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SeO_2/H_2O_2 OXIDATIONS OF EXOCYCLIC OLEFINS

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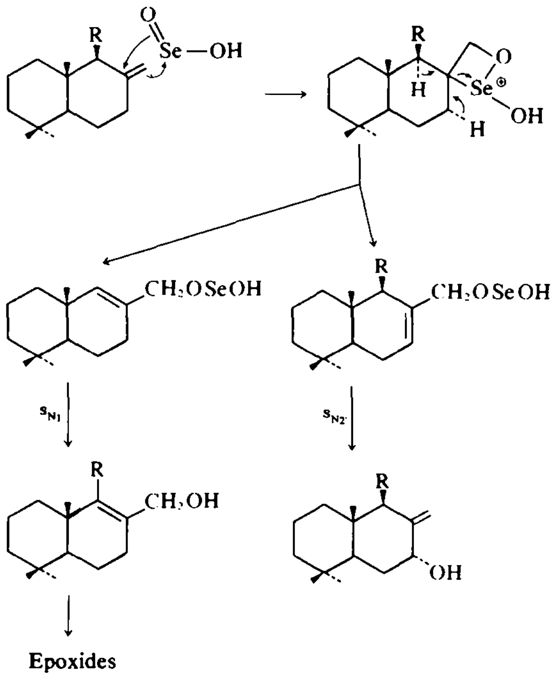
Abstract—Unlike endocyclic olefins the major product from the SeO_2/H_2O_2 oxidation of exocyclic olefins is the same allylic alcohol as from the uncatalysed oxidation. Minor products derived from epoxide intermediates were investigated. The use of SeO_2 as an allylic oxidant for olefins has been extensively investigated, the functionality of the product being to a degree solvent dependent. Although the earlier mechanism of Guillemonat[2] is incorrect, his rules for the prediction of the position of oxidation still remain valid. A survey by Tratchenburg[3] of the current position in SeO_2 oxidation postulates allylic oxidation as proceeding through the intermediacy of an oxaselenocyclobutane to a selenite ester which is solvated by competitive unimolecular (S_N1) and bimolecular (S_N2') processes (Scheme 1).



Scheme 1.

Metal oxide catalysed hydrogen peroxide oxidation is known as an effective method[4] for the hydroxylation of olefins. Whether the product is the *cis* or *trans* diol depends on the choice of metal oxide catalyst, a wide range of which have been investigated. Using selenium dioxide as catalyst gave trans diols and product analyses suggested the intermediacy of epoxide moieties, although in the first reported oxidations no epoxides were isolated. Tanaka[5] later reported the isolation of epoxides exclusively (independent of solvent or water content) in an investigation of 8- and 12-membered cyclic olefins. The formation of diols, attributed to the hydrolytic opening of the oxirane ring, was dependent on steric hindrance and internal strain. In view of the isolation of epoxides and epoxide ring opening products, together with the reported Baeyer–Villiger oxygen insertion reactions on ketones, the presence of an oxidising species having a peroxy acid function, peroxyselenous acid, was postulated.[3]

Few examples of the selenium dioxide/hydrogen peroxide oxidation of terminal exocyclic olefins have been reported; α-pinene gave the allylic alcohol as the only reported product.[6] In this instance the product is the same as the normal (uncatalysed) selenium dioxide oxidation product.

We have investigated the SeO_2/H_2O_2 oxidation of a range of terminal exocyclic methylenes and have established that in contrast to endocyclic olefins the addition of H_2O_2 to the conventional SeO_2 allylic oxidation does not alter the nature of the major oxidation products which are still those predicted by the Tratchenburg mechanism. Additional minor products were isolated which can be accounted for by epoxidation after allylic oxidation followed by neighbouring group participation. Although a simple epoxide product was isolated for one substrate no diol products from epoxide openings were detected from any of the substrates investigated.

The alkene system most extensively examined was the 8(17)-exocyclic methylene of various labdane derivatives. In all SeO_2 oxidations of this olefinic system the major product was the allylic 7α-alcohol. The orientation of the OH group was unequivocally established by the unusually low-field signal of the 7β carbinol proton which, being coplanar with the exocyclic double bond, was extensively deshielded.

14,15 - *Dinorlabd* - 8(17) - *ene* (**1**). SeO_2/H_2O_2 oxidation gave 14,15 - dinorlabd - 8(17) - en - 7α - ol (**2**) together with three isomeric minor products, all $C_{18}H_{32}O_2$ epoxides. The first of these was established as 8,17 - epoxy - 14,15 - dinorlabdan - 7α - ol (**3**) by its synthesis from the allylic alcohol product (**2**) by epoxidation. The remaining two epoxides possessed spectral data (Table 1) consistent with their formulation as the isomers 8,9 - epoxy - 14,15 - dinorlabdan - 17 - ol (**4**) and 8β,9β - epoxy - 14,15 - dinorlabdan - 17 - ol (**5**).

The isomer with the C-17 protons at lowest field was assigned as the β-epoxide since models show that the C-17 hydroxymethyl group is more axial in this isomer. In addition the C-10 Me group was at lower field being closer to the epoxidic oxygen, although it is to be noted that an α-epoxide, αβ to an angular Me produces a large shift in that Me signal.[7] Further, the C-4β Me appeared at higher

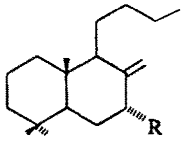
Table 1. PMR data for 8,9-epoxides and reduction products

	Ring A Methyls			
	10β	4β	4α	C-17 protons
8,9-Epoxy-14,15-dinorlabdan-17-ol (4)	1.03	0.81	0.83	3.52
8β,9β-Epoxy-14,15-dinorlabdan-17-ol (5)	1.06	0.78	0.84	3.62
14,15-Dinor-8α-labdane-9α,17-diol (7)	0.89	0.83	0.89	4.04, 3.52, J_{AB}12, J_{BX}2.2, J_{BX}1.8
14,15-Dinorlabdane-8β,17-diol (6)	0.98	0.85	0.87	3.52, 3.23, J_{AB}11

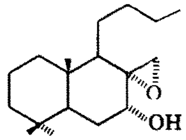
field due to increased shielding of the epoxide ring. Confirmation of these assignments was obtained by LAH reductions; in each case the C-17 OH group enhanced the diaxial opening of the epoxides. The β epoxide (**5**) gave 14,15 - dinorlabdane - 8β, 17-diol (**6**) having a low-field C-10 Me signal (δ 0·98) consistent with an 8β OH group while the C-17 protons appeared as an AB system (H_A 3·52, H_B 3·23, J_{AB} 11 Hz), typical of an equatorial hydroxymethyl group.[8] Reduction of the α epoxide (**4**) gave 14,15 - dinor - 8α - labdane - 9α,17 - diol (**7**) in which the C-17 protons appeared as the AB part of an ABX system. The C-10 Me signal (δ 0·89) was consistent with the presence of a 9α-OH grouping.[9]

8(17) - *Labden* - 13 - *ol* (**8**). SeO_2/H_2O_2 oxidation gave two products, the allylic alcohol, 8(17)-labdene-7α,13-diol (**9**) and a compound $C_{20}H_{34}O_3$ which showed OH (3400 cm^{-1}) and extensive C–O (1104, 1045, 991 cm^{-1}) absorptions and was identified from spectral and degradative data as 9,13 - epoxylabdane - 8β,17 - diol (**10**). The lower than normal C-13 Me signal (δ 1·21) implied an ether linkage to C-13 while the AB system (H_A 3·71, H_B 3·46, J_{AB} 10 Hz) was consistent with an equatorial or axial hydroxymethyl at C-8. The presence of a low-field ring A Me signal (δ 1·08) indicated an 8β-OH and consequently an 8α-hydroxymethyl. Thus the ether was probably attached to C-9.

