded the hydroxy-acetate [(37) or (38)] as an oil, (10 mg, 7%), homogeneous to t.l.c., ν_{max}. 740, 865, 920, 970, 1025, 1055, 1145, 1255, 1385, 1735, and 3600 cm⁻¹, τ 4·55 (1H, t, *J* 3·5 Hz, -C=C*H*·CH₂-), 5·25 [1H, sextet, *J* 6·5 Hz, -CH₂C*H*(OAc)Me], 8·12 (3H, s, OAc), 8·84 [3H, d, *J* 6·5 Hz, -CH(OAc)*Me*], 8·96 [3H, s, -C(OH)*Me*], and 9·03 (3H, s) and 9·12 (6H, s) (Me's at C-4 and C-9).

Hydrolysis of 5β,8β-*Epoxy*-14,15-*bisnor*-8,5-friedo-*labdan*-13(R *and* S)-*yl Acetates* (36).—The acetates (36) (200 mg) were treated with methanolic potassium hydroxide (5%; 20 ml) for 24 h at 30°. Isolation through ether gave an oil which was applied to one large preparative plate and this was eluted 15 times with light petroleum–ether (5 : 1). The band of higher R_F afforded 5β,8β-*epoxy*-14,15-*bisnor*-8,5-friedo-*labdan*-13ξ₁-*ol* as an oil, homogeneous to t.l.c.,

ν_{max} 760, 855, 865, 900, 940, 990, 1035, 1045, 1070, 1080, 1120, 1370, 1390, and 3450 cm^{-1}, τ 6·37 [1H, m, $W_{\frac{1}{2}}$ 25 Hz, -CH$_2$CH(OH)Me], 8·84 (3H, s, -O·CR$_2$$Me$), 8·86 [3H, d, J 6 Hz, -CH(OH)Me], and 9·07 (3H, s), 9·09 (3H, s), and 9·21 (3H, s) (Found: C, 76·85; H, 11·3. C$_{18}$H$_{32}$O$_2$ requires C, 77·1; H, 11·5%).

The band of lower R_F afforded 5β,8β-epoxy-14,15-bisnor-8,5-friedo-labdan-13ξ$_2$-ol as an oil, homogeneous to t.l.c., i.r. spectrum identical with that of the 13ξ$_1$-isomer, τ 6·35 [1H, m, $W_{\frac{1}{2}}$ 25 Hz, -CH$_2$CH(OH)Me], 8·83 (3H, s, -O·CR$_2$-Me), 8·86 [3H, d, J 6 Hz, -CH(OH)Me], and 9·08 (3H, s), 9·10 (3H, s), and 9·21 (3H, s) (Me's at C-4 and C-9) (Found: C, 76·8; H, 11·25. C$_{18}$H$_{32}$O$_3$ requires C, 77·1; H, 11·5%). The yield of each isomer was 45%.

Oxidation of the mixture of alcohols gave 5β,8β-epoxy-14,15-bisnor-8,5-friedo-labdan-13-one characterised as the semicarbazone (plates from aqueous ethanol), m.p. 187—189° (Found: C, 67·7; H, 9·7; N, 12·2. C$_{19}$H$_{33}$N$_3$O$_2$ requires C, 68·0; H, 9·9; N, 12·5%).

Hydroxylation of Keto-acetate (42).—The keto-acetate (42) (15 mg) was treated with osmium tetraoxide in pyridine by the method described earlier. The crude product obtained showed $\nu_{max.}$ 1705, 1730, and 3450 cm^{-1}. It was applied to one small preparative plate and this was eluted 3 times with light petroleum–ether (1 : 1). The major band was removed; a check by t.l.c. indicated that the diol had been converted into a new much less polar compound which was purified by p.l.c. [3 elutions with light petroleum–ether (30 : 1)] to give 9-(3-acetoxybutyl)-3,6:3,7-diepoxy-2,2,6,7-tetramethylcyclodecane (43) as an oil, $\nu_{max.}$ 840, 920, 960, 1020, 1080, 1120, 1180, 1245, 1375, and 1735 cm^{-1}, τ (c.a.t.) 5·20 [1H, m, $W_{\frac{1}{2}}$ 22 Hz, -CH$_2$CH(OAc)Me], 8·02 (3H, s, OAc), 8·77 [3H, d, J 6 Hz, -CH(OAc)Me], 8·93 (6H, s, -O·CR$_2$-Me), and 9·10—9·19 (6H, complex pattern for *gem*-dimethyl due to the presence of stereoisomers), *m/e* 338.

Methyl 14,15,16-Trisnorlabd-8-en-13-oate.—Sodium hydroxide solution (5%; 4 ml) was added to 14,15-bisnorlabd-8-en-13-one (200 mg) in dioxan (10 ml). Iodine (10 g) and potassium iodide (20 g) in water (100 ml) were then added dropwise with shaking until a definite excess of iodine was present (as indicated by the colour of the solution). Additional dioxan was added as required to maintain a homogeneous solution. The mixture was finally heated at 60° for 30 min, iodine solution being added to maintain an excess of iodine. The solution was cooled, diluted with sodium hydroxide solution, and extracted twice with ether. The ethereal extracts were discarded and sodium thiosulphate (solid) added to the aqueous layer prior to acidification with hydrochloric acid (2N). Isolation through ether afforded crude 14,15,16-trisnorlabd-8-en-13-oic acid: this was dissolved in ether and an ethereal solution of diazomethane added. After 30 s the excess of diazomethane was destroyed by the addition of acetic acid. Isolation through ether gave an oil which was applied to one small preparative plate. After 3 elutions with light petroleum–ether (20 : 1), the major band was removed and afforded *methyl 14,15,16-trisnorlabd-8-en-13-oate* (60 mg, 30%) as an oil, homogeneous to t.l.c., $\nu_{max.}$ 750, 780, 970, 1040, 1160, 1185, 1260, 1735, and 3600 cm^{-1}, τ 6·37 (3H, s, CO$_2$Me), 7·6—8·1 (6H, complex, -CH$_2$·CO$_2$Me and -CH$_2$·C=C·CH$_2$-), 8·41 (3H, s, -C=CMe), 9·03 (3H, s, Me at C-10), and 9·10 (3H, s) and 9·15 (3H, s) (*gem*-dimethyl) (Found: C, 77·2; H, 10·8. C$_{18}$H$_{30}$O$_2$ requires C, 77·6; H, 10·9%).

