4-(4-*o*-Chlorobenzyloxycarbonylaminobutyl)-3-(9-fluorenylmethyloxycarbonyl)-5-oxooxazolidine (7). α-[(9-fluorenylmethyloxycarbonyl)amino]pimelic acid **5** was prepared from α-aminopimelic acid (**4**) according to standard procedures.[18] Compound **5** (10 g, 25 mmol) in toluene (485 mL) was heated at reflux with paraformaldehyde (4.85 g) and *p*-toluenesulfonic acid monohydrate (485 mg, 2.55 mmol) for 2.5 h with azeotropic water removal. Formation of a new less polar spot with concomitant disappearance of the starting material spot was observed on TLC. This observation was consistent with formation of oxazolidinone **6**.

Compound **6** was not isolated. To the above reaction solution corresponding to 25 mmol of crude **6** were added *o*-chlorobenzyl alcohol (4.0 g, 28.05 mmol), triethylamine (3.8 mL, 2.76 g, 27.3 mmol), and diphenylphosphoryl azide (5.9 mL, 7.53 g, 27.4 mmol). The resultant solution was heated at 90–95 °C for 4 h. After cooling, the reaction mixture was washed with aqueous citric acid (2 × 150 mL), 1 N aqueous $NaHCO_3$ (2 × 150 mL), water (150 mL), and saturated aqueous NaCl (150 mL) and dried (Na_2SO_4). Concentration in vacuo gave 15.45 g of crude **7**. Preparative TLC (silica gel, 99:1 $CHCl_3$–MeOH) of the concentrate from a 10-mL aliquot gave 70 mg of an oil: IR ($CHCl_3$) 1800, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.0–1.8 (m, 6), 3.12 (m, 2), 3.90 (br m, 1), 4.21 (t, 1, J = 5 Hz), 4.67 (d, 2, J = 5 Hz), 4.77 (m, 1), 5.02 (d, 1, J = 4.5 Hz), 5.23 (s, 2), 5.32 (d, 1, J = 4.5 Hz), 6.9–7.9 (m, 12).

N^{α}-Fmoc-N^{α}-methyl-N^{ϵ}-(*o*-chlorobenzyloxycarbonyl)-lysine (8). Crude oxazolidinone **7** (~13.5 g, 24.5 mmol) was dissolved in $CHCl_3$ (70 mL), and Et_3SiH (11.7 mL, 8.5 g, 73 mmol) was added. Trifluoroacetic acid (70 mL) was then added, and the resultant solution was stirred at room temperature for 18 h. Concentration in vacuo and reconcentration twice from $CHCl_3$ gave 18.5 g of yellow oil. Flash chromatography (silica gel, 120:5:0.5:0.1 $CHCl_3$–MeOH–H_2O–HOAc) followed by repeat chromatography of side cuts yielded 2.0 g (15%) of amorphous product: NMR ($CDCl_3$) δ 1.1–2.0 (m, 6), 2.83 (s, 3), 3.16 (m, 2), 4.23 (m, 1), 4.45 (d, 2, J = 5.5 Hz), 4.80 (m, 1), 5.23 (s, 2), 6.90 (m, 1), 7.2–7.9 (m, 12), 8.10 (m, 1).

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Cationic Cyclizations and Rearrangements as Models for Strobane and Hispanane Biogenesis[1]

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In contrast to methyl 15(*R*)-hydroxypimar-8(14)-en-oate (**5a**) the 15(*S*)-epimer **9a** gave a stable toluenesulfonate. Solvolysis of the latter gave, depending upon the conditions, the 15(*R*)-epimer **5a**, the methoxy derivative **9d**, or, with rearrangement, the strobane derivative **10a** and the cyclopropane resin acid ester **11a**. Treatment of methyl 15-hydroxy-16-nor-8(14)-pimaren-18-oate (**9e**) with toluenesulfonyl chloride–pyridine resulted, as in the case of **5a**, in spontaneous rearrangement to **10b** and **11b**. The difference in behavior of **5a** and **9e** on the one hand and **9a** on the other is attributed to different spatial demands in the homoallylic cations produced from the starting materials. The reactions provide laboratory analogies for postulated biogenetic pathways to diterpenoids of the strobane and hispanane families. In an effort to test an alternative proposal for biogenesis of the strobanes, the epimeric labda-8(17),13-dien-12(*S*)- and -12(*R*)-ols **22** and **23** were synthesized and subjected to reagents known to effect cationic cyclizations. These experiments failed to provide compounds with the strobane carbon skeleton. Formic acid converted **23**, but not **22**, to the tricyclic hydrocarbon **31**.

One of the possible biogenetic pathways to diterpenoids with the strobane skeleton **2** involves vinyl migration in cation A or its equivalent which is generated from an appropriate pimaradiene precursor, **1** (Scheme I).[2] A second possibility is that the strobanes are formed by direct cyclization of a labdane derivative rather than through the intermediacy of a pimarane, e.g., by cyclization (Scheme II) of a bicyclic ion D or its equivalent theoretically derivable from *cis*-biformene (**3**) or alcohol **4**.

Some years ago,[3] upon attempting to mimic the pathway sketched in Scheme I, we obtained from **1a** by way of **5a** the cyclopropane resin acid ester **7** and the strobane-like isomer **6** whose C-14 stereochemistry was opposite those of the naturally occurring strobanes (Scheme III).[4,5] In the present paper we report the biogenetic-type solvolytic rearrangement of tosylate **9c** to the strobic acid derivative **10a** and to **11a** with the correct C-14 stereochemistry as well as the facile transformation of **9e**, by way of a *primary*

(1) This work was supported in part by a grant (CHE-7801 191) from the National Science Foundation.

(2) For a review see: Coates, R. M. *Fortschr. Chem. Org. Naturst.* **1976**, *33*, 73.

(3) Herz, W.; Hall, A. L. *J. Org. Chem.* **1974**, *39*, 14.

(4) (a) Zinkel, D. F.; Spalding, B. F. *Tetrahedron Lett.* **1971**, 2459. (b) Zinkel, D. F.; Spalding, B. F. *Tetrahedron* **1973**, 29, 1441. (c) Zinkel, D. F.; Evans, B. B. *Phytochemistry* **1972**, *11*, 1441.

(5) Numbering in formulas **6** and **10** differs from that employed previously[3,4] and is based on the systematic name strobane for a hydrocarbon skeleton which was not known at the time commonly accepted proposals[6] for naming cyclic diterpenes were formulated. Strobic acid would thus be stroba-8(15),12-dien-18-oic acid. The discoverers[4a] originally used the systematic name abeopimarane, in terms of which strobic acid should be formulated as 14(13→15α*H*)-abeopimara-8(14),12-dien-18-oic acid, and subsequently[4b] corrected it to that of a cyclolabdane [14(*S*),17-cyclolabda-8(17),12-dien-18-oic acid]. Coates[2] has used strobane numbering. The abeopimarane or cyclolabdane nomenclature would probably be preferable to the strobane nomenclature if the actual biosynthesis route were known.

(6) Rowe, J. W. "The Common and Systematic Nomenclature of Cyclic Diterpenes"; Forest Products Laboratory, U.S. Department of Agriculture: Madison, WI, 1968 (with Additions and Corrigenda, 1969).

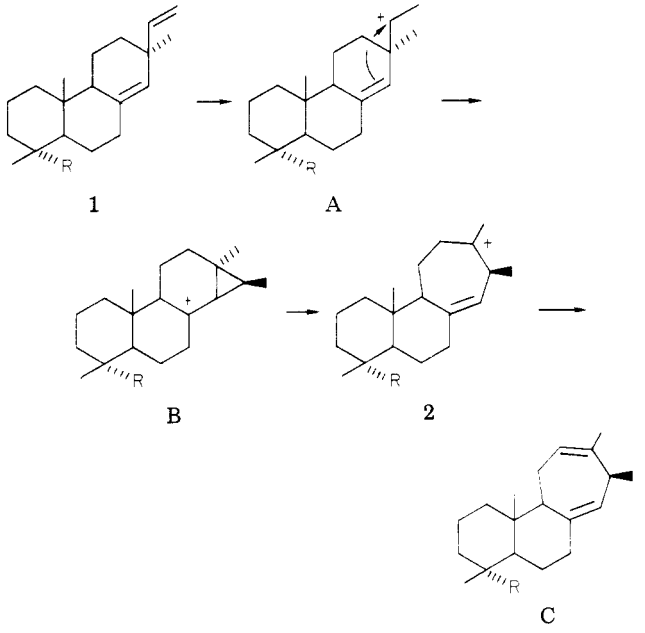
0022-3263/83/1948-0081$01.50/0

Table I. ^{13}C NMR Spectral Data of Compounds 5a-11a

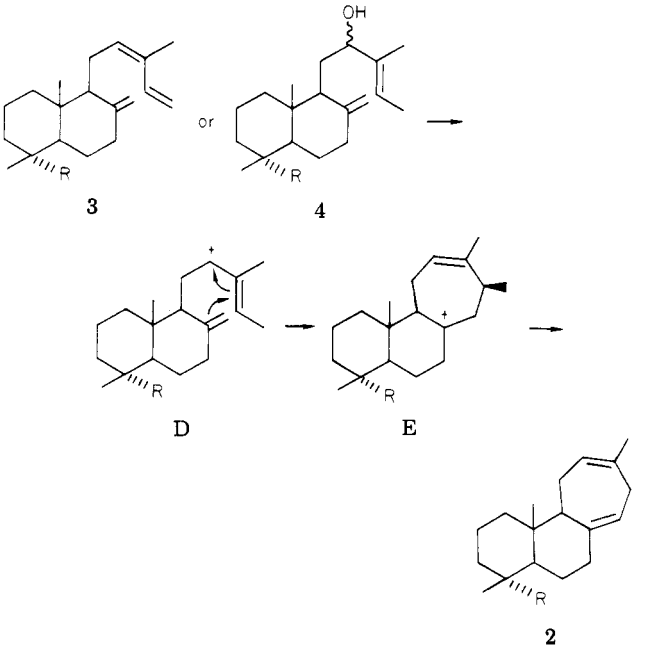
	chemical shift, ppm										
carbon	5a	5b	6	7	8	9a	9b	9e	10a	10b	11a
1	38.22	38.06	38.83	36.64	37.92	38.24	38.33	38.25	38.87	38.60	36.71
2	18.17	18.12	18.06	18.44	18.06	18.19	18.33	18.15	18.06	18.30	18.46
3	37.05	37.05	37.11	36.01	37.05	37.06	37.07	36.98	37.24	37.10	35.27
4	47.48	47.49	47.59	47.88	47.45	47.50	47.55	47.49	47.11	47.59	47.82
5	49.33	49.38	50.47	46.36	49.19	49.33	49.31	49.20	49.16	50.23	46.48
6	24.93	24.95	27.08	21.90	26.85	25.28	25.11	25.66	23.46	26.88	21.73
7	35.76	35.71	37.41	31.00	35.47	35.90	35.87	35.55	33.19*	37.59	31.48
8	138.77	138.99	140.93	128.50	140.49	138.08	137.35	139.45	141.44	142.61	125.16
9	50.72	50.72	59.55	136.43	50.91	50.45	50.28	50.77	56.47	59.56	141.63
10	37.80	37.83	39.77	36.99	38.03	38.00	38.06	36.34	37.05	39.77	37.53
11	18.30	18.12	18.28	18.82	19.91	18.53	18.20	18.69	21.38	18.87	21.70
12	30.59	31.87	40.82	32.06	31.95	32.15	31.59	31.14	39.85*	37.81*	26.28
13	38.66	37.51	76.79	21.14	49.03	38.24	56.97	37.64	85.15	75.43	17.27
14	128.99	127.84	37.73	31.10	125.89	128.53	128.15	127.65	41.48	39.31*	27.09
15	71.92	73.72	126.16	22.15	212.31	74.12	76.66	69.85	127.54	117.74	25.03
16	17.41	14.95	15.53	13.83	26.62	17.82	15.42		17.84		8.60
17	22.42	22.47	24.63	19.56	26.86	22.28	22.86	25.66	25.31	30.40	26.84
18	179.14	179.30	179.20	117.38	179.28	179.09	179.36	179.31	179.50	179.25	179.37
19	17.00	17.02	16.64	16.39	16.98	16.99	17.00	17.02	16.95	16.64	16.42
20	15.06	14.96	14.60	20.21	14.50	15.28	14.88	15.01	15.99	14.62	19.60
21	57.76	57.84	57.81	57.73	57.89	57.76	57.84	57.86	57.76	57.84	57.75
Ac		170.53, 21.28					170.62, 21.28				

[a] An asterisk indicates that the assignments may be interchanged.

