Cationic Cyclizations of Labda-8(17),12- and Labda-8(17),13(16)-dien-14-ol[1]

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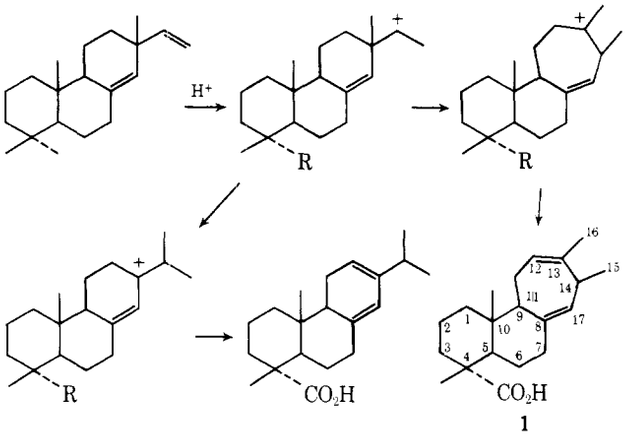
Received September 1, 1976

Syntheses of the labda-8(17),13-dien-12-ols (**6**) from sclareol and of the labda-8(17),12- (**16**) and labda-8(17),13(16)-dien-14-ols (**29**) from manool are described. On treatment with Collins reagent, the secondary allylic alcohols **6** and **16** undergo an oxidative rearrangement to α-epoxy ketones later found characteristic of tertiary allylic alcohols. Cationic cyclizations of **16, 29,** and **29** acetate did not result in the hoped-for biogenetic-type strobane synthesis, but yielded tricyclic systems containing five- or six-membered rings (**28** from **16, 32** and **36a** from **29,** and **29** acetate, respectively) as well as a phyllocladane **37** (from **29** acetate). A simple, high-yield preparation of **22** from manool is described.

Strobic acid (**1**) and its congeners[2] are representatives of a diterpene group whose biogenesis may involve a variant of the scheme previously[3] proposed for biogenesis of the abietanes. This is shown in Scheme I. (In this and subsequent schemes representation of formulas in the form of discrete carbonium ions is done for convenience only and implies no judgment as to concertedness or lack thereof.)

Scheme I



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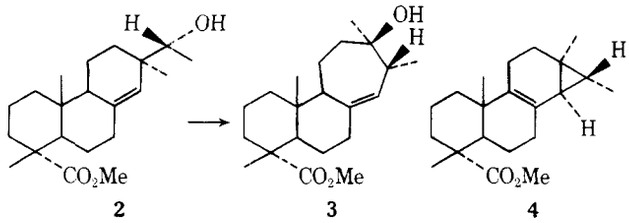
The postulated rearrangement–ring expansion sequence was realized in our laboratory some time ago.[4] Treatment of the hydroxy ester **2** with tosyl chloride–pyridine resulted in genesis of the stroban derivative **3** and the cyclopropane resin acid **4,** apparently by way of a stereospecific homoallylic–cyclopropylcarbinyl–homoallylic pathway. Since the stereochemistry of the C-14 methyl group was opposite of that found in strobic acid, the C-15 epimer of **2** might be expected to

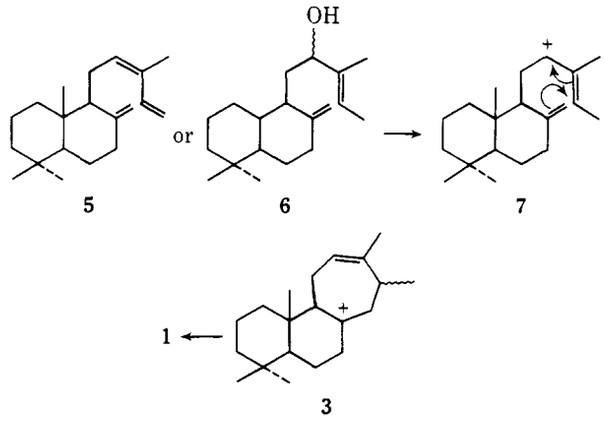


2 3 4

furnish a product with proper C-14 orientation. However, at the time the work was carried out, it proved impossible to separate the 1:1 mixture of C-14 alcohols produced by $NaBH_4$ reduction of the corresponding ketone.

An alternative biogenetic pathway to the strobanes is cyclization (arrows) of the bicyclic ion **7** theoretically derivable from *cis*-biformene (**5**) or the alcohol **6** (Scheme II).[4,5] In the present communication we describe attempts to duplicate this route and variants thereof in the laboratory. Although there are precedents for the formation of seven-membered rings by

Scheme II



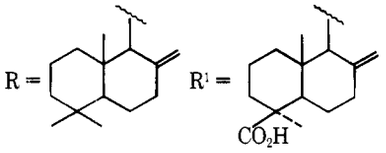
cationically induced cyclization,[6-11] the hoped-for ring closures either did not take place in the desired manner or proceeded beyond the strobane stage.

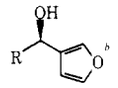
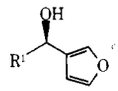
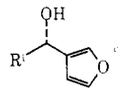
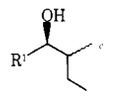
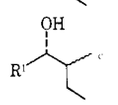
Results and Discussion

Synthesis of Alcohols 6 and 16. The proposed approach required the synthesis of alcohol **6,** which, as depicted in Scheme II, is a mixture of epimers. One possible starting point for the synthesis of this material was lactone **8** from sclareol.[12] $LiAlH_4$ reduction of **8** gave the diol **9a.** The corresponding monoacetate **9b** on dehydration with $POCl_3$–pyridine afforded a mixture of olefinic acetates **10a, 11,** and **12** in the ratio 5:4:1 which was separated by chromatography over silver nitrate–alumina. The structures were established by NMR spectroscopy, **10a** exhibiting two broadened vinylic singlets at 4.65 and 4.85 ppm, **11** a vinyl methyl resonance at 1.69 ppm and no vinylic protons, and **12** a vinyl methyl at 1.72 ppm and a vinyl proton multiplet at 5.05 ppm. Removal of the acetate protecting group by reduction of **10a** with $LiAlH_4$ and oxidation of the resulting alcohol **10b** with either Collins reagent[13] or Ag_2CO_3 on Celite[14] led to aldehyde **13** which exhibited the requisite spectral properties (NMR two broadened vinylic singlets at 4.40 and 4.83 ppm, aldehyde triplet at 9.7 ppm, two-proton doublet at 2.46 ppm, $J_{11,12}$ = 1 Hz).

Addition of *cis*-2-butenyllithium (THF, −78 °C) to **13** gave a 50% yield of alcohols **6a** and **6b** which were separated chromatographically. The NMR spectra of the two products were very similar except for the chemical shifts of H-12 [broadened doublet at 4.60 ($J \sim 10$ Hz) and triplet at 4.73 ppm (J = 6 Hz)], H-14 (broadened quartets due to allylic coupling at 5.24 and 5.37 ppm, J = 6 and 7 Hz), and H-17 (two broadened singlets at 4.40, 4.77 and at 4.73, 4.87 ppm). A comparison of the chemical shifts of H-17 with those reported for other 12-hydroxylabdanes[15,16] indicates (see Table I) that the isomer

Table I. H-17 Resonances of 12-Hydroxylabdanes[a]



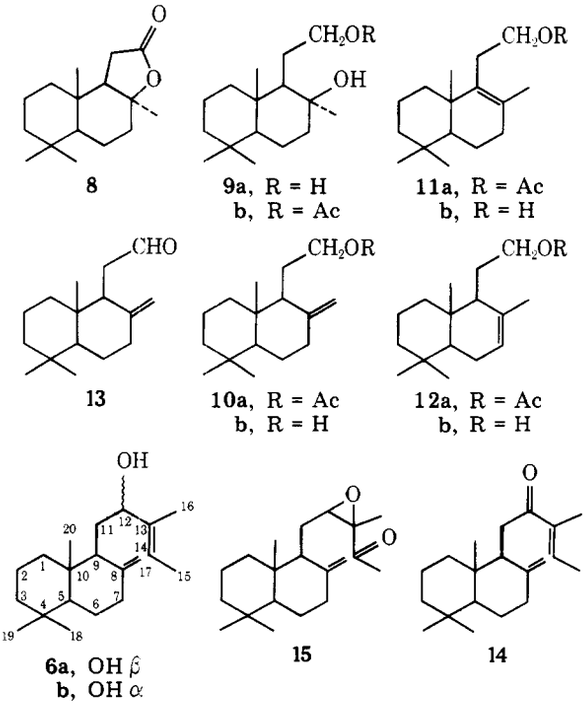
Compd	H-17a	H-17b
6a	4.40	4.77
6b	4.73	4.87
	4.47	4.85
	4.48	4.86
	4.72	4.88
	4.40	4.83
	4.72	4.88

[a] In $CDCl_3$. [b] Taken from ref 16. [c] Taken from ref 15.

