3a–c and higher oligomers. High dilution or slow addition techniques did not improve the yields of lactones or change the monomer–dimer ratios. Only part of the sodium hydride reacts and the reaction mixture remains heterogeneous. These facts suggest that lactonization occurs on the surface of the sodium hydride rather than in homogeneous solution. The use of benzene or toluene as solvent[4] decreased the reaction rate and gave only traces of lactone.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and are uncorrected. Proton NMR chemical shifts were recorded with a Varian HA-100 spectrometer and are reported in parts per million downfield from internal Me_4Si. Mass spectra were measured on a Varian CH-4 spectrometer. Preparative TLC was performed with a Harrison Research Model 7924 centrifugal thin-layer chromatograph.

Standard Procedure for Alkylation of Cyclohexane-1,3-dione.[5] 2-Allyl-2-(9-hydroxynonyl)cyclohexane-1,3-dione (1c). Cyclohexane-1,3-dione (20 g, 0.178 mol) was dissolved in a solution of potassium hydroxide (10 g, 0.178 mol) in 250 mL of water containing a trace of copper powder (50 mg). The solution was heated on a steam bath, and 9-iodononanol (48 g, 0.178 mol) was added, followed by sufficient methanol to give a clear hot solution. After 4 h the methanol was removed under vacuum and 3 N sodium hydroxide solution was added until a pH of 11 was obtained. Neutral material was removed by six extractions with ether and the aqueous solution was then acidified with concentrated hydrochloric acid to pH 1. The oily suspension was allowed to solidify during 24 h of stirring. Filtration gave 10.4 g (23%) of 2-(9-hydroxynonyl)cyclohexane-1,3-dione: mp 123–124 °C after recrystallization from ethyl acetate–hexane; NMR ($CDCl_3$) δ 1.25 (s, 14 H, CH_2), 1.30–2.55 (m, 9 H, CH_2CO, $CH_2C{=}$, CH_2, OH exchanged by D_2O), 3.35 (s, 1 H, OH exchanged by D_2O), 3.62 (t, 2 H, CH_2O); mass spectrum, m/e 254 (M^+, 5%), 113 (100%). Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.80; H, 10.68.

A solution of this dione (6.2 g, 24 mmol, unpurified) in 25 mL of aqueous potassium hydroxide (1.5 g, 27 mmol) was stirred with excess allyl bromide (5 mL) for 18 h at room temperature. Ether (250 mL) was added and the solution was washed with small volumes of 1 N sodium hydroxide solution until the washings were strongly basic. After a further washing with water, the solution was dried ($MgSO_4$) and evaporated in vacuo. Chromatography of the residue on silica gel (ethyl acetate–hexane, 1:1) gave 6.0 g (84%) of 1c as an oil: NMR ($CDCl_3$) δ 1.25 (s) and 1.4–2.0 (m) (18 H, CH_2), 1.75 (s, 1 H, OH exchanged by D_2O), 2.5 (q, 6 H, CH_2CO, $CH_2C{=}$), 3.60 (t, 2 H, CH_2O), 4.85–5.10 (m, 2 H, $CH_2{=}$), 5.2–5.9 (m, 1 H, CH=); mass spectrum, m/e 294 (M^+, 15%), 152 (100%). Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.24; H, 10.59.

Standard Procedure for Formation of Lactones. 6-Allyl-5-oxopentadecanolide (2c). Sodium hydride (100 mg, 50% in oil, 2.1 mmol) was suspended in 2 mL of dry toluene and added in one portion to a stirred solution of diketone 1c (2.94 g, 10 mmol) in dry (molecular sieves) toluene–tetrahydrofuran (300 mL, 1:1) under a nitrogen atmosphere. The mixture was heated to reflux with a preheated oil bath and maintained at reflux for 45 min. The cooled mixture was treated with acetic acid (1 mL) and methanol (20 mL) to destroy unreacted sodium hydride and was then evaporated to dryness in vacuo. Preparative centrifugal TLC on silica gel (ethyl acetate–hexane, 1:19) gave the lactone 2c (1.65 g, 56%) as an oil: NMR ($CDCl_3$) δ 1.25 (s) and 1.4–2.1 (m) (18 H, CH_2), 2.1–2.7 (m, 7 H, CH_2CO, CHCO, CH_2CO_2, $CH_2C{=}$), 3.9–4.5 (m, 2 H, CH_2O), 4.85–5.15 (m, 2 H, $CH_2{=}$) 5.3–5.9 (m, 1 H, CH=); mass spectrum, m/e 294 (M^+, 40%), 152 (80%), 115 (100%). Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.47; H, 10.41.