Acetylation with acetic anhydride/pyridine gave the hydroxy-acetate (**11**) [3480 cm^{-1} (OH); 1720, 1232 cm^{-1}, δ 2·08 (acetate)]. The slightly lower field signal for the equatorial acetoxymethyl (δ H_A 4·22, H_B 4·10, J_{AB} 11 Hz) was consistent with the proposed environment. Treatment of the epoxy diol (**10**) with lead tetraacetate gave the ketone, 9,13 - epoxy - 17 - norlabdan - 8 - one (**12**), showing CO absorption at 1719 cm^{-1}. The C-13 Me resonance at δ 1·01 indicated extensive shielding consistent with a cyclic ether holding the side chain in a fixed position. Dreiding models show that such shielding is expected for the proposed structure (**12**), provided that the normal labdane C-13 stereochemistry has been retained. The octant rule[10] predicts a more positive C.E. maximum for **12** than for 13 - acetoxy - 17 - norlabdan - 8 - one (**13**) where the side chain is not fixed in a positive octant. This is in accord with the observed *a* values (−42·70 and −65·88 respectively). The structure of the ketone was unequivocally established as 9,13 - epoxy - 17 - norlabdan - 8 - one (**12**) by its synthesis from 9,13 - epoxy - 8(17) - labdene (**14**), a by-product from the allylic



1: R = H
2: R = OH



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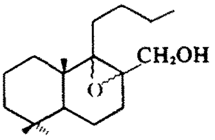
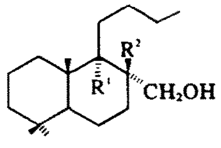
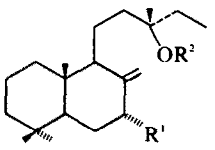


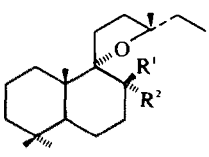
4: α epoxide
5: β epoxide



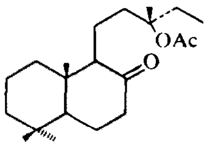
6: R¹ = H, R² = OH
7: R¹ = OH, R² = H



8: R¹ = R² = H
9 R¹ = OH, R² = H
16: R¹ = H, R² = Ac
17: R¹ = OH, R² = Ac
46: R¹ = OAc, R² = H



10: R¹ = OH, R² = CH₂OH
11: R¹ = OH, R² = CH₂OAc
12: R¹,R² = =O
14: R¹,R² = =CH₂
15: R¹ = CH₂OH, R²OH



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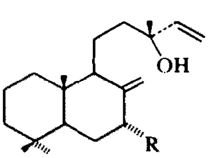
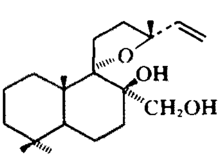


18: R = H
19: R = OH



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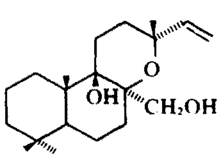

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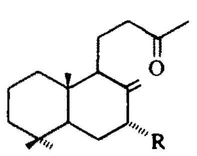
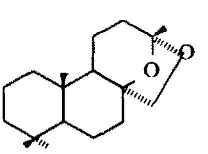


22: R = H
23: R = OH



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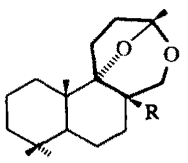


25: R = OH
26: R = Cl

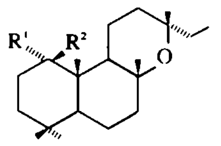
bromination/hydrolysis[11] of 8(17) - labden - 13 - ol (8). Treatment of the epoxy-alkene with osmic acid in pyridine gave 9,13 - epoxylabdane - 8,17 - diol (15) which was cleaved with tetraacetate to 9,13 - epoxy - 17 - norlabdan - 8 - one (13) identical to that previously obtained. As the SeO_2/H_2O_2 product was different from the 8α,17-diol (15) yet cleaved to the same ketone it must be the C-8 epimer, 9,13 - epoxylabdane - 8β,17 - diol (10). This product is derived through the intermediacy of the β-epoxide corresponding to 5 which undergoes nucleophilic attack by the suitably placed C-13 OH group. The corresponding oxidation of 13 - acetoxy - 8(17) - labdane (16) where the C-13 OH group is protected from participation gave only the allylic alcohol, 13 - acetoxy - 8(17) - labdan - 7α - ol (17).

8(17),14 - *Labdadien* - 13 - *ol* (18). SeO_2/H_2O_2 oxidation gave two products. The allylic alcohol, 8(17),14 - labdadiene - 7α,13 - diol (19) obtained was identical in all respects with that from *Dacrydium kirkii.*[12] The fact that the optical rotations were the same established conclusively that the naturally occurring compound has the normal labdane C-13 stereochemistry. The other product was the epoxy diol, 9,13 - epoxy - 14 - labdene - 8β,17 - diol (20), analogous to 10. Despite considerable effort the epoxy diol (21) corresponding to nucleophilic opening of the α-epoxide by the C-13 OH could not be detected.

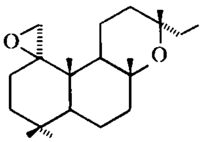
It is significant that no product derived from an 8α,9α-epoxide was isolated from the oxidation of an olefin containing an oxygen function at C-13. It is possible that H-bonding to the peracid species directs epoxidation to the β-face.

14,15 - *Dinorlabd* - 8(17) - *en* - 13 - *one* (22). SeO_2/H_2O_2 oxidation gave two products, the major one again being the allylic alcohol, 7α - hydroxy - 14,15 - dinorlabd - 8(17) - en - 13 - one (23). The second product, $C_{18}H_{30}O_3$ showed OH absorption (3420 cm^{-1}) and extensive C–O (1070, 1052, 1020 cm^{-1}) absorption. The Me signal at δ 1·44 was characteristic of a $CH_3{-}\underset{\overset{|}{O}}{C}{-}O$ moiety as in the intramolecular ketal (24) and a low-field ring A Me signal (δ 1·05) indicated an 8β oxygen function. The magnitude of J_{AB} (11 Hz) for the C-17 methylene protons eliminated the possibility of the usual 5-membered ketal system. It was shown to be a tertiary alcohol since it did not acetylate with acetic anhydride/pyridine and showed no other low-field carbinol proton signals so that the C-17 methylene must be involved in a 6- or larger-membered ring system. This data, together with previous product analyses lead to its formulation as the intramolecular ketal, 9,13; 13,17 - diepoxy - 14,15 - dinorlabdan - 8β - ol (25) formed via the intermediacy of an 8β,9β - epoxy - 17 - hydroxymethyl derivative (analogous to 5) with concomittant ketalisation. An 8α, 9α-epoxide would give rise to the normal 5-membered ketal system. Attempts to dehydrate the hydroxy ketal (25) using thionyl chloride/pyridine gave the chloro derivative (26).