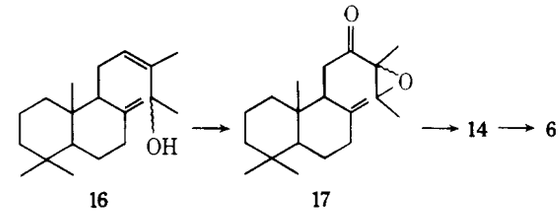
with H-17 resonances at 4.73 and 4.87 ppm is **6b** [(*E*)-labda-8(17),13-dien-(12*S*)-ol].

Oxidation of **6a** and **6b** with active MnO_2 to the ketone **14** failed. Oxidation of **6b** with Collins reagent quite unexpectedly gave a substance $C_{20}H_{32}O_2$ which had the properties of an α-epoxy ketone **15** [IR bands at 1705 and 1640 cm^{-1}, significant signals in the NMR spectrum at 1.41 (singlet of methyl on carbon attached to oxygen), 1.97 (methyl ketone), 3.00 (multiplet of H-12), 4.35 and 4.85 ppm (broad singlets of H-17)]. The observation of this unusual oxidative transformation prompted a more extended study[17] which has demonstrated that formation of rearranged α-epoxy aldehydes is a general phenomenon when tertiary allylic alcohols are oxidized with Collins reagent. Apparently, certain secondary allylic alcohols are also subject to this rearrangement (see also below). In accordance with the results of this parallel investigation,[17] C-12 of **15** retains the configuration of the precursor alcohol, but the configuration at C-13 is unknown.

Scheme III

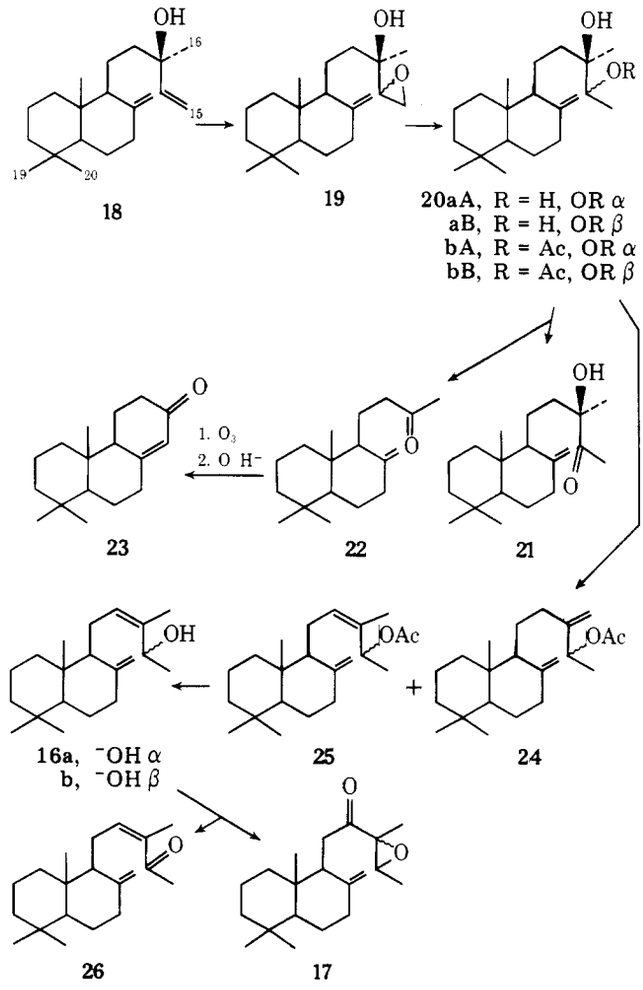


The overall yield of alcohols **6** was rather low, owing to the need of separating **10a** from **11** and **12**, and the lithium reagent needed for the last step was difficult to handle. These problems and the interesting oxidative rearrangement of **6b** discussed in the preceding paragraph suggested a different approach to **6**. It was hoped that oxidation of the allylic alcohol **16** with Collins reagent might also be accompanied by rearrangement and lead to epoxy ketone **17** which after reduction with chromous chloride to **14** and further reduction with hydride would yield **6**.



The point of departure for synthesis of **16** was manool (**18**, Scheme IV). Epoxidation with vanadyl acetylacetonate and *tert*-butyl hydroperoxide[18] resulted in selective attack on the terminal double bond. The resulting epoxide mixture **19** was reduced with $LiAlH_4$ to **20a** which was a mixture of epimers.[19]

Scheme IV



The original plan for converting **20a** to **16** involved oxida-

Table II. Oxidation of 20a with Various Oxidizing Agents

Reagent	Yield, % 21	22
Jones reagent	15	65
Collins reagent	20	76
Pyridinium chlorochromate	15	59
Ag_2CO_3–Celite	28	68
Active MnO_2	5	95

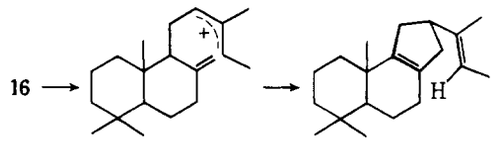
tion to **21** (thus removing the center of asymmetry giving rise to the diastereomeric mixture), dehydration to labda-8(17),12-diene-14-one, and lithium aluminum hydride reduction of the latter. However, exposure of **20a** to a variety of oxidizing agents invariably produced **21** only as a minor product (5–28%, depending on reagent, see Table II). The major product (59–95%) was the well-known ketone **22** which is usually made directly from manool by oxidation with $KMnO_4$.[20]

The formation of ketone **22**, particularly in the high yield shown in the last entry of Table II, while not unprecedented from the chemical point of view,[21] is very interesting because it is an intermediate in the synthesis of **23**, a substance which has proved to be a "versatile starting material" [21] for diterpene synthesis.[23] The maximum yield of **22**, when prepared directly from manool, is about 65%,[20] but this requires work on a relatively small scale and extensive chromatography over $AgNO_3$-impregnated silica gel. The method described here, while involving three steps **18** → **19** → **20** → **21**, seems at least comparable, if not superior. Since each step yields only one product, the operations can be carried through on a large scale without purification of intermediates. In this manner we have achieved overall yields of 90–95% from manool.

Because the yield of **21** was low regardless of the choice of oxidizing agent, the approach to **16** was modified. Dehydration of the monoacetate mixture **20b** ($POCl_3$–pyridine) gave a 1:2 mixture of olefinic acetates **24** and **25** which were separated by preparative TLC. $LiAlH_4$ reduction of **25** then gave the required alcohol **16** as an inseparable mixture of epimers **16a** and **16b**. Subsequently, it was discovered that one of the epimers **20b** could be crystallized from hexane. This isomer (mp 105 °C) was converted in the same way to one of the components of mixture **16** which was needed for another study.[17] Application of Horeau's method[24] showed that the pure substance was labda-8(17),12-dien-(14*S*)-ol (**16b**); consequently the isomer of mp 105 °C was **20bB**.