Further elution with ethyl acetate–hexane (1:9) gave the dimeric lactone 3c (0.35 g, 12%): mp 52 °C from ethyl acetate–hexane; NMR ($CDCl_3$) δ 1.25 (s) and 1.4–2.1 (m) (36 H, CH_2), 2.1–2.7 (m, 14 H, CH_2CO, CHCO, CH_2CO_2, $CH_2C{=}$), 3.9–4.25 (t, 4 H, CH_2O), 4.85–5.15 (m, 4 H, $CH_2{=}$), 5.3–5.9 (m, 2 H, CH=); mass spectrum, m/e 588 (M^+, 80%), 152 (100%). Anal. Calcd for $C_{36}H_{60}O_6$: C, 73.43; H, 10.27. Found: C, 73.10; H, 10.54.

20-Acetoxy-1-bromoeicosane. A solution of 1,20-dibromoeicosane[6] (8.8 g, 20 mmol) in dimethylformamide (75 mL) containing sodium acetate (1.65 g, 20 mmol) was heated at 80 °C for 1 h. The solution was diluted with water and the products were extracted into ether. After the solution was washed with water and dried ($MgSO_4$), the solvent was removed in vacuo and the products were chromatographed on silica gel, using ethyl acetate–hexane. Crystallization from methanol gave 2.8 g (33%): mp 52 °C; mass spectrum, m/e 419 and 421 ($M^+ + H$). Anal. Calcd for $C_{22}H_{43}BrO_2$: C, 62.99; H, 10.33. Found: C, 63.13; H, 10.58.

2-Allyl-2-(4-hydroxybutyl)cyclohexane-1,3-dione (1a) and 2-Allyl-2-(20-hydroxyeicosyl)cyclohexane-1,3-dione (1d). The standard procedure for alkylation of cyclohexane-1,3-dione was modified for these preparations. Alkylation was performed first with allyl bromide then with the ω-acetoxyalkyl halide. The standard procedure gave only O-alkylated products. Hydrolysis of the acetoxy group was achieved by heating a solution in ethanol–0.5 N hydrochloric acid (2:1) at reflux for 2 h.

Registry No. 1a, 76334-20-8; 1b, 76346-75-3; 1c, 76334-21-9; 1d, 76334-22-0; 2a, 76334-23-1; 2b, 76334-24-2; 2c, 76334-25-3; 2d, 76334-26-4; 3a, 76334-27-5; 3b, 76334-28-6; 3c, 76334-29-7; cyclohexane-1,3-dione, 504-02-9; 9-iodononanol, 76334-30-0; allyl bromide, 106-95-6; 20-acetoxy-1-bromoeicosane, 76334-31-1; 1,20-dibromoeicosane, 14296-16-3.

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C(14) Configuration of 8,13-Epoxylabdan-14-ols

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Recently interest has been focused on ^{13}C NMR spectroscopy as a tool for the determination of C(15) configurations in pimarene- and isopimarene-15,16-diols.[1,2] The determination of the C(14) configuration of 8,13-epoxylabdanes with C(14)- or C(14),C(15)-oxygenated side chains by ^{13}C NMR spectroscopy is the subject of the present paper.

The natural diterpenoid borjatriol (1,[3,4] Chart I) was used as a representative of the 8,13-epoxylabdane diterpenes (manoyl oxide derivatives) and used as starting material for obtaining all the products here described. Compounds with a C(13),C(14)-threo configuration (13*R*,14*R*, 1–6) were directly synthetized from the natural product 1 by acetylation (2), acetone–anhydrous $CuSO_4$ treatment (3), selective C(15)-OH tosylation and subsequent reaction with Na_2CO_3–EtOH–H_2O (4),[5] $LiAlH_4$ reduction of compound 4 (5), and acetylation of product 5 to yield 6. The preparation of the C(14) epimeric series [13*R*,14*S*,C(13),C(14)-erythro compounds 7–13] was achieved as follows. The acetonide 3 was acetylated at its C(7) OH and then transformed into (14*R*)-7β-acetoxy-8,13-epoxylabdane-14,15-diol[3] by acid treatment. Selective C(15)-OH benzoylation and subsequent C(14)-OH tosyla-

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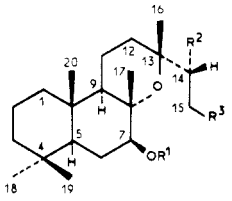
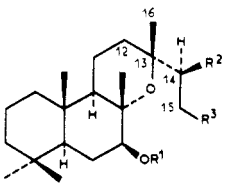
Table I. ^{13}C Chemical Shifts of Compounds 1–13[a]