1 - *Methylene* - 8,13 - *epoxylabdane* (27). An epoxide (28), identical to the epoxide prepared by treatment of the alkene (27) with *m*-chloroperbenzoic acid, was the sole product; no allylic alcohol was detected. The epoxide was assigned a 1β,1′-configuration since the downfield spin-pair of the epoxidic AB system exhibited large long-range coupling (J 2·2 Hz), consistent with a pseudo-axial methylene group.[13] Epoxidation of the alkene (27) from the β face is also consistent with the hydride reduction of 8,13 - epoxylabdan - 1 - one (29) which gives the α(axial) and β(equatorial) alcohols in a 9:1 ratio.[14] LAH reduction of the epoxide gave 1α - methyl - 8,13 - epoxylabdan - 1β - ol (31). This assignment was confirmed by a comparison



27: R¹,R² = =CH₂
29: R¹,R² = =O
30: R¹ = R² = H
31: R¹ = CH₃, R² = OH
32: R¹ = H, R² = OH
33: R¹ = OH, R² = H
34: R¹ = OH, R² = CH₃



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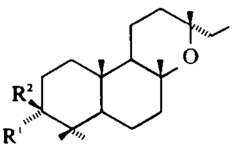
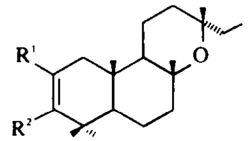
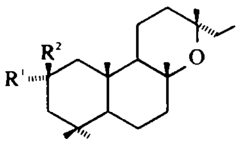


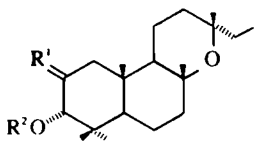
35: R¹,R² = =CH₂
36: R¹,R² = =O
44: R¹ = OH, R² = H
45: R¹ = OAc, R² = H



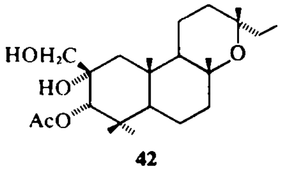
37: R¹ = H, R² = CH₂OH
47: R¹ = CH₂OH, R² = H
48: R¹ = CH₂OCH₃, R² = H
51: R¹ = CHO, R² = H



38: R¹,R² = =CH₂
39: R¹,R² = =O
50: R¹ = OH, R² = CH₂OH



40: R¹ = CH₂, R² = H
41: R¹ = CH₂, R² = Ac
43: R¹ = O, R² = Ac



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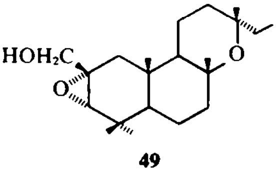

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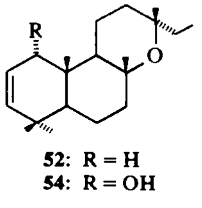
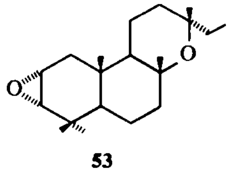


52: R = H
54: R = OH



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of the ring A Me signals in pyridine with those of the epimeric 8,13 - epoxylabdan - 1 - ols (**32** and **33**) (Table 2).

Methyl magnesium iodide on 8,13 - epoxylabdan - 1 - one (**29**) gave 1β - methyl - 8,13 - epoxylabdan - 1α - ol (**34**) and 1α - methyl - 8,13 - epoxylabdan - 1β - ol (**31**) in a 5:2 ratio, the latter product being identical to the LAH reduction product of the epoxide (**28**). Methyl lithium on the ketone (**29**) gave only 1β - methyl - 8,13 - epoxylabdan - 1α - ol (**34**).

Table 2. PMR data for 1-substituted 8,13-epoxylabdane derivatives (C_5D_5N)

	Methyl signals						
	10β	4β	4α	C-14	C-1	13β	8β
8,13-Epoxylabdane (30)	0.72	0.76	0.82	0.89(t)		1.16	1.24
1α-Methyl-8,13-epoxylabdan-1β-ol (31)	0.81	0.84	1.11	0.91(t)	1.41	1.17	1.34
8,13-Epoxylabdan-1β-ol (32)	0.79	0.81	1.00	0.91(t)		1.18	1.32
8,13-Epoxylabdan-1α-ol (33)	0.79	0.82	0.88	0.87(t)		1.20	1.33
1β-Methyl-8,13-epoxylabdan-1α-ol (34)	0.78	0.85	0.85	0.84(t)	1.43	1.15	1.32

3 - *Methylene* - 8,13 - *epoxylabdane* (**35**). The rearranged allylic alcohol, 3 - hydroxymethyl - 8,13 - epoxylabd - 2 - ene (**37**) was the sole product. The C-2 olefinic proton appeared as a doublet since models show that the dihedral angle (2,1α) is close to 90°.

2 - *Methylene* - 8,13 - *epoxylabdane* (**38**). SeO_2/H_2O_2 oxidation gave four products. Although not the major component the allylic alcohol, 2 - methylene - 8,13 - epoxylabdan - 3α - ol (**40**) was isolated. That the OH group was at C-3 and not at the alternative allylic position, C-1, was established by conversion to the acetate (**41**) which was hydroxylated with osmic acid in pyridine to the diol acetate (**42**). Periodate cleavage of **42** gave the ketoacetate, 3α - acetoxy - 8,13 - epoxylabdan - 2 - one (**43**) identical with a sample prepared by the acetoxylation of 8,13 - epoxylabdan - 2 - one (**39**) with lead tetraacetate.[15] This interconversion also established the α orientation of the OH group in **40** which was initially in doubt when the C-3 carbinol proton appeared at markedly higher field (δ 3·61) than usual (*cf* 8(17) - labdene - 7α,13 - diol, **9** at δ 5·03). Ring A Me signals were in good agreement with those predicted from addivity values and thus eliminated the possibility that ring A existed in a twist conformation in which the 3β proton was removed from the deshielding zone of the exocyclic methylene at C-2. In contrast the allylic acetate (**41**) showed the expected deshielding of the carbinol proton (δ 5·12) (*cf* 7α - acetoxy - 8(17) - labden - 13 - ol, **46** at δ 5·40).

The major product of the oxidation, $C_{21}H_{36}O_2$, showed OH absorption (3400 cm^{-1}) and was identified as the unsaturated alcohol, 2-hydroxymethyl-8,13-epoxylabd-2 - ene (**47**) from spectroscopic data. The C-3 olefinic proton (δ 5·37) was long-range coupled to the 1α-proton ($\theta_{3/1\alpha}$ 90°). The third product, $C_{21}H_{36}O_3$, was identified as the epoxy alcohol, 2β - hydroxymethyl - 2α,3α;8,13 - diepoxylabdane (**49**) and its structure confirmed by epoxidation of the previously isolated unsaturated alcohol (**47**). The direction of opening of this epoxide on LAH reduction was controlled by the β-hydroxymethyl group and the abnormal opening product obtained, 2β - hydroxymethyl - 8,13 - epoxylabdan - 2α - ol (**50**), was cleaved by periodate to 8,13 - epoxylabdan - 2 - one (**39**). The fourth product, $C_{21}H_{34}O_2$ showed aldehyde absorption (2710, 1695 cm^{-1}, δ 9·44) and was formulated as 2 - formyl - 8,13 - epoxylabd - 2 - ene (**51**). The C-3 olefinic proton was long range coupled ($J_{3/\alpha}$ 3 Hz) to the 1α-proton. The UV absorption maximum at 231 nm was consistent with this structure.

SeO_2 oxidation of 8(17),14 - labdadien - 13 - ol (**18**) gave allylic alcohol 8(17),14 - labdadiene - 7α,13 - ol (**19**) in 54% yield but none of the other products which were isolated when using the SeO_2/H_2O_2 oxidant.

SeO_2/H_2O_2 oxidation of the endocyclic olefin 8,13 - epoxylabd - 2 - ene (**52**) was in accord with the findings of Tanaka[5] and gave only 2α,3α;8,13 - diepoxylabdane (**53**), no hydroxylated product or allylic alcohol being detected. Oxidation of the olefin (**52**) with SeO_2 alone gave a good yield of the allylic alcohol, 8,13-epoxylabd-2-en-1-ol (**54**).