Epoxidation of Methyl 14,15,16-Trisnorlabd-8-en-13-oate.—Methyl 14,15,16-trisnorlabd-8-en-13-oate (200 mg) was

treated with perbenzoic acid in benzene by the method described above. The product obtained was applied to 2 small preparative plates and these were eluted 10 times with light petroleum–ether (50 : 1). The band of higher R_F afforded *methyl 8α,9α-epoxy-14,15,16-trisnorlabdan-13-oate* (5) (105 mg, 50%) as an oil, homogeneous to t.l.c., $\nu_{max.}$ 730, 850, 890, 900, 1060, 1080, 1170, 1200, 1270, and 1735 cm^{-1}, τ 6·40 (3H, s, CO$_2$Me), 7·80 (2H, m, -CH$_2$CH$_2$·CO$_2$Me), 8·83 (3H, s, -C-CMe), 8·99 (3H, s, Me at C-10), and 9·15 (3H, s)

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and 9·20 (3H, s) (Me's at C-4) (Found: C, 73·9; H, 10·4. C$_{18}$H$_{30}$O$_3$ requires C, 73·45; H, 10·25%).

The band of lower R_F afforded *methyl 8β,9β-epoxy-14,15,16-trisnorlabdan-13-oate* (15) (70 mg, 32%) as an oil, homogeneous to t.l.c., $\nu_{max.}$ 700, 850, 890, 900, 1000, 1080, 1170, 1195, 1270, and 1735 cm^{-1}, τ 6·39 (3H, s, CO$_2$Me), 7·63 (2H, m, -CH$_2$CH$_2$·CO$_2$Me), 8·74 (3H, s, -C-CMe), 8·98 (3H, s,

$$\begin{array}{c} \diagdown / \\ O \end{array}$$

Me at C-10), and 9·17 (3H, s) and 9·22 (3H, s) (Me's at C-4) (Found: C, 73·7; H, 10·3. C$_{18}$H$_{30}$O$_3$ requires C, 73·45; H, 10·25%).

Treatment of Methyl 8α,9α-Epoxy-14,15,16-trisnorlabdan-13-oate (5) with Boron Trifluoride–Ether Complex.—The epoxy-ester (5) (100 mg) was treated with boron trifluoride-ether complex in benzene in the manner described previously. The product was applied to one small preparative plate and this was eluted 7 times with light petroleum–ether (20 : 1). The band of highest R_F gave a mixture of dienyl-esters (10 mg, 10%), as indicated by t.l.c. on silica gel–silver nitrate plates, and was not investigated further.

The second band afforded *methyl 9-oxo-14,15,16-trisnor-10(9 ⟶ 8)abeo-labdan-13-oate* (44) (40 mg, 40%) as an oil, homogeneous to t.l.c., $\nu_{max.}$ 985, 1080, 1160, 1210, 1260, 1695, and 1740 cm^{-1}, τ 6·37 (3H, s, CO$_2$Me), 7·30 (2H, m, -CH$_2$CH$_2$·CO$_2$Me), 7·60 (2H, m, -CO·CH$_2$CH$_2$·CO$_2$Me), 8·78 [3H, s, -CO·C(Me)-], and 9·12 (9H, s, Me's at C-4 and C-10) (Found: C, 73·2; H, 10·0. C$_{18}$H$_{30}$O$_3$ requires C, 73·45; H, 10·25%).

The third band afforded *methyl 5α,8α-epoxy-14,15,16-trisnor-9,5-friedo-labdan-13-oate* (34) (20 mg, 20%) as an oil, homogeneous to t.l.c., $\nu_{max.}$ 860, 1000, 1050, 1080, 1140, 1170, 1205, and 1740 cm^{-1}, τ 6·38 (3H, s, CO$_2$Me), 7·82 (2H, m, -CH$_2$CH$_2$·CO$_2$Me), 8·76 (3H, s, -O·CR$_2$$Me$), 8·93 (3H, s, Me at C-9), and 9·02 (3H, s) and 9·28 (3H, s) (Me's at C-4) (Found: C, 73·15; H, 9·9. C$_{18}$H$_{30}$O$_3$ requires C, 73·45; H, 10·25%).

Treatment of Methyl 8β,9β-Epoxy-14,15,16-trisnorlabdan-13-oate (15) with Boron Trifluoride–Ether Complex.—The epoxy-ester (15) (100 mg) was treated with boron trifluoride-ether complex in benzene in the usual manner. Gel formation took place almost instantly. After 1 min potassium carbonate and a few drops of water were added. The product was isolated through chloroform and was applied to one small preparative plate which was then eluted 4 times with light petroleum–ether (4 : 1). The major band afforded 8β-hydroxy-14,15,16-trisnorlabdan-13,19α-olactone (46) (82 mg, 85%) as prisms (from light petroleum), m.p. 168—169°, $\nu_{max.}$ 840, 905, 915, 960, 1000, 1050, 1120, 1185, 1220, 1240, 1775, and 3650 cm^{-1}, τ (CDCl$_3$) 7·45 (2H, m, -CH$_2$CH$_2$·CO·O-), 7·80 (2H, m, -CH$_2$CH$_2$·CO·O-), 8·87 and 8·89 [6H, 2s, -C(OH)Me and Me at C-10), and 9·10 (3H, s) and 9·14 (3H, s) (Me's at C-4) (Found: C, 72·4; H, 9·8%; *m/e*, 280. C$_{17}$H$_{28}$O$_3$ requires C, 72·8; H, 10·05%; *M*, 280).

