we examined the reaction with phenanthro[9,10-c]-thiophene (9).[8] Treatment of 9 with NBS in acetone is reported to cause oxidation to sulfoxide 10 (Scheme II). We found that NBS in acetic acid, however, gave the dibromo compound 11 which, on further bromination gave 12 and 13.

We note that in the conversion of 4 to 5 and 11 to 12, one destroys the aromaticity of a thiophene ring but gains a benzenoid ring, and this may be a factor which facilitates the observed further electrophilic bromination.

Experimental Section

Bromination of Naphtho[1,2-c]thiophene (3). (a) With Bromine. Bromine (320 mg, 2 mmol) in 5 mL of chloroform was added to a solution of 3 (180 mg, 1 mmol) in 10 mL of chloroform. The mixture was stirred at room temperature for 2 min and then was washed with aqueous sodium bisulfite, sodium bicarbonate, and water. The organic layer was dried over magnesium sulfate, and the solvent was removed under vacuum. The residue was chromatographed on silica gel with 30% of benzene in hexane as the eluent to give 140 mg (41%) of 1,3-dibromonaphtho[1,2-c]thiophene (4), which could be recrystallized from hexane: mp 89–91 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.25 (m, 1 H), 7.65 (m, 1 H), 7.52 (m, 2 H), 7.28 (d, J = 10 Hz, 1 H), 7.27 (d, J = 10 Hz, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 132.00, 131.53, 128.64, 128.06, 127.88, 127.59, 127.11, 127.06, 123.65, 119.41, 104.94, 103.24; IR (KBr) 3060 (m), 1460 (s), 1380 (s), 1220 (m), 890 (s), 870 (w) cm^{-1}; mass spectrum, m/e (relative intensity) 344 (50), 342 (100), 340 (53), 263 (22), 261 (22); high-resolution mass spectrum calcd for $C_{12}H_6Br_2S$ m/e 341.853 83, found m/e 341.854 12.

(b) With 2 Equiv of N-Bromosuccinimide. NBS (360 mg, 2 mmol) was added to a solution of 3 (180 mg, 1 mmol) in 20 mL of acetic acid. The mixture was stirred at room temperature for 20 min, and then 100 mL of water was added. The solution was extracted with 30 mL of ether three times. The combined organic layers were washed with aqueous sodium bicarbonate and dried over magnesium sulfate. The solvent was removed under vacuum to give a solid which was chromatographed on silica gel with 20% of benzene in hexane as the eluent to give 74 mg (22%) of 4, mp 89–91 °C.

In addition to 4, compounds 5 and 6 were isolated in 13% and 21% yields respectively. For 5: mp 113–114 °C; ^{1}H NMR (250 HMz, $CDCl_3$) δ 8.97 (m, 1 H), 8.10 (m, 1 H), 8.09 (d, J = 8.0 Hz, 1 H), 7.85 (m, 2 H), 7.81 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 189.18, 148.42, 137.49, 133.10, 129.58, 129.52, 129.25, 127.66, 127.37, 126.70, 118.27, 44.43; IR (KBr) 3080 (w), 1700 (s), 1500 (m), 1350 (m) cm^{-1}; mass spectrum, m/e (relative intensity) 360 (0.78), 358 (1.6), 356 (0.73), 279 (73.6), 277 (77.4), 198 (17), 170 (100); high-resolution mass spectrum calcd for $C_{12}H_6Br_2OS$ m/e 357.848 75, found m/e 357.846 07.

For 6: mp 115–117 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.17 (m, 1 H), 8.23 (d, J = 8.5 Hz, 1 H), 7.95 (m, 1 H), 7.94 (d, J = 8.5 Hz, 1 H), 7.77 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 190.50, 190.04, 139.46, 136.84, 136.17, 133.55, 130.67, 129.58, 128.53, 128.14, 126.20, 118.53; IR (KBr) 3060 (m), 1690 (s), 1400 (m), 1250 (m) cm^{-1}; mass spectrum, m/e (relative intensity) 214 (79.6), 186 (31), 158 (20), 126 (100); high-resolution mass spectrum calcd for $C_{12}H_6O_2S$ m/e 214.008 85, found m/e 214.009 07.

Hydrolysis of 6. Compound 6 (30 mg, 0.14 mmol) was suspended in 30 mL of hydrochloric acid (20%), and the mixture was refluxed for 6 h. After the solution was cooled to room temperature, it was extracted with 25 mL of ether. The organic layer was washed with water and dried over magnesium sulfate. The solvent was evaporated to give a yellow solid which was recrystallized from ethanol to give 15 mg (50%) of naphthalene-1,2-dicarboxylic acid: mp 175–176 °C (lit.[7] mp 175 °C); mass spectrum, m/e (relative intensity) 216 (29), 198 (81), 172 (10), 154 (65.6), 126 (100).