The Tratchenburg mechanism as applied to the oxidation of the 8(17)-exocyclic methylene compounds is shown in Scheme 1. Preferential abstraction of the proton from the allylic methylene (C-7) rather than from the allylic methine (C-9) is in accord with the observations of Guillemonat.[2] An experiment using 7β - deuterio - 14,15 - dinorlabd - 8(17) - ene (**1** with 7βD) yielded 7β - deuterio - 14,15 - dinorlabd - 8(17) - en - 7α - ol (**2** with 7βD), showing that the initial hydrogen abstraction occurs from the α-face.

The tetrasubstituted olefinic selenite esters undergo S_N1 hydrolysis whereas the trisubstituted olefinic selenite esters predominantly undergo S_N2' hydrolysis since the stereochemical requirements are more readily attained. The greater reactivity of the more highly substituted double bond to electrophilic attack accounts for the greater predominance of products derived from the epoxidation of the Δ^8 alcohols as compared to those from the disubstituted double bonds. The oxidation of 1 - methylene - 8,13 - epoxylabdane (**28**) is anomalous. The isolation, in low yield, of only an epoxide and no product derived from the intermediate selenite ester suggests steric hindrance to its formation from the C-11 methylene.

EXPERIMENTAL†

Selenium dioxide on 14,15 - *dinorlabd* - 8(17) - *ene* (1)

Compound **1** (5·4 g) in dioxan (100 ml) was stirred with SeO_2 (2·5 g) and H_2O_2 (20 ml, 30%) at r.t. for 2½ days. Work up by dilution and ether extraction gave crude material (6·1 g). Chromatography (180 g alumina) gave:

(i) 20% EtOAc/Hexane—14,15 - *dinorlabd* - 8(17) - *en* - 7α - *ol* (**2**) (2·9 g) distilled 74°/0·03 mm., m.p. 43–45°; ν_{max} 3340(OH); 3080, 1635, 1408, 895(C=CH_2); 1198, 1163, 1140, 1117, 1080, 1045, 1033, 994(CO) cm^{-1}; PMR: Me's at δ 0·65, 0·80, 0·88, 0·93 (tr, J 7 Hz); C=$C\underline{H}_2$ 4·35, 4·62; $C\underline{H}OH$ as a multiplet 5·02 (W/2 3 Hz). (Found: C, 81·5; H, 12·1. $C_{18}H_{32}O$ requires: C, 81·8; H, 12·2%).

(ii) EtOAc—A mixture which further resolved on PLC (6 × 30% ether/hexane) into:

(a) The upper band—8(17) - *epoxy* - 14,15 - *dinorlabdan* - 7α - *ol* (**3**) (0·2g), distilled 85°/0·02 mm, m.p. 69–70°; ν_{max} 3400 (OH); 3030, 1480, 963, 943, 914, 886, 842, 811, 770, 720 (epoxide); 1193, 1105, 1054, 1034 (CO) cm^{-1}; PMR: Me's at δ 0·78, 0·82, 0·85 (tr, J 7 Hz), 0·91; epoxide protons as an AB system H_A 2·83, H_B 2·54 (J_{AB} 4 Hz); $C\underline{H}OH$ as a multiplet 3·44 (W/2 4Hz). (Found: C, 77·1; H, 11·5. $C_{18}H_{32}O_2$ requires: C, 77·1; H, 11·5%).

(b) The middle band—8,9 - *epoxy* - 14,15 - *dinorlabdan* - 17 - *ol* (**4**) (0·5 g), distilled 90°/0·2 mm; ν_{max} 3435 (OH); 970, 940, 910, 877, 860, 838, 814, 770, 730, 690, 662 (epoxide); 1170, 1110, 1038 cm^{-1}; PMR: Me's at δ 0·81, 0·83, 0·88 (tr, J 7 Hz), 1·03; C-17 protons

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†For general details see Part 1.[16]

3·52. (Found: C, 76·9; H, 11·5. $C_{18}H_{32}O_2$ requires: C, 77·1; H, 11·5%).

(c) The lower band—8β,9β - *epoxy* - 14,15 - *dinorlabdan* - 17 - *ol* (**5**) (0·3 g), distilled 90°/0·02 mm. ν_{max} 3435 (OH); 974, 820, 889, 877, 862, 839, 818, 724, 694 (epoxide); 1160, 1096, 1036, 1000, 974 (CO) cm^{-1}; PMR: Me's at δ 0·78, 0·84, 0·88 (tr, J 7 Hz), 1·06; C-17 protons 3·64. (Found: C, 77·3; H, 11·5. $C_{18}H_{32}O_2$ requires: C, 77·1; H, 11·5%).

Selenium dioxide on 7β - *deuterio* - 14,15 - *dinorlabd* - 8(17) - *ene* (**1** *with* 7βD)

Repetition of the above experiment using **1**[13] with 7βD gave **2** with 7βD. PMR. showed no multiplet at δ 5·02; *m/e* 265 (M^+).

14,15 - *Dinor* - 8α - *labdane* - 9,17 - *diol* (**7**). Compound **4** (450 mg) in dry ether (15 ml) was refluxed with excess LAH for 6 hr. Excess LAH was destroyed with wet ether and then water, the complex hydrolysed with H_2SO_4 (10 ml, 10%) and the mixture ether extracted. Removal of solvent followed by PLC, (70% ether/hexane) gave 14,15 - *dinor* - 8α - *labdane* - 9,17 - *diol* **7** (408 mg), sublimed 100°/0·015 mm., m.p. 128–129°; ν_{max} 3300 (OH); 1165, 1112, 1068, 1045, 1013 (CO) cm^{-1}; PMR: Me's at δ 0·83, 0·89, 0·89, 0·90 (tr, J 7 Hz); C-17 protons as the AB portion of an ABX system H_A 4·04, H_B 3·52 (Apparent coupling constants, J_{AB} 12, J_{AX} 2·2, J_{BX} 1·8 Hz). (Found: C, 76·7; H, 12·1. $C_{18}H_{36}O_2$ requires: C, 76·5; H, 12·1%).

14,15 - *Dinorlabdane* - 8β,17 - *diol* (**6**). Compound **5** (180 mg) in dry ether (10 ml) was refluxed with excess LAH for 6 hr. Work up as for **7** followed by PLC (70% ether/hexane) gave 14,15 - *dinorlabdane* - 8β,17 - *diol* **6** (160 mg), sublimed 96°/0·02 mm., m.p. 123–124°. ν_{max} 3395 (OH); 1179, 1053, 1040 (CO) cm^{-1}; PMR: Me's at δ 0·85, 0·87, 0·88 (tr, J 7 Hz), 0·98; C-17 protons as an AB system H_A 3·52, H_B 3·23 (J_{AB} 11 Hz). (Found: C, 76·8; H, 12·1. $C_{18}H_{36}O_2$ requires: C, 76·5; H, 12·1%).

Selenium dioxide/hydrogen peroxide on 8(17) - *labden* - 13 - *ol* (**8**)

A soln of **8** (15 g) in dioxan (70 ml) with H_2O_2 (25 ml, 30%) and SeO_2 (2 g) was stirred at r.t. for 24 hr. The product (14·9 g) was absorbed onto alumina (1000 g deactivated with 80 ml water). Elution gave:

(i) 45% ether/hexane—9,13 - *epoxylabdane* - 8β,17 - *diol* (**10**) (1·7 g), distilled 104°/0·015 mm., m.p. 53–56°; ν_{max} 3405 (OH); 1104, 1045, 1001, (CO) cm^{-1}; PMR: methyls at δ 0·83, 0·87, 0·92 (tr, J 7 Hz), 1·08, 1·21; C-17 protons as an AB system H_A 3·71, H_B 3·46 (J_{AB} 10 Hz). (Found: C, 74·4; H, 11·2. $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%).