Scheme I



Scheme II

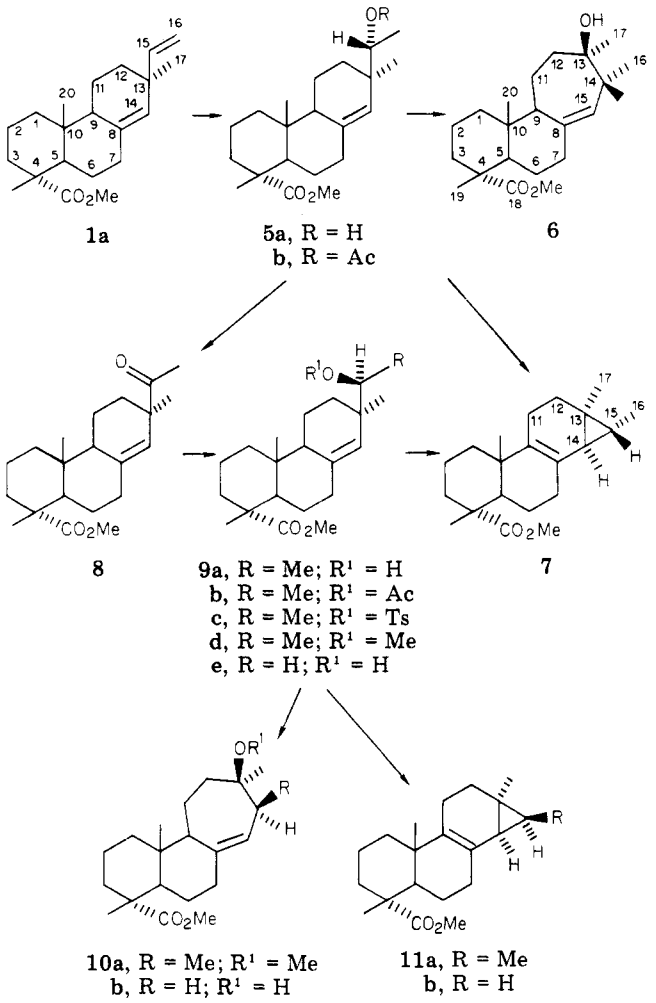


cation or its equivalent, to **10b** and **11b**. The rearrangement of **9e** serves as a model for the crucial step in the biogenesis of the recently discovered diterpenes hispanonic acid (**13**) and hispaninic acid (**14**)[7] from a C-17 functionalized sandaracopimaradiene precursor **12** (Scheme IV). We also describe new experiments designed to provide a laboratory analogy for the proposal adumbrated in Scheme II which, like an earlier related study, failed to provide compounds with the strobane carbon skeleton.

Biogenetic-Type Cyclizations of Pimaranes. Our previous results[3] indicated that genesis of **6** and **7** on treatment of **5a** with tosyl chloride–pyridine proceeded by a stereospecific homoallyl–cyclopropylcarbinyl–homoallyl pathway. If this interpretation were correct, the C-14 epimer **9a** of **5a** might be expected to furnish products **10a** and **11a** with the C-14 stereochemistry of the naturally occurring strobanes. An early effort[9] to verify this supposition foundered because $NaBH_4$ reduction of ketone **8** gave a 1:2 mixture (NMR analysis) of **5a** and **9a** which were not separated as such or as the acetates **5b** and **9b** by the means then available. Various subsequent attempts to invert the C-15 configuration of alcohol **5a** also failed, apparently due to participation by the 8,14 double bond. In particular, treatment with triphenylphosphine–diethyl azodicarboxylate[10] resulted in recovery of **5a** under all conditions tried. Finally, HPLC of the alcohol mixture by using the peak shaving–recycle technique earlier found useful for the near-quantitative separation of closely re-

(7) Rodriguez, B.; Savona, G.; Piozzi, F. *J. Org. Chem.* **1979**, *44*, 2219.
(8) Sundararaman, P.; Herz, W. *J. Org. Chem.* **1977**, *42*, 806.
(9) Hall, A. L. Ph.D. dissertation, The Florida State University, 1973.
(10) Mitsunobu, O. *Synthesis* **1981**, 1.

Scheme III



lated labdadiene isomers[11] afforded pure **5a** and **9a** in 20% and 56% yields. Spectroscopically, **9a** and **9b** can be distinguished from **5a** and **5b** of established 15(*R*) configuration in the frequencies of H-14 (near δ 5.3 for **9a,b** and δ 5.1 and **5a,b**) anc C-15 (δ 2–3 downfield for the **9** series; Table I).

Unexpectedly, reaction of **9a** with tosyl chloride–pyridine under conditions which had resulted in rearrangement of **5a** to **6** and **7** gave tosylate **9c** (93%) without rearrangement. Subsequent solvolysis of **9c** (MeOH–NaOAc) furnished after extensive chromatographic purification three substances **9d**, **10a**, and **11a** in 6%, 14%, and 21% yields, respectively. Solvolysis of **9c** in acetone–H_2O gave 44% of **11a**, 23% of **5a**, and smaller amounts of unidentified mixtures. Structure assignments were based on the following evidence.

The least polar and noncrystalline product **9d** was obtained pure in a very small amount only. Its identification as the methyl ether of alcohol **9a** rests on its spectroscopic properties, particularly on the frequency of the H-14 signal at δ 5.39 which indicated that it belonged to the 15(*S*) rather than the 15(*R*) series.

The most polar product **10a** which could not be induced to crystallize had the molecular formula $C_{22}H_{35}O_3$ (high-resolution mass spectroscopy) and contained in addition to the methyl ester function an ethereal methoxyl group attached to a quaternary carbon which was represented in the ^{13}C NMR spectrum by a singlet at δ 85.13 and which must be C-13. Its paramagnetic shift of 9–10 ppm in comparison with the C-13 signals of **6** and **10b** (Table I) is in accord with expectations.[12,13] A vinylic proton (H-15) represented in the ^1H NMR spectrum by a broadened doublet at δ 5.16 (J = 6 Hz) was coupled vicinally to neighboring H-14, a quintet at δ 2.35 (J = 6 Hz), which was in turn coupled to the protons of a methyl doublet at δ 1.06. Hence **10a** was the methyl ether of a stereoisomer of **6**. Because H-14 was not deshielded by the adjacent oxygen-bearing group as in **6** where its signal is found at δ 2.78, it was cis to the methyl group on C-13 and hence α.

The molecular formula $C_{21}H_{32}O_2$ and the ^1H and ^{13}C NMR spectra of the crystalline substance formed in largest amount were consistent with structure **11a**. The absence of a vinylic proton signal and the presence of two quaternary vinylic carbon signals located the double bond at the 8-position; comparison with the ^1H NMR spectrum of **7** evidenced the relative stereochemistries. At 270 MHz the C-15 methyl signal of **7** was clearly visible as a doublet at δ 1.03 (J = 5.5 Hz) spin coupled to H-15 at δ 0.91 (dd, J's $\approx$ 4.5 and 5.5 Hz) which was in turn coupled to H-14 at δ 0.28. In the spectrum of **11a** the proximity of these resonances at δ 0.77 (broadened singlet of H-16), 0.75 (apparent doublet), and 0.71 (broad singlet) did not permit decoupling and determination of coupling constants, but the paramagnetic shift of H-14 indicated that it was no longer shielded by the adjacent methyl group and hence was trans to it in the new compound. The appearance of H-16 is due to the same second-order NMR phenomenon previously[3] observed for H-16 of **7** at 90 MHz.

That **7** and **11a** are C-14 epimers is also supported by their ^{13}C NMR spectra (Table I). Assignments for C-1 through C-7, C-10, and C-18 through C-20 which are least affected by the presence of the cyclopropane ring were deduced by comparison with literature values for methyl Δ^8-pimarate and its 13-epimer.[14] Assignments for C-14, C-15, and C-17 were based on selective decoupling; while no such experiments could be carried in the case of **11a** because of the proximity of the respective proton signals, the assignments seemed straightforward. The δ 6 diamagnetic shift of C-16 in **11a** can be ascribed to its proximity to the shielding zone of the 8,9 double bond, the frequencies of whose carbons are affected in an opposite manner (relative to C-8 and C-9 of the Δ^8-pimarates) by the change in configuration at C-15. The δ 7 diamagnetic shift of C-17 in **7** relative to that of **11a** is due to its cis relationship with C-16; analogously, C-12 experiences a δ 6 upfield shift in going from **7** to **11a**.

In summary, attempted tosylation of the 15(*R*)-epimer **5a** results in products representing the homoallylic–cyclopropylcarbinyl–homoallylic system **5a**, **6**, and **7** with 100% retention of configuration, whereas the 15(*S*)-epimer **9a** forms the expected tosylate. Hydrolysis of the latter

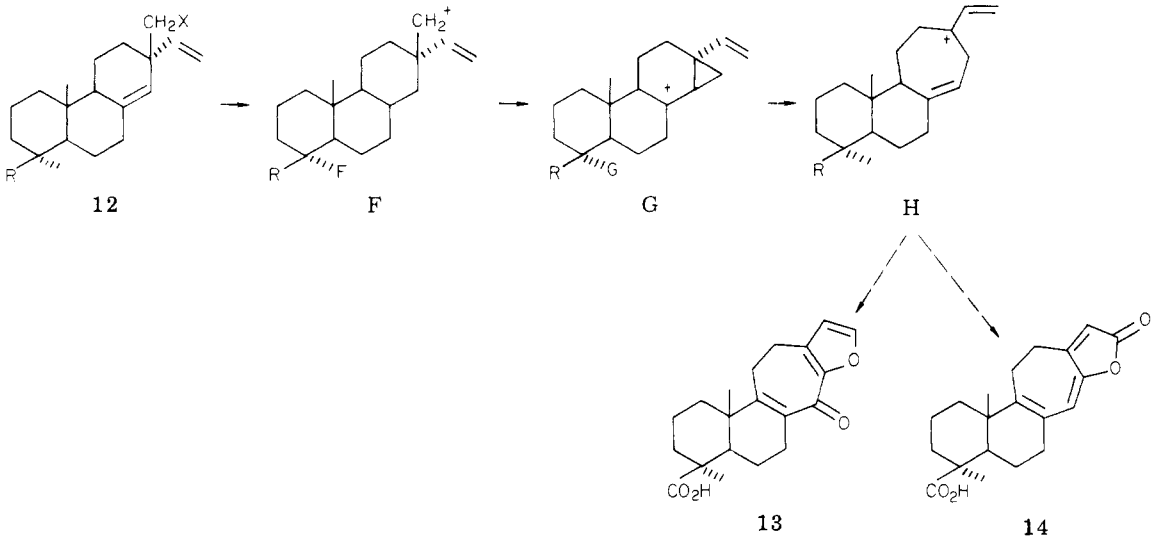
(11) Mohanraj, S.; Herz, W. *J. Liq. Chromatogr.* **1981**, *4*, 525.