	1	2[b]	3[c]	4	5	6[d]	7	8[e]	9[f]	10	11	12[g]	13[h]
C(1)	38.9	38.7	38.8	38.8	39.0	38.9	38.9	38.7	38.9	38.8	38.9	38.8	38.9
C(2)	18.5	18.4	18.5	18.5	18.5	18.5	18.5	18.4	18.5	18.5	18.5	18.4	18.5
C(3)	41.9	41.8	41.9	41.9	41.9	41.9	41.9	41.8	41.9	41.9	41.9	41.8	41.9
C(4)	33.2	33.1	33.1	33.1	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2
C(5)	54.2	53.8	54.1	53.9	54.3	53.9	54.1	54.0	54.1	54.1	54.1	54.0	54.1
C(6)	27.4	25.5	27.1	26.8	27.1	25.6	27.3	25.5	26.6	26.9	26.9	25.6	26.8
C(7)	80.3	81.0	80.2	80.5	80.7	81.3	80.5	81.1	80.8	80.5	80.8	81.4	80.8
C(8)	78.9	76.9	78.6	78.4	78.4	76.5	79.1	77.0	78.3	78.6	79.1	76.6	78.9
C(9)	56.2	56.0	56.2	54.8	56.4	56.3	56.4	56.0	55.9	55.5	56.2	56.3	56.0
C(10)	36.9	36.6	36.9	37.0	36.9	36.7	37.0	36.7	37.1	37.0	37.0	36.7	37.1
C(11)	14.3	14.1	14.1	14.4	14.6	14.3	14.3	14.1	14.3	14.2	14.2	14.3	14.2
C(12)	34.0	32.0	31.3	33.6	34.8	31.8	32.7	34.6	35.4	32.7	29.3	34.7	32.3
C(13)	74.9	73.2	73.4	70.6	75.4	73.4	75.6	73.0	73.2	70.8	76.3	73.1	74.7
C(14)	79.7	77.0	82.5	59.5	76.7	76.8	78.7	77.9	83.6	59.8	73.3	77.4	77.3
C(15)	62.6	63.0	65.1	43.6	16.3	14.1	62.8	63.1	65.3	43.7	15.6[i]	13.9	66.6
C(16)	22.7	25.0	24.8	23.9	19.8[i]	23.8	24.2	22.4	21.7	24.1	23.8	21.5	23.3
C(17)	19.5	20.2	19.4	19.7	19.6[i]	20.2	19.5	20.1	19.6	19.5	19.4	20.1	19.6
C(18)	33.3	33.1	33.2	33.3	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2
C(19)	21.3	21.2	21.2	21.3	21.4	21.2	21.3	21.2	21.3	21.3	21.3	21.2	21.3
C(20)	15.8	15.7	15.8	15.7	15.8	15.8	15.8	15.7	15.8	15.7	15.9[i]	15.7	15.8

[a] In parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm; for other data see the Experimental Section. [b] C(7)-OAc, 169.7, 21.1; C(14)-OAc, 170.4,[i] 20.9;[i] C(15)-OAc, 170.1,[i] 20.7.[i] [c] C(14),C(15)-acetonide, 109.0, 26.2, 25.0. [d] C(7)-OAc, 169.9, 21.1; C(14)-OAc, 170.2, 21.2. [e] C(7)-OAc, 170.1, 21.1; C(14)-OAc, 170.7,[i] 20.9; C(15)-OAc, 170.1,[i] 20.9. [f] C(14),C(15)-acetonide, 108.9, 26.3, 25.1. [g] C(7)-OAc, 170.0, 21.2; C(14)-OAc, 170.0, 21.2. [h] Ethoxy group, 70.8, 15.2. [i,j] Values bearing the same superscript may be interchanged.

Chart I





	R^1	R^2	R^3
1	H	OH	OH
2	Ac	OAc	OAc
3	H	$-OCMe_2O-$	
4	H	$-O-$	
5	H	OH	H
6	Ac	OAc	H

	R^1	R^2	R^3
7	H	OH	OH
8	Ac	OAc	OAc
9	H	$-OCMe_2O-$	
10	H	$-O-$	
11	H	OH	H
12	Ac	OAc	H
13	H	OH	OC_2H_5
14	Ac	OAc	OC_2H_5

tion gave the (14*R*)-7β-acetoxy-14-(tosyloxy)-15-(benzyloxy) derivative which was refluxed with Na_2CO_3 in EtOH–H_2O solution[5] (see Experimental Section) to yield compounds **7**, **10**, and **13** with inversion of the C(14) center. Derivatives **8** and **9** and derivatives **11** and **12** were obtained from compounds **7** and **10**, respectively. Ac_2O–pyridine treatment of compound **13** yielded the diacetate **14**, the ^1H NMR spectrum of which showed a two-H signal at δ 4.95 (H-7 and H-14) and a four-H multiplet at δ 3.60 (2 H-15 and OCH_2CH_3); thus the attachment of the ethoxy group in these compounds is at the C(15) position.