As hoped for, the epimeric mixture **16** underwent at least partial oxidative rearrangement with Collins reagent to a mixture of the epimeric α-keto epoxides **17** and the α,β-unsaturated ketone **26** which was separated by high-pressure liquid chromatography. Both fractions exhibited the requisite spectral properties; **17** had methyl singlets at 0.75, 0.83, 0.90, and 1.41 ppm, a methyl doublet at 1.38 ppm due to CH_3CHO, the hydrogen of which appeared as a quartet at 3.16 ppm, and an IR band at 1700 cm^{-1}; whereas **26** exhibited methyl singlets at 0.75, 0.80, 0.90, and 2.20 ppm, the triplet of H-12 at 6.61 ppm, and IR bands at 1675 and 1640 cm^{-1}. Unfortunately the attempted reduction of **17** with chromous chloride for eventual conversion to **6** resulted only in quantitative recovery of starting material.

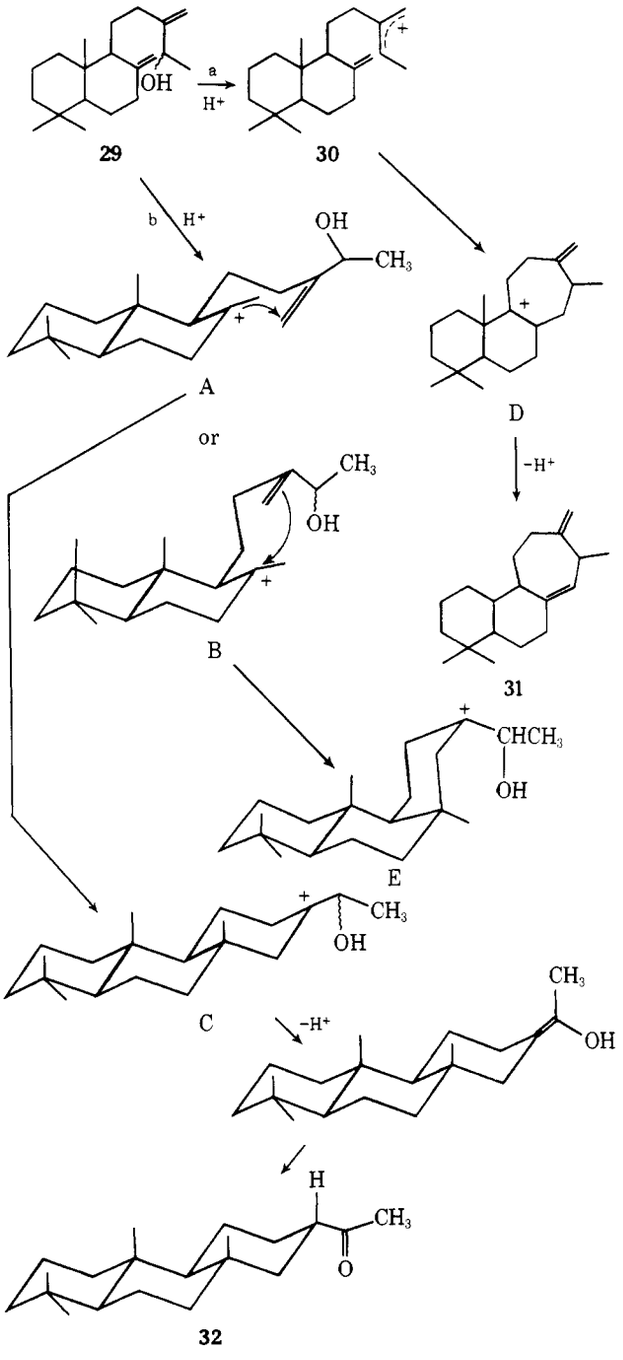
Cyclization Studies. Failure to obtain **6** in reasonable yield prompted a study of the cationic cyclization of alcohol **16** as a possible biogenetic-type route to strobanes since either **6** or **16** could serve as a precursor of the requisite allylic cation **27**. Attempted cyclization of **16** with $SnCl_4$ in CH_2Cl_2 or CH_3NO_2 gave a complex hydrocarbon mixture which could not be separated satisfactorily. Cyclization using formic acid furnished the formate of **16**, and a small amount of a hydrocarbon **28**. The structure assignment was based on the absence of functional groups evidenced by the IR spectrum and the NMR spectrum which showed the presence of a vinylic methyl singlet with fine splitting, a vinylic methyl doublet and a downfield quartet corresponding to one proton, coupling to which was responsible for the fine splitting of the vinyl methyl singlet, as well as three singlets of the three methyl groups attached to ring A. Formation of this hydrocarbon suggests that ion **27**, if formed, undergoes preferential cyclization to a five- instead of a seven-membered ring.



27 **28**

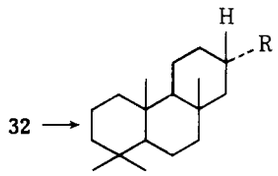
Attention was therefore turned to the cyclization of the

Scheme V

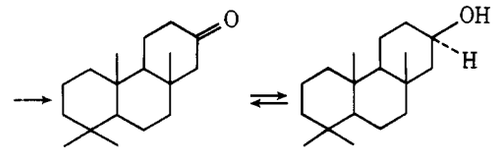


isomeric alcohol **29**, which it was hoped might undergo cyclization to strobane derivative **31** by path a of Scheme V via allylic carbonium ion **30**. Its synthesis was accomplished by $LiAlH_4$ reduction of **24**, a by-product in the preparation of **16**. However, cyclization of **29** with $SnCl_4$–CH_2Cl_2 at −78 °C or $SnCl_4$-nitromethane at 0 °C led in 60% yield to a tricyclic methyl ketone **32** by path b of Scheme V, i.e., by initial protonation at C-17, in a manner reminiscent of the acid-catalyzed cyclizations of labda-8,13-dienes.[23] The IR spectrum of the product had a carbonyl band at 1725 cm^{-1}, but lacked the frequency at 1640 cm^{-1} characteristic of the olefinic methylene group attached to C-8 of the precursor. The NMR spectrum displayed four methyl singlets in the range 0.7–1.0 ppm, a fifth methyl singlet at 2.06 ppm (acetyl methyl), and no downfield signals characteristic of vinylic protons. The absence of unsaturation was confirmed by the ^{13}C NMR spectrum. The stereochemistry of the new angular methyl group at C-8 was assumed to be β since models indicate that attack of the C-13 methylene group on C-8 should occur from the bottom face (ion A) rather than from the top face (ion B) due to steric interactions in ion B between the axial methyl group on -10 and the side chain. The acetyl group attached to C-13 of the product was expected to be equatorial (see Scheme V).

Structure and stereochemistry of **32** were confirmed by the following transformations. Baeyer–Villiger oxidation of **32** gave ester **33a** which was reduced to alcohol **33b** with loss of two carbon atoms. Oxidation of **33b** (Jones reagent) furnished a cyclohexanone **34** (IR band at 1720 cm^{-1}). Reduction of **34** with lithium tri-*tert*-butoxyaluminum hydride afforded a new alcohol **35**. Since the reagent reduces cyclohexanones to axial alcohols, the hydroxyl group of **33b**, and hence the side chain of **32**, must be equatorial. Furthermore, comparison of the NMR spectra of **33a** and **35** revealed that in **35** one of the methyl singlets is downfield as compared with **33a** due to deshielding by the hydroxyl group. This can occur only if the C-8 methyl group is axial to ring C, which would be true of either trans-anti-trans alcohol **35** deived from **32** or a trans-anti-cis alcohol (C-8 methyl α, C-13 hydroxyl α) derived from ion E, Scheme V.