(12) The methoxyl carbon displays an unusual shift of δ 46.64, apparently as the result of shielding by the 8(15) double bond (model).

(13) Chemical shifts of C-1 through C-6 and of the methyls in ring A of **6**, **10a**, and **10b** are essentially identical with those of methyl pimarate (**1a**) and its derivatives. The C-8, C-13, and C-15 frequencies are readily identified as is C-10 which is found at δ 37.05 in **10a** and at δ 39.77 in **6** and **10b**. Relative to **1a** and its analogues, C-9 of **6** and **10b** exhibits a paramagnetic shift of ca. δ 8 and C-9 of **10a** a paramagnetic shift of δ 5.6 as the result of deshielding by the hydroxyl (or methoxyl) on C-13. In **6** the doublet at δ 37.73 can be assigned to C-14 by exclusion. Due to the alteration of ring C, the triplet of C-7 in **6** and **10b** exhibits a small downfield shift of ca. δ 2.5; the upfield shift of C-7 in **10a**, tentatively identified with a triplet at δ 33.19, may be due to steric compression. Comparison of the spectra of **6** and **10b** makes a decision about assignment of the triplets at δ 39.31 and 37.81 (or 37.59), which are associated with C-12 and C-14, in the spectrum of the latter difficult.

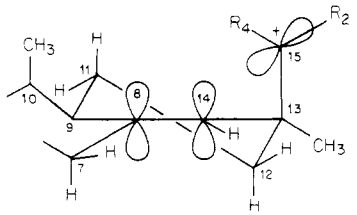
(14) Delmond, B.; Pappillaud, B.; Vallade, J.; Petraud, M.; Barbe, B. *Org. Magn. Reson.* **1981**, *17*, 201.

Scheme IV



results in predominant rearrangement to the cyclopropylcarbinyl product **11a** and a lesser amount of direct displacement product **5a** with inversion. Methanolysis yields components of the homoallylic–cyclopropylcarbinyl–homoallylic system **9d**, **10a** and **11a**; since the material balance is poor, the formation of other products cannot be excluded.

We ascribe the difference in the behavior of **5a** and **9a** to different spatial demands in the two homoallylic ions produced from **5a** and **9a**. In the former (I, R_1 = H, R_2 = Me) C-16 is directed away from ring C of the pimarane



I

ring system; in the latter (I, R^1 = Me, R_2 = H) C-16 is directed toward ring C with a considerable increase in energy. Thus tosylation of **9a** proceeds normally, and under certain conditions, "normal" nucleophilic displacement in **9c** to give **5a** may compete successfully with rearrangement which proceeds by way of I.

If this were so **9e** should behave like **5a**, and its rearrangement would at the same time provide a laboratory analogy for the biogenesis of the hispananes.[7] This was found to be the case. The required substance was synthesized by OsO_4–$NaIO_4$ cleavage of **1a**[12] followed by reduction with $NaBH_4$. Treatment of **9e** with tosyl chloride–pyridine in the manner described for **5a** and **9a** followed by extensive chromatographic purification indeed gave no tosylate but the two substances **10b** and **11b** in 30% and 5% yields, respectively. The structure of the major product was deduced by comparison of its ^1H and ^{13}C NMR spectra with those of **6** and **10a**. The ^1H NMR spectrum lacked the methyl doublet found in these substances, and the vinylic proton signal at δ 5.29 (H-15) was coupled to two mutually coupled doublets (H-14a,b, $J_{a,b}$ = 12 Hz) at δ 2.59 and 1.81. The ^1H NMR spectrum of the minor product lacked the methyl doublets of **7** and **11a** but exhibited an AMX spin system of three cyclopropane protons at δ 0.46 (dd), 0.59 (t), and 0.69 (dd) (J_{AM} = J_{MX} = 4 Hz, J_{AX} = 8 Hz). Thus, the major and minor products **10b** and **11b** from **9e** are lower homologues of **6** (or **10a**) and **11a** (or **7**) with the same stereochemistry at C-13.

Biogenetic-Type Cyclizations of Labdanes. An attempt to duplicate in the laboratory the second possible biogenetic route to the strobanes requires synthesis of an alcohol of type **4**. Earlier efforts in this direction[8] had produced the C-12 epimers **22a** and **23a** from sclareol, but in yields insufficient to study their cyclization. We now describe preparation of **22a,b** and **23a,b** from manool (**15**) as mixtures of *E* and *Z* isomers and the results of our attempts to effect their cyclization to strobanes.

The key step in the synthesis of **22** [12(*S*) series] and **23** [12(*R*) series] was an allylic transposition[15] of the alcohol function of **18b,d** (3:1 mixture of C-14 epimers).[8,16] Epoxidation of **18b,d** with vanadyl acetylacetonate and *tert*-butyl hydroperoxide[18] yielded a 77:23 mixture of epoxides **20a** and **21a** (Scheme V) which were separated by HPLC. **20a** was obviously a mixture of C-14 epimers (NMR analysis) whereas **21a** appeared to be homogeneous. The assignment of stereochemistry follows from the subsequent transformation of these compounds to **22** and **23**. Conversion to the mesylates followed by reduction with sodium naphthalenide–THF at −20 °C gave **22** (from **20b**) and **23** (from **21b**) in 63–83% yield as well as some **20a** (from **20b**) and **21a** (from **21b**) as the result of S–O cleavage.[19] **22** was a 2:3 mixture of the previously known *E* alcohol **22a**[8] with the new *Z* isomer **22b**, and **23** was a 1:2 mixture of known *E* alcohol **23a**[8] with *Z* isomer **23b**. As has been pointed out earlier,[8,20–22] compounds of the 12(*R*) series such as **23a,b** can be differentiated from compounds of the 12(*S*) series such as **22a,b** by the $\Delta\delta$ for

(15) Yasuda, A.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1976**, 2621.

(16) Alcohols **18b,d** which are prepared by dehydration of **16a,b** and subsequent hydrolysis were erroneously depicted as *Z* isomers earlier.[8] That they are *E* isomers is clearly shown by the chemical shift of H-12 (δ 6.56) in the ^1H NMR spectrum of the oxidation product **19** (cf. H-14 of **24a** and **24b** at δ 6.76 and 5.76, respectively).[8,17]

(17) Sundararaman, P.; Herz, W. *J. Org. Chem.* **1977**, *42*, 813.

(18) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.

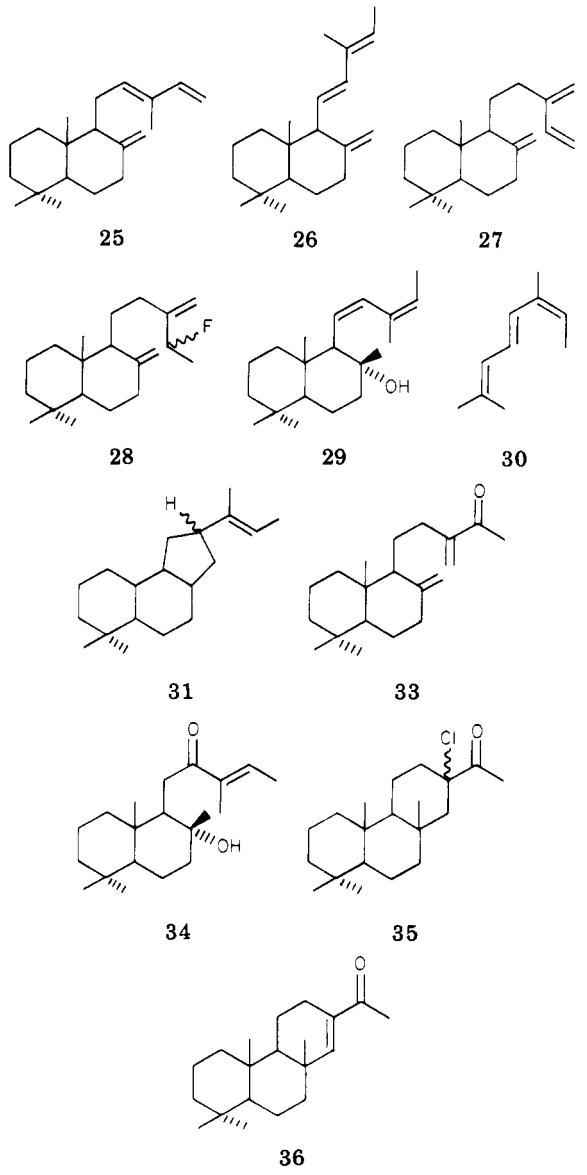
(19) The conditions are critical. Reduction was slow at temperatures below −20 °C; higher temperatures favored S–O over C–O cleavage. Na–NH_3 reduction gave lower yields and altered the ratio of *E* to *Z* isomers (see Experimental Section).

(20) Bell, R. A.; Gravestock, M. B.; Taguchi, V. Y. *Can. J. Chem.* **1972**, *50*, 3749; **1975**, *53*, 2869.

(21) Turner, J. A.; Herz, W. *J. Org. Chem.* **1977**, *42*, 1900.

(22) Mohanraj, S.; Herz, W. *J. Org. Chem.* **1981**, *46*, 1362.

Chart I



H-17a and H-17b, which for the 12(*R*) series is more than twice as great as that for the 12(*S*) series. On the other hand, the components of the *E*,*Z* pairs **22a,b** and **23a,b** can be distinguished most conveniently by the strikingly different chemical shifts of H-12: δ 4.74 (t, J = 7 Hz) and 4.58 (br d, J = 10 Hz) for **22a** and **23a**, δ 4.08 (dd, J = 9, 5 Hz) and 4.01 (br d J = 10 Hz) for **22b** and **23b**, respectively.

Our first attempts at cyclization utilized the method of Mukaiyama and co-workers, who achieved biomimetic cyclizations of nerol, geraniol, and farnesol with 2-fluoro-1-methylpyridinium tosylate in the presence of tri-*n*-butylamine.[23] Application of this procedure to **22a,b** gave no cyclic products but led to **18b,d** as a 1:1 mixture of epimers (18%) and 46% of a mixture of *trans*-biformene (**25**) and the labdatriene **26** (Chart I). The reaction with **23a,b** was somewhat slower and gave only **25** and **26** (81%). Reaction with 2-fluoro-1,3-dimethylpyridinium tosylate was again slower for **23a,b** than for **22a,b**; **23a,b** now gave **18b,d** (40%) and the **25**/**26** mixture (30%) whereas **22a,b** afforded **18b,d** (14%), the **25**/**26** mixture (33%), and 13-(*Z*),12(*R*) alcohol **23b** (20%) free of the *E* isomer. Under comparable conditions, **18b,d** gave only the mixture of **25** and **26**, whereas **17b,d** gave **25**/**26** (23%), sclarene (**27**, 13%), and a mixture of epimeric fluorides **28** (10%).