A ^{13}C NMR spectral analysis of compounds **1–13** led to the needed stereochemical information. The carbon shifts are listed in Table I and were assigned on the basis of ^{13}C NMR off-resonance-decoupled spectra, comparison of pairs of compounds, consideration of β, γ, and δ substituent effects, general chemical shift arguments, and literature data on related structures.[4,6,7]

The data collected in Table I show that the comparison of C(12) and C(16) shifts of one of the C(14) epimers of these 8,13-epoxylabdane derivatives with those of the other (pairs of compounds: **1**, **7**; **2**, **8**; **3**, **9**; **5**, **11**; **6**, **12**) distinguishes the two compounds easily and reveals their C(14) configurations, since the γ effects exerted by the C(14)-oxygenated function on C(12) and C(16) are different in each isomer. Only in the C(14),C(15)-epoxy derivatives (**4** and **10**) are the observed differences in the chemical shifts of C(12) and C(16) not adequate for the sterochemical diagnosis of these compounds.

The differences in the C(12) and C(16) chemical shifts of these substances may be clearly explained when it is considered that in compounds **1**, **5**, **7**, **11**, and **13** there exists an intramolecularly hydrogen bonded [8,13-epoxy→C(14)-OH] form, which causes a preferred conformation of the diterpenoid side chain. In addition, the C(14),C(15)-diol system can adopt several conformations as reflected by the differences in $\delta_{C(12)}$ and $\delta_{C(16)}$ observed for compound **1** vs. **7** ($\Delta\delta_{C(12)} = 1.3$ ppm, $\Delta\delta_{C(16)} = -1.5$ ppm) as opposed to those observed for compound **5** vs. **11** ($\Delta\delta_{C(12)} = 5.5$ ppm, $\Delta\delta_{C(16)} = -4.0$ ppm). A simple explanation for this observed variation in magnitude of $\Delta\delta_{C(12)}$ and $\Delta\delta_{C(16)}$ is found in a difference of rotamer population and also in the different magnitude of the γ effects exerted by the C(14)-OH and C(15) groups on C(12) and C(16), taking into account that the preferred C(13),C(14) conformation in each compound is probably that represented in Chart II.

In the case of the acetyl and acetonide derivatives (compounds **2**, **3**, **6**, **8**, **9**, and **12**), it is evident that their preferred side-chain conformations must be different from those of the corresponding C(14)-hydroxy derivatives. A simple consideration of the greater shielding magnitude of the γ-gauche effect than the γ-trans effect exerted by the C(14) and C(15) groups on C(12) and C(16) allowed the assignment of a preferred rotamer for each compound (Chart II), which explains the $\delta_{C(12)}$ and $\delta_{C(16)}$ variations

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(Table I). In particular, the influence of steric effects in the rotamer population is clearly reflected in the $\delta_{C(12)}$ values shown by the acetonide derivatives (**3** and **9**, 31.3 and 35.4 ppm, respectively), whereas the $\delta_{C(16)}$ in the same compounds are also almost the maximum values (24.8 ppm in **3** and 21.7 ppm in **9**), and the small irregularities (25.0 ppm in compound **2** and 21.5 ppm in **12**) may be due to the C(16) methyl group–acetonide interactions, which are not expected between C(12) and the acetonide. The small differences shown by the epimeric C(14),C(15)-epoxides (compounds **4** and **10**) are also in agreement with all the above considerations.

It is very important to note that the C(14)-OH configuration in these 8,13-epoxylabdane derivatives must be firmly established by acetylation of the alcohol or by C-(14),C(15)-acetonide formation. Effectively, in the C-(13),C(14)-threo series the acetylation of the C(14)-hydroxyl group causes an upfield shift of C(12) ($\Delta\delta$ = −2.0 ppm for compounds **1** and **2** and −3.0 ppm for **5** and **6**) and a downfield shift of C(16) [$\Delta\delta$ = 2.3 ppm (**1** and **2**) and 4.0 ppm (**5** and **6**)], whereas in the C(13),C(14)-erythro series the same structural variation causes a downfield shift of C(12) ($\Delta\delta$ = 1.9 ppm for compounds **7** and **8** and 5.4 ppm for **11** and **12**) and an upfield shift of C(16) [$\Delta\delta$ = −1.8 ppm (**7** and **8**) and −2.3 ppm (**11** and **12**)]. Identical variations, but of different magnitude, are observed between compounds **1** and **3** and between **7** and **9** (Table I).