Bromination of Phenanthro[9,10-c]thiophene (9). Bromination of 9[8] (85 mg, 0.36 mmol) with NBS (150 mg, 0.72 mmol) in 30 mL of acetic acid was carried out as described for the preparation of 4. The workup gave a solid which was recrystallized from hexane to yield 100 mg (65%) of 11: mp 170–172 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.33 (m, 2 H), 8.40 (m, 2 H), 7.55 (m, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 131.79, 130.55, 127.97, 127.67, 127.09, 124.32, 123.44, 105.04; IR (KBr) 3010 (w), 1450 (s), 1040 (w), 750 (s), 720 (s) cm^{-1}; mass spectrum, m/e (relative intensity) 394 (53), 392 (100), 390 (50), 313 (21), 311 (22); high-resolution mass spectrum calcd for $C_{16}H_8Br_2S$ m/e 391.869 49, found m/e 391.870 42.

Treatment of 11 with NBS. Compound 11 (80 mg, 0.2 mmol) was treated with NBS (36 mg, 0.2 mmol) in 20 mL of acetic acid with stirring at room temperature for 20 min. Then water (20 mL) was added, and the solution was extracted with ether (20 mL) three times. The combined organic layers were washed with aqueous sodium bicarbonate and water. The organic solution was dried over magnesium sulfate and evaporated to give a residue. The residue was chromatographed on silica gel with 20% of benzene in hexane as the eluent to yield 12 (62%) and 13 (15%).

For 12: mp 150–152 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.90 (m, 2 H), 7.83 (m, 2 H), 7.76 (m, 2 H), 7.73 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 190.07, 150.84, 134.32, 131.85, 131.84, 129.44, 129.08, 128.44, 126.61, 125.97, 125.50, 125.14, 122.79, 43.69; IR (KBr) 3030 (w), 1695 (s), 1495 (m), 1380 (m), 1080 (m) cm^{-1}; mass spectrum, m/e (relative intensity) 410 (2), 408 (3.5), 406 (1.8), 329 (83), 327 (70), 220 (100); high-resolution mass spectrum calcd for $C_{16}H_8Br_2OS$ m/e 407.864 40, found m/e 407.868 41.

For 13: mp 160–162 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.35 (m, 2 H), 8.71 (m, 2 H), 7.82 (m, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 191.38, 135.46, 133.87, 130.04, 129.22, 127.93, 125.81, 122.99; IR (KBr) 3020 (w), 1690 (s), 1500 (w), 1360 (w) cm^{-1}; mass spectrum, m/e (relative intensity) 264 (76), 236 (45), 208 (30), 176 (100); high-resolution mass spectrum calcd for $C_{16}H_8O_2S$ m/e 264.024 50, found m/e 264.024 50.

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(8) Shields, J. E.; Remy, D. E.; Bornstein, J. J. Org. Chem. 1975, 40, 477.

C(13) and C(14) Configurations of 8,13- and 8,13β-Epoxylabdane-14,15-diols: A Method Based on Boric Acid Induced ^{13}C NMR Shifts[1]

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Among natural substances of the diterpene type there exist an increasing number containing a vicinal glycol unit in the form of a 13-dihydroxyethyl group.[3] Whereas the stereochemistry of their rigid nuclear framework and of the substituents attached to it could be easily determined by spectral methods, the configuration of their secondary hydroxy group of the dihydroxyethyl moiety has remained

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(3) (a) Wenkert, E.; Ceccherelli, P.; Raju, M. S.; Polonsky, J.; Tingoli, M. J. Org. Chem. 1979, 44, 146, and references therein. (b) Rodríguez, B.; Valverde, S. Tetrahedron 1973, 29, 2837. (c) Valverde, S.; Rodríguez, B. Phytochemistry 1977, 16, 1841. (d) de Quesada, T. G.; Rodríguez, B.; Valverde, S. Phytochemistry 1975, 14, 517. (e) von Carstenn-Lichterfelde, C.; Rodríguez, B.; Valverde, S. Experientia 1975, 31, 757.

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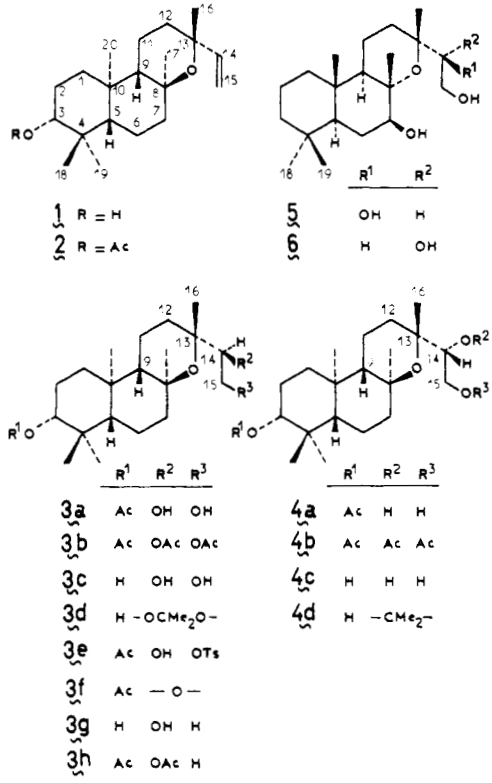
Chart I



obscure in some cases because of the nonrigid nature of the C(13)-attached side chain.