Table II. ^{13}C NMR Spectral Data of 19 and 31

carbon	chemical shift, ppm 19	31
1	38.79 t[a]	37.40 t
2	18.91 t	19.04 t
3	41.65 t	42.20 t
4	33.02	33.18
5	54.94 d	52.22 d
6	23.94 t	19.19 t
7	37.49 t[a]	35.14 t
8	147.68	139.70[a]
9	56.12 d	144.30
10	39.04	36.12
11	23.73 t	27.16 t
12	144.14 d	45.52 d
13	136.51	131.12[a]
14	197.94	116.49 d
15	24.65 q	12.70 q[b]
16	10.75 q	13.19 q[b]
17	107.17 t	41.08 t
18	33.15 q	33.40 q
19	21.30 q	21.52 q
20	13.95 q	19.48 q

[a, b] Assignments may be interchanged.

Substance **26** which is new was recognized by its ^{1}H NMR spectrum which exhibited a doublet at δ 6.02 (J = 15 Hz) and a double doublet at δ 5.58 (J = 15.5, 9.5 Hz) characteristic of the trans double bond as well as signals characteristic of the H-17a,b protons, the quartet of H-14, the vinyl methyl doublet of H-15, and the vinyl methyl singlet of H-16. The *E* rather than the *Z* configuration was assigned to the double bond because H-14 appeared at lower field (δ 5.46) than in neoabienol **29** (δ 5.27)[24] and 4(*E*),6(*Z*)-alloocimene (**30**, δ 5.29).[25,26] Structure assignment for **28** was based on the molecular formula and the characteristic ^{1}H NMR spectrum.

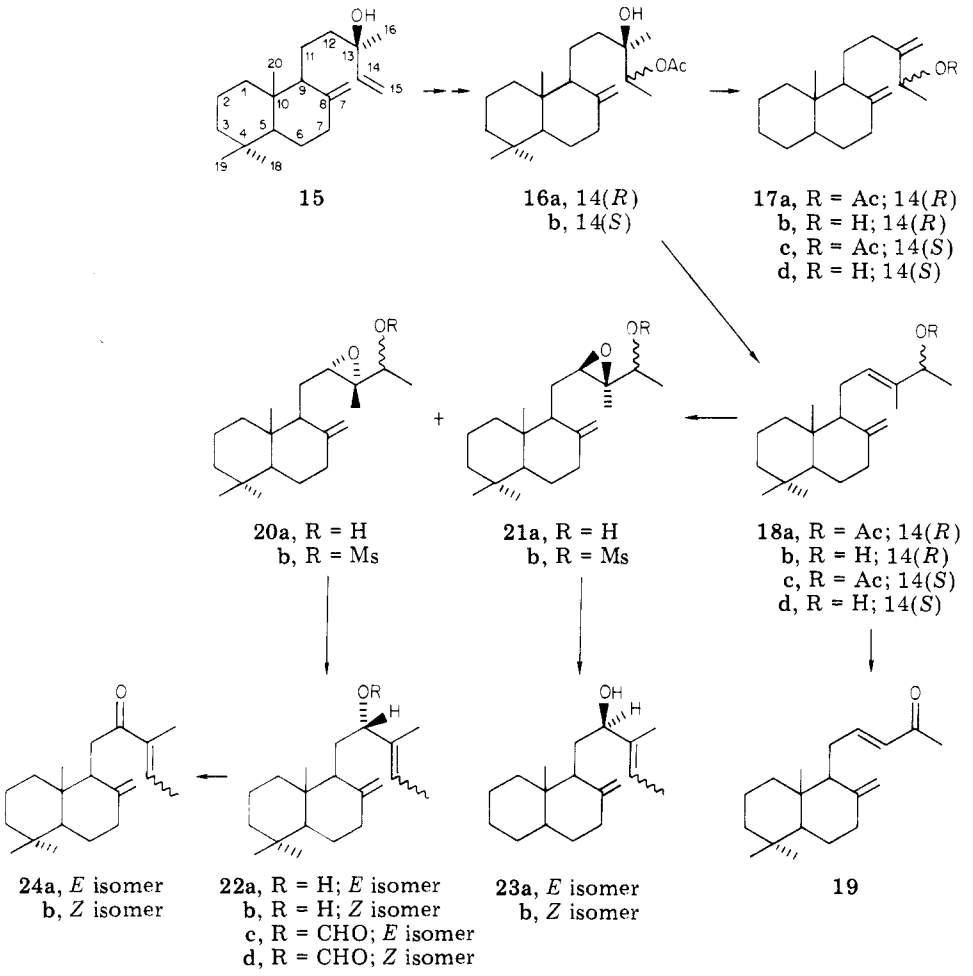
Decomposition of the 2-alkoxypyridinium salts derived from **22** and **23** (as well as those from **17** and **18**) was therefore not accompanied by π cyclization, either by direct displacement of the leaving group as in the formic acid treatment of **23a,b** (vide infra) or by the "zipper" mechanism sketched in Scheme II. Superficially the products can be accounted for most readily in terms of intermediate allylic cations. However, formation of an appreciable amount of **23b** from **22a,b** with 2-fluoro-1,3-dimethylpyridinium tosylate hints at competition from a localized ion pair in the case of **22**.

Failure to observe π cyclization in the reactions of **22** and **23** with 2-fluoro-1-methylpyridinium tosylates led us to study the action of other agents known to effect cyclizations. Attempts to prepare mesylates or tosylates from **22a,b** or **23a,b** for eventual solvolysis studies failed (at low temperature) or effected dehydration to mixtures of triolefins (at room temperature). Reaction with $SnCl_4$ gave polymeric material, treatment with boron trifluoride etherate or toluenesulfonic acid gave ill-defined mixtures, and trifluoroacetic acid produced complex mixtures containing mainly compounds resulting from isomerization of the 8(17) double bond.[27] Formic acid (97%) at room tem-

(23) Kobayashi, S.; Tsutsui, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 1137.

(24) Raldugin, V. A.; Pentegova, V. A. *Khim. Prir. Soedin.* **1971**, *7*, 595.
(25) Sasaki, T.; Eguchi, S., Yamada, H. *Tetrahedron Lett.* **1971**, *99*.
(26) *E* and *Z* isomers **23a,b** also exhibit this characteristic difference (δ 5.44 for **23a**, δ 5.24 for **23b**), but the chemical shifts of H-14 in the **22a,b** isomer pair are almost the same (δ 5.38 for **22a**, δ 5.35 for **22b**). The situation is reversed for H-15, with $\Delta\delta$ = 0.1 for **22a,b** and 0 for **23a,b**.

Scheme V



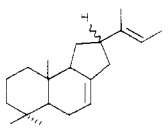
perature slowly converted **22a,b** to formate mixture **22c,d**, but under the same conditions this reagent effected relatively fast cyclization of **23a,b** in 54% yield to the same tricyclic hydrocarbon **31** previously[8] isolated in low yield from 90% formic acid treatment of **18**, together with 32% of a mixture of olefins.

Examination of the previously unreported ^{13}C NMR spectrum of **31** (Table II) demonstrated that the substance was indeed homogeneous and probably possessed the *E* configuration shown in the formula, the two quartets at δ 12.70 and 13.19 being assignable to C-15 and C-16 because the chemical shifts of C-18, C-19, and C-20 in Δ^8-pimaranes and similar compounds hover in the range δ 33–34, 21.5–22, and 19–20, respectively[14,28,29] (cf. also compounds **7** and **11a** in Table I). If **31** were a (*Z*)-alkene, the C-16 signal would be expected at lower field.[30] Seemingly then, cyclization of **23a,b** to **31** is accompanied or followed, at least in part, by double bond isomerization from *Z* to *E*, as *E* alcohol **23a** was the minor component (~33%) of the **23a,b** mixture.

The stereochemistry of **31** at C-12 remains unknown; the coupling constants involving H-12 are equally consonant with α and β orientation of the unsaturated side chain, and several attempts to oxidize the 13,14 double bond selectively in order to shed light on this matter were ineffective. This is unfortunate since the important question of whether π cyclization of **23a,b** to **31** involves retention or inversion at C-12 must in consequence remain unanswered for the time being. In view of the quite different behavior of **22a,b** and **23a,b**, intervention of an entirely free allylic cation in the cyclization process leading to **31** seems quite unlikely; hence inversion appears inherently more probable.[27] However, regardless of the mechanism, inspection of molecular models offers no simple clue to account for the observation that π cyclization in the presence of formic acid proceeds easily in the 12(*R*) series and not at all in the 12(*S*) series.

Finally, in the hope of inducing π cyclization in a more electrophilic metalloenolate, we studied the behavior of

(27) Chromatography of the mixture from trifluoroacetic acid treatment of **23a,b** gave a small amount (~5%) of tricyclic hydrocarbon **31** admixed with its Δ^7 isomer **32**. The presence of the latter was revealed in the ^1H NMR spectrum by a multiplet at δ 5.32, irradiation at whose frequency did not affect the H-12 signal. Hence, the substance was not a $\Delta^{8(17)}$ isomer.



32

(28) Wahlberg, I.; Almqvist, S.-O; Nishida, T.; Enzell, C. R. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 1047.

(29) Wehrli, F. W.; Nishida, T. *Fortschr. Chem. Org. Naturst.* **1979**, *36*, 1.

(30) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.

(31) Whether the previously reported formation of **31** from **18a,b**[8] involves allylic cations is uncertain. That π participation is not important in intramolecular cationic π cyclization reactions of Δ^2-cyclohexenol derivatives and that allylic cations are the first formed intermediates have been shown recently. Ladika, M.; Bregovec, I.; Sunko, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 1285.

ketones **24** and **33** in the presence of $SnCl_4$ at −78 °C. The major product from **24** was **34**, the *E* configuration for the α,β-unsaturated ketone being based on the frequency of the H-14 signal (δ 6.80) and the configuration at C-8 on the chemical shift of H-20.[32] Reaction of **33** with $SnCl_4$ afforded two identifiable fractions. The less polar material, $C_{20}H_{33}OCl$, was a mixture of epimeric chloro ketones **35**; the second was the α,β-unsaturated ketone **36**. Thus all three compounds are the result of initial protonation of the 8(17) double bond, with **35** and **36** arising by subsequent π cyclization onto electron-deficient C-8 in the manner previously observed[8] for **17a,c** and **17b,d**. Cyclizations of this type which have been carried out with copalic acid derivatives[33,34] presumably simulate the biogenesis of a group of tricyclic diterpenoids which have so far been isolated only from marine organisms.[35] Compounds of type **32** have so far not been found in nature.

In view of the results reported in the present paper, it is tempting to speculate that a path akin to Scheme I, which requires the intermediacy of a pimarane, rather than to Scheme II is involved in the biogenesis of the strobanes, especially since it can also encompass the biogenesis of the abietanes[3] and, if modified as in Scheme IV, the biogenesis of the hispananes as well. However, the possibility that the enzymes which mediate strobane biosynthesis can modify the inherent chemical properties of substrates like **18**, **22**, or **23** cannot be neglected.