Reduction of the Lactone (46).—Reduction of the lactone

(46) with lithium aluminium hydride in ether for 30 min under reflux afforded 14,15,16-*trisnorlabdane*-8β,9α,13-*triol* as needles, m.p. 123—124°, τ (CDCl$_3$) 6·34 (2H, m, $W_{\frac{1}{2}}$ 15 Hz, $-CH_2CH_2\cdot OH$), 8·81 [3H, s, $-C(OH)Me$], 8·92 (3H, s, Me at C-10), and 9·12 (3H, s) and 9·16 (3H, s) (Found: C, 71·4; H, 11·5%; *m/e*, 284. C$_{17}$H$_{32}$O$_3$ requires C, 71·8; H, 11·35%; *M*, 284).

Preparation of 6β-*Benzoyloxy*-5,5,9β-*trimethyl*-trans-*decalin*-1-*one* (56).—The method used is indicated in outline only.[16] Resorcinol ⟶ cyclohexane-1,3-dione ⟶ 9-methyl-Δ$^{5(10)}$-octalin-1,6-dione (47% yield) ⟶ 5β-hydroxy-10β-methyl-Δ$^{1(9)}$-octalin-2-one monohydrate (64%) ⟶ 5β-benzyloxy-10β-methyl-Δ$^{1(9)}$-octalin-2-one (86%) ⟶ 5β-benzoyloxy-1,1,10β-trimethyl-Δ^8-octalin-2-one (56%) [plus 5β-benzoyloxy-1,1,3α,10β-tetramethyl-Δ^8-octalin-2-one (18%) (see below)] ⟶ 5β-hydroxy-1,1,10β-trimethyl-Δ^8-octalin-2-one (97%) ⟶ 5β-hydroxy-1,1,10β-trimethyl-*trans*-decalin-2-one (94%) [plus 5,5,9β-trimethyl-*trans*-decalin-1β,6β-diol (4%)] ⟶ 6β-benzoyloxy-5,5,9β-trimethyl-*trans*-decalin-1β-ol (59%) [plus 6α-benzoyloxy-5,5,9β-trimethyl-*trans*-decalin-1β-ol (7%) (see below)] (*via* 1,1,10β-trimethyl-5β-tetrahydropyranyloxy-*trans*-decalin-2-one, 1,1,10β-trimethyl-5β-tetrahydropyranyloxy-*trans*-decalin-2-ol, and 6-benzoyloxy-5,5,9β-trimethyl-1β-tetrahydropyranyloxy-*trans*-decalin: these compounds were not isolated but used directly for the next steps) ⟶ 6β-benzoyloxy-5,5,9β-trimethyl-*trans*-decalin-1-one (95%), m.p. 103—105° (lit.,[10] 92—93·5°). 5β-*Benzoyloxy*-1,1,3α,10β-*tetramethyl*-Δ^8-*octalin*-2-*one* was obtained as prisms (from light petroleum), m.p. 97—99°, ν$_{max.}$ 705, 800, 985, 1025, 1115, 1270, 1655, and 1720 cm^{-1}, τ (CDCl$_3$) 1·87 (2H, m, aromatic), 2·44 (3H, m, aromatic), 4·37 (1H, t, *J* 4 Hz, $-C=CY\cdot CH_2-$), 4·95 (1H, ABX, q, J_{ax-ax} 10, J_{ax-eq} 5 Hz, $-CH\cdot OBz$), 7·35 (1H, m, $-CH\cdot CO-$), 8·69 (3H, s) and 8·71 (3H, s) (*gem*-dimethyl), 8·75 (3H, s, Me at C-10), and 8·87 (3H, d, *J* 7 Hz, $-CO\cdot CH\cdot CH_3$) (Found: C, 77·6; H, 8·2. C$_{21}$H$_{28}$O$_5$ requires C, 77·3; H, 8·05%). 6α-*Benzoyloxy*-5,5,9β-*trimethyl*-trans-*decalin*-1β-*ol* was obtained as needles (from light petroleum), m.p. 131—133°, ν$_{max.}$ 720, 940, 980, 1040, 1120, 1280, 1715, and 3600 cm^{-1}, τ (CDCl$_3$) 1·90 (2H, m, aromatic), 2·50 (3H, m, aromatic) 5·20 [1H, t, *J* 6·5 Hz, $-CH(OBz)-$], 6·00 [1H, m, $W_{\frac{1}{2}}$ 18 Hz, $-CH(OH)-$], and 8·82 (3H, s) and 8·98 (6H, s) (3 × Me) (Found: C, 75·4; H, 8·65. C$_{20}$H$_{28}$O$_3$ requires C, 75·9; H, 8·9%).

Preparation (*in Outline*) *of* 6β-*Hydroxy*-2α,5,5,9β-*tetra-methyl*-trans-*decalin*-1-*one* (57).[11]—This was prepared in 55% yield by reaction of 6β-benzoyloxy-5,5,9β-trimethyl-*trans*-decalin-1-one with diethyl oxalate in benzene in the presence of sodium hydride and the resulting product was methylated with methyl iodide in acetone in the presence of potassium carbonate. Strict control of reaction times was necessary to obtain the yield quoted. The $-CO\cdot CO_2Et$ group was then removed with sodium ethoxide in ethanol.