Recently there were described two procedures for the determination of the C(15) configuration by ^{13}C NMR spectral analysis of cyclization products of pimarene-, isopimarene-, and sandaracopimarene-15,16-diols.[3a,4] Moreover, some of us have recently reported a simpler and better criterion for the assignment of the C(14) stereochemistry of 8,13-epoxylabdanes with C(14)- or C(14),C(15)-oxygenated side chains.[5] This method is based on the variation of $\delta_{C(12)}$ and $\delta_{C(16)}$ in the ^{13}C NMR spectra of the C(14),C(15)-dihydroxy compound and its 14,15-diacetyl or 14,15-acetonide derivative. The determination of the C(14) configuration of 8,13β-epoxylabdane-14,15-diols by ^{13}C NMR spectroscopy and an improvement of the previously described method[5] for establishing the C(14) configuration of either the 8,13 or 8,13β series are the subjects of the present paper.

The natural diterpenoid ribenol[6] [*ent*-3β-hydroxy-8,13β-epoxylabd-14-ene (**1**) Chart I] was used as the starting material for obtaining all the products belonging to the 8,13β-epoxylabdane series. Treatment of the acetyl derivative of ribenol (compound **2**) with osmium tetroxide yielded a mixture of the C(14),C(15)-dihydroxy derivatives epimeric at their C(14) centers. This mixture was easily separated on column chromatography, yielding pure the major constituent (**3a**), as well as the minor one (**4a**) [for the assignment of the configurations at their C(14) centers see following discussion]. Acetylation of both compounds yielded the triacetyl derivatives **3b** and **4b**, respectively. Alkaline hydrolysis of **3a** and **4b** gave compounds **3c** and **4c**, respectively, which were transformed into their C-(14),C(15)-acetonide derivatives (compounds **3d** and **4d**, respectively) by acetone–anhydrous $CuSO_4$ treatment. On the other hand, selective C(15)-OH tosylation of compound **3a** yielded the derivative **3e**, which was treated with Na_2CO_3–EtOH–H_2O to give[5] the oxirane **3f**. $LiAlH_4$ reduction of compound **3f** yielded the diol **3g**, which was acetylated to give substance **3h**.[7]

Table I. ^{13}C Chemical Shifts of Compounds 3a,b,d,g,h and 4a,b,d[a,b]

	3a[c]	3b[d]	3d[e]	3g[f]	3h[g]	4a[h]	4b[i]	4d[j]
C(1)	36.8	37.1	37.4	37.5	37.1	37.0	36.8	37.3
C(2)	23.4	23.5	27.2	27.5	23.5	23.5	23.5	27.2
C(3)	80.6	80.5	78.6	77.9	80.6	80.5	80.5	78.8
C(4)	37.6	37.7	38.8	39.0	37.7	37.8	37.7	38.8
C(5)	55.4	55.4	55.2	55.6	55.4	55.5	55.5	55.5
C(6)	19.6	19.6	19.8	20.0	19.7	19.7	19.6	19.8
C(7)	43.6	43.2	43.4	44.1	43.4	43.7	43.5	43.8
C(8)	75.2	75.3	74.6	74.7	74.9	75.3	74.5	74.6
C(9)	53.3	56.1	56.5	54.0	56.0	53.6	53.0	54.0
C(10)	36.7	36.7	36.7	36.9	36.7	36.8	36.8	37.0
C(11)	14.2	14.9	14.9	14.5	14.9	14.6	14.5	14.7
C(12)	28.8	33.0	34.2	28.1	32.2	29.5	28.6	29.5
C(13)	74.9	73.4	73.7	76.0	73.9	75.6	73.0	72.9
C(14)	76.7	74.0	78.3	71.7	72.9	76.1	76.7	81.2
C(15)	63.0	63.7	65.2	17.1	14.5	63.4	63.5	65.7
C(16)	24.6	24.8	24.4	24.5	24.4	25.2	26.3	25.4[k]
C(17)	25.5	25.2	25.3	25.5	24.7	25.2	25.3	25.3[k]
C(18)	27.9	27.9	28.0	28.3	28.0	28.0	28.0	28.1
C(19)	16.4	16.3	15.6[k]	15.8	16.4	16.4	16.5	15.4[l]
C(20)	15.2	15.6	15.3[k]	15.3	15.6	15.3	15.0	15.1[l]

[a] In parts per million downfield from Me_4Si; δ (Me_4Si) = δ ($CDCl_3$) + 76.9 ppm. [b] All in $CDCl_3$ solution, except for **3g**, which was taken in $CDCl_3$-pyridine-d_5 (9:1). [c] OAc, 170.6, 21.1. [d] OAc, 170.3, 170.2, 170.0, 21.1, 20.9, 20.7. [e] Acetonide, 109.0, 26.0, 24.4. [f] No variations were observed on addition of H_3BO_3. [g] OAc, 170.4, 170.1, 21.3, 21.1. [h] OAc, 170.5, 21.1. [i] OAc, 170.6, 170.5, 170.3, 21.2, 21.0, 20.8. [j] Acetonide, 109.1, 26.5, 25.3 (see footnote *k*). [k,l] Values bearing the same superscript may be interchanged.