(ii) 60% ether/hexane—8(17) - *labdene* - 7α,13 - *diol* **9** (5·1 g), identical (mmp, IR, PMR) with an authentic sample;[12] ν_{max} 3320, 3280 (OH); 3080, 1640, 900 ($C{=}CH_2$); 1145, 1045, 1030 (CO) cm^{-1}; PMR: Me's at δ 0·68, 0·81, 0·89, 0·89 (tr, J 7 Hz), 1·15: $C{=}CH_2$ 4·38, 4·68; $C\underline{H}OH$ 5·04 (W/2 3 Hz).

17 - *Acetoxy* - 9,13 - *epoxylabdan* - 8β - *ol* (**11**). Compound **10** (80 mg) was treated for 24 hr at r.t. with dry pyridine (1·5 ml) and Ac_2O (1·5 ml). Dilution with water, ether extraction, washing with dil HCl, sat $NaHCO_3$ and water and removal of solvent followed by PLC (65% ether/hexane) gave 17 - *acetoxy* - 9,13 - *epoxy labdan* - 8β - *ol* **11** (80 mg), distilled 90°/0·02 mm., m.p. 84–84·5°; ν_{max} 3480 (OH); 1720, 1232 (acetate); 1185, 1130, 1099, 1049, 990 (CO) cm^{-1}; PMR: Me's at δ 0·82, 0·86 (tr, J 7 Hz), 0·88, 1·09, 1·25; acetate methyl 2·08; C-17 protons as an AB system H_A 4·22, H_B 4·10 (J_{AB} 11 Hz). (Found: C, 72·1; H, 10·6. $C_{22}H_{38}O_4$ requires: C, 72·1; H, 10·5%).

9,13 - *Epoxy* - 17 - *norlabdan* - 8 - *one* (**12**). To a stirred soln of **10** (90 mg) in dry benzene (10 ml) was added lead tetraacetate (150 mg) in dry benzene (15 ml) over a period of ½ hr. Stirring was continued at r.t. for 1 hr. Excess $Pb(OAc)_4$ was destroyed by the addition of ethane diol (0·5 ml) and filtration and evaporation of the solvent gave 9,13 - *epoxy* - 17 - *norlabdan* - 8 - *one* **12** (85 mg), distilled 65°/0·03 mm. ν_{max} 1719 (C=O); 1131, 1110, 1059, 1022 (CO) cm^{-1}; PMR: Me's at δ 0·72, 0·82, 0·92 (tr, J 7 Hz), 0·95, 1·01; perturbed methylene 2·10–2·60. CD (*c*, 0·165; MeOH) $[\theta]_{260}$ O; $[\theta]_{309}$ −3500 (138 nm); $[\theta]_{338}$ O. (Found: C, 78·2; H, 11·1. $C_{19}H_{32}O_2$ requires: C, 78·0; H, 11·0%).

9,13 - *Epoxylabdane* - 8,17 - *diol* (**15**). To OsO_4 (100 mg) in pyridine (20 ml) was added **14**[11] (100 mg) in pyridine (8 ml). After stirring at r.t. for 24 hr, sodium metabisulphite (3 g) in water (10 ml) was added and stirring continued for a further 24 hr. The mixture was diluted with water (300 ml), extracted with $CHCl_3$ (3 × 70 ml) which was washed with 2M HCl, sat $NaHCO_3$ and water. Drying and evaporation of the solvent followed by PLC (70% ether/hexane) gave 9,13 - *epoxylabdan* - 8,13 *diol* **15** (45 mg), distilled 90°/0·015 mm; ν_{max} 3635 (OH); 1137, 1108, 1089, 1054, 1032, 1020, 984 (CO) cm^{-1}; PMR: Me's at δ 0·77, 0·81, 0·87, 0·97 (tr, J. 7 Hz), 1·25; C-17 protons as an AB system H_A 3·72, H_B 3·43 (J_{AB} 10 Hz). (Found: 74·1; H, 11·1. $C_{20}H_{36}O_2$ requires: C, 74·0; H, 11·2%).

Lead tetraacetate on 9,13 - *epoxylabdane* - 8,17 - *diol* (**15**). Compound **15** (19 mg) in dry benzene (5 ml) was cleaved with lead tetraacetate (25 ml) in dry benzene (10 ml) as described for **10**. Work up gave 9,13 - *epoxy* - 17 - *norlabdan* - 8 - *one* **12** (17 mg), identical (IR, PMR) with that obtained from cleavage of **10**.

Selenium dioxide/hydrogen peroxide on 8(17),14-*labdadien*-13-*ol* (**18**)

A soln of **18** (10 g) in dioxan (100 ml) was stirred at r.t. with H_2O_2 (25 ml, 30%) and SeO_2 (3 g) for 24 hr. The product (9·8 g) was adsorbed onto alumina (500 g deactivated with 40 ml water). Elution gave:

(i) 40% ether/hexane—9,13 - *Epoxy* - 14 - *labdene* - 8β,17 - *diol* **20** (2·1 g), distilled 100°/0·1 mm., m.p. 100–101°; ν_{max} 3370 (OH); 3080, 1630, 1400, 980, 902 ($CH{=}CH_2$); 3080. 1630, 870 ($C{=}CH_2$); 1170, 1140, 1090, 1070, 1033, 980 (CO) cm^{-1}; PMR: Me's at δ 0·82, 0·88, 1·09, 1·31; C-17 protons as an AB system H_A 3·77, H_B 3·46 (J_{AB} 10 Hz); $C\underline{H}{=}C\underline{H}_2$ as an ABX system H_X 6·06, H_A 5·07, H_B 4·91 (J_{AX} 17·5, J_{AB} 1·5, J_{BX} 11 Hz). (Found: C, 74·7; H, 10·9. $C_{20}H_{34}O_3$ requires: C, 74·5; H, 10·6%).

(ii) 80% E/H—8(17),14 - *labdadiene* - 7α,13 - *diol* **19** (4·5 g), (identical m.m.p., IR, PMR) with the naturally occurring compound, $[\alpha]_D^{25}$ +17°; ν_{max} 3320, 3260, (OH); 3085, 1640, 1410, 998, 913 ($CH{=}CH_2$); 3080, 1640, 900($C{=}CH_2$); 1120, 1105, 1060, 1030 (CO) cm^{-1}; PMR: Me's at δ 0·65, 0·79, 0·87, 1·26; $C{=}C\underline{H}_2$ 4·35, 4·63; $C\underline{H}OH$ 5·01; $C\underline{H}{=}C\underline{H}_2$ as an ABX system H_X 5·90, H_A 5·20, H_B 5·04 (J_{AX} 17, J_{AB} 1·5, J_{BX} 10·5 Hz). (Found: C, 78·3; H, 11·2. $C_{20}H_{34}O_2$ requires: C. 78·3; H, 11·2%).