33a, R = OAc
b, R = OH



34 **35**

That formulas **32–35** are indeed correct is evident from the CD curve of ketone **34**. As a *trans*-decalone derivative of the *t*3, *t*2 type,[26] it should exhibit a reasonably strong *positive* Cotton effect ($\Delta\epsilon \sim 1$ or larger), whereas a trans-anti-cis ketone resulting from degradation of E (Scheme V) would be *c*3′ *eq*, *t*4′[26] and should exhibit a relatively weak negative Cotton effect.[27] In fact, $[\theta]_{287}$ of ketone **34** (methanol solution) was +3280 ($\Delta\epsilon \sim 1$) which shows that it and its relatives **32**, **33**, and **35** are *trans-anti-trans*-perhydrophenanthrene derivatives.

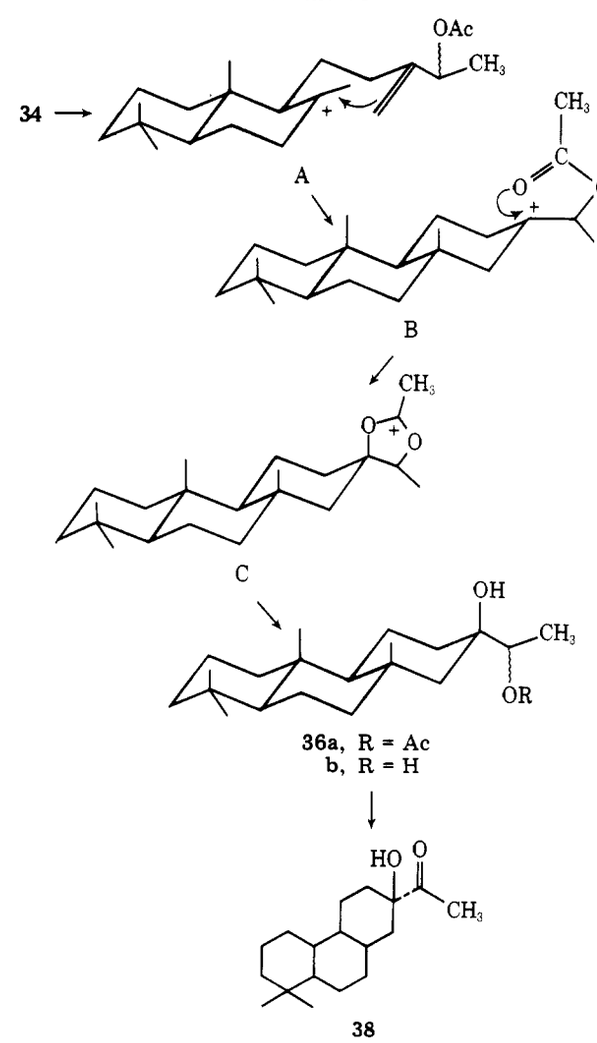
Cyclization of acetate **24** ($SnCl_4$–CH_2Cl_2, −78 °C) proceeded by two competing pathways to yield a mixture of tricyclic hydroxy acetates $C_{22}H_{38}O_3$ (**36a**, Scheme VI) and a tetracyclic substance $C_{20}H_{33}Cl$ (**37**, Scheme VII). The structure of the more polar product **36a** was established as follows. $LiAlH_4$ reduction furnished a diol (**36b**) which was oxidized (Ag_2CO_3–Celite, benzene) to a hydroxy ketone **38** exhibiting a $CH_3C{=}O$ singlet at 2.16 ppm. Further oxidation of **38** with Jones reagent yielded the previously encountered ketone **34** whose formation was not particularly surprising since the reagent is known to cleave 1,2-diols, especially if one of the hydroxyl groups is tertiary.[21] The axial orientation of the

Table III. ^{13}C NMR Spectrum of 37 [a]

Carbon	Chemical shifts	Carbon	Chemical shifts
C-1	41.8 t	C-11	19.5 t[b]
C-2	18.3 t[b]	C-12	32.5 t
C-3	39.7 t	C-13	75.5
C-4	33.1	C-14	38.7 t[c]
C-5	56.3 d	C-15	35.3 t
C-6	21.0 t	C-16	46.4 d
C-7	39.2 t[c]	C-17	6.9 q
C-8	45.1	C-18	33.6 q
C-9	53.9	C-19	21.8 q
C-10	37.3	C-20	15.1 q

[a] Run in $CDCl_3$ at 67.905 MHz, using Me_4Si as internal standard. Assignments are based on predicted shifts and comparison with spectra of kaurenoids: J. R. Hanson, M. Siverns, F. Piozzi, and G. Savona, *J. Chem. Soc., Perkin Trans. 1*, 114 (1976). Unmarked signals are singlets. [b,c] Assignments may be interchanged.

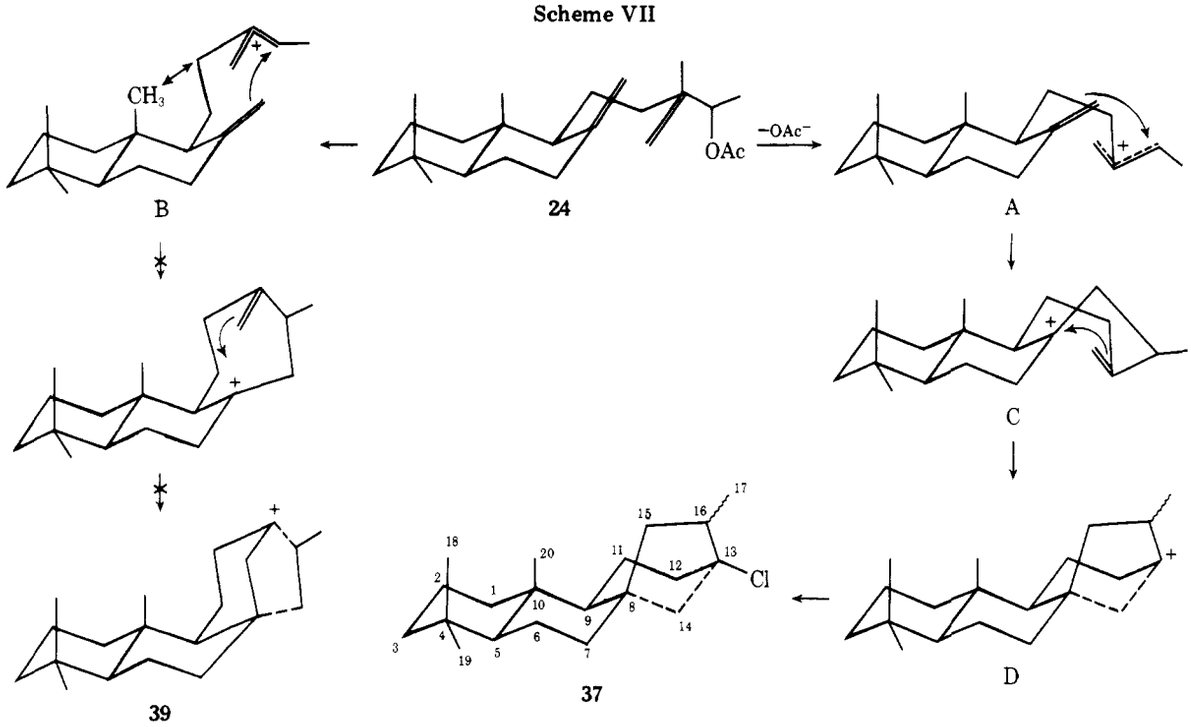
Scheme VI



36a, R = Ac
b, R = H

38

Scheme VII



tertiary hydroxyl group of **36a** was deduced by comparing the chemical shift of the C-8 methyl resonances in **36a, 36b,** and **38** with those in the NMR spectra of **33** and **35.**

The formation of **36a** from **24** is rationalized in Scheme VI. Protonation of the exocyclic double bond attached to ring B leads to ion A which undergoes cyclization with participation of the second $=CH_2$ group to ion B. The latter is stabilized by participation of the acetate group as in C. As in Scheme V, attack on C-8 is expected to occur preferentially from the α face of the molecule, thus leading to β orientation of the methyl group on C-8. Degradation of **38** to ketone **34** confirms this hypothesis.