The 14*S* configuration of the major epimer (**3a**) and its derivatives (**3b–h**), as well as the 14*R* configuration of compounds **4a–d**, was first inferred from the fact that oxidation of the C(14)–C(15) double bond of these *ent*-8,13β-epoxylabd-14-enes with osmium tetroxide mainly affords the 14(*S*)-hydroxy epimer.[3e] This conclusion was then confirmed by application of Horeau's method of partial resolution[8] to compounds **3d** and **3g**, which defined as 14*S* the absolute configuration of the diol **3g** (see also the Experimental Section).

The ^{13}C shifts of compounds **3a,b,d,g,h** and **4a,b,d** are listed in Table I and were assigned on the basis of ^{13}C NMR off-resonance-decoupled spectra, comparison of pairs of compounds, general chemical shift arguments, and literature data on closely related structures.[5]

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 the 13*R*,14*S*,C(13),C(14)-erythro series with those of the 13*R*,14*R*,C(13),C(14)-threo series (pairs of compounds: **3a**, **4a**; **3b**, **4b**; **3d**, **4d**) distinguished the two compounds easily, since the γ effects exerted by the C(14)-oxygenated function on C(12) and C(16) are different in each isomer.

An identical behavior in the $\delta_{C(12)}$ and $\delta_{C(16)}$ values between the pairs of epimers, as well as a similar variation of $\Delta\delta_{C(12)}$ and $\Delta\delta_{C(16)}$ between a C(14)-hydroxy compound and its acetyl or C(14),C(15)-acetonide derivative, has been

(4) (a) Wenkert, E.; Raju, M. S.; Ceccherelli, P.; Curini, M.; Tingoli, M.; Pellicciari, R. *J. Org. Chem.* **1980**, *45*, 741. (b) Wenkert, E.; Halls, T. D. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R. *J. Org. Chem.* **1981**, *46*, 3135.

(5) García-Alvarez, M. C.; Rodríguez, B. *J. Org. Chem.* **1981**, *46*, 1915.

(6) González, A. G.; Fraga, B. M.; Hernández, M. G.; Luis, J. G. *Phytochemistry* **1973**, *12*, 1113.

(7) Due to the low quantity of compound **4a**, which is the minor product obtained from OsO_4 treatment of **2**, it was not possible to prepare 15-deoxy derivarives of the C(13),C(14)-threo series.

(8) Horeau, A.; Nouaille, A. *Tetrahedron Lett.* **1971**, 1939.

Table II. ^{13}C Chemical Shifts and Boric Acid Shifts of Compounds 3a, 4c, 5, and 6[a,b]

	3a[c]	Δδ (H_3BO_3)[d]	4c	Δδ (H_3BO_3)[d]	5	Δδ (H_3BO_3)[d]	6	Δδ (H_3BO_3)[d]
C(1)	36.8	−0.2	37.5	−0.1	38.9	0.0	38.9	0.0
C(2)	23.6	0.0	27.4	0.0	18.6	0.0	18.5	0.0
C(3)	80.4	0.1	77.9	0.1	42.0	0.0	42.0	−0.1
C(4)	37.7	0.1	39.0	0.0	33.2	0.0	33.1	0.0
C(5)	55.5	−0.1	55.6	0.1	54.2	0.0	54.2	−0.1
C(6)	19.7	0.0	19.8	0.1	27.5	−0.2	27.6	−0.1
C(7)	43.8	−0.4	43.8	0.2	80.5	−0.1	80.3	−0.2
C(8)	75.6	−1.0	75.0[e]	−0.2	79.1	−0.4	78.7	0.0
C(9)	54.6	1.7	54.7	−1.4	56.3	−0.1	56.3	−0.1
C(10)	37.0	0.1	36.8	0.2	37.0	0.0	36.8	0.0
C(11)	14.7	0.2	14.9	−0.4	14.4	−0.1	14.5	−0.2
C(12)	31.1	2.8	30.6	−1.1	33.2	0.5	34.0	−1.0
C(13)	74.6	2.4	75.1[e]	2.1	75.5	−0.1	74.8	−0.4
C(14)	76.3	0.5	76.8	0.2	78.9	1.2	80.1	0.8
C(15)	63.2	2.2	63.4	2.0	62.8	2.0	62.5	1.3
C(16)	24.4	−1.1	24.8	2.5	23.6	−1.0	22.5	0.4
C(17)	25.4	−0.3	25.2	0.0	19.6	0.0	19.6	−0.1
C(18)	28.0	−0.1	28.2	0.1	33.3	0.0	33.3	0.0
C(19)	16.4	0.0	15.7	0.0	21.3	0.0	21.3	0.0
C(20)	15.3	0.3	15.3	−0.3	15.8	0.0	15.8	0.0

[a] In parts per million downfield from Me_4Si; δ (Me_4Si) = δ ($CDCl_3$) + 76.9 ppm. [b] In $CDCl_3$-pyridine-d_5 (9:1) solution. [c] OAc, 170.0, 21.0. [d] After saturation with H_3BO_3. [e] These assignments may be interchanged.

previously found[5] in the 8,13-epoxylabdane-14(*R*),15- or -14(*S*),15-diol series: compounds **5** [13*R*,14*S*,C(13),C(14)-erythro isomer] and **6** [13*R*,14*R*,C(13),C(14)-threo isomer].