Selenium dioxide/hydrogen peroxide on 13 - *acetoxy* - 8(17) - *labdene* (**16**)

A soln of **16** (2 g) in dioxan (20 ml) with H_2O_2 (10 ml, 30%) and SeO_2 (0·5 g) was stirred at r.t. for 4 days. The product (1·9 g) was adsorbed onto alumina (100 g). Elution with 25% ether/hexane gave 13 - *acetoxy* - 8(17) - *labden* - 7α - *ol* **17** (0·7 g), distilled 95°/0·02 mm; ν_{max} 3420 (OH); 1730, 1250 (acetate); 3080, 1640, 895 ($C{=}CH_2$); 1126, 1067, 1018, 990 (CO) cm^{-1}; PMR: Me's at δ 0·68, 0·82, 0·86 (tr, J 7 Hz), 0·90, 1·41; acetate methyl 1·98; $C{=}C\underline{H}_2$ 4·36, 4·67; $C\underline{H}OH$ 5·04 (W/2 3 Hz). (Found: C, 75·5; H, 10·8. $C_{22}H_{38}O_3$ requires: C, 75·4; H, 10·9%).

Selenium dioxide on 14,15 - *dinorlabd* - 8(17) - *en* - 13 - *one* (**22**)

Compound **22** (1·2 g) in dioxan (30 ml) was stirred with SeO_2 (0·5 g) and H_2O_2 (3 ml, 30%) at r.t. for 36 hr. $NaHCO_3$ wash of the crude product (1·26 g) gave a neutral fraction (1·1 g) which was separated by PLC (100% ether).

(i) Upper band—9,13-8α,13 - *diepoxy* - 14,15 - *dinorlabdan* - 8β - *ol* **25** (0·25 g) sublimed 76°/0·04 mm, m.p. 77–78°; ν_{max} 3420 (OH); 1070, 1052, 1020 (C–O) cm^{-1}; PMR: Me's at δ 0·83, 0·90, 1·05, 1·44; $-C\underline{H}_2O$ as AB system H_A 3·52. H_B 3·29 (J_{AB} 11 Hz). (Found: C, 73·6; H, 10·4. $C_{18}H_{30}O_3$ requires: C, 73·4; H, 10·3%).

(ii) Lower band—7α - *hydroxy* - 14,15 - *dinorlabd* - 8(17) - *en* - 13 - *one* **23** (0·4 g), distilled 68°/0·04 mm; ν_{max} 3520 (OH), 1705 (>C=O), 3080, 1645, 890 ($C{=}CH_2$) cm^{-1}; PMR: Me's at δ 0·68, 0·79, 0·87, $C\underline{H}_3CO$ 2·10; $C{=}C\underline{H}_2$ 4·37, 4·58, $C\underline{H}OH$ as a multiplet 5·05 (W/2 3 Hz). (Found: C, 77·6; H, 10·9. $C_{18}H_{30}O_2$ requires: C, 77·6; H, 10·9%).

8β - *Chloro* - 9,13;8α,13 - *diepoxylabdane* (**26**). The hydroxy ketal (0·1 g) was reacted with thionyl chloride (4 ml) in redistilled pyridine (20 ml) at r.t. with stirring for 24 hr. Dilution, ether extraction and washing the ether extract with dil. HCl and then water followed by evaporation of the solvent gave a product which on PLC (50% ether/hexane) gave 8β - *chloro* - 9,13;8α,13 - *diepoxy* - 14,15 - *dinorlabdane* **26** (0·095 g) m.p. 84–85°, sublimed 78°/0·05 m.m.; ν_{max} 1073, 1057, 1030 (C–O); 673 (C–Cl) cm^{-1}; PMR: Me's at δ 0·84, 0·90, 1·14, 1·43; $C\underline{H}_2O$ as AB system H_A 3·93, H_B 3·53 (J_{AB} 12 Hz) (Found: C, 69·0; H, 9·3; Cl, 11·2. $C_{18}H_{29}ClO_2$ requires: C, 69·1; H, 9·3; Cl, 11·3%).

1 - *Methylene* -8,13 - *epoxylabdane* (**27**). A soln of **29** (0·5 g) and methylene iodide (0·5 ml) in dry ether (10 ml) was added to Mg/Hg amalgam (101 g; 1:100) covered by dry ether (10 ml) and the mixture stirred for 1 hr. The ethereal fraction was decanted and the amalgam washed several times with ether and the combined ether extracts washed with 10% Na_2SO_3 aq. to remove iodine released during the reaction. PLC (20% ether/hexane) gave 1 - *methylene* - 8,13 - *epoxylabdane* **27** (120 mg) as an oil, distilled 65°/0·04 mm; ν_{max} 3100, 1635, 890 ($C{=}CH_2$); 1115, 1034 (C–O) cm^{-1}; PMR: Me's at δ 0·85, 0·91, 0·97, 1·22, 1·36, 0·84 (tr, J 7 Hz); $C{=}C\underline{H}_2$ 4·49, 4·76. (Found: C, 82·9; H, 11·8. $C_{21}H_{36}O$ requires: C, 82·8; H, 11·9%.).

Selenium dioxide/hydrogen peroxide on 1 - *methylene* - 8,13 - *epoxylabdane* (27)

Compound **27** (100 mg) in dioxan (10 ml) was stirred with SeO_2 (0·06 g) and H_2O_2 (0·5 ml, 30%) for 48 hr. PLC (30% ether/hexane) gave two bands. The upper band was unchanged 1-*methylene*-8,13 - *epoxylabdane* **27** (30 mg). The lower band was 1β,1′;8,13 - *diepoxylabdane* **28** (20 mg) as an oil, distilled 60°/0·03 mm; ν_{max} 1110, 1085 (C–O); 900, 850 (epoxide) cm^{-1}; PMR: Me's at 0·90, 0·90, 1·08, 1·15, 1·30, 0·83 (tr, J 7 Hz); epoxidic protons as an AB system H_A 2·90, H_B 2·42 (J_{AB} 4 Hz with H_A long-range coupled J 2 Hz). (Found: C, 78·9; H, 11·5. $C_{21}H_{36}O_2$ requires: C, 78·8; H, 11·3%).

Epoxidation of 1 - *methylene* - 8,13 - *epoxylabdane* (**27**). Compound **27** (0·18 g) in $CHCl_3$ (20 ml) was stirred with *m*-chloroperbenzoic acid (0·11 g) at r.t. for 15 hr. Dilution, work up with 10% $Na_2S_2O_3$ to remove excess peracid followed by PLC (1:10 ether/hexane) gave 1β,1′;8,13 - *diepoxylabdane* **28** (0·12 g) identical to the product from the SeO_2/H_2O_2 oxidation.

Lithium aluminium hydride reduction of epoxide (**28**). Compound **28** (0·1 g) in dry ether (15 ml) and excess LAH was left at r.t. for 15 hr. Work up as for **7** and PLC (30% ether/hexane) gave 1α - *methyl* - 8,13 - *epoxylabdan* - 1β - *ol* **31** (0·07 g), distilled 87°/0·03 mm; ν_{max} 3600, 3470 (OH), 1170, 1105, 1050, 1030, 995 (C–O) cm^{-1}; PMR: Me's at δ 0·80, 0·86, 0·94, 1·17, 1·32, 1·32, 0·84 (tr, J 7 Hz); PMR (C_5D_5N): Me's at δ 0·81, 0·84, 1·11, 1·17, 1·34, 1·41, 0·91 (tr, J 7 Hz). (Found: C, 78·4; H, 11·7. $C_{21}H_{38}O_2$ requires: C, 78·2; H, 11·9%).

Methyl magnesium iodide on 8,13 - *epoxylabdan* - 1 - *one* (**29**). Compound **29** (0·4 g) in dry ether (20 ml) was reacted with an ethereal soln of MeMgI prepared from Mg turnings (0·5 g) and redistilled MeI (1·5 ml). The mixture was refluxed for 3 hr and the excess reagent destroyed by the addition of saturated NH_4Cl aq. Ether extraction and removal of solvent gave three bands on PLC (15% ether/hexane)

(i) The upper band of 8,13 - *epoxylabdan* - 1 - *one* **29** (0·165 g), identical to an authentic sample (IR, TLC).