Although the C(14)-OH configurations of some of these compounds have also been studied by ^{1}H NMR spectroscopy,[8] the ^{13}C NMR analysis here reported is a simpler and better criterion for this purpose and provides a sure method for establishing the relative C(13),C(14) stereochemistry of this class of diterpenoids.

Experimental Section

Melting points were determined in a Kofler apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter with a 1-dm cell. Elemental analyses were carried out in our Institute with the help of a Perkin-Elmer 240 analyzer. IR spectra were determined on a Perkin-Elmer 257 spectrometer. Mass spectra were obtained on a JEOL MS-01SG-2 instrument. ^{1}H NMR spectra were measured at 90 or 60 MHz of $CDCl_3$ solutions with Me_4Si as an internal standard.

All ^{13}C NMR spectra were obtained on a Varian XL-100(15) spectrometer equipped with Nicolet TT-100PFT accessory. The spectra were recorded at the frequency of 25.2 MHz over a spectral width of 6 kHz with the solvent (commercial NMR grade $CDCl_3$) providing an internal deuterium lock. A total of 8K data points was collected in the FID. A pulse width of 10.0 μs was used to aid in the acquisition of the slower relaxing carbons, and the pulse flip angle was 52°. The total time delay between pulses was 1.3 s. The proton-decoupled spectra were obtained by using a square-wave-modulated noise band centered in the proton spectrum. All samples were prepared as 0.6 M $CDCl_3$ solutions in 12-mm sample tubes. The probe temperature in each case was 36 °C. Chemical shifts are accurate to ±0.05 ppm.

Compounds **1**–**4** have been previously described.[3-5]

(14*R*)-8,13-Epoxylabdane-7β,14-diol (5). The (14*R*)-14,15-epoxy derivative[5] (**4**, 1 g) was treated with $LiAlH_4$ in Et_2O solution at room temperature for 3 h, yielding compound **5** (890 mg after crystallization from aqueous MeOH): mp 150–151 °C; $[\alpha]^{15}_D$ −2.7° (*c* 0.89, $CHCl_3$); IR (KBr) 3400, 1465, 1390, 1300, 1130, 1105, 1080, 1025, 1000, 990, 965, 903 cm^{-1}; ^{1}H NMR δ 3.50 (2 H, complex signal, H-7 and H-14), 1.06 (3 H, d, *J* = 7 Hz, 3 H-15), CMe singlets at 1.31 (3 H), 1.18 (3 H), 0.89 (3 H), 0.82 (3 H), and 0.80 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 324 (M^+, 0.3), 309 (0.6), 291 (3), 279 (100), 261 (80), 243 (34), 203 (26), 141 (61), 123 (80), 95 (69), 81 (54), 69 (67). Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18. Found: C, 74.13; H, 11.23.

(14*R*)-7β,14-Diacetoxy-8,13-epoxylabdane (6). Ac_2O–pyridine treatment of compound **5** (850 mg) gave the corresponding diacetate **6** (850 mg, a syrup): IR (film) 1730, 1470, 1375, 1250, 1105, 1080, 1040, 980 cm^{-1}; ^{1}H NMR δ 4.80 (2 H, complex signal, H-7 and H-14), 2.05 (6 H, s, 2 OAc), 1.12 (3 H, d, *J* = 6 Hz, 3 H-15), CMe singlets at 1.30 (3 H), 1.15 (3 H), 0.85 (3 H), and 0.78 (6 H).