As in compounds **5** and **6** and their derivatives,[5] the $\delta_{C(12)}$ and $\delta_{C(16)}$ variations shown by the substances collected in Table I may be explained for compounds **3a**, **3g**, and **4a** on the basis of a preferred side-chain conformation due to an intramolecularly hydrogen bonded [8,13β-epoxy → C(14) OH] form, whereas in their C(14),C(15)-diacetyl or -acetonide derivatives (except in compound **4d**) the preferred side-chain rotamer must be different from those of the corresponding C(14)-hydroxy compounds.

As in the case of the 8,13-epoxylabdane derivatives **5** and **6**,[5] the C(14)-OH configuration of their C(13) epimers[9] (compounds **3** and **4**, respectively) must be firmly established by acetylation of the alcohol or by C(14),C(15)-acetonide formation. Effectively, in the C(13),C(14)-erythro series the acetylation of the C(14)-hydroxy group causes a large downfield shift of C(12) (Δδ = 4.2 ppm for compounds **3a** and **3b**, and 4.1 ppm for **3g** and **3h**) and no substantial shift of C(16) [Δδ = 0.2 ppm (**3a** and **3b**) and −0.1 ppm (**3g** and **3h**)], whereas in the C(13),C(14)-threo series the same structural variation causes an upfield shift of C(12) (Δδ = −0.9 ppm for compounds **4a** and **4b**) and a downfield shift of C(16) [Δδ = 1.1 ppm (**4a** and **4b**)]. Identical variations, but of different magnitude, are observed between compounds **3a** and **3d** but not between compounds **4a** and **4d** (Table I). Thus, an identical preferred side-chain rotamer must be considered for these two last compounds.

However, there are some differences between the ^{13}C NMR spectroscopic behavior of the 14,15-dihydroxy-8,13β-epoxylabdane derivatives (compounds **3a** and **4a**) and their C(13) epimers[9] (compounds **5** and **6**).[5] In compounds **5** and **6**, epimerization of the C(14) OH or derivatization of it does not causes any variation larger than ±0.5 ppm in $\delta_{C(9)}$.[5] The same behavior was now found in the C(13),C(14)-threo series of the 8,13β-epoxylabdane-14(*R*),15-diol derivatives (compounds **4a**,**b**,**d**); in contrast, compounds **3a** and **3g** showed a large downfield shift of C(9) when the C(14) OH was acetylated [Δδ = 2.8 and 2.0 ppm (compounds **3b** and **3h**, respectively)] or when it formed an acetonide derivative [Δδ = 3.2 ppm (**3d**)] (Table I). Thus, it is clear that a ring-C conformatonal difference exists between compounds **3a**, **3g**, **4a**, **4b**, and **4d** [$\delta_{C(9)}$ 53.3, 54.0, 53.6, 53.0, and 54.0 ppm, respectively] and the derivatives **3b**, **3d**, and **3h** [$\delta_{C(9)}$ 56.1, 56.5, and 56.0, respectively].

Table III. Width (Hertz) at Half Height of the ^{13}C NMR Signals[a] Affected by H_3BO_3 Addition

	3a		4c		5		6	
	b	*c*	*b*	*c*	*b*	*c*	*b*	*c*
C(9)	4	22	4	19	4	4	5	5
C(12)	5	28	5	20	5	28	7	37
C(13)	3	7	3	8	3	6	3	5
C(14)	4	23	5	21	4	40	5	20
C(15)	4	30	5	25	4	45	5	28
C(16)	6	14	6	12	5	19	5	9

[a] Proton-decoupled spectra. [b] In $CDCl_3$-pyridine-d_5 (9:1) solution. [c] After saturation with H_3BO_3 (see the Experimental Section).

Furthermore, a study of boric acid induced shifts in the ^{13}C NMR spectra of compounds **3a**, **3g**, **4c**, **5**, and **6** allowed an improvement of the method for establishing the C(13) configuration and the C(13),C(14) relative stereochemistry of these diterpenoids, because derivatization is not necessary and the signals of C(12) and C(16) in all the compounds and of C(9) in compounds of the 13β series are clearly distinguished from the others, which is a great advantage in the elucidation of the structures of new 8,13- and 8,13β-epoxylabdane-14,15-diol derivatives.

It is known[10] that addition of boric acid to either 1,2- or 1,3-diols produces substantial alterations in the ^{13}C chemical shifts of the parent compounds and also a marked broadening[10a] of the lines associated with the hydroxy-bearing carbons forming the borate ester. In the experimental conditions used by us (see the Experimental Section), compounds **5** and **6** showed induced shifts in C(12)–C(16) and also a marked broadening of the C(12) and

(9) From the point of view of the NMR spectroscopy without chiral interactions and omitting the carbocyclic oxygenated function, compounds **5** and **6** may be considered as the C(13) epimers of compounds **3a** and **4a**, respectively, because **5** and **6** belong to the *nor*-8,13-epoxylabdane series, whereas **3a** and **4a** belong to the *enantio*-8,13β-epoxylabdane series.