The NMR spectrum of the less polar product $C_{20}H_{33}Cl$ (**37**) displayed three methyl singlets, a methyl doublet, and no resonances indicative of the presence of vinylic hydrogen. The IR spectrum showed the absence of functionality; the ^{13}C NMR spectrum established the absence of olefinic carbon and the presence of a tertiary C–Cl bond. On the basis of these observations and the following arguments the phyllocladane structure **37** (Scheme VII) rather than the kaurane formula **39** was assigned to this substance.

Loss of acetate ion from **24** leads to an allylic carbonium ion. Molecular models suggest that conformation A is preferred over conformation B due to steric interaction between C-10 methyl and the side chain of the latter. Cyclization of A to C and then to D leads to a tertiary ion with phyllocladane stereochemistry which reacts with Cl^- derived from $SnCl_4$ or abstracts Cl^- from the solvent[29] to form **37.** Cyclization from the unfavorable conformation B would have led to compound **39** with kaurane stereochemistry.

Thus carbonium ion D of Scheme V (equivalent to ion C of Scheme VII) can be generated from allylic carbonium ion **30,** but appears prone to further cyclization rather than deprotonation to a strobane derivative. The possibility exists that it could be trapped if the reaction were carried out in a highly nucleophilic medium. The behavior of allylic carbonium **7** remains to be investigated in more detail although there is evidence that it cyclizes to a five- rather than a seven-membered ring.

Experimental Section[30]

Reduction of Lactone 8. A solution of 20 g of **8** in 25 ml of THF was added dropwise with stirring to a slurry of 1 g of $LiAlH_4$ in 250 ml of THF (nitrogen atmosphere). Stirring was continued for 2 h, excess reducing agent was destroyed by addition of wet ethyl acetate, and the complex was destroyed by addition of water. The mixture was filtered and the residue was thoroughly washed with ethyl acetate. The combined filtrate and washings were evaporated to yield 18.7 g (92%) of **9a,** mp 135 °C after recrystallization from hexane–$CHCl_3$, which had IR absorption at 3250 cm^{-1} and NMR signals (90 MHz) at 0.66, 0.66, 0.73, 1.0 (C-4, C-8, and C-10 methyls), and 3.0 ppm m (two protons, H-12).

Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.89; O, 12.58. Found: C, 75.40; H, 11.89; O, 12.71.

A solution of 18.7 g of **9a** in 10 ml of pyridine was stirred with 10 ml of acetic anhydride at room temperature for 8 h, poured onto crushed ice, and extracted with ether. The washed and dried ether extracts were evaporated, yield of gummy **9b** 21 g (88%). After purification by column chromatography, it had IR bands at 3450, 1740, and 1240 cm^{-1}, NMR signals (90 MHz) at 0.72, 0.72, 0.80, 1.10 (C-4, C-8, and C-10 methyls), 1.98 (acetate), and 4.05 ppm t (J = 7 Hz, H-12).

Anal. Calcd for $C_{18}H_{32}O_3$: C, 72.93; H, 10.80; O, 16.19. Found: C, 73.19; H, 11.01; O, 15.51.

Dehydration of 9b. To a solution of 21 g of **9b** in 10 ml of anhydrous pyridine cooled to 0 °C was added 5 ml of $POCl_3$. The mixture was stirred for 8 h, poured onto crushed ice, and extracted with ether. The washed and dried ether layer was evaporated and the gummy residue, wt 18.6 g, was chromatographed over an alumina column impregnated with $AgNO_3$. The first component **11a,** wt 1.9 g, had IR bands at 1740 and 1240 cm^{-1}, NMR signals (60 MHz) at 0.83, 0.88, 0.93 (C-4 and C-10 methyls), 1.62 (C-8 methyl), 2.05 (acetate), and 4.05 ppm t (J = 8 Hz, H-12).

Anal. Calcd for $C_{18}H_{30}O_2$: mol wt, 278. Found: mol wt (MS), 278.

Reduction of **11a** with $LiAlH_4$ in the usual fashion (see below for **10a**) yielded **11b,** NMR signals at 0.80, 0.83, 0.90 (C-4 and c C-10 methyl), 1.5 g (C-8 methyl), and 3.56 ppm t (two protons, H-12), IR band at 3350 cm^{-1} (br).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 80.92; H, 12.04.

The second component **12a,** wt 7.4 g, had IR bands at 1740 and 1235 cm^{-1}, NMR signals (60 MHz) at 0.78, 0.90, 0.90 (C-4 and C-10 methyls), 1.72 br (C-8 methyl), 2.06 (acetate), 4.2 m (H-12), and 5.5 ppm br (H-7).

Anal. Calcd for $C_{18}H_{30}O_2$: mol wt, 278. Found: mol wt (MS), 278.

Reduction of **12a** with $LiAlH_4$ in the usual fashion (see below for **10a**) yielded **12b,** NMR signals at 0.79, 0.86, 0.87 (C-4 and C-10 methyls), 1.67 (C-8 methyl), 3.7 m (two protons, H-12), 5.43 ppm m (H-7), IR band at 3380 cm^{-1} (br).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 80.74; H, 12.06.

The last component (**10a**), wt 9.3 g, had IR bands at 1740, 1640, and 1240 cm^{-1}, NMR signals (90 MHz) at 0.57, 0.68, 0.73 (C-4 and C-10

methyls), 1.75 (acetate), 3.3 m (H-12), 4.65 and 4.85 ppm br (exocyclic methylene).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86; O, 11.49. Found: C, 77.04; H, 10.82; O, 11.91.

A solution of 5 g of **10a** in 10 ml of THF was added dropwise with stirring to a slurry of 0.25 g of $LiAlH_4$ in 50 ml of Thf and stirred for 4 h. The usual workup yielded 4.0 g of **10b** as a gum, which was purified by column chromatography and had IR bands at 3340 and 1640 cm^{-1}, NMR signals (60 MHz) at 0.7, 0.82, 0.89 (C-4 and C-10 methyls), 3.6 m (H-12), 4.55 br and 4.81 ppm br (exocyclic methylene group).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94; O, 6.77. Found: C, 81.10; H, 12.14; O, 6.76.

Oxidation of 10b. A. A solution of 3.2 g of **10b** in 5 ml of CH_2Cl_2 was added in one portion to a suspension of 2.4 g of CrO_3·2pyridine in 500 ml of CH_2Cl_2 (nitrogen atmosphere). The mixture was stirred for 15 min at room temperature, and filtered through a Florisil column. The residue was washed thoroughly with CH_2Cl_2 and the washings again filtered through Florisil. The combined filtrates were evaporated. The gummy residue was chromatographed over Florisil, yield of gummy **13**, wt 2.5 g (78%), which could be crystallized from hexane (mp 32–34 °C, lit. 35.6 °C),[27] IR bands at 1720 and 1640 cm^{-1}, NMR signals (90 MHz) at 0.71, 0.83, 0.91 (C-4 and C-10 methyls), 2.46 d (J = 1–2 Hz, H-11), 4.40 br and 4.83 br (exocyclic methylene), and 9.7 ppm t (J = 1–2 Hz, H-12).

B. Oxidation of 0.400 g of **10b** with a suspension of silver carbonate on Celite in refluxing benzene for 18 h followed by filtration through a Celite column and evaporation of the solvent yielded 0.315 g (80%) of **13**.

(*E*)-Labda-8(17),13-dien-(12*R*)- and -(12*S*)-ols (6a and 6b). To a solution of 0.368 g of *cis*-2-bromo-2-butene in anhydrous ether kept at −78 °C was added 0.255 g of *tert*-butyllithium in ether. The mixture was stirred at −78 °C for 1 h; this was followed by dropwise addition of 0.177 g of aldehyde **13** in anhydrous ether. The reaction was monitored by TLC. When it was complete, the mixture was poured onto crushed ice, neutralized with NH_4Cl, and extracted with ether. The washed and dried extract was evaporated and the residue separated by preparative TLC into two components, **6a** (36 mg, 18%) and **6b** (70 mg, 35%). Alcohol **6a** had IR bands at 3600, 3450 (br), and 1640 cm^{-1}, and NMR signals (270 MHz) at 0.65, 0.78, 0.86 (C-4 and C-10 methyls), 1.58 d (J = 6 Hz, C-14 methyl), 1.68 br (C-13 methyl), 4.40 br and 4.77 br (H-17), 4.60 dbr (J = 10 Hz, H-12), 5.24 ppm qbr (J = 6 Hz, H-14).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.50; H, 11.68; O, 5.68.