6β-*Acetoxy*-1,2α,5,5,9β-*pentamethyl*-trans-*decalin*-1-*ols*.—6β-Hydroxy-2α,5,5,9β-tetramethyl-*trans*-decalin-1-one (57) (200 mg) was dissolved in ether (2 ml) and methyl-lithium (1·5M; 5 ml) in ether was added dropwise with stirring under nitrogen. After 30 min saturated ammonium chloride solution was added cautiously; isolation through ether gave an oil which was acetylated. The resulting product was adsorbed on 2 small preparative plates which were eluted 10 times with light petroleum–ether (10 : 1). The

[16] Full details are to be found in M. S. Hadley, D.Phil. Thesis, Oxford University, 1969.

band with higher R_F afforded 6β-*acetoxy*-1β,2α,5,5,9β-*pentamethyl*-trans-*decalin*-1α-*ol* (58) (110 mg, 51%) as prisms (from light petroleum), m.p. 121—122°, ν$_{max.}$ 920, 980, 1035, 1245, 1380, 1730, and 3550 cm^{-1}, τ (CDCl$_3$) 5·46 [1H, m, $W_{\frac{1}{2}}$ 20 Hz, $-CH(OAc)-$], 7·96 (3H, s, OAc), 8·93 [3H, s, $-C(OH)Me$], 9·03 (3H, s, Me at C-9), 9·12 (3H, s) and 9·14 (3H, s) (*gem*-dimethyl), and 9·14 (3H, d, *J* 6·5 Hz, $-CHMe$) (Found: C, 72·1; H, 10·65. C$_{17}$H$_{30}$O$_3$ requires C, 72·3; H, 10·7%).

The band with lower R_F afforded 6β-*acetoxy*-1α,2α,5,5,9-β-*pentamethyl*-trans-*decalin*-1β-*ol* (59) (70 mg, 33%) as prisms (from light petroleum), m.p. 128—130°, ν$_{max.}$ 920, 980, 1035, 1245, 1380, 1730, and 3550 cm^{-1}, τ (CDCl$_3$) 5·49 [1H, m, $W_{\frac{1}{2}}$ 20 Hz, $-CH(OAc)-$], 7·95 (3H, s, OAc), 8·91 [3H, s, $-C(OH)Me$], 8·95 (3H, s, Me at C-9), 9·11 (3H, s) and 9·14 (3H, s) (*gem*-dimethyl), and 9·13 (3H, d, *J* 6·5 Hz, $-CHMe$) (Found: C, 72·05; H, 10·65. C$_{17}$H$_{30}$O$_3$ requires: C, 72·3; H, 10·7%).

Dehydration of 6β-*Acetoxy*-1β,2α,5,5,9β-*pentamethyl*-trans-*decalin*-1α-*ol* (58).—The decalol (58) (100 mg) was dissolved in dry pyridine (1 ml) and phosphoryl chloride (0·3 ml) added dropwise with swirling. The solution was maintained at 45—50° for 8 h, cooled, and poured cautiously onto crushed ice. Isolation through light petroleum gave an oil which was adsorbed from light petroleum on silica gel (5 g). Elution with progressively graded mixtures of light petroleum and ether afforded 6β-*acetoxy*-1,2,5,5,9β-*pentamethyl*-Δ^1-trans-*octalin* (62) (90 mg, 92%) as prisms (from light petroleum), m.p. 55—56°, ν$_{max.}$ 910, 985, 1030, 1240, 1370, and 1730 cm^{-1}, τ 5·58 [1H, ABX q, J_{ax-ax} 11, J_{ax-eq} 5 Hz, $-CH(OAc)-$], 8·02 (3H, s, OAc), 8·48 (6H, s, MeC=CMe), 9·03 (3H, s, Me at C-9), and 9·13 (3H, s) and 9·15 (3H, s) (*gem*-dimethyl), *m/e* 264 (Found: C, 77·0; H, 10·65. C$_{17}$H$_{28}$O$_2$ requires C, 77·2; H, 10·65%).

Dehydration of 6β-*Acetoxy*-1α,2α,5,5,9β-*pentamethyl*-trans-*decalin*-1β-*ol* (59).—The decalol (59) (100 mg) was dehydrated as described above to give 6β-*acetoxy*-2α,5,5,9β-*tetramethyl*-1-*methylene*-trans-*decalin* (64) (90 mg, 92%) as prisms (from light petroleum), m.p. 53—54°, ν$_{max.}$ 900, 980, 1030, 1240, 1370, and 1730 cm^{-1}, τ 5·37 and 5·50 (2H, 2s, $-C=CH_2$), 5·57 [1H, ABX q, J_{ax-ax} 11, J_{ax-eq} 5 Hz, $-CH_2CH(OAc)-$], 7·72 (1H, m, $W_{\frac{1}{2}}$ 35 Hz, $-CH_2CH\cdot Me$), 8·02 (3H, s, OAc), 8·93 (3H, s, Me at C-9), 9·00 (3H, d, *J* 6 Hz, $-CHMe$), and 9·12 (3H, s) and 9·17 (3H, s) (*gem*-dimethyl), *m/e* 264 (Found: C, 77·2; H, 10·5. C$_{17}$H$_{28}$O$_2$ requires C, 77·2; H, 10·65%).