Experimental Section

IR spectra were recorded on neat samples on a Perkin-Elmer 257 spectrophotometer unless specified otherwise. ^1H NMR spectra were recorded in $CDCl_3$ at 270 MHz on a Bruker HX-270 spectrometer with Me_4Si as an internal standard and ^{13}C NMR spectra at 67.89 MHz on the same instrument. High-resolution mass spectra were determined on an AEI MS-902 instrument and low-resolution mass spectra on a Finnigan 4510 GC/MS at 70 eV. High-pressure LC separations were carried out on a Waters Prep LC/System 500 liquid chromatography by using two Prep PAC-500/silica cartridges (5.7 × 30 cm). Precoated silica gel sheets (60F-254, 0.2 mm thick, EM Reagents) were used for analytical TLC. Silica gel 60 (230–460 mesh, EM Reagents) was used for flash chromatography. Preparative TLC was carried out on glass silica gel plates (60 PF 254 + 366, EM Reagents) with a layer thickness of 1.5 mm. Silica gel (70–230 mesh, particle size 0.063–0.200 mm, EM Reagents) was used for column chromatography. Argon was used to maintain an inert atmosphere in all experiments.

Methyl 15(*R*)-Hydroxy-8(14)-pimaren-18-oate (5a). The acetate **5b** was prepared in 67% overall yield as described earlier. Its hydrolysis with K_2CO_3–MeOH effected an improvement in the yield of **5a**. Anhydrous K_2CO_3 (7 g) was added in portions to a cooled solution (ice–water) of 5 g of **5b** in dry MeOH which was stirred at room temperature for 50 h. The reaction was monitored by TLC. The mixture was diluted with H_2O, acidified with dilute HCl and extracted thoroughly with ether. The usual work up of the organic layer furnished crude **5a**. Recrystallization from MeOH gave 4.0 g (92%) of product, mp 104–106 °C.

Methyl 15-Oxo-8(14)-pimaren-18-oate (8). Oxidation of **5a** by Jones reagent[3] was superior to oxidation with pyridinium chlorochromate and gave 3.5 g (87%) of **8** from 4.0 g of **5a**.

Methyl 15(*S*)-Hydroxy-8(14)-pimaren-18-oate (9a). $NaBH_4$ reduction of 2.0 g of **8** in 50 mL of MeOH as described[3] gave 1.8 g (89%) of a 1:2 mixture of **5a** and **9a** as a colorless solid which showed a single spot on TLC in various solvent systems. For the LC separation of the two substances, we used a hexane–ethyl acetate (4:1) solvent system at a flow rate of 0.25 L/min, a chart speed of 2 min/cm and a radial compression pressure of 400 psi. Injection of 0.8 g of mixture and initial attempts to achieve separation by several recycles were not successful although there were indications that in the tenth recycle some separation was being achieved. Hence the peak shaving–recycling technique was adopted from the sixth recycle onward. NMR analysis of all the fractions indicated that the left-hand-side shavings from the sixth cycle onward contained pure **5a** and that the right-hand-side shaving pure **9a**. Because of continuous recycling the last three fractions gave only mixtures of **5a** and **9a**. Injection of more than 0.5 g of the mixture and collection of large volumes during the peak shaving process resulted in no separation. Overall, a 0.5-g mixture after 15 peak shaving–recycling repetitions yielded 0.28 g of pure **9a**, 0.10 g of pure **5a**, and 0.05 g of mixture with a solvent consumption of 14 L and a recovery of 86%. The total time involved for one injection was approximately 2.5 hr. Pure **9a** melted at 136–137 °C after recrystallization from MeOH: IR (KBr) 3300, 1725, 1390, 1260, 1248, 1185, 1150, 1090, 1075, 1035, 920 cm^{-1}; NMR δ 5.32 (br, H-14), 3.66 (4 H, H-15 and OCH_3), 1.18, 1.11 (d J = 7 Hz), 0.87 and 0.81 (H-19, H-]6, H-17, and H-20); mol wt calcd for $C_{21}H_{34}O_3$ 334.2507, found (MS) 334.2507.

The high-resolution mass spectrum also exhibited a peak at m/z 335.2585 of composition $C_{21}H_{35}O_3$ resulting from intermolecular proton transfer. Other significant peaks in the mass spectrum were at m/z 316 ($C_{31}H_{32}O_2$), 289 ($C_{19}H_{29}O_2$), 229 ($C_{17}H_{25}$), 181, and 121.

Methyl 15(*S*)-Acetoxy-8(14)-pimaren-18-oate (9b). Acetylation of 0.75 g of the mixture of **5a** and **9a** produced by $NaBH_4$ reduction of **8** with acetic anhydride–pyridine at room temperature overnight followed by the usual workup gave 0.7 g (80%) of a mixture of **5b** and **9b**. Separation of the mixture after purification by preparative TLC (hexane–ether, 8:2) was achieved by preparative LC with the solvent system hexane-ethyl acetate (92:8) and the peak shaving–recycle technique. A 0.5-g portion of the mixture was separated in approximately 2 h into 0.25 g of pure **9b** and 0.12 g of pure **5b** with a solvent consumption of 12 L. The 15(*S*) isomer **9b** could not be induced to crystallize. It had the following: IR 1732, 1728, 1250, 1155, 1140, 1115, 1070, 960, 870, 770 cm^{-1}; NMR δ 5.20 (br, H-14), 4.87 (q, J = 7 Hz, H-15), 3.65 (OMe), 2.01 (Ac), 1.18, 1.11 (d, J = 7 Hz), 0.90 and 0.81 (H-19, H-16, H-17, and H-20); mol wt calcd for $C_{23}H_{36}O_4$ 376.2614, found (MS) 376.2614. Other significant peaks in the mass spectrum were at m/z 316 ($C_{31}H_{32}O_2$), 301 ($C_{20}H_{29}O_2$), 289 ($C_{19}H_{29}O_2$), 181, and 121.

Methyl 15(*S*)-(Tosyloxy)-8(14)-pimaren-18-oate (9c). A solution of 0.23 g of **9a** and 0.20 g of freshly crystallized *p*-toluenesulfonyl chloride in 3 mL of pyridine was left in a freezer at −15 °C for 30 days. The mixture was poured into H_2O, extracted with ether, washed with dilute HCl and water, dried, and evaporated at room temperature. The residual gum was purified by preparative TLC (hexane–ether, 7:3) to yield 0.25 g (93%) of **9c** as a glassy solid: IR 1730, 1600, 1365, 1350, 1315, 1260, 1195, 1180, 1110, 1070, 1060, 910, 825, 860 cm^{-1}; NMR δ 7.76 (d) and 7.29 (d) (2 H each, J = 8 Hz, aromatic protons), 4.96 (br, H-14), 4.41 (q, J = 8 Hz, H-15), 3.63 (OMe), 2.41 ($ArCH_3$), 1.31 (d, J = 8 Hz), 1.17, 0.86, and 0.59 (H-16, H-19, H-17, and H-20). The product was somewhat unstable and was therefore not analyzed.

Solvolyses of 9c. (a) A solution of 0.080 g of **9c** and 0.050 g of freshly fused NaOAc in 3 mL of dry MeOH was stirred at room temperature for 5 days, the reaction being monitored by TLC, at which time most of the tosylate had disappeared. Dilution with H_2O, extraction with ether, washing, and solvent removal furnished a gum (0.065 g) which was purified by extensive preparative TLC (hexane–ether, 17:3). Of the several bands being examined by NMR spectroscopy, only three proved significant.

The least polar fraction **9d** (4 mg, 6%) remained a gum: IR 1730, 1252, 1115, 1055, 1012, 960, 880 cm^{-1}; NMR δ 5.39 (br, H-14), 3.66 (ester OMe), 3.32 (ether OMe), 3.17 (q, J = 7 Hz, H-15), 1.23, 108 (*d*, J = 7 Hz), 0.90 and 0.88 (H-19, H-16, H-17, and H-20). The low-resolution mass spectrum did not contain the molecular ion. The following significant peaks were observed: m/z (relative

(32) A β-oriented hydroxyl would be expected to deshield the C-10 methyl.

(33) Bory, S.; Fetizon, M.; Laszlo, P. *Bull. Soc. Chim. Fr.* **1963**, 2310 Bory, S.; Manh Duc, D. K.; Fetizon, M.; Kone, M.; Trang Anh, N. *Ibid.* **1975**, 2347.

(34) Gonzalez, A. G.; Martin, J. D. *Tetrahedron Lett.* **1972**, 2259.

(35) Gonzalez, A. G.; Darias, J.; Martin, J. D. *Tetrahedron Lett.* **1971**, 2729. Cimino, G.; DeRosa, D.; De Stefano, S.; Minale, L. *Tetrahedron* **1974**, *30*, 645. Yamamura, S.; Terada, Y. *Tetrahedron Lett.* **1977**, 2171. Kazlauskas, R.; Murphy, P. T.; Wells, R. J.; Noack, K.; Oberhänsli, W. E.; Schönholzer, A. B. *Aust. J. Chem.* **1979**, *32*, 867. Kazlauskas, R.; Murphy, P. T.; Wells, R. J. *Tetrahedron Lett.* **1979**, 903.

intensity 289 (55), 257 (12), 229 (39), 181 (22), 121 (100), 107 (33), 95 (40), 85 (42).

A somewhat more polar fraction was **11a** which was crystallized from $CHCl_3$–hexane: 14 mg (21%); mp 85–87 °C; IR (KBr) 1728, 1260, 1195, 1180, 1140, 1128, 1050, 880, 850, 835, 790, 780, 760, 732 cm^{-1}; NMR δ 3.66 (OMe), 1.17 (H-19), 1.06 (H-17), 0.94 (H-20), 0.77 (br, H-16), 0.75 (d, ?), 0.71 (br, H-14 and H-15); mol wt calcd for $C_{21}H_{32}O_2$ 316.2394, found (MS) 316.2493. Other significant peaks were at m/z (relative intensity, composition) 301 (55.8, $C_{20}H_{29}O_2$), 288 (13.6, $C_{19}H_{28}O_2$), 257 (14.1, $C_{19}H_{29}$), 241 (94.9, $C_{18}H_{25}$), 175 (10.5, $C_{12}H_{19}$), 161 (7.2, $C_{12}H_{17}$), 159 (27.2, $C_{12}H_{15}$), 149 (51.8, $C_{11}H_{17}$), 135 (81.1, $C_{10}H_{15}$), 121 (100, C_9H_{13}), 105 (86.1, C_8H_9), and 91 (53.5, C_7H_7).

The most polar fraction was **10a** (10 mg) which could not be induced to crystallize: IR 1730, 1390, 1370, 1250, 1138, 1090, 1070, 960, 880 cm^{-1}; NMR δ 5.16 (br d J = 6 Hz, H-15), 3.64 (ester OMe) 3.13 (ether OMe), 2.35 (quintet, J = 6 Hz, H-14), 1.20, 1.10, 1.08 (d, J = 6 Hz), 0.88 (H-17, H-19, H-16, H-20); mol wt calcd for $C_{22}H_{36}O_3$ 348.2655, found (MS) 348.2604. Other significant peaks in the mass spectrum were at m/z (relative intensity, composition) 333 (0.1, $C_{21}H_{33}O_3$), 316 (11.2, $C_{21}H_{32}O_2$), 289 (10.6, $C_{19}H_{29}O_2$), 261 (9.0, $C_{17}H_{25}O_2$), 257 (7.1, $C_{19}H_{29}$), 203 (5.8, $C_{15}H_{23}$), 201 (10.2, $C_{15}H_{21}$), 181 (2.1, $C_{11}H_{17}O_2$), and 121 (36.2, C_9H_{13}).