(10) (a) Smith, W. B. *J. Org. Chem.* **1979**, *44*, 1631. (b) Pasdeloup, M.; Brisson, C. *Org. Magn. Reson.* **1981**, *16*, 164.

Table IV. Effects of H_3BO_3 in the ^{13}C NMR Spectra of Compounds 3a, 4c, 5, and 6

no.	C(13) config	C(13),C(14) stereochem	C(9)	C(12)	C(16)
3a	13β (= 13 epi)	erythro	Δδ(+),[a] br[b]	Δδ(+), br	Δδ(−), br
4c	13β	threo	Δδ(−), br	Δδ(−), br	Δδ(+), br
5	13α (= 13 normal)	erythro	Δδ(0), s[b]	Δδ(+), br	Δδ(−), br
6	13α	threo	Δδ(0), s	Δδ(−), br	Δδ(+), br

[a] Δδ(+), downfield shift; Δδ(−), upfield shift; Δδ(0), no shift. [b] br, broadened signal; s, sharp signal.

C(14)–C(16) signals; compounds **3a** and **4c** showed the same induced shifts and broadenings as **5** and **6**, but also their C(9) signals were broadened. Moreover, in compound **4c**, C(9) showed an upfield shift, whereas in compound **3a**, C(9) was downfield shifted (Tables II and III). On the other hand, the ^{13}C NMR spectrum of compound **3g** was not affected by boric acid addition (Table I).

The boric acid induced shifts in compounds **3a**, **4c**, **5**, and **6** may be explained by considering that a C(14),C(15)-borate ester is formed and that it causes a preferred side-chain conformation, which must be different from those of the corresponding C(14),C(15)-dihydroxy derivatives. This borate ester is also responsible of a ring-C conformational change in compound **3a**. In fact, the observed boric acid shifts in C(12) and C(16) of compounds **5** and **6**, and in C(9), C(12), and C(16) of compound **3a**, are of the same sign, although of different magnitude, as the ones observed for the acetonide derivatives of these compounds (Table I and ref 5), whereas the borate ester of compound **4c** causes shifts in C(9), (C12), and C(16), which are not observed for acetonation (**4d**, Tables I and II).

As a consequence of all the above results, the C(13) configuration and the C(13),C(14) relative stereochemistry of these labdane derivatives can be firmly established by boric acid induced ^{13}C NMR shifts. Table IV summarizes these conclusions.

Finally, it is very important to note that boric acid may be more specific and adequate than lanthanide chemical shift reagents in the NMR spectroscopic study of some organic compounds.[10a,11]

Experimental Section

Melting points were determined on 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[2a] 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. ^1H NMR spectra ($CDCl_3$) were measured at 90 MHz, 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 a frequency of 25.2 MHz over a spectral width of 5 kHz with the solvent [commercial NMR grade $CDCl_3$ or $CDCl_3$–pyridine-d_5 (9:1, v/v)] 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 proton-decoupled spectra were obtained by using a square-wave-modulated noise band centered in the proton spectrum. All samples were prepared as 0.5 M $CDCl_3$ or $CDCl_3$–pyridine-d_5 (9:1, v/v) solutions in 5-mm sample tubes. The probe temperature in each case was 36 °C. To observe H_3BO_3 shifts, pure boric acid was added in small amounts to the $CDCl_3$–C_5D_5N solution of the sample tube until a thin layer of H_3BO_3 (≃2-mm high) appeared in the bottom after stirring (saturated solution). The substrate sample was easily recovered by addition of 0.1 N HCl solution and extraction with $CHCl_3$. Chemical shifts are accurate to ±0.05 ppm. Compounds 1,[6] **2**,[6] **5**,[5] and **6**[3b,c] have been previously described.

(14*S*)-*ent*-3β-Acetoxy-8,13β-epoxylabdane-14,15-diol (3a) and (14*R*)-*ent*-3β-Acetoxy-8,13β-epoxylabdane-14,15-diol (4a) from Ribenol Acetate (2). To an Et_2O–dioxane (2:1, v/v, 100 mL) solution of compound **2**[6] (720 mg), an excess of OsO_4 (650 mg) was added, and the solution was left standing at room temperature for 1 week. Workup in the usual manner yielded a mixture of compounds **3a** and **4a**. This mixture was chromatographed on a silica gel (300 g, Merck no. 7734, deactivated with 10% H_2O) dry column; elution with $CHCl_3$ yielded compound **4a** (105 mg), and elution with $CHCl_3$–MeOH (49:1) yielded derivative **3a** (608 mg).