Compounds 7, 10, and 13 from Borjatriol (1). The acetonide **3** (11.5 g), obtained from the natural diterpenoid **1**, was treated with Ac_2O–pyridine to yield the 7-acetyl derivative (12.7 g) previously described,[3,4] which was transformed into (14*R*)-7β-acetoxy-8,13-epoxylabdane-14,15-diol, which is also known,[3,4] by acid treatment (yield 11.4 g). An 11-g sample of this last compound (28.8 mmol) was treated with 29 mmol of benzoyl chloride in pyridine solution (200 mL) at room temperature during 1 h; workup in the usual manner yielded the 15-benzoyl derivative in almost quantitative yield: ^{1}H NMR δ 8.12 (2 H, dd, J_o = 7.3 Hz, J_m = 2.6 Hz) and 7.50 (3 H, m) (aromatic protons), 4.70 (1 H, q, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 5.5 Hz, H-7), 4.58 and 4.37 (AB part of an ABX system, J_{AB} = 11.3 Hz, 2 H-15), 3.52 (1 H, dd, X part of an ABX system, J_{XA} = 6.6 Hz, J_{XB} = 4.0 Hz, H-14), 2.05 (3 H, s, OAc), CMe singlets at 1.28 (6 H), 0.85 (3 H), 0.78 (3 H) and 0.75 (3 H). This compound was treated with excess tosyl chloride in pyridine solution to yield the (14*R*)-14-tosyl-15-benzoyl derivative: ^{1}H NMR δ 8.05 (2 H, dd, J_o = 7.3 Hz, J_m = 2.6 Hz) and 7.50 (3 H, m) (benzoyl group), 7.80 and 7.17 (A_2B_2 system, *J* = 8 Hz, tosyl group), 4.95–4.25 (4 H, complex signal, H-7, H-14, and 2 H-15), 2.29 (3 H, s, MePh, tosyl group), 2.05 (3 H, s, OAc), CMe singlets at 1.31 (3 H), 1.22 (3 H), 0.82 (3 H), 0.76 (3 H), and 0.72 (3 H). Treatment of this last compound under reflux for 20 h with Na_2CO_3 in 80% aqueous EtOH solution (2% w/v, 500 mL) yielded a mixture of compounds **7**, **10**, and **13**.[5] This mixture was chromatographed on a silica gel column eluted with *n*-hexane–EtOAc (4:1) to yield, in the order of elution, **10** (4.6 g), **13** (1.2 g), and **7** (3.1 g).

(14*S*)-8,13-Epoxylabdane-7β,14,15-triol (7): mp 171–174 °C (from Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ −0.95° (*c* 1.41, MeOH); IR (KBr) 3500, 3360, 2990, 2950, 2930, 1465, 1445, 1380, 1315, 1140, 1095, 1080, 1070, 1050, 1010, 1000, 965, 905, 875 cm^{-1}; mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 340 (M^+, 0.5), 291 (3), 279 (100), 261 (70), 243 (20), 203 (20), 141 (55), 123 (75), 95 (60), 81 (54), 69 (77). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.40; H, 10.71.

(14*S*)-8,13;14,15-Diepoxylabdan-7β-ol (10): mp 124–127 °C (*n*-hexane); $[\alpha]^{18}_D$ +6.6° (*c* 0.60, $CHCl_3$); IR (KBr) 3495, 3005, 2970, 2870, 1470, 1390, 1075, 1050, 995, 885 cm^{-1}; ^{1}H NMR δ 3.60 (1 H, m, $W_{1/2}$ = 18 Hz, H-7), 3.10–2.66 (3 H, complex signal, H-14 and 2H-15), CMe singlets at 1.31 (3 H), 1.27 (3 H), 1.01 (3 H), 0.94 (3 H), and 0.91 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 322 (M^+, 4), 307 (2), 289 (2), 279 (100), 261 (60), 243 (24), 203 (16), 141 (28), 123 (48), 109 (24), 95 (28), 81 (27). Anal. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63. Found: C, 74.61; H, 10.49.

(14*S*)-8,13-Epoxy-15-ethoxylabdane-7β,14-diol (13): a syrup; IR (NaCl) 3420, 1470, 1390, 1105, 1075, 1000, 915 cm^{-1}; ^{1}H NMR δ 3.80–3.00 (6 H, complex signal, H-7, H-14, 2 H-15, and OCH_2CH_3), 1.20 (3 H, t, *J* = 7 Hz, OCH_2CH_3), CMe singlets at 1.28 (3 H), 1.25 (3 H), 0.88 (3 H), 0.80 (3 H), and 0.77 (3 H); mass spectrum, *m/z* 368 (M^+; $C_{22}H_{40}O_4$ requires *m/e* 368).