(b) A solution of 0.050 g of **9c** in 3 mL of acetone–H_2O (4:1) was stirred at room temperature for 72 h and then heated at 60–65 °C for 1 h at which time TLC indicated almost complete disappearance of starting material. The solution was poured into H_2O, extracted with ether, washed, and dried. Evaporation of the solvent gave a gummy residue which was purified by preparative TLC (hexane–ether 17:3) to give two main fractions, **11a** (18 mg, 44%) and **5a** (10 mg, 23%). The material recovered from the other bands (total weight 11 mg) was highly impure as indicated by NMR spectrometry.

Methyl 15-Hydroxy-16-nor-8(14)-pimaren-18-oate (9e). To a mixture of 3.0 g of **1a** and 9.5 g of $NaIO_4$ in 100 mL of dioxane–H_2O (7:3) was added approximately 0.6 g of OsO_4 with due precautions. The flask was stoppered and stirred in the dark for 12 h, after which time the mixture was filtered quickly, and the precipitate was washed thoroughly with dry ether. The combined filtrate and washings were washed with H_2O, dried, and evaporated at reduced pressure. The residual gummy black material was dissolved in 60 mL of dry MeOH and reduced with 0.7 g of added $NaBH_4$. Reduction was complete after 40 min as indicated by TLC. The usual workup provided tarry material which was purified by silica gel column chromatography. Elution with hexane–ether (78:22) yielded the desired **9e** as a gum: 1.1 g (36%); IR 3580–3200 (br), 1730, 1250, 1140, 1110, 1030 cm^{-1}; NMR δ 5.11 (br, H-14), 3.63 (OMe), 3.37 and 3.29 (2 AB d, J = 10 Hz, H-15), 1.18, 0.92, and 0.72 (H-19, H-17, and H-20). The low-resolution mass spectrum exhibited a weak peak for the molecular ion at m/z 320 which could not be observed in the high-resolution mass spectrum. The ion of highest m/z corresponded to $M^+ - OCH_3$: mol wt calcd for $C_{20}H_{32}O_3OCH_3$ 289.2160, found (MS) 289.2140.

Reaction of 9e with Tosyl Chloride. A solution of 0.4 g of **9e** and 0.35 g of tosyl chloride in 3.5 mL of pyridine was kept at −15 °C for 30 days. TLC indicated disappearance of all starting material. The mixture was divided into two equal portions, each of which was diluted with water and extracted with ether. The organic layer from the first portion was washed with 5% HCl and brine and dried. Removal of solvent furnished semicrystalline material which was purified by preparative TLC (hexane–ether, 3:2). One major band and five minor bands were observed. NMR analysis of the fractions from the minor bands (less than 10–12 mg each) indicated them to be mixtures. Substance **10b** from the major band (0.06 g, 30%) melted at 149–150 °C and had the following: IR (KBr) 3300 (center of broad adsorption), 1725, 1390, 1375, 1252, 1200, 1180, 1140, 1115, 1050, 970, 905, 860, 770, 730 cm^{-1}; NMR δ 5.28 (br dd, J = 9, 5 Hz, H-15) 3.64 (OMe), 2.59 (br dd, J = 12, 5 Hz, H-14a), 1.81 (br dd, J = 12, 9 Hz, H-14b), 1.22, 1.17, and 0.96 (H-17, H-19, and H-20). The low-resolution mass spectrum showed a weak peak for the molecular ion at m/z 320 which could not be observed in the high-resolution mass spectrum. The ion of highest m/z corresponded to $M^+ - H_2O$: mol wt calcd for $C_{20}H_{32}O_3 \cdot H_2O$ 302.2238, found (MS) 302.2209. Other significant peaks in the high-resolution mass spectrum were at m/z (relative intensity, composition) 287 (2.9, $C_{19}H_{27}O_2$), 243 (2.9, $C_{17}H_{29}$), 181 (13.0, $C_{11}H_{17}O_2$), and 121 (100, C_9H_{13}).

The organic layer from the second portion was washed only with water, dried, and concentrated at reduced pressure and room temperature. The residual gum was purified by preparative TLC first with 24:1 hexane–ether which gave the less polar product **11b** (10 mg, 5%) and then with 3:2 hexane–ether which gave 40 mg of **10b**. Substance **11b** could not be induced to crystallize: IR 1730, 1255, 1200, 1145, 1120, 1050, 770 cm^{-1}; NMR δ 3.65 (OMe), 1.18 (H-19), 1.11 (H-17), 0.92 (H-20), 0.69 (dd, J = 8, 4 Hz, H-15a), 0.59 (t, J = 4 Hz, H-14), 0.46 (dd, J = 8, 4 Hz, H-15b); mol wt calcd for $C_{20}H_{30}O_2$ 302.2209, found (MS) 302.2220. Other significant peaks in the high-resolution mass spectrum were at m/z (relative intensity, composition) 287 (1.7, $C_{19}H_{27}O_2$), 243 (1.6, $C_{18}H_{27}$), 242 (12.3, $C_{18}H_{26}$), 227 (16, 8, $C_{17}H_{23}$), 161 (0.8, $C_{12}H_{17}$), 141 (2.0, $C_{11}H_{15}$), and 121 (34.2, C_9H_{13}).

(*E*)-Labda-8(17),12-dien-14(*RS*)-ol (18b,d). The previously used procedure[8] was improved as follows. Dehydration of 20 g of **16a,b** from manool[8] and flash chromatography of the crude product over silica gel gave 15.9 g of a 2:5 mixture of **17a,c** and **18a,c**. Separation of the mixture by preparative HPLC (hexane containing 2.5% ethyl acetate) by using the peak shaving–recycle technique (three recycles, peak shaving after one recycle, solvent consumption per 6 g of mixture 5.4 L, total recovery 99% time consumed 40 min, **17a,c** in the left-hand-side shavings, **18a,c** on the righ-hand side) gave 4.1 g of **17a,c** and 10.95 g of **18a,c** which exhibited NMR signals at δ 5.37 and 5.34 (br t J = 7 Hz, H-12 of two epimers), 5.22 and 5.19 (q, J = 7 Hz, H-14), 4.78 (br, H-17a of both epimers), 4.43 and 4.38 (br, H-17b), 2.00 (Ac), 1.63 (H-16) 1.25 (d, J = 7 Hz, H-15), and 0.87, 0.81, and 0.71 (H-18, H-19, and H-20). Reduction of 10.95 g of **18a,c** with $LiAlH_4$[8] gave 9.23 g of a 3:1 mixture of **18b** and **18d** which had NMR signals at 5.30 (br t J = 7 Hz, H-12), 4.80 (br, H-17a), 4.44 and 4.42 (br, H-17b), 4.16 (q, J = 7 Hz, H-14), 1.63 and 1.61 (H-16), 1.20 (d, J = 7 Hz, H-15), and 0.87, 0.81, and 0.71 (H-18, H-19, and H-20).

(*E*)-Labda-8(17),12-dien-14-one (19). The preparation of this substance was improved by oxidation with active MnO_2 (1 g) which was added in portions to a stirred solution of 0.3 g of **18b,d** in 20 mL of pentane. After 24 h the starting material had disappeared. Filtration, washing of the precipitate with pentane, and evaporation of the filtrate and washings gave a gum which was purified by preparative TLC (hexane–ether, 4:1) to give 0.28 g (94%) of **19**.[8] The ^{13}C NMR spectrum is given in Table II.

Epoxidation of 18b,d. To a solution of 8.54 g of **18b,d** and 0.25 g of vanadium(III) 2,4-pentanedionate in 60 mL of refluxing benzene was added 5 mL of 70% *tert*-butyl hydroperoxide, the progress of the reaction being monitored by TLC. When reaction was complete, the solution was washed with H_2O and brine. Removal of solvent gave a gummy residue (9.2 g) which was purified by flash chromatography to give 8.44 g of a 7:2 mixture of epoxides **20a** and **21a**. Separation by preparative HPLC (hexane containing 9% ethyl acetate, two recycles, solvent consumed 6.6 L, total recovery 99%, time consumed 40 min) gave 6.10 g of **20a** (3:1 mixture of epimers) and 1.78 g of **21a**.

Epimer mixture **20a**: IR 3450, 3080, 1640, 900, 865 cm^{-1}; NMR δ 4.90 and 4.85 (br, H-17a), 4.73 and 4.73 (br, H-17b), 3.72 (q, J = 7 Hz, H-14 of both epimers), 3.06 and 3.00 (dd, J = 7, 5 Hz, H-12), 1.30 and 1.28 (H-16), 1.18 and 1.17 (d, J = 7 Hz, H-15), 0.89, 0.82 (H-18, H-19), 0.71 and 0.69 (H-20); mol wt calcd for $C_{20}H_{34}O_2$ 306.2558, found (MS) 306.2580. Other significant peaks in the high-resolution mass spectrum were at m/z (relative intensity, composition) 288 (4, $C_{20}H_{32}O$), 273 (3, $C_{19}H_{29}O$), 204 (16, $C_{15}H_{24}$), 190 (22, $C_{14}H_{22}$), 175 (17, $C_{13}H_{19}$), 147 (15, $C_{11}H_{15}$), 137 (100, $C_{10}H_{17}$), 136 (23, $C_{10}H_{16}$), 123 (26, C_9H_{15}), 107 (33, C_8H_{11}), and 105 (29, C_8H_9).

Substance or epimer mixture **21a**: IR 3430, 3075, 1645, 895, 865 cm^{-1}; the ^1H NMR spectrum did not indicate the presence of an epimer mixture and had signals at δ 4.84 and 4.43 (br, H-17a,b), 3.39 (q, J = 7 Hz, H-14), 2.85 (dd, J = 6.5, 4 Hz, H-12), 1.29 (H-16), 1.18 (d, J = 7 Hz, H-15), and 0.88, 0.81, and 0.69 (H-18, H-19 and H-20); the high-resolution mass spectrum was very similar to that of **20a**; mol wt calcd for $C_{20}H_{34}O_2$ 306.2558, found (MS) 306.2591.

Addition of 3 g of Et_3N to 6.0 g of **20a** in CH_2Cl_2 at −20 to −30 °C followed by dropwise addition of 3.5 g of methanesulfonyl chloride, stirring at −20 to −30 °C for 1 h under nitrogen, decomposition by pouring over ice, ether extraction, washing, and drying gave 7.13 g of **20b** (3:1 mixture of epimers): IR 3075, 1645, 1360, 1185, 980, 925, 830, 760 cm^{-1}; NMR δ 4.91 and 4.88 (br, H-17a), 4.70 and 4.51 (br, H-17b), 4.39 and 4.34 (q, J = 7 Hz, H-14), 3.02 (t, J = 4 Hz, H-12), 3.00 and 2.99 (Ms), 1.44 (d, J = 7 Hz, H-15), 1.35 and 1.33 (H-16), 0.90 and 0.82 (H-18 and H-19), 0.71 and 0.70 (H-20); mol wt calcd for $C_{21}H_{36}O_4S$ 384.2334, found (MS) 384.2330.