3a: mp 173 °C (from Me_2CO–*n*-hexane); $[\alpha]^{21}_D$ −27.5° (*c* 0.77, $CHCl_3$); IR (KBr) 3350 (OH), 1725, 1250 (OAc) cm^{-1}; ^1H NMR δ 4.50 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 3.80–3.50 (3 H, complex signal, H-14 and 2 H-15), 2.03 (3 H, s, OAc) CMe singlets at 1.22 (3 H), 1.17 (3 H), 0.85 (3 H), and 0.83 (6 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) M^+ absent, 367 (M^+–15, 6), 321 (20), 261 (75), 243 (52), 203 (12), 201 (12), 135 (100). Anal. Calcd for $C_{22}H_{38}O_5$: C, 69.07; H, 10.01. Found: C, 68.96; H, 10.13.

4a: mp 164–165 °C (Me_2CO–*n*-hexane); $[\alpha]^{21}_D$ −25.5° (*c* 0.165, $CHCl_3$); IR (KBr) 3420 (OH), 1725, 1255 (OAc) cm^{-1}; ^1H NMR δ 4.53 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 3.73–3.40 (3 H, complex signal, H-14 and 2 H-15), 2.08 (3 H, s, OAc), CMe singlets at 1.33 (3 H), 1.15 (3 H), and 0.90 (9 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) M^+ absent, 367 (M^+ − 15, 11), 321 (26), 261 (60), 243 (40), 203 (6), 201 (5), 135 (80), 123 (100), 109 (65). Anal. Calcd for $C_{22}H_{38}O_5$: C, 69.07; H, 10.01. Found: C, 69.13; H, 10.16.

(14*S*)-*ent*-3β,14,15-Triacetoxy-8,13β-epoxylabdane (3b). This was obtained from compound **3a** by Ac_2O–pyridine treatment: mp 174–175 °C (MeOH); $[\alpha]^{21}_D$ −33.1° (*c* 0.51, $CHCl_3$); IR (KBr) 1730 (br), 1250 (OAc) cm^{-1}; ^1H NMR δ 5.42 (1 H, dd, X part of an ABX system, J_{XA} = 9 Hz, J_{XB} = 3 Hz, H-14), 4.62 (1 H, dd, B part of an ABX system, J_{BA} = 12 Hz, H-15), 4.49 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 5.5 *Hz*, H-3), 4.19 (1 H, dd, A part of an ABX system, H′-15), 2.09, 2.05, and 2.02 (3 H each, singlets, 3 OAc), CMe singlets at 1.32 (3 H), 1.14 (3 H), 0.87 (3 H), 0.85 (3 H), and 0.81 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) M^+ absent, 451 (M^+ − 15, 2), 407 (1), 391 (4), 331 (5), 321 (40), 261 (100), 243 (82), 203 (20), 201 (23), 135 (84). Anal. Calcd for $C_{26}H_{42}O_7$: C, 66.92; H, 9.07. Found: C, 67.04; H, 9.05.

(14*S*)-*ent*-8,13β-Epoxylabdane-3β,14,15-triol (3c). This was obtained from **3a** by alkaline hydrolysis with ethanolic KOH (5%, w/v): mp 122–124 °C (Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ −17.0° (*c* 0.74, MeOH); IR (KBr) 3280 br (OH) cm^{-1}; ^1H NMR ($CDCl_3$–C_5D_5N, 1:1) δ 4.10–3.55 (3 H, complex signal, H-14 and 2 H-15), 3.25 (1 H, dd, $J_{aa'}$ = 10 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), CMe singlets at 1.28 (3 H), 1.23 (3 H), 1.05 (3 H), 0.85 (3 H), and 0.80 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) M^+ absent, 325 (M^+ − 15, 1), 291 (3), (30), (3), 261 (38), 243 (41), 203 (14), 144 (30), 135 (26), 84 (35), 69 (40), 57 (100). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.39; H, 10.37.

(14*S*)-*ent*-8,13β-Epoxy-14,15-(isopropylidenedioxy)labdan-3β-ol (3d). Treatment of compound **3c** with anhydrous $CuSO_4$ in acetone solution gave compound **3d**: mp 137–139 °C (Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ −8.0° (*c* 0.67, $CHCl_3$); IR (KBr) 3530, 3300 br (OH) cm^{-1}; ^1H NMR δ 4.35 (1 H, dd, X part of an ABX system, J_{XA} = 5 Hz, J_{XB} = 8 Hz, H-14), 4.01 (1 H, dd, B part of an ABX system, J_{BA} = 8.5 Hz, H-15), 3.96 (1 H, dd, A part of an ABX system, H′-15), 3.25 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), CMe singlets at 1.43 and 1.35 (acetonide), 1.17 (3 H), 1.10 (3 H),

(11) A ^{13}C NMR study of boric acid induced shifts in some natural diterpenoids will be published elsewhere.

1.00 (3 H), and 0.80 (6 H); mass spectrum (75 eV, direct inlet), m/z (relative intensity) M^+ absent, 365 ($M^+ - 15$, 2), 279 (18), 261 (21), 243 (26), 2 03 (7), 135 (30), 121 (15), 95 (20), 81 (22), 69 (20), 55 (32), 43 (100). Anal. Calcd for $C_{23}H_{40}O_4$: C, 72.59; H, 10.60. Found: C, 72.48; H, 10.53.