(14*S*)-7β,14,15-Triacetoxy-8,13-epoxylabdane (8). This was obtained from compound **7** by Ac_2O–pyridine treatment: mp 146–148 °C (MeOH); $[\alpha]^{18}_D$ −4.8° (*c* 1.44, $CHCl_3$); IR (KBr) 1750, 1740, 1725, 1270, 1245, 1230, 1070, 1045 cm^{-1}; ^{1}H NMR δ 4.93 (1 H, X part of an ABX system, J_{XA} = 8 Hz, J_{XB} = 2.5 Hz, H-14), 4.80 (1 H, q, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 5.5 Hz, H-7), 4.40 (1 H, B part of an ABX system, J_{AB} = 11.5 Hz, H-15), 4.09 (1 H, A part of an ABX system, H'-15), 2.05 (6 H, s, 2 OAc), 2.00 (3 H, s, OAc), CMe singlets at 1.30 (3 H), 1.20 (3 H), 0.87 (3 H), and 0.80 (6 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) M^+ absent, 391 (2.4), 321 (24), 279 (6), 261 (100), 243 (30), 203 (18), 123 (24), 95 (18), 81 (17), 69 (31). Anal. Calcd for $C_{26}H_{42}O_7$: C, 66.92; H, 9.07. Found: C, 66.86; H, 9.16.

(14*S*)-8,13-Epoxy-14,15-(isopropylidenedioxy)labdan-7β-ol (9). Treatment of compound **7** with anhydrous $CuSO_4$ in acetone solution gave compound **9**: mp 97–101 °C (*n*-hexane); $[\alpha]^{18}_D$ +3.1°

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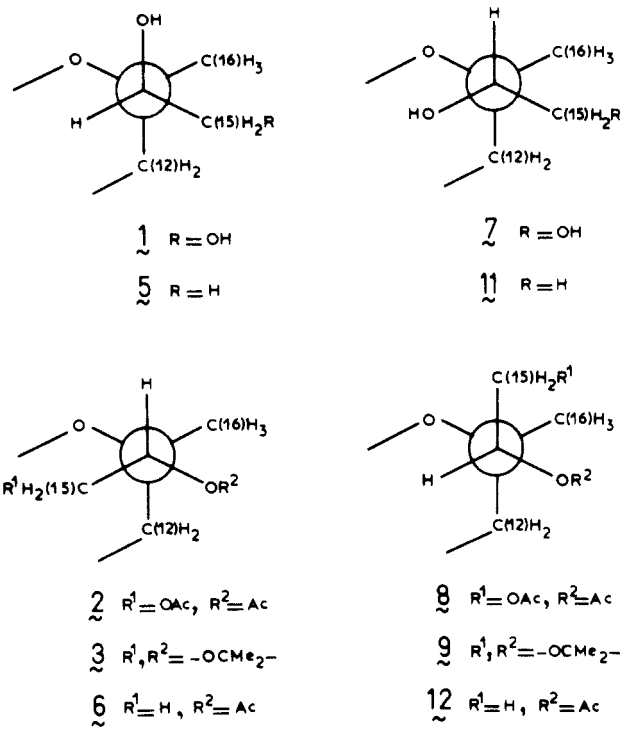
Chart II



(*c* 0.32, $CHCl_3$); IR (KBr) 3600, 3490, 2990, 2940, 1470, 1385, 1215, 1080, 865 cm^{-1}; ^1H NMR δ 4.16–3.45 (4 H, complex signal, H-7, H-14, and 2 H-15), CMe singlets at 1.45 and 1.38 (acetonide), 1.31 (3 H), 1.26 (3 H), 0.92 (3 H), 0.84 (3 H), and 0.81 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 380 (M^+, 0.3), 365 (7), 347 (4), 279 (100), 261 (54), 243 (16), 203 (14), 141 (34), 123 (40), 95 (30), 81 (23), 69 (37). Anal. Calcd for $C_{23}H_{40}O_4$: C, 72.59; H, 10.60. Found: C, 72.64; H, 10.56.

(14*S*)-8,13-Epoxylabdane-7β,14-diol (11). Treatment of compound **10** as previously described for preparation of compound **5** yielded the derivative **11**: mp 156–158 °C (Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ +10.8° (*c* 1.21, $CHCl_3$); IR (KBr) 3440, 3350, 1145, 1075, 1000, 900 cm^{-1}; ^1H NMR δ 3.55 (2 H, complex signal, H-7 and H-14), 1.04 (3 H, d, J = 6.5 Hz, 3 H-15), CMe singlets at 1.30 (3 H), 1.18 (3 H), 0.87 (3 H), 0.80 (3 H), and 0.77 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) 324 (M^+, 1.2), 309 (1.1), 291 (2.4), 279 (100), 261 (63), 243 (24), 203 (22), 141 (48), 123 (60), 95 (51), 81 (38), 69 (56). Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18. Found: C, 73.97; H, 11.29.