Mesylation of 1.75 g of **21a** with 0.75 g of triethylamine and 0.98 g of methanesulfonyl chloride furnished 2.1 g of **21b**: IR 3075, 1640, 1360, 1185, 980, 920, 825, 760 cm^{-1}; NMR δ 4.86 and 4.39 (br, H-17a,b), 4.19 (q, J = 7 Hz, H-14), 3.07 (Ms), 2.80 (br dd, J = 6, 4 Hz, H-12), 1.40 (d, J = 7 Hz, H-15), 1.36 (H-16), 0.87, 0.80, and 0.67 (H-18, H-19, and H-20); mol wt calcd for $C_{21}H_{36}O_4S$ 384.2334, found (MS) 384.2298.

(*E*)- and (*Z*)-Labda-8(17),13-dien-12(*S*)-ol (22a,b). To 150 mL of a 1 M solution of naphthalene in THF (freshly distilled over sodium–benzophenone and $LiAlH_4$) was added (N_2 atmosphere) 6 g of freshly cut sodium. The mixture was stirred for 3 h; the resulting sodium naphthalenide solution remained satisfactory for use at least 4 days if kept under N_2 with stirring. Approximately 60 mL of this solution was added by using a 10-mL dropping funnel and a gas-tight syringe to 7.0 g of **20b** in 60 mL of THF at −20 °C under N_2 until the green color persisted, the reaction being monitored by TLC. When the reaction was complete after 10 h, excess sodium naphthalenide was quenched with water. Extraction with ether and evaporation of the washed and dried extract followed by flash chromatography over silica gel furnished 3.32 g (63%) of a 2:3 mixture of **22a**[8] and **22b** and 1.7 g of **20a**. The reaction was very slow with a 0.3 M solution of sodium naphthalenide (giving a 45% yield of **22a,b**) or at −30 to −40 °C. At temperatures above −20 °C, the reaction was faster, but the yield of **22a,b** decreased in favor of **20a**. Reversal of the mode of addition lowered the yield of **22a,b** to ca. 30%. Very slow addition of freshly cut sodium to 0.1 g of **20b** in 15 mL of dry THF and 15 mL of liquid NH_3 at −35 to −40 °C followed by the usual workup gave a 3:2 mixture of **22a** and **22b**. The mixture of **22a** and **22b** had the following: NMR δ 5.38 (q) and 5.35 (q) (J = 7 Hz, H-14 of E and Z isomers), 4.87 (br) and 4.73 (br) (H-17a,b of E), 4.84 (br) and 4.67 (br) (H-17a,b of Z), 4.74 (t, J = 7 Hz), 4.08 (dd, J = 9, 5 Hz, H-12 of E and Z), 1.66 (br) and 1.59 (br) (H-16 of E and Z), 1.60 (d) and 1.50 (d) (J = Hz, H-15 of Z and E), 0.86, 0.79, and 0.69 (H-18, H-19, and H-20); mol wt calcd for $C_{20}H_{34}O$ 290.2609, found (MS) 290.2575.

(*E*)- and (*Z*)-Labda-8(17),13-dien-12(*R*)-ol (23a,b). Reduction of 2.0 g of **21b** in 30 mL of THF with ca. 20 mL of 1 M sodium naphthalenide in the manner described for **20b** afforded 0.16 g of **21a** and 1.25 g (85%) of a 1:2 mixture of **23a**[8] and **23b** which had NMR signals at δ 5.44 (q) and 5.24 (q) (J = 7 Hz, H-14 of Z and E), 4.86 (br) and 4.46 (br) (H-17a,b of E), 4.84 (br) and 4.46 (br) (H-17a,b of Z), 4.58 (br d) and 4.01 (br d) (J = 10 Hz, H-12 of E and Z), 1.70 (br) and 1.63 (br) (H-16 of E and Z), 1.60 (d, J = 7 Hz, H-15 of E and Z), and 0.87, 0.80, and 0.66 (H-18, H-19, and H-20); mol wt calcd for $C_{20}H_{34}O$ 290.2609, found (MS) 290.2581.

(*E*)- and (*Z*)-Labda-8(17),13-dien-12-one (24a,b). Oxidation of **22a** or **23a** with active MnO_2 was previously reported[8] as unsuccessful, apparently because of the slowness of the reaction. In the present work 0.3 g of mixture **22a,b** in 30 mL of pentane was successfully oxidized with 3.5 g of MnO_2, the reaction being monitored by TLC. After 4 days all the starting material had disappeared. A workup as described for **19** followed by preparative TLC (hexane–ether, 17:3) gave 0.21 g (73%) of **24a,b** which despite its melting point of 54–55 °C was a mixture of E and Z isomers: IR 3070, 1690, 1670, 1642, 1205, 1100, 1070, 890 cm^{-1}; NMR δ 6.76 (q), J = 8 Hz, H-14 of E), 5.70 (q, J = 8 Hz, H-14 of Z), 4.71 (br) and 4.33 (br) (H-17a,b of Z), 4.67 (br) and 4.17 (br) (H-17a,b of E), 2.92 (dd) and 2.68 (dd) (J = 16, 8 Hz, H-11a of E and Z), 2.3–2.6 (complex multiplets containing H-11b of both isomers), 1.92 (t, J = 1 Hz), 1.77 (s, H-16 of Z and E), 1.85 (d) and 1.77 (d) (J = 7 Hz, H-15 of E and Z), 0.89, 0.82, 0.74, 0.72 (H-18, H-19, and H-20); mol wt calcd for $C_{20}H_{32}O$ 288.2453, found (MS) 288.2443. Other significant peaks in the high-resolution mass spectrum were at m/z (relative intensity, composition) 273 (3.9, $C_{19}H_{29}O$), 191 (5.8, $C_{13}H_{22}$), 137 (12.5, C_9H_{16}), 95 (15.4, C_7H_{11}), and 83 (100, C_5H_7O).

Reactions with 2-Fluoro-1-methylpyridinium Tosylates. (a) A solution of 0.1 g of **22a,b** and 0.4 g of tri-*n*-butylamine in methylene chloride was added to a suspension of 0.2 g of 2-fluoro-*N*-methylpyridinium tosylate in CH_2Cl_2 at −20 to −30 °C and the mixture stirred for 7 h at the same temperature. The progress of the reaction was monitored by TLC. The mixture was quenched with water and extracted with hexane. Evaporation of the washed and dried organic extract gave a gummy residue which was purified by preparative TLC (hexane–ether, 9:1) to give (1) 0.043 g (46%) of a 1:1 mixture of **25** and **26** [NMR signals for **25** δ 6.33 (dd, J = 17.5, 11 Hz, H-14), 5.42 (br t J = 7 Hz, H-12), 5.04 (d, J = 17.5 Hz, H-15$_{trans}$), 4.87 (d, J = 11 Hz, H-15$_{cis}$), 4.82 (br) and 4.45 (br) (H-17a,b), 1.77 (br, H-16), 0.90, 0.83, and 0.74 (H-18, H-19, and H-20); NMR signals for **26** δ 6.02 (d, J = 15.5, H-12), 5.58 (dd, J = 15.5, 9.5 Hz, H-11), 5.46 (q, J = 7 Hz, H-14), 4.73 (br) and 4.50 (br) (H-17a,b), 1.75 (br, H-16), 1.71 (d, J = 7 Hz, H-15), 0.89, 0.84, and 0.83 (H-18, H-19, and H-20)] and (2) 0.018 g (19%) of a 1:1 mixture of **18b,d**. When the reaction was carried out at −78 °C for 10 days, the entire amount of starting material was recovered.

(b) Reaction of 0.1 g of **23a,b** with 2-fluoro-1-methylpyridinium tosylate in the manner described above gave 0.076 g (81%) of a 1:1 mixture of **25** and **26** and no **18**.

(c) Reaction of 0.07 g of **22a,b** and 0.1 g of tri-*n*-butylamine with 0.07 g of 2-fluoro-1,3-dimethylpyridinium tosylate in CH_2Cl_2 at −78 °C for 50 h and at room temperature for 18 h gave after TLC purification 0.022 g (33%) of the mixture of **25** and **26**, 0.014 g (20%) of pure 13(*Z*),12(*R*) alcohol **23b** [NMR δ 5.44 (q, J = 8 Hz, H-14), 4.84 (br) and 4.46 (br) (H-17a,b), 4.02 (br d J = 10 Hz, H-12), 1.64 (H-16), 1.60 (d, J = 8 Hz, H-15), 0.87, 0.81, and 0.67 (H-18, H-19, and H-20)], and 0.1 g (14%) of **18b,d**.

(d) Reaction of 0.07 g of **23a,b** and 0.08 g of tri-*n*-butylamine with 0.07 g of 2-fluoro-1,3-dimethylpyridinium tosylate in $CHCl_2$ at room temperature for 18 h, at −40 °C for 3 h, and finally at 0 °C for 5 h was carried out, at which time starting material had disappeared. The usual workup followed by preparative TLC gave 0.025 g (40%) of **18a,b** and 0.02 g (30%) of a **25/26** mixture.

(e) Reaction of 0.072 g of **17b,d** and 0.045 g to tri-*n*-butylamine with 0.07 g of 2-fluoro-1,3-dimethylpyridinium tosylate at −78 °C for 3 h and at room temperature for 30 h followed by the usual workup and preparative TLC (hexane) gave 0.022 g (23%) of **25/26**, 0.12 g (13%) of sclarene (**27**) [NMR δ 6.37 (dd, J = 17, 12 Hz, H-14), 5.22 (d, J = 16 Hz, H-15$_{trans}$), 5.04 (d, J = 8 Hz, H-15$_{cis}$), 4.98 (br), 4.96 (br), 4.82 (br), and 4.53 (br), (H-16a,b and H-17a,b), 0.80, 0.79, and 0.66 (H-18 H-19, and H-20)], and 0.01 g (10%) of 14(*RS*)-fluoro-8(17),13(16)-labdadiene (**28**): IR 3080, 1640, 1390, 910, 900 cm^{-1}; NMR δ 5.03 (br), 4.88 (br), and 4.82 (br) (H-16a,b and H-17a, obscuring the one-proton multiplets of H-14), 4.51 (br) and 4.49 (br) (H-17b of both epimers), 1.45 (d) and 1.35 (d) (J = 22 Hz, H-15), 0.85, 0.79, and 0.68 (H-18, H-19, and H-20); mol wt calcd for $C_{20}H_{33}F$ 292.2565, found (MS) 292.2545 (4.3%). Other significant peaks in the high-resolution mass spectrum were at m/z (composition, relative intensity) 277 ($C_{19}H_{30}F$, 20.5), 272 ($C_{20}H_{32}$, 5.5), 257 ($C_{19}H_{29}$, 13.2), 201 ($C_{15}H_{21}$, 10.4), 189 ($C_{14}H_{21}$, 11.3), 177 ($C_{13}H_{21}$, 11.4), 149 (C_{11H17}, 24.7), 137 ($C_{10}H_{17}$, 63.2), 135 ($C_{10}H_{15}$, 24.5), 123 (C_9H_{15}, 41.2), 109 (C_8H_{13}, 52.0), 107 (C_8H_{11}, 40.4), 105 (C_8H_9, 36.2), 95 (C_7H_{11}, 83.3), and 93 (C_7H_9, 55.8).