(ii) The lower band as a mixture of three compounds which on further PLC (30% ether/hexane) gave

(a) 1β - *methyl* - 8,13 - *epoxylabdan* - 1α - *ol* **34** (0·05 g) distilled 91°/0·3 mm. crystallized on long standing. ν_{max} 3600, 3470 (OH), 1160, 1105, 1080, 1030, 995 (CO) cm^{-1}; PMR: Me's at δ 0·77, 0·86, 0·88, 1·13, 1·28, 1·31, 0·83 (tr, J 7 Hz); PMR (C_5D_5N): Me's at δ 0·78, 0·85, 1·15, 1·31, 1·45, 0·83 (tr, J 7 Hz). (Found: C, 78·0; H, 12·1. $C_{21}H_{38}O_2$ requires: C, 78·2; H, 11·9%).

(b) 1α - *methyl* - 8,13 - *epoxylabdan* - 1β - *ol* **31** (0·02 g) identical (IR, TLC) to the sample prepared from the LAH reduction of epoxide (**28**).

(c) Unidentified compound (0·03 g) ν_{max} 1700 (C=O) cm^{-1}.

Methyl lithium on 8,13 - *epoxylabdan* - 1 - *one* (**29**). Compound **29** (0·12 g) in LAH dried ether was reacted with an ethereal soln of MeLi (1·2 ml, 1·4 M) in a N_2 atmosphere for 36 hr. Excess reagent was destroyed by the careful dropwise addition of water. The combined ethereal extracts were washed with $Na_2S_2O_3$ aq (20 ml; 10%) and then water. Removal of the solvent under vacuum and PLC (50% ether/hexane) of the product gave 1β - *methyl* - 8,13 - *epoxylabdan* - 1α - *ol* **34** (0·09 g) identical (IR, TLC) to the sample prepared above.

3 - *Methylene* - 8,13 - *epoxylabdane* (**35**). A soln of **36** (1·0 g) and CH_2I_2 (1 ml) in dry ether (20 ml) was added to Mg/Hg amalgam (203 g; 3:200) covered by dry ether (10 ml). After stirring for 1 hr and work up as for **27**, PLC (6% ether/hexane) gave 3 - *methylene* - 8,13 - *epoxylabdane* **35** (150 mg) as an oil, distilled 70°/0·04 mm; ν_{max} 3095, 1635, 885 ($C{=}CH_2$); 1100 (C–O) cm^{-1}; PMR: Me's at δ 0·85, 0·86, 1·07, 1·18, 1·28, 0·83 (tr, J. 7 Hz); $C{=}C\underline{H}_2$ 4·64, 4·68. (Found: C, 82·8; H, 12·0. $C_{21}H_{36}O$ requires: C, 82·8; H, 11·9%).

Selenium dioxide/hydrogen peroxide on 3 - *methylene* - 8,13 - *epoxylabdane* (35)

Compound **35** (120 mg) in dioxane (10 ml) was stirred with SeO_2 (0·07 g) and H_2O_2 (1 ml; 30%) at r.t. for 45 hr. PLC (10% ether/hexane) gave an upper band of unchanged 3 - *methylene* - 8,13 - *epoxylabdane* **35** (30 mg) and a lower band, 3 - *hydroxymethyl* - 8,13 - *epoxylabd* - 2 - *ene* **37** (20 mg) m.p. 94–95°, sublimed 80°/0·03 mm; ν_{max} 3400 (OH); 1110, 1053 (C–O) cm^{-1}; PMR: Me's at δ 0·78, 0·85, 1·04, 1·20, 1·29, 0·84 (tr, J 7 Hz); $-C\underline{H}_2OH$ as A_2 system 4·14; $C{=}C\underline{H}$ 5·66 (d, J 5 Hz). (Found: C, 78·8; H, 11·4. $C_{21}H_{36}O_2$ requires: C, 78·8; H, 11·3%).

2 - *Methylene* - 8,13 - *epoxylabdane* (**38**). A soln of **39** (6·0 g) and CH_2I_2 (2 ml) in dry ether (25 ml) was added to Mg/Hg amalgam (203 g; 3:200) covered by dry ether (10 ml). The reaction refluxed of its own accord and after ½ hr was worked up as for **27**. The crude produce was adsorbed on alumina (100 g) and elution with hexane gave 2 - *methylene* - 8,13 - *epoxylabdane* **38** (3·20 g), m.p. 67–68°, sublimed 68°/0·03 mm; ν_{max} 3060, 1645, 870, 865 ($C{=}CH_2$); 1115, 1070, 1035, 1000 (C–O) cm^{-1}; PMR: Me's at δ 0·70, 0·73, 0·91, 1·19, 1·26, 0·85 (tr, J 7 Hz); $C{=}C\underline{H}_2$ 4·65, 4·72. (Found: C, 82·9; H, 11·9. $C_{21}H_{36}O$ requires: C, 82·8, H, 11·9%).

Selenium dioxide/hydrogen peroxide on 2 - *methylene* - 8,13 - *epoxylabdane* (38)

The olefin **38** (1·5 g) in dioxan (50 ml) was stirred with SeO_2 (0·3 g) and H_2O_2 (5 ml, 30%) at r.t. for 48 hr. PLC (30% ether/hexane) gave five compounds.

Band I—(the upper band) (0·13 g) was identified as unchanged 2 - *methylene* - 8,13 - *epoxylabdane* (**38**).

Band II—2 - *formyl* - 8,13 - *epoxylabd* - 2 - *ene* **51** (0·06 g) m.p. 135–136°, sublimed 64°/0·045 mm; λ_{max} 231 nm (ε 4650); ν_{max} 1653 (C=C) 2710, 1695 (CHO); 1120, 1078 (C–O) cm^{-1}; PMR: Me's at δ 0·71, 1·01, 1·10, 1·20, 1·30, 0·85 (tr, J 7 Hz); 1β-H as A part of AB system H_A 2·47 (J_{AB} 16 Hz); $C{=}C\underline{H}$ 6·45 (d, long range coupled $J_{3,1\alpha}$ 3 Hz); $-C\underline{H}O$ 9·44 (s). (Found: C, 79·3; H, 10·85. $C_{21}H_{34}O_2$ requires: C, 79·2; H, 10·8%).

Band III—2 - *methylene* - 8,13 - *epoxylabdan* - 3α - *ol* **40** (0·04 g) m.p. 93–94°, sublimed 80°/0·03 mm; $\nu_{max}^{CCl_4}$ 3620 (non-bonded OH) 3450 (bonded OH); 3080, 1650, 900 ($C{=}CH_2$); 1120, 1075 (C–O) cm^{-1}; PMR: Me's at δ 0·71, 0·75, 1·00, 1·20, 1·27, 0·85 (t, J 7 Hz); $-\overset{|}{C}\underline{H}OH$ 3·61 (s); $C{=}C\underline{H}_2$ 4·82, 4·97. (Found: C, 78·7; H, 11·4. $C_{21}H_{36}O_2$ requires: C, 78·8; H, 11·3%).

Band IV—2 - *hydroxymethyl* - 8,13 - *epoxylabd* - 2 - *ene* **47** (0·35 g) m.p. 116–118°, sublimed 100°/0·03 mm; ν_{max} 3400 (OH); 1120, 1080 (C–O) cm^{-1}; PMR: Me's at δ 0·76, 0·87, 0·97, 1·20, 1·30, 0·85 (tr, J 7 Hz); $C\underline{H}_2OH$ as A_2 system 3·94; $C{=}C\underline{H}$ 5·37 (W/2 4 Hz due to long-range coupling with 1α-H). (Found: C, 78·9; H, 11·6. $C_{21}H_{36}O_2$ requires: C, 78·8; H, 11·3%).