Alcohol **6b** had IR bands at 3600, 3400 (br), and 1640 cm^{-1}, and NMR signals at 0.67, 0.77, 0.84 (C-4 and C-10 methyls), 1.50 d (J = 6 Hz, C-14 methyl), 1.66 br (C-13 methyl), 4.73 t (J = 6 Hz, H-12), 4.73 br and 4.87 br (H-17), and 5.37 ppm qbr (J = 6 Hz, H-14).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.52; H, 11.74; O, 5.17.

Oxidation of 6b. A. A solution of 35 mg of **6b** in 2 ml of CH_2Cl_2 was oxidized with 0.35 g of Collins reagent as described above for **10b.** The crude gummy product was purified by TLC, yield 20 mg of **15** (57%), which had an IR band at 1640 cm^{-1}, NMR signals (60 MHz) at 0.70, 0.80, 0.86 (C-4 and C-10 methyls), 1.45 (C-13 methyl), 2.00 (methyl ketone), 3.00 m (H-12), 4.73 br and 4.95 ppm br (H-17).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59; O, 10.51. Found: C, 79.00; H, 10.40; O, 10.60.

B. Attempts to oxidize 35 mg of **6a** or **6b** with active MnO_2 in $CHCl_3$ solution for 8 hr at room temperature resulted in complete recovery of the starting materials.

Epoxidation of Manool. To a solution of 20 g of manool and 0.5 g of vanadyl acetylacetonate in 150 ml of refluxing benzene was added dropwise 7.5 g of 80% *tert*-butyl hydroperoxide. The progress of the reaction was monitored by TLC. When reaction was complete, the solvent was evaporated. Chromatography of the residue over silica gel (solvent hexane–ether, 9:1) yielded 20 g (96%) of **19** as a gummy mixture of C-14 epimers, which exhibited NMR signals (60 MHz) at 0.70, 0.83, 0.90 (C-4 and C-10 methyls), 1.20 and 1.30 (together three protons, C-13 methyl), 2.80 m (H-14 and H-15), 4.53 br and 4.83 ppm br (H-17).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.33; H, 11.04; O, 10.63.

Labd-8(17)-ene-(13*R*,14*RS*)-diol (20a). A solution of 20 g of **19** in THF was added dropwise to 1 g of $LiAlH_4$ in 250 ml of THF with stirring (nitrogen atmosphere). After 1 h the mixture was worked up as usual, yielding 20 g (99%) of **20a** as a mixture of C-14 epimers, which had IR bands at 3400 and 1640 cm^{-1}, NMR signals (270 MHz) at 0.70, 0.81, 0.86 (C-4 and C-10 methyls), 1.13 (C-13 methyl), 1.08 d and 1.09 d (J = 7 Hz, together three protons, C-14 methyl), 3.63 q and 3.64 q (J = 7 Hz, together one proton, H-14), 4.58 br and 4.82 ppm br (H-17).

Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76; O, 10.37. Found: C, 77.98; H, 11.71; O, 10.31.

Acetylation of 15 g of **20a** in 10 ml of pyridine with 10 ml of acetic anhydride for 8 h at room temperature followed by the usual workup and chromatography over Florisil gave 13 g (80%) of **20b** as a mixture of C-14 epimers which had IR bands at 3490, 1740, 1640, and 1240 cm^{-1}, NMR signals (270 MHz) at 0.66, 0.80, 0.86 (C-4 and C-10 methyls), 1.13 (C-13 methyl), 1.15 d and 1.17 d (J = 7 Hz, C-14 methyl), 2.03 (acetate), 4.50 br and 4.80 br (H-17), and 4.8 ppm m (two superimposed quartets, together one proton, H-14).

Anal. Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93; O, 13.69. Found: C, 75.80; H, 10.96; O, 13.24.

Acetate of Labd-8(17)-ene-(13*R*,14*S*)-diol (20dB). The mixture of acetates **20b** was dissolved in hexane and cooled to 0 °C. Compound **20bB** crystallized out and had mp 105 °C. The IR and NMR spectra were identical with those of **20b** except for the absence of the doublet at 1.15 ppm and the appearance of H-14 as a sharp quartet at 4.80 ppm.

Oxidations of 20a. A. To an ice-cold solution of 3.6 g of **20a** in 20 ml of acetone was added dropwise a solution of Jones reagent until the reaction was completed. The solvent was evaporated at reduced pressure and the residue was taken up in ether. Evaporation of the washed and dried extract gave a gum which was chromatographed over Florisil. Fraction 1, wt 1.8 g (65%), corresponded to ketone **22.**[20] Fraction 2, wt 0.54 g (15%), was **21** as a gum which had IR bands at 3450, 1700, and 1640 cm^{-1}, NMR signals (60 MHz) at 0.62, 0.76, 0.83 (C-4 and C-10 methyls), 1.31 (C-13 methyl), 2.16 (methyl ketone), 4.40 br and 4.80 ppm br (H-17).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.52; H, 11.33; O, 10.15.

B. Oxidation of 0.40 g of **20a** with 5 g of Collins reagent in CH_2Cl_2 (15 min) and chromatography gave 0.26 g (76%) of **22** and 0.08 g (20%) of **21.** Oxidation of 0.20 g of **20a** with 0.50 g of pyridinium chlorochromate in CH_2Cl_2 until reaction was complete (TLC) and preparative TLC of the crude product gave 100 mg (59%) of **22** and 30 mg (15%) of **21.** Oxidation of 1.4 g of **20a** with slver carbonate on Celite in refluxing benzene for 18 h followed by the usual workup (see oxidation of **10b**) and chromatography over Florisil gave 0.80 g (68%) of **22** and 0.40 g (28%) of **21.** Oxidation of 0.375 g of **20a** with 0.6 g of active MnO_2 in boiling $CHCl_3$ until the reaction was complete (TLC analysis), filtration, and evaporation of the filtrate gave 0.31 g of a gum which was **22** (95%) containing a trace of **21** (<5%, TLC analysis).

Dehydration of 20b. An ice-cold solution of 4.10 g of **20b** in 15 ml of pyridine was mixed with 5 ml of $POCl_3$ and allowed to stand, with stirring, at room temperature for 12 h until reaction was complete (TLC). The mixture was poured onto ice and extracted with ether. The washed and dried ether extract was evaporated. Chromatography over Florisil gave 2.93 g (80%) of a mixture containing **24** and **25** in the ratio 1:2 (NMR analysis). The two substances were separated by pressure liquid chromatography (Porasil column, eluting solvent 1:1 hexane–ether). Acetate **24**[31] had IR bands at 1740, 1640, and 1240 cm^{-1}; NMR signals (270 MHz) at 0.75, 0.81, 0.88 (C-4 and C-10 methyls), 1.30 d (J = 7 Hz, C-14 methyl), 2.03 (acetate), 4.50 br, 4.83 br (H-17), 4.87 br (H-17), 5.03 br (H-16b), and 5.30 ppm q (J = 7 Hz, H-14).

Acetate **25** had IR bands at 1740, 1640, 1240, and 740 cm^{-1}; NMR signals (270 MHz) at 0.70, 0.83, 0.90 (C-4 and C-10 methyls), 1.26 d (J = 7 Hz, C-14 methyl), 1.66 br (C-13 methyl), 2.00 (acetate), 4.43 br and 4.83 br (H-17), 5.41 t (J = 6 Hz, H-12), and 5.25 ppm q (J = 7 Hz, H-14).