Epoxidation of 6β-*Acetoxy*-1,2,5,5,9β-*pentamethyl*-Δ^1-trans-*octalin* (62).—The octalin (62) (350 mg) was treated with perbenzoic acid in benzene in a similar manner to that previously described. The oil obtained was applied to one large preparative plate and this was eluted 8 times with light petroleum–ether (9 : 1). The band of higher R_F afforded 5β,6β-*epoxy*-1,1,5α,6α,10β-*pentamethyl*-trans-*decalin*-2β-*yl acetate* (70) (100 mg, 27%) as prisms (from light petroleum), m.p. 72—73°, ν$_{max.}$ 890, 910, 955, 990, 1015, 1040, 1100, 1245, 1375, and 1735 cm^{-1}, τ 5·61 [1H, ABX q, J_{ax-ax} 10, J_{ax-eq} 5 Hz, $-CH_2CH(OAc)-$], 8·03 (3H, s, OAc), 8·79 (3H, s, $-\underset{O}{\underset{|}{C}}-C\cdot Me$ at C-6), 8·89 (3H, s, $-\underset{O}{\underset{|}{C}}-C\cdot Me$ at C-5), 8·98 (3H, s, Me at C-10), and 9·18 (3H, s) and 9·20 (3H, s) (*gem*-dimethyl), *m/e* 280 (Found: C, 73·0; H, 10·15. C$_{17}$H$_{28}$O$_3$ requires C, 72·8; H, 10·05%).

The band at lower R_F afforded 5α,6α-*epoxy*-1,1,5β,6β,10β-*pentamethyl*-trans-*decalin*-2β-*yl acetate* (66) (200 mg, 54%) as prisms (from light petroleum), m.p. 69—70°, ν$_{max.}$ 890, 910,

945, 990, 1015, 1040, 1100, 1245, 1375, and 1735 cm⁻¹, τ 5·55 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, -CH(OAc)·CH₂⁻], 8·04 (3H, s, OAc), 8·81 (3H, s, $\overset{-C-C\cdot Me}{\underset{O}{\diagdown\diagup}}$ at C-6, 8·86 (3H, s, $\overset{-C-C\cdot Me}{\underset{O}{\diagdown\diagup}}$ at C-5), 8·99 (3H, s, Me at C-10), and 9·17 (3H, s) and 9·19 (3H, s) (gem-dimethyl), m/e 280 (Found: C, 72·95; H, 10·2. $C_{17}H_{28}O_3$ requires: C, 72·8; H, 10·05%).

Hydrolysis of 5,6-Epoxy-1,1,5,6,10β-pentamethyl-trans-decalin-2β-yl Acetates.—Hydrolysis of the 5α,6α-epoxide (66) with methanolic potassium hydroxide (1%) for 48 h and purification of the product by p.l.c. afforded 5α,6α-*epoxy*-1,1,5β,6β,10β-*pentamethyl*-trans-decalin-2β-*ol* (67) as feathery needles (from light petroleum), m.p. 72—73°, $v_{max.}$ 885, 940, 1010, 1055, 1100, 1385, and 3600 cm⁻¹, τ (CDCl₃) 6·77 [1H, m, $W_{\frac{1}{2}}$ 16 Hz, -CH(OH)·CH₂], 8·75 (3H, s, $\overset{-C-}{\underset{O}{\diagdown\diagup}}$ ·Me at C-6), 8·79 (3H, s, $\overset{-C-C\cdot Me}{\underset{O}{\diagdown\diagup}}$ at C-5), 8·98 (3H, s, Me at C-10), and 9·04 (3H, s) and 9·21 (3H, s) (gem-dimethyl) (Found: C, 75·75; H, 11·15. $C_{15}H_{26}O_2$ requires C, 75·6; H, 11·0%).

Similar hydrolysis of the 5β,6β-epoxide (70) furnished 5β,6β-*epoxy*-1,1,5α,6α,10β-*pentamethyl*-trans-decalin-2β-ol (71) as needles (from light petroleum), m.p. 125—126°, $v_{max.}$ 950, 1020, 1050, 1100, 1385, and 3600 cm⁻¹, τ (CDCl₃) 6·75 [1H, ABX q, J_{ax-ax} 10, J_{ax-eq} 5 Hz, -CH₂CH(OH)-], 8·74 (3H, s, $\overset{-C-C\cdot Me}{\underset{O}{\diagdown\diagup}}$ at C-6), 8·83 (3H, s, $\overset{-C-C\cdot Me}{\underset{O}{\diagdown\diagup}}$ at C-5), 8·96 (3H, s, Me at C-10), and 9·04 (3H, s) and 9·25 (3H, s) (gem-dimethyl) (Found: C, 75·8; H, 11·0. $C_{15}H_{26}O_2$ requires: C, 75·6; H, 11·0%).

6β-Acetoxy-1,5,5,9β-tetramethyl-trans-decalin-1-ols.— The decalone (56) (400 mg) was dissolved in dry ether (4 ml) and an excess of methyl-lithium in ether was added dropwise with stirring under nitrogen. After 30 min saturated ammonium chloride solution was added cautiously; isolation through ether by continuous (12 h) extraction gave an oil which was treated with acetic anhydride (0·4 ml) in pyridine (4 ml) and left at 20° for 24 h. Isolation through ether gave an oil which was adsorbed on one large preparative plate and eluted 10 times with light petroleum–ether (9 : 1). The band of highest R_F gave an oil which was distilled to give 2-phenylpropan-2-ol, b.p. 88—89° at 11 mmHg, m.p. 30—32° (lit.,[17] b.p. 94° at 13 mmHg, m.p. 35—37°). The next band afforded 6β-*acetoxy*-1β,5,5,9β-*tetramethyl*-trans-*decalin-1α-ol* (60) (160 mg, 47%) as prisms (from light petroleum), m.p. 115—116°, τ (CDCl₃) 5·45 [1H, ABX q, J_{ax-ax} 10, J_{ax-eq} 5 Hz, -CHCH(OAc)-], 7·95 (3H, s, OAc), 8·90 [3H, s, -C(OH)Me], 9·02 (3H, s, Me at C-9), and 9·12 (6H, s, Me's at C-5) (Found: C, 71·4; H, 10·3. $C_{16}H_{28}O_3$ requires C, 71·6; H, 10·5%). The third band afforded 6β-*acetoxy*-1α,5,5,9β-*tetramethyl*-trans-*decalin*-1β-*ol* (61) (130 mg, 38%) as prisms (from light petroleum), m.p. 95—96°, τ (CDCl₃) 5·52 [1H, m, $W_{\frac{1}{2}}$ 22 Hz, -CH₂CH(OAc)-], 7·95 (3H, s, OAc), 8·72 [3H, s, -C(OH)Me], 8·94 (3H, s, Me at C-9), and 9·10 (3H, s) and 9·13 (3H, s) (Me's at C-5) (Found: C, 71·7; H, 10·55. $C_{16}H_{28}O_3$ requires C, 71·6; H, 10·5%).