(14*S*)-7β,14-Diacetoxy-8,13-epoxylabdane (12). Obtained from compound **11** by Ac_2O–pyridine treatment. Compound **12** was a syrup: IR (NaCl) 1730, 1250, 1105, 1080, 1065, 1035, 980 cm^{-1}; ^1H NMR δ 4.80 (2 H, complex signal, H-7 and H-14), 2.06 and 2.03 (3 H each, s, 2 OAc), 1.10 (3 H, d, J = 7 Hz, 3 H-15), CMe singlets at 1.31 (3 H), 1.17 (3 H), 0.87 (3 H), and 0.80 (6 H).

(14*S*)-7β,14-Diacetoxy-8,13-epoxy-15-ethoxylabdane (14). Acetylation of compound **13** gave compound **14**: a syrup; IR (NaCl) 1735, 1240 cm^{-1}; ^1H NMR δ 4.95 (2 H, complex signal, H-7 and H-14), 3.60 (4 H, complex signal, 2 H-15 and OCH_2CH_3), 2.09 and 2.07 (3 H each, s, 2 OAc), 1.15 (3 H, t, J = 7.5 Hz, OCH_2CH_3), CMe singlets at 1.31 (3 H), 1.18 (3 H), 0.88 (3 H), and 0.80 (6 H).

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Registry No. 1, 52591-03-4; 2, 76499-23-5; 3, 76499-24-6; 4, 76499-25-7; 5, 76499-26-8; 6, 76499-27-9; 7, 76549-11-6; 8, 76581-98-1; 9, 76549-12-7; 10, 76549-13-8; 11, 76549-14-9; 12, 76549-15-0; 13, 76499-28-0; 14, 76499-29-1; (14*R*)-7β-acetoxy-8,13-epoxylabdane-14,15-diol, 76499-30-4; (14*R*)-7β-acetoxy-15-(benzoyloxy)-8,13-epoxylabdan-14-ol, 76499-31-5; (14*R*)-7β-acetoxy-14-tosyloxy-15-(benzoyloxy)-8,13-epoxylabdane, 76499-32-6.

Phenolysis of Spiro[(binaphthylenedioxy)cyclophosphazenes]

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During the last few years (aryloxy)cyclophosphazenes containing reactive functional groups have become of great interest due to their relevance to high molecular weight chemistry. Recently series of hexa(*p*-halogenophenoxy)-cyclophosphazenes[1] and hexa(*p*-hydroxymethylphenoxy)cyclophosphazenes[2] have been synthesized as well as a number of cyclophosphazenes with mixed substituents: phenoxy(hydroxyalkoxy),[3] phenoxy(hydroxyphenoxy),[4] and phenoxyisothiocyanato.[5] Kajiwara has prepared a series of cyclolinear spiro-type polymers by the reactions of *gem*-diphenylcyclophosphazene with aromatic *p*-dihydroxy compounds[6] among which the product obtained from hydroquinone was the most interesting.

In our previous paper[7] we reported the synthesis of two isomeric spiro[(binaphthylenedioxy)cyclophosphazenes], **1** and **2**. Both these compounds contain two PCl_2 groups in their molecules. Such a structure (monogem substituted) offers possibilities for the preparation of cyclolinear derivatives. However, it was suspected that the steric hindrance imposed on **1** and **2** by the presence of bulky spiro substituents would significantly restrain, if not prevent completely, substitution of the remaining chlorine atoms in these compounds. In order to establish the possibility of partial (two atoms) and total (four atoms) substitution of chlorine atoms in **1** and **2**, we have studied their reaction with phenol at various molar ratios of reagents.

Results and Discussion

Phenolysis of either $(PNCl_2)_3$ itself[8] or that of its *gem*-diphenyl derivative[8,9] is known to follow a nongeminal substitution pattern due to the steric factors hindering the attachment of the second phenoxy group to the phosphorus atoms already bearing one such a substituent. Therefore, the replacement of chlorine atoms with phenoxy groups in **1** and **2**, which are monogem derivatives could also be expected to follow a nongeminal reaction pattern and to produce diphenoxy derivatives **3** or **4**, respectively, containing two P(OPh)Cl groups as shown in reaction a of Scheme I.

In actual fact the reaction of the isomeric 3,3,5,5-tetrachloro(binaphthylenedioxy)cyclotriphosphazenes **1** and **2** with sodium phenolate (**7**) in tetrahydrofuran at molar ratios of 1:2 (Scheme Ia) or 1:4 (Scheme Ib) proceeds quantitatively and leads, depending upon the stoichiom-

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