Anal. Calcd for $C_{22}H_{36}O_2$: C, 79.46; H, 10.91; O, 9.62. Found: C, 79.47; H, 10.88; O, 9.65.

(*Z*)-Labda-8(17),12-dien-(14*RS*)-ol (16). Reduction of 0.400 g of **25** with 0.03 g of $LiAlH_4$ in THF followed by the usual workup gave 0.188 g of **16** as a mixture of C-14 epimers which had IR bands at 3350, 1640, and 898 cm^{-1}; NMR signals at 0.66, 0.76, 0.83 (C-4 and C-10 methyls), 1.15 d (J = 7 Hz, C-14 methyl), 1.60 br (C-13 methyl), 3.96 q (J = 7 Hz, H-14), 4.25 br and 4.63 br (H-17), and 5.16 ppm t br (J = 6 Hz, H-12).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.49; H, 11.83; O, 5.68.

(*Z*)-Labda-8(17),12-dien-(14*S*)-ol (16b). A solution of 0.760 g of **20bB** in 1 ml of pyridine was dehydrated with 0.1 ml of pyridine as described above for **20b** and gave 0.600 g of a mixture of acetates. Reduction with 5 mg of $LiAlH_4$ in THF by the usual procedure yielded 0.480 g of a mixture of alcohols which was separated by high-pressure liquid chromatography using a Porasil column (solvent hexane–5% ether) to furnish 0.300 g of alcohol **16b.** The IR and NMR spectra were

similar to those of mixture **16.**

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.65; H, 11.80; O, 5.55.

Absolute Configuration of 16b. A solution of 400 mg of α-phenylbutyric anhydride (1.29×10^{-2} M) and 50 mg of **16b** (1.72×10^{-3} M) in 2 ml of pyridine was allowed to stand at room temperature for 48 h. Excess anhydride was destroyed by adding 1 ml of water and allowing to stand for 12 h at room temperature. The solution was extracted with ether. The extract was washed with water, three 10-ml portion of 5% sodium bicarbonate solution, and again several times with water. The combined aqueous extracts were washed with chloroform and acidified with an excess of 1 N sulfuric acid solution. The acidified solution was extracted with chloroform and the chloroform extract was dried and evaporated. This afforded 318 mg of α-phenylbutyric acid (pure on TLC), α_D in 5 ml of benzene (0.4-dm tube) 0.0179, $[\alpha]_D$ 1.22, theoretical $[\alpha]_D$ 96.5/[2 × 7.48 − 1] = 6.91. The optical yield therefore was 1.22/6.91 = 17.6%.

Oxidation of 16. Oxidation of 0.385 g of the mixture of epimers **16** with 3 g of Collins reagent in CH_2Cl_2 followed by the usual workup gave 0.375 g of a gummy mixture which was separated by pressure liquid chromatography on Porasil (eluent 1% ether in hexane). Fraction 1 (**17,** 0.123 g, 32%) was a solid, mp 91–93 °C, which had IR bands at 1700, 1640, 1450, 1370, and 900 cm^{-1}; NMR signals (270 MHz) at 0.70, 0.80, 0.88 (C-4 and C-10 methyls), 1.36 d (J = 6 Hz, C-14 methyl), 1.40 (C-13 methyl), 3.16 m (J = 6 Hz, H-14), 4.43 br and 4.73 ppm br (H-17).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59; O, 10.51. Found: C, 79.00, H, 10.40; O, 10.60.

The second fraction (**26,** 103 mg, 27%) was a gum which had IR bands at 1670, 1640, and 900 cm^{-1}; NMR signals (270 MHz) at 0.75, 0.83, 0.88 (C-4 and C-10 methyls), 1.80 br (C-13 methyl), 2.20 (methyl ketone), 4.43 br and 4.86 br (H-17), and 6.55 ppm tbr (J = 6Hz, H-12).

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18; O, 5.55. Found: C, 82.65; H, 11.24; O, 6.11.

When chromous chloride was added to 43 mg of **17** in 2 ml of acetic acid, the color of the solution remained blue. The usual workup resulted in recovery of 40 mg of starting material.

Labda-8(17),13(16)-dien-14-ol (29). Reduction of 0.260 g of **24** with 0.03 g of $LiAlH_4$ in the manner described for **25** gave 0.17 g (75%) of **29** as a mixture of C-14 epimers which had IR bands at 3350, 1640, and 900 cm^{-1}; NMR signals (270 MHz) at 0.66, 0.80, 0.83 (C-4 and C-10 methyls), 1.31 d (J = 7 Hz, C-14 methyl), 4.05 q (J = 7 Hz, H-14), 4.33 br (H-17), 4.60 br (H-16), and 4.80 ppm br (H-17).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.49; H, 183; , 5.68.

Cyclization of 16. A mixture of 3.6 g of **16** and 1 ml of 90% formic acid was allowed to stand at room temperature for 1 h, diluted with water, and extracted with ether. The washed and dried extract was evaporated and the gummy residue was chromatographed over Florisil. Hexane eluted 0.43 g of a gum which was further separated by pressure liquid chromatography (eluent hexane) into two fractions. Fraction 1 (120 mg) was an inseparable mixture of hydrocarbons; fraction 2 (300 mg, 8%) was identified as **28.** The NMR spectrum (270 MHz) exhibited signals at 0.83, 0.86, 0.95 (C-4 and C-10 methyls), 1.5 d ($J \sim 1$ Hz, vinyl methyl), 1.50 d (J = 6 Hz, vinyl methyl) 2.78 m (two protons), and 5.2 ppm qbr (J = 6 Hz, vinyl proton). Owing to facile decomposition of this substance the elementary analysis was not satisfactory. The high-resolution mass spectrum indicated decomposition. The low-resolution mass spectrum gave the correct molecular ion.

Anal. Calcd for $C_{20}H_{32}$: mol wt, 274. Found: mol wt (MS), 274.

Elution of the Florisil column with hexane–ether (19:1) produced 1.25 g (38%) of the formate of **16** which had NMR signals at 0.72, 0.84, 0.89 (C-4 and C-10 methyls), 1.30 d (J = 7 Hz, C-14 methyl), 1.67 br (C-13 methyl), 4.40 and 4.80 br (H-17), 5.3 q br (J = 7 Hz, H-14), and 8.00 ppm (formyl proton).

Anal. Calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76; O, 10.05. Found: C, 79.42; H, 10.56; O, 10.02.

Further elution of the Florisil column with hexane–ether (9:1) gave 0.20 g of starting material **16.**

Reaction of 0.21 g of **16** in CH_2Cl_2 with $SnCl_4$ in CH_2Cl_2 at −78 °C for 5 min followed by the usual workup gave 0.19 g of a hydrocarbon mixture (NMR analysis) which could not be separated chromatographically.

Cyclization of 29. To a solution of 0.14 g of **29** in 10 ml of CH_2Cl_2 kept at −78 °C was added dropwise with stirring (nitrogen atmosphere) 0.18 g of anhydrous $SnCl_4$ in 10 ml of CH_2Cl_2. Stirring was continued at room temperature for 30 min, at which time there was added 5 ml of pyridine. The mixture was poured into 10 ml of 1 N hydrochloric acid and extracted with ether. The washed and dried ether extract was evaporated and the residual gum was purified by preparative TLC. This yielded 0.10 g (60%) of ketone **32** (mp 86 °C, crystallized from hexane–chloroform) which had IR bands at 1725, 1460, and 1375 cm^{-1}, NMR signals (270 MHz) at 0.82, 0.83, 0.86, 0.96 (C-4, C-8 and C-10 methyls), and 2.06 ppm (methyl ketone).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.45; H, 11.81; O, 5.74.

A solution of 0.275 g of **32** and 0.200 g of *m*-chloroperbenzoic acid in 10 ml of $CHCl_3$ was allowed to stand for 24 h in the dark. The washed and dried $CHCl_3$ was evaporated at reduced pressure; the residual gum upon purification by preparative TLC yielded 0.267 g (92%) of **33a** which had IR bands at 1725, 1460, 1440, 1380, 1360, and 1240 cm^{-1}; NMR signals (270 MHz) at 0.77, 0.80, 0.83, 0.96 (C-4, C-8 and C-10 methyls), 1.96 (acetate), and 4.88 ppm m (H-13).