Dehydration of 6β-Acetoxy-1β,5,5,9β-tetramethyl-trans-decalin-1α-ol (60).—The decalol (60) (150 mg) was dehydrated with phosphoryl chloride in pyridine as described above. The oily product was applied to two small preparative plates which were eluted 3 times with light petroleum–ether (20 : 1). The major band gave a compound with m.p. 72—73°.

[17] G. W. Capp and E. G. E. Hawkins, *J. Chem. Soc.*, 1953, 4106.

The n.m.r. spectrum showed it to be only 85% pure, the impurity being the exo-methylene compound. This crude product was applied to two small silica gel–silver nitrate plates which were eluted 5 times with light petroleum–ether (20 : 1). The major band afforded 6β-*acetoxy*-1,5,5,9β-*tetramethyl*-Δ¹-trans-*octalin* (63) (100 mg, 70%) as prisms (from light petroleum), m.p. 79—80°, $v_{max.}$ 810, 920, 1040, 1075, 1180, 1250, 1380, and 1735 cm⁻¹, τ 4·85br (1H, s, $W_{\frac{1}{2}}$ 3·5 Hz, -C=CH·CH₂-), 5·57 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, -CH₂CH-(OAc)-], 8·02 (3H, s, OAc), 8·98 (3H, s, Me at C-9), 9·12 (6H, s, Me's at C-5) (Found: C, 76·6; H, 10·3. $C_{16}H_{26}O_2$ requires C, 76·75; H, 10·45%).

Dehydration of 6β-Acetoxy-1α,5,5,9β-tetramethyl-trans-decalin-1β-ol (61).—The decalol (61) (120 mg) was dehydrated in an analogous manner to that described above. The olefin obtained, m.p. 40—43°, was shown by n.m.r. to consist of 80% exo-methylene compound, the impurity being the olefin obtained as major product in the previous experiment. Purification by p.l.c. using silica gel–silver nitrate plates afforded 6β-*acetoxy*-5,5,9β-*tetramethyl*-1-*methylene*-trans-*decalin* (65) (80 mg, 70%) as prisms (from light petroleum), m.p. 49—50°, $v_{max.}$ 890, 905, 985, 1040, 1100, 1150, 1250, 1380, 1735, and 3030 cm⁻¹, τ 5·53 [3H, s for -C=CH₂ superimposed on m for -CH₂CH(OAc)-], 8·02 (3H, s, OAc), 8·93 (3H, s, Me at C-9), and 9·13 (3H, s) and 9·16 (3H, s) (Me's at C-5) (Found: C, 76·4; H, 10·2. $C_{16}H_{26}O_2$ requires C, 76·75; H, 10·45%).

Isomerisation of 6β-Acetoxy-5,5,9β-tetramethyl-1-methylene-trans-decalin (65).—The decalin (65) (200 mg) was dissolved in benzene (2 ml) and heated under reflux for 4 h with sulphuric acid in methanol (6 ml, 7%). Excess of sodium hydrogen carbonate was then added and the mixture evaporated. The product, isolated by extraction with ether, was acetylated. The acetylated product was applied to two small preparative plates (silica gel–silver nitrate) which were eluted 6 times with light petroleum–ether (20 : 1). The band of higher R_F afforded 6β-*acetoxy*-1,1,5,5-*tetramethyl*-Δ⁹-*octalin* (74) (30 mg, 15%) as needles, m.p. 35—37°, τ 5·37 [1H, ABX q, J_{ax-ax} 8·5, J_{ax-eq} 4·5 Hz, -CH₂CH(OAc)-], 8·01 (7H, s for OAc superimposed on m for -CH_2·C=C·CH_2-), and 9·02 (6H, s) and 9·04 (6H, s) (Me's at C-1 and C-5) (Found: C, 76·2; H, 10·2. $C_{16}H_{26}O_2$ requires C, 76·75; H, 10·45%). The band of lower R_F afforded 6β-acetoxy-1,5,5,9β-tetramethyl-Δ¹-*trans*-octalin (63) (150 mg, 75%) identical by i.r. and n.m.r. with that obtained previously.