Reaction of 22a,b with Formic Acid. A mixture of 0.1 g of **22a,b** and 2 mL of 97% formic acid was stirred (N_2 atmosphere) at room temperature, the reaction being monitored by TLC. After 72 h the mixture was diluted with ether. The organic layer was washed with bicarbonate solution and brine, dried, and evaporated. The residue was purified by preparative TLC (hexane–ether, 9:1) to give 0.08 g (76%) of a **22c,d** mixture: IR 3080, 1730, 1645, 1190, 980 cm^{-1}; NMR δ 8.01 (CH=O), 5.92 (dd, J = 10, 5 Hz), 5.36 (dd, J = 8 and 4 Hz, H-12 of Z and E), 5.46 (q, J = 7, H-14 of both isomers), 4.90 (br), 4.87 (br), 4.85 (br), and 4.78 (br) (H-17a,b of both isomers), 1.64 (d) and 1.63 (d) (J 7 Hz, H-15), 1.60 (H-16 of both isomers), 0.87, 0.86, 0.81, 0.80, 0.71, and 0.69 (H-18, H-19 and H-20 of E and Z). The low-resolution mass spectrum exhibited a weak peak for the molecular ion at m/z 318; this could not be observed in the high-resolution mass spectrum where the

peak of highest amu was seen at m/z 303 ($C_{20}H_{31}O_2$, $M^+ - CH_3$). Other significant peaks were at m/z (relative intensity, composition) 272 (18.6, $C_{20}H_{32}$) 257 (12.4, $C_{19}H_{29}$), 191 (1.0, $C_{14}H_{23}$), 149 (21.6, $C_{11}H_{17}$), 137 (62.2, $C_{10}H_{17}$), 135 (47.3, $C_{10}H_{15}$), 109 (65.0, C_8H_{13}), and 95 (100, C_7H_{11}).

Reduction of 0.05 g of **22c,d** with $LiAlH_4$ gave **22a,b**.

Reaction of 23a,b with Formic Acid. A mixture of 0.17 g of **23a,b** and 2 mL of 97% formic acid was stirred at room temperature (N_2 atmosphere). The reaction was complete after 1 h. The mixture was neutralized with $NaHCO_3$ and extracted with ether. The usual workup followed by preparative TLC (hexane) gave 0.086 g of gummy **31** and 0.052 g of a mixture of olefins. The tricyclic hydrocarbon had the following: IR 2900 (br), 1445 (br), 1370, 968, 835 cm^{-1}; NMR δ 5.24 (q, J = 8 Hz, H-14), 2.8 (septet, J = 8 Hz, H-12), 1.56 (d, J = 8, H-15), 1.54 (d, J = 1 Hz, H-16), 0.97, 0.88, 0.88 (H-18, H-19, and H-20). Attempts to oxidize the 13,14-double bond selectively failed. An incorrect value was reported previously[8] for the molecular weight. The ^{13}C NMR spectrum is listed in Table II: mol wt calcd for $C_{20}H_{32}$ 272.2503, found (MS) 272.2519 (55.7%). Other significant ions in the high-resolution mass spectrum were at m/z (relative intensity composition) 257 (100, $C_{19}H_{29}$), 215 (14.7, $C_{16}H_{23}$), 201 (15.1, $C_{15}H_{21}$), 175 (14.1, $C_{13}H_{19}$), 161 (14.8, $C_{12}H_{17}$), 147 (16.1, $C_{11}H_{15}$), 133 (29.6, $C_{10}H_{13}$), 121 (16.8, C_9H_{13}).

8(17),13(16)-Labdadien-14-one (33). Oxidation of 0.3 g of **17b,d** in 20 mL of pentane with 4 g of active MnO_2 in the manner described for oxidation of **18b,d** required 72 h for completion of the reaction. After the usual workup and preparative TLC (hexane–ether, 17:3) of the crude product there was obtained 0.26 g (89%) of **33** as a gum which slowly solidified and then melted at 58–59 °C: IR 3080, 1675, 1640, 1625, 1130, 980, 945, 890 cm^{-1}; NMR δ 5.97 (br) 5.75 (br) (H-16a,b), 4.84 (br) and 4.60 (br) (H-17a,b), 2.34 (Ac), 0.89, 0.81, and 0.68 (H-18, H-19, and H-20); mol wt calcd for $C_{20}H_{32}O$ 288.2453, found (MS) 288.2432 (10.2%). Other significant peaks in the high-resolution mass spectrum were at m/z (composition, relative intensity) 273 ($C_{19}H_{29}O$, 14.6), 177 ($C_{13}H_{21}$, 14.2), 149 ($C_{10}H_{16}$, 23.4), and 137 ($C_{10}H_{17}$, 100).

Reactions with $SnCl_4$. (a) To a solution of 0.05 g of **24** in 8 mL of CH_2Cl_2 kept at −78 °C was added slowly with stirring 0.06 mL of $SnCl_4$. After 30 min the reaction was quenched with 10% $NaHCO_3$ solution and extracted with ether. After the usual workup the crude product was purified by preparative TLC (hexane–ether, 1:1) to give 0.02 g (40%) of a crystalline solid (**34**): 99–100 °C; IR (KBr) 3475, 1670, 1285, 1170, 1090, 950 cm^{-1}; NMR δ 6.80 (q, J = 8 Hz, H-14), 2.81 (dd, J = 18, 4 Hz, H-11a), 2.61 (dd, J = 18, 4 Hz, H-11b), 1.85 (dd, J = 8, 1 Hz, H-15), 1.70 (t, J = 1 Hz, H-16), 1.12 (H-17), 0.87, 0.83, and 0.78 (H-18, H-19, and H-20); mol wt calcd for $C_{20}H_{34}O_2$ 306.2558, found (MS) 306.2517 (3.3%). Other significant peaks in the high-resolution mass spectrum were at m/z (composition, relative intensity) 291 ($C_{19}H_{31}O_2$, 1.8), 288 ($C_{20}H_{32}O$, 19.9), 273 ($C_{19}H_{29}O$, 14.0), 221 ($C_{15}H_{25}O$, 18.4), 191 ($C_{14}H_{23}$, 26.8), 177 ($C_{13}H_{21}$, 25.3), and 175 ($C_{13}H_9$, 19.1).

(b) Ketone **33** (0.10 g) on treatment with 0.015 mL of $SnCl_4$ for 30 min at −78 °C in the manner described in the previous paragraph, a workup in the usual fashion, and preparative TLC (hexane–ether, 47:3) of the crude product afforded 0.015 g (15%) of gummy **35** which was a mixture of C-13 epimers as indicated by doubling of the methyl signals: IR 1690 (br), 1240, 1130, 1115 cm^{-1}; NMR δ 2.08 (Ac), 1.26 and 1.24 (H-17 of epimers), 0.88, 0.85, 0.84, 0.83, 0.80, and 0.79 (H-18, H-19, H-20, and epimers); mol wt calcd for $C_{20}H_{33}OCl$ 324.2219, found (MS) 324.2197 (12.1%). Other significant peaks in the high-resolution mass spectrum were at m/z (composition, relative intensity) 309 ($C_{19}H_{30}OCl$, 10.4), 288 ($C_{20}H_{32}O$, 29.6), 273 ($C_{19}H_{29}O$, 29.5), and 266 ($C_{17}H_{27}Cl$, 54.1).

The more polar fraction yielded 0.022 g (23%) of **36** as a gum: IR 1665, 1640, 1290, 1255, 1180, 1145, 925, 875 cm^{-1}; NMR δ 6.34 (br, H-14), 2.27 (Ac), 1.11 (H-17), 0.96, 0.87, and 0.87 (H-18, H-19, and H-20); mol wt calcd for $C_{30}H_{32}O$ 288.2953, found (MS) 288.2464 (12.2%). Other significant peaks in the high-resolution mass spectrum were at m/z (composition, relative intensity) 273 ($C_{19}H_{29}O$, 14), 191 ($C_{14}H_{22}$, 21), and 175 ($C_{13}H_{19}$, 9.7).

Registry No. **1a**, 3730-56-1; **5a**, 42401-43-4; **5b**, 42401-44-5; **8**, 42401-48-9; **9a**, 42401-49-0; **9b**, 83815-99-0; **9c**, 83816-00-6; **9d**, 83816-01-7; **9e**, 83816-02-8; **10a**, 83816-03-9; **10b**, 83816-04-0; **11a**, 83860-56-4; **11b**, 83816-05-1; **16a**, 61046-88-6; **16b**, 61091-77-8; **17a**, 83830-91-5; **17b**, 61091-79-0; **17c**, 83816-06-2; **17d**, 61091-80-3; **18a**, 83860-57-5; **18b**, 83860-58-6; **18c**, 83860-59-7; **18d**, 83860-60-0; **19**, 83860-61-1; **20a** (isomer 1), 83860-62-2; **20a** (isomer 2), 83860-68-8; **20b** (isomer 1), 83816-07-3; **20b** (isomer 2), 83860-69-9; **21a** (isomer 1), 83860-63-3; **21a** (isomer 2), 83860-70-2; **21b** (isomer 1), 83860-64-4; **21b** (isomer 2), 83860-71-3; **22a**, 61091-81-4; **22b**, 83860-65-5; **22c**, 83816-08-4; **22d**, 83860-66-6; **23a**, 61047-01-6; **23b**, 83860-67-7; **24a**, 83816-09-5; **24b**, 83816-10-8; **25**, 10395-42-3; **26**, 83816-11-9; **27**, 511-02-4; **28**, 83816-12-0; **31**, 83816-13-1; **33**, 20046-46-2; **34**, 83816-14-2; **35** (isomer 1), 83830-87-9; **35** (isomer 2), 83816-16-4; **36**, 83816-15-3; 2-fluoro-*N*-methylpyridinium tosylate, 58086-67-2; 2-fluoro-1,3-dimethylpyridinium tosylate, 59387-91-6.

Photochemistry of (*o*-Methylphenyl)alkadienes: Attempted Intramolecular Trapping of the Resulting *o*-Xylylenes[1a]

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The photochemistry of a series of *o*-methylphenyl dienes was investigated in order to determine if the resulting *o*-xylylenes could be trapped in an intramolecular Diels–Alder reaction in synthetically useful yields. Irradiation of **3** gave meta-isomer **4** as the major product along with lower yields of double bond migration product **5** and the desired cycloadduct **6**. The best yield of **6** (24%) was obtained by irradiation of **3** with a low-pressure mercury vapor lamp at low temperatures. The other compounds investigated gave none of the intramolecular Diels–Alder product of the *o*-xylylene. Irradiation of **17** gave only double bond migration product **18**. Irradiation of **22** gave an excellent yield of (2 + 2) cycloadduct **23**. Irradiation of **26** gave meta-isomer **28**, double bond migration product **27**, and **29**, a (2 + 2) cycloadduct of **28**.

Intramolecular Diels–Alder reactions of *o*-xylylenes (*o*-quinodimethanes) have been extensively applied to the synthesis of polycyclic ring systems containing at least one aromatic ring (especially steroids) in recent years.[2] Al-

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