Band V—2β - *hydroxymethyl* - 2α,3α;8,13 - *diepoxylabdane* **49** (0·3 g) m.p. 127–128°, sublimed 115°/0·03 mm; ν_{max} 3400 (OH); 1120, 1080 (C–O); 915, 810 (epoxide) cm^{-1}; PMR: Me's at δ 0·77, 0·98, 1·09, 1·18, 1·25, 0·82 (tr, J 7 Hz); $\underline{H}{-}\overset{O}{\overset{/\ \backslash}{C{-}C}}$ 2·91 (s), $-C\underline{H}_2OH$ as AB system H_A 3·63, H_B 3·52 (J_{AB} 13 Hz). (Found: C, 75·1; H, 10·8. $C_{21}H_{36}O_3$ requires: C, 75·0; H, 10·7%).

3α - *Acetoxy* - 2 - *methylene* - 8,13 - *epoxylabdane* (**41**). The alcohol **40** (40 mg) in Ac_2O/pyridine (3 ml; 1:1) was left at r.t. for 24 hr. Work up as for **11** gave, after PLC (15% ether/hexane), 3α - *acetoxy* - 2 - *methylene* - 8,13 - *epoxylabdane* **41** (40 mg) as an oil b.p. 90°/0·01 mm; ν_{max} 1745, 1230 ($OCOCH_3$); 3080, 1655, 905

($C{=}CH_2$); 1120, 1075, 1030 (C–O) cm^{-1}; PMR: Me's at δ 0·71, 0·79, 0·89, 1·19, 1·27, 0·87 (tr, J 7 Hz); $OCOC\underline{H}_3$ 2·05; $C{=}C\underline{H}_2$ 4·91; –C$\underline{H}$OAc 5·12 (d, J 3 Hz, long range coupling with 1αH). (Found: C, 76·5; H, 10·7. $C_{23}H_{36}O_3$ requires: C, 76·2; H, 10·5%).

3α - Acetoxy - 8,13 - epoxylabdan - 2 - one (**43**). The acetate **41** (40 mg) in pyridine (2 ml) was treated with OsO_4 (50 mg) in pyridine (2 ml) and the mixture allowed to stand at r.t. for 24 hr $NaIO_4$ (10 ml; 3%) was added and stirring continued for a further 24 hr. Dilution and ether extraction gave 3α - *acetoxy* - 8,13 - *epoxylabdan* - 2 - *one* **43** (20 mg) m.p. 69·5–70·5° (aqueous MeOH); ν_{max} 1752, 1230 ($OCOCH_3$); 1730 (C=O) cm^{-1}; PMR: Me's at δ 0·97, 0·98, 0·98, 1·20, 1·30, 0·86 (tr, J 7 Hz); $OCOC\underline{H}_3$ 2·15; C-1 methylene as AB system H_A 2·35, H_B 2·25 (J_{AB} 12 Hz); –CHOAc 4·97 (s). (Found: C, 72·2; H, 10·0. $C_{22}H_{36}O_4$ requires: C, 72·5; H, 10·0%).

Epoxidation of 2 - hydroxymethyl - 8,13 - epoxylabd - 2 - ene (**47**). Compound **47** (20 mg) in $CHCl_3$ (10 ml) was stirred at r.t. with excess *m*-chloroperbenzoic acid in $CHCl_3$ (5 ml) for 20 hr. Washing with water and treatment with 10% $Na_2S_2O_3$ aq gave after PLC (25% ether/hexane) 2β - hydroxymethyl - 2α,3α;8,13 - *diepoxylabdane* (**49**) identical to the product from the SeO_2/H_2O_2 oxidation.

Lithium aluminium hydride reduction of 2β - hydroxymethyl - 2α,3α;8,13 - diepoxylabdane (**49**). The epoxide **49** (60 mg) in dry ether (20 ml) was refluxed with excess LAH for 2 hr. Excess LAH was destroyed with wet ether and then water. The complex was hydrolysed with H_2SO_4 (10 ml, 10%) and the mixture ether extracted. PLC (20% ether/hexane) gave 2β - *hydroxymethyl* - 8,13 - *epoxylabdan* - 2α - *ol* **50** (50 mg) as an oil (distilled 130°/0·3 mm); ν_{max} 3400 (OH); 1118, 1065 (C–O) cm^{-1}; PMR: Me's at δ 0·82, 0·86, 1·12, 1·18, 1·27, 0·83 (tr, J 7 Hz); –$C\underline{H}_2OH$ as A_2 system, 3·34. (Found: C, 74·2; H, 11·6. $C_{21}H_{38}O_3$ requires: C, 74·5; H, 11·3%).

Cleavage of 2β - hydroxymethyl - 8,13 - epoxylabdan - 2α - ol (**50**). To diol **50** (40 mg) in $CHCl_3$/HOAc (5 ml, 1:1) was added excess $Pb(OAc)_4$. After stirring for 5 hr at r.t. excess $Pb(OAc)_4$ was destroyed by the addition of ethylene glycol. Work up by filtration and evaporation of the solvent gave 8,13 - *epoxylabdan* - 2 - *one* **39** (30 mg) identical with an authentic sample (m.m.p., IR, NMR).

Selenium dioxide on 8(17),14 - *labdadien* - 13 - *ol* (**18**)

Compound **18** (0·5 g) in dioxan (20 ml) was refluxed with SeO_2 (0·15 g) and water (1·5 ml) for 2·5 hr by which time all the starting material had reacted (TLC). PLC (70% ether/hexane) of the product gave 8(17),14 - *labdadiene* - 7α,13 - *diol* **19** (0·27 g) identical (m.m.p., PMR, IR) with an authentic sample. TLC examination of the crude product shown none of the other products isolated from the corresponding SeO_2/H_2O_2 oxidation.

Selenium dioxide/hydrogen peroxide on 8,13 - *epoxylabd* - 2 - *ene* (**52**)

A soln of **52** (400 mg) in dioxan (20 ml) with H_2O_2 (3 ml; 30%) and SeO_2 (0·2 g) was stirred at r.t. for 48 hr. PLC (10% ether/hexane) gave unchanged **52** (80 mg) and 2α,3α;8,13 - *diepoxy* - *labdane* **53** (280 mg), identical with an authentic sample (m.m.p., IR, PMR).

Selenium dioxide on 8,13 - *epoxylabd* - 2 - *ene* (**52**)

(a) A soln of **52** (300 mg) and SeO_2 (600 mg) in dioxan (30 ml) and water (2·0 ml) was refluxed for 10 hr. PLC (70% ether/hexane) of the product gave 8,13 - *epoxylabd* - 2 - *en* - 1α - *ol* **54** (220 mg) m.p. 54–55°, sublimed 50°/0·03 mm; ν_{max} 3430 (OH); 1659 (C=C) cm^{-1}; PMR: Me's at δ 0·87, 0·87, 0·99, 1·20, 1·31, 0·85 (tr, J 7 Hz); $C\underline{H}{=}C\underline{H}{-}C\underline{H}OH$ as ABX system H_A 5·71, H_B 5·53, H_X 3·65 (J_{AB} 10 Hz, J_{BX} 5 Hz). (Found: C, 78·2; H, 11·1. $C_{20}H_{34}O_3$ requires: C, 78·5; H, 11·1%).

(b) A soln of **52** (0·20 g) in dioxan (10 ml) with H_2O (1·5 ml) was stirred at r.t. for 120 hr and gave unchanged starting material (0·19 g) on workup.

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