Epoxidation of 6β-Acetoxy-1,5,5,9β-tetramethyl-Δ¹-trans-octalin (63).—The octalin (63) (200 mg) was treated with perbenzoic acid in the usual way. The oil obtained was applied to the top of an alumina column (200 g). Careful elution with graded mixtures of light petroleum and ether afforded 5β,6β-*epoxy*-1,1,6α,10β-*tetramethyl*-trans-*decalin*-2β-*yl acetate* (72) (75 mg, 35%) as prisms (from light petroleum), m.p. 69—70°, $v_{max.}$ 720, 775, 905, 955, 1035, 1250, 1380, and 1730 cm⁻¹, τ 5·62 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, -CH₂CH(OAc)-], 7·23 (1H, t, J 1·5 Hz, $\overset{-CH_2C H-C-}{\underset{O}{\diagdown\diagup}}$), 8·02 (3H, s, OAc), 8·89 (3 H, s, $\overset{-C-C-Me}{\underset{O}{\diagdown\diagup}}$), 8·96 (3H, s, Me at C-10), and 9·17 (3H, s) and 9·20 (3H, s) (gem-dimethyl) (Found: C, 72·45; H, 9·85. $C_{16}H_{26}O_3$ requires C, 72·15; H, 9·85%). Further elution afforded 5α,6α-*epoxy*-1,1,5β,10β-*tetramethyl*-trans-*decalin*-2β-*yl acetate* (68) (115 mg, 54%) as plates (from light petroleum), m.p. 119—120°, $v_{max.}$ 680, 920, 960, 990, 1035, 1250, 1380,

and 1730 cm⁻¹, τ 5·57 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, $-CH_2CH(OAc)-$], 7·30 (1H, t, J 2·5 Hz, $-CH_2CH-C-$), 8·86 (3H, s, $-C-C\cdot Me$),
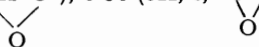
8·94 (3H, s, Me at C-10), and 9·16 (3H, s) and 9·18 (3H, s), (gem-dimethyl) (Found: C, 72·25; H, 9·75. $C_{16}H_{26}O_3$ requires: C, 72·15; H, 9·85%). Hydrolysis of the acetate (68) with methanolic potassium hydroxide (1%) for 48 h and purification of the product by p.l.c. afforded 5α,6α-epoxy-1,1,5β,10β-tetramethyl-trans-decalin-2β-ol (69) as plates, m.p. 129—130° (from light petroleum), τ (CDCl₃) 6·75 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, $-CH_2CH(OH)-$], 7·11 (1H, t, J 2·5 Hz, $-CH_2CH-C-$), 8·80 (3H, s, $-C-C\cdot Me$), 8·93 (3H, s, Me at C-10), and 9·03 (3H, s) and 9·20 (3H, s) (gem-dimethyl) (Found: C, 74·7; H, 10·6. $C_{14}H_{24}O_2$ requires C, 74·95; H, 10·8%). Similar hydrolysis of the acetate (72) afforded 5β,6β-epoxy-1,1,5α,10β-tetramethyl-trans-decalin-2β-ol (73) as prisms (from light petroleum), m.p. 71—72°, τ (CDCl₃) 6·77 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, $-CH_2CH(OH)-$], 7·09br (1H, s, $W_{\frac{1}{2}}$ 4 Hz, $-CH_2CH-C-$), 8·83 (3H, s, $-C-C\cdot Me$), 8·94 (3H, s, Me at C-10), and 9·03 (3H, s) and 9·25 (3H, s) (gem-dimethyl) (Found: C, 74·85; H, 10·9. $C_{14}H_{24}O_2$ requires: C, 74·95; H, 10·8%).

Reduction of 5α,6α-Epoxy-1,1,5β,10β-tetramethyl-trans-decalin-2β-ol (69) with Lithium in Ethylamine.—The decalol (69) (30 mg) was reduced with lithium in ethylamine for 30 min by the procedure described above. The crude product was acetylated; the acetylated product was purified by p.l.c. [one small plate eluted 3 times with light petroleum-ether (4:1)] and proved to be 6β-acetoxy-1β,5,5,9β-tetra-methyl-trans-decalin-1α-ol by m.p., i.r., and n.m.r. comparisons with authentic material.

Reaction of 5α,6α-Epoxy-1,1,5β,6β,10β-pentamethyl-trans-decalin-2β-ol (67) with Boron Trifluoride–Ether Complex.—One drop of a solution (1%) of boron trifluoride ether complex in dry benzene was added to the epoxide (67) (100 mg) in dry benzene (2 ml). Further boron trifluoride–ether solution was added at 15 min intervals until t.l.c. indicated that no starting material remained. After the usual work-up the mixture was acetylated. The crude product was applied to two small preparative plates and these were eluted 6 times with light petroleum-ether (10:1). The band with highest R_F afforded 1,1,6,10β-tetramethyl-5-methylene-Δ⁶-trans-octalin-2β-yl acetate (76) (200 mg, 18%) as an oil, homogeneous to t.l.c., $ν_{max}$ 710, 840, 905, 940, 995, 1035, 1060, 1090, 1115, 1160, 1250, 1380, 1650, and 1735 cm⁻¹, $λ_{max}$ 235 nm (ε 16,000), τ 4·40br (1H, m, $W_{\frac{1}{2}}$ 4 Hz, $-CH_2CH=C-$), 5·22 (2H, s, $-C=CH_2$), 5·55 [1H, m, $W_{\frac{1}{2}}$ 17 Hz, $-CH_2CH(OAc)-$], 8·02 (3H, s, OAc), 8·24 (3H, d, J 1·5 Hz, $-C=C\cdot Me$), and 9·03 (3H, s), 9·05 (3H, s), and 9·13 (3H, s) (Me's at C-1 and C-10), m/e 262. The band with lowest R_F afforded 3β-acetoxy-7α-acetyl-2,2,6β,7β-tetramethyl-trans-bicyclo[4.3.0]nonane (77) (75 mg, 70%) as plates (from light petroleum), m.p. 106—107°, $ν_{max}$ 910, 920, 975, 990, 1005, 1040, 1080, 1100, 1120, 1200, 1250, 1380, 1695, and 1735 cm⁻¹, τ 5·68 [1H, ABX q, J_{ax-ax} 10, J_{ax-eq} 5·5 Hz, $-CH_2CH(OAc)-$], 7·94 (3H, s, COMe), 8·04 (3H, s, OAc), 8·83 [3H, s, $-C(Me)\cdot CO-$], 9·05 (3H, s), 9·09 (3H, s), and 9·13 (3H, s), m/e 280 (Found: C, 72·9; H, 10·1. $C_{17}H_{28}O_3$ requires C, 72·8; H, 10·05%).