Anal. Calcd for $C_{20}H_{34}O_2$: mol wt, 306. Found: mol wt (MS), 306.

Reduction of 0.230 g of **33a** in 2 ml of THF with 50 mg of $LiAlH_4$ in 10 ml of THF followed by the usual workup and purification of the crude product by preparative TLC gave 0.19 g (96%) of gummy **33b** which had IR bands at 3290, 1460, 1380, and 1360 cm^{-1}; NMR signals (270 MHz) at 0.79, 0.80, 0.83, 0.93 (C-4, C-8 and C-10 methyls), and 3.66 ppm m (H-13).

Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20; O, 6.05. Found: C, 81.52; H, 12.09; O, 6.39.

Oxidation of 0.21 g of **33b** in 10 ml of acetone with Jones reagent as described for **20a** and preparative TLC of the crude product afforded 0.175 g of gummy **34** which had an IR band at 1720 cm^{-1} and NMR signals (270 MHz) at 0.84, 0.86, 0.89, and 0.90 ppm (C-4, C-8, and C-10 methyls).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52; O, 6.10. Found: C, 82.62; H, 11.41; O, 5.97.

$LiAl(t\text{-}BuO)_3H$ reduction of 0.12 g of **34** followed by the usual workup and purification by preparative TLC yielded 0.10 g of **35** (mp 126–128 °C, crystallized from hexane–chloroform) which had NMR signals at 0.80, 0.82, 0.84 (C-4 and C-10 methyls), 1.12 (C-8 methyl), and 4.05 ppm m (H-13).

Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20; O, 6.05. Found: C, 81.50; H, 12.10; O, 6.40.

Cyclization of 24. To a solution of 2.8 g of **24** in 125 ml of CH_2Cl_2 cooled to −78 °C was added dropwise, with stirring, 2.5 g of anhydrous $SnCl_4$ in 20 ml of CH_2Cl_2. Stirring was continued at −78 °C for 1 h, and 20 ml of pyridine was added. The mixture was worked up as described for the cyclization of **29.** Chromatography of the crude product over silica gel gave two fractions. Fraction 1 (a mixture of epimers at C-15), wt 1 g (36%), was **36a** which had IR bands at 3530 and 1715 cm^{-1}; NMR signals (270 MHz) at 0.81, 0.82, 0.83 (C-4 and C-10 methyls), 1.10 (C-8 methyl), 1.15 d and 1.16 d (together three protons, C-15 methyl), 2.05 and 2.06 (together three protons, acetate), 4.61 q and 4.62 ppm q (J = 7 Hz, together one proton, H-15).

Anal. Calcd for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93; O, 13.69. Found: C, 75.60; H, 10.86; O, 13.54.

Fraction 2, wt 0.5 g (18%), was **37.** The IR spectrum had bands at 1460, 1440, 1390, 1370, and 970 cm^{-1}; the NMR spectrum exhibited signals (270 MHz) at 0.78, 0.85, 0.9 (C-4 and C-10 methyls), and 0.98 ppm d (J = 6 Hz, C-16 methyl).

Anal. Calcd for $C_{20}H_{33}Cl$: C, 77.50; H, 11.05; Cl, 11.43. Found: C, 77.45; H, 10.91; Cl, 11.57.

Reduction of 0.290 g of **36a** with 30 mg of $LiAlH_4$ in the usual fashion and preparative TLC of the crude product gave 0.173 g of diol **36b** which had IR absorption at 3500 cm^{-1} and NMR signals (60 MHz) at 0.83, 0.83, 0.83 (C-4 and C-10 methyls), 1.11 (C-8 methyl), 1.11 d (J = 7 Hz, C-15 methyl), and 3.40 ppm q (J = 7 Hz, H-15).

Anal. Calcd for $C_{20}H_{36}O_2$: mol wt, 308. Found: mol wt (MS), 308.

Oxidation of 0.10 g of **36b** with silver carbonate on Celite in refluxing benzene for 18 h, filtration, and purification of the crude product by preparative TLC furnished hydroxy ketone **38,** wt 0.09 g (90%): IR absorption at 3500 and 1705 cm^{-1}; NMR signals at 0.80, 0.83, 0.83 (C-4 and C-10 methyls), 1.13 (C-8 methyl), and 2.16 ppm (methyl ketone).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.19; H, 11.32; O, 10.49.

Oxidation of 0.173 g of **38** in acetone with Jones reagent at 0 °C for 15 min followed by the usual workup yielded 0.15 g of ketone **34** which was identical with material obtained by degradation of **32.**

Registry No.—6a, 61047-01-6; **6b,** 61091-81-4; **8,** 30450-17-0; **9a,** 41747-05-1; **9b,** 61047-02-7; **10a,** 61047-03-8; **10b,** 31207-72-4; **11a,** 61047-04-9; **11b,** 31222-15-8; **12a,** 61047-05-0; **12b,** 31207-73-5; **13,** 3243-36-5; **15,** 61046-83-1; **16a,** 61046-84-2; **16a** formate, 61046-85-3; **16b,** 61091-75-6; **16b** formate, 61091-76-7; **17,** 61046-86-4; **18,** 596-85-0;

19 14α isomer, 54780-63-1; **19** 14β isomer, 54809-24-4; **20aA,** 61046-87-5; **20aB,** 61116-61-8; **20bA,** 61046-88-6; **20bB,** 61091-77-8; **21,** 61091-78-9; **24,** 19884-98-1; **25,** 61046-89-7; **26,** 61046-90-0; **28,** 61046-91-1; **29** 14α epimer, 61091-79-0; **29** 14β epimer, 61091-80-3; **32,** 61046-92-2; **33a,** 61046-93-3; **33b,** 61046-94-4; **34,** 18102-90-4; **35,** 61046-95-5; **36a** 15α epimer, 61046-96-6; **36a** 15β epimer, 61046-97-7; **36b,** 61046-98-8; **37,** 61046-99-9; **38,** 61047-00-5; *cis*-2-bromo-2-butene, 3017-71-8.

References and Notes

(1) Supported in part by grant from the National Science Foundation (GP-12582).
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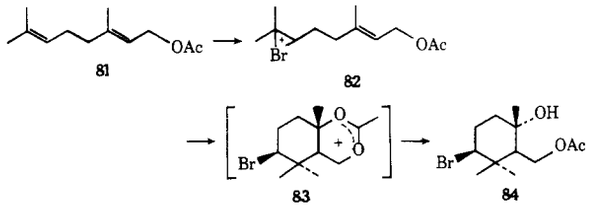

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Oxidative Rearrangements of Tertiary and Some Secondary Allylic Alcohols with Chromium(VI) Reagents. A New Method for 1,3-Functional Group Transposition and Forming Mixed Aldol Products[1]

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Received September 1, 1976

Oxidation of tertiary allylic and some secondary allylic alcohols with Collins reagent results in oxidative rearrangement to α-epoxy aldehydes or ketones. Oxidation of tertiary allylic alcohols and some secondary alcohols with pyridinium chlorochromate results in oxidative rearrangement to α,β-unsaturated aldehydes or ketones. These reactions are useful for effecting the 1,3-transposition of oxygen and for carrying out mixed aldol condensations. A detailed study of the reaction of labda-8(17),12-dien-14-ol with Cr(VI) reagents was carried out. Possible mechanisms for the oxidative rearrangements are discussed.

In connection with work on a biogenetic-type synthesis of the strobanes, we had occasion to attempt the oxidation of the allylic alcohol **1** to the α,β-unsaturated ketone **2**.[2] Oxidation with active manganese dioxide failed; oxidation with Collins reagent[3] furnished as sole product and in good yield the epoxy ketone **3**.

The formation of an epoxy ketone from an allylic alcohol with Collins reagent was unprecedented, although there are