Reaction of 5β,6β-Epoxy-1,1,5α,6α,10β-pentamethyl-trans-decalin-2β-ol (71) with Boron Trifluoride–Ether Complex.—Similar treatment of the epoxide (71) (100 mg) with boron trifluoride–ether gave a very complex mixture (t.l.c. indicated at least 8 components). After acetylation, the mixture was chromatographed first on a silica gel column and then on preparative plates. This afforded two pure compounds; the first was 6β,9β-epoxy-1,1,2α,5,5-pentamethyl-trans-decalin-2β-ol (80) (10 mg, 9%), prisms, m.p. 75—76°, $ν_{max}$ 735, 780, 920, 940, 980, 1015, 1050, 1085, 1125, 1170, 1195, 1235, 1340, 1380, and 3550 cm⁻¹, τ 6·17 (1H, d, J 4 Hz, $-CH_2CH\cdot O-$), 6·87 (1H, s, D₂O exchangeable, $-OH$), 8·97 (9H, s), 9·00 (3H, s), and 9·10 (3H, s), m/e 238.

The second compound was 6β-acetoxy-1,1,2α,5,5-penta-methyl-Δ⁹-octalin-2β-ol (81) (30 mg, 27%), prisms, m.p. 117—118°, $ν_{max}$ 930, 990, 1045, 1080, 1250, 1380, 1735, and 3600 cm⁻¹, τ 5·36 [1H, ABX q, J_{ax-ax} 9, J_{ax-eq} 4 Hz, $-CH_2CH-(OAc)-$], 7·98 (3H, s, OAc), 8·90 [3H, s, $-C(OH)Me$], and 8·99 (6H, s), 9·02 (3H, s), and 9·04 (3H, s) (gem-dimethyls), m/e 280 (Found: C, 72·3; H, 9·8. $C_{17}H_{28}O_3$ requires C, 72·8; H, 10·05%).

Reaction of 5α,6α-Epoxy-1,1,5β,10β-tetramethyl-trans-decalin-2β-ol (69) with Boron Trifluoride–Ether Complex.—Similar treatment of the epoxide (69) (80 mg) with boron trifluoride–ether complex in benzene gave a product which t.l.c. showed to be almost exclusively one component. The product was acetylated and then applied to one small preparative plate which was eluted 5 times with light petroleum-ether (10:1). The only significant band was removed and afforded 1,1,5,5-tetramethyl-Δ⁹-octalin-2β,6α-diyl diacetate (82) (90 mg, 85%) as needles, m.p. 131—132° (from light petroleum), $ν_{max}$ 970, 1035, 1055, 1185, 1250, 1380, and 1735 cm⁻¹ τ 5·28 [2H, ABX q, J_{ax-ax}, J_{ax-eq} 4 Hz, $-CH_2CH(OAc)-$], 7·99 [10H, 6H s for $-(OAc)_2$ superimposed on 4H m for $-CH_2\cdot C=C\cdot CH_2-$], 8·23 (4H, m, $-CH_2CH_2\cdot C=C\cdot CH_2CH_2-$), and 8·98 (6H, s) and 9·01 (6H, s) (gem-dimethyl), m/e 308 (Found: C, 69·65; H, 8·8. $C_{18}H_{28}O_4$ requires: C, 70·1; H, 9·15%).

Reaction of 5β,6β-Epoxy-1,1,5α,10β-tetramethyl-trans-decalin-2β-ol (73) with Boron Trifluoride–Ether Complex.—Similar treatment of the epoxide (73) (60 mg) with boron trifluoride–ether complex in benzene gave a product which was applied to one small preparative plate and this was eluted 6 times with light petroleum-ether (1:1). The band with higher R_F afforded 6β,9β-epoxy-1,1,5,5-tetramethyl-trans-decalin-2β-ol (84) (9 mg, 15%) as plates, m.p. 45—47°, $ν_{max}$ 820, 915, 970, 1050, 1100, 1160, 1240, 1300, 1340, 1375, and 3500 cm⁻¹, τ 6·15 (1H, d, J 4·5 Hz, $-CH_2CH\cdot O-$), 6·75 [1H, m, $W_{\frac{1}{2}}$ 16 Hz, $-CH_2CH(OH)-$], and 8·95 (3H, s), 8·98 (6H, s), and 9·12 (3H, s) (gem-dimethyls), m/e 224 ($C_{14}H_{24}O_2$ requires m/e, 224). The band with lower R_F afforded a *diol* which was acetylated to give 1,1,5,5-tetra-methyl-Δ⁹-octalin-2β,6β-diyl diacetate (86) (55 mg, 70%) as rods (from light petroleum), m.p. 105—107°, $ν_{max}$ 915, 985, 1035, 1100, 1250, 1380, and 1735 cm⁻¹, τ 5·38 [2H, ABX q, J_{ax-ax} 10, J_{ax-eq} 4 Hz, $-CH_2CH(OAc)-$], 7·99 [10H, 6H s for (OAc)₂ superimposed on 4H m for $-CH_2\cdot C=C\cdot CH_2$], 8·23 (4H, m, $-CH_2CH_2\cdot C=C\cdot CH_2CH_2-$), and 8·99 (6H, s), and 9·01 (6H, s), m/e 308 (Found: C, 69·95; H, 9·2. $C_{18}H_{28}O_4$ requires C, 70·1; H, 9·15%).