(14*S*)-*ent*-3β-Acetoxy-8,13β:14,15-diepoxylabdane (3f). A 246-mg sample of compound **3a** (0.715 mmol) was treated with 0.8 mmol of tosyl chloride in pyridine solution (12 mL) at room temperature during 24 h; workup in the usual manner yielded (14*S*)-*ent*-3β-acetoxy-15-(tosyloxy)-8,13β-epoxylabdan-14-ol (**3e**): ^1H NMR δ 7.82 and 7.33 (A_2B_2 system, J = 8 Hz, tosyl group), 4.50–3.80 (4 H, complex signal, H-3, H-14, and 2 H-15), 2.43 (3 H, s, MePh, tosyl group), 2.03 (3 H, s, OAc), CMe singlets at 1.10 (3 H), 1.05 (3 H), 0.85 (6 H), and 0.79 (3 H). Treatment of this last compound under reflux for 2 h with Na_2CO_3 in 90% aqueous EtOH solution (0.1%, w/v, 15 mL)[5] quantitatively yielded compound **3f**: mp 159–161 °C (MeOH); $[\alpha]^{18}_D$ –34.1° (*c* 0.41, $CHCl_3$); IR (KBr) 3070 (oxirane), 1735, 1245 (OAc) cm^{-1}; ^1H NMR δ 4.51 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 3.12 (1 H, dd, J_1 = 3 Hz, J_2 = 4 Hz, oxirane), 2.80 (1 H, t, J = 4 Hz, oxirane), 2.50 (1 H, dd, J_1 = 3 Hz, J_2 = 4 Hz, oxirane), 2.07 (3 H, s, OAc), CMe singlets at 1.43 (3 H), 1.11 (3 H), 0.89 (3 H), 0.85 (3 H), and 0.81 (3 H); mass spectrum (75 eV, direct inlet), m/z (relative intensity) M^+ absent, 349 ($M^+ - 15$, 8), 321 (32), 251 (52), 243 (42), 203 (16), 201 (18), 135 (70), 121 (32), 109 (31), 95 (40), 81 (43), 69 (50), 55 (62), 43 (100). Anal. Calcd for $C_{22}H_{36}O_4$: C, 72.49; H, 9.96. Found: C, 72.39; H, 10.03.

(14*S*)-*ent*-8,13β-Epoxylabdane-3β,14-diol (3g). The (14*S*)-14,15-epoxy derivative (**3f**) was treated with $LiAlH_4$ in Et_2O solution at room temperature for 3 h, yielding compound **3g**: mp 90–91 °C (Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ –15.5° (*c* 0.43, MeOH); IR (KBr) 3480, 3300 (br, OH) cm^{-1}; ^1H NMR ($CDCl_3$–C_5D_5N, 9:1) δ 3.70 (1 H, q, J = 6 Hz, H-14), 3.27 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 1.17 (3 H, d, J = 6 Hz, 3 H-15), CMe singlets at 1.23 (3 H), 1.17 (3 H), 1.05 (3 H), 0.85 (3 H), and 0.80 (3 H); mass spectrum (75 eV, direct inlet), m/z (relative intensity) M^+ absent, 309 ($M^+ - 15$, 2) 279 (62), 261 (68), 243 (91), 203 (21), 135 (100), 121 (68), 95 (65), 81 (72). Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18. Found: C, 73.96; H, 11.26.

(14*S*)-*ent*-3β,14-Diacetoxy-8,13β-epoxylabdane (3h). Acetylation of compound **3g** gave compound **3h**: mp 119–121 °C (MeOH); $[\alpha]^{18}_D$ –33.3° (*c* 0.74, $CHCl_3$); IR (KBr) 1730, 1245 (OAc) cm^{-1}; ^1H NMR δ 5.13 (1 H, q, J = 6 Hz, H-14), 4.47 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 2.07 (6 H, s, 2 OAc), 1.23 (3 H, d, J = 6 Hz, 3 H-15), CMe singlets at 1.29 (3 H), 1.13 (3 H), 0.89 (3 H), 0.86 (3 H), and 0.82 (3 H); mass spectrum (75 eV, direct inlet), m/z (relative intensity) M^+ absent, 393 ($M^+ - 15$, 1), 349 (3), 333 (9), 321 (20), 251 (52), 243 (38), 203 (11), 201 (14), 135 (54), 121 (18), 95 (21), 81 (26), 69 (32), 55 (41), 43 (100). Anal. Calcd for $C_{24}H_{40}O_5$: C, 70.55; H, 9.87. Found: C, 70.63; H, 9.57.

Application of Horeau's method to compounds 3d and 3g was performed in the usual manner.[8] Compound **3d** (59.81 mg, 0.1574 mmol) and (±)-α-phenylbutyric anhydride (148.54 mg, 0.4792 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.335$, 3*R* configuration. Compound **3g** (51.000 mg, 0.1574 mmol) and (±)-α-phenylbutyric anhydride (148.54 mg, 0.4792 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.128$ for the two 3*R* and 14 centers. Thus, 0.128 – 0.335 = –0.207 for the C(14)-hydroxyl group, configuration 14*S*. This experiment was performed with identical time reaction (16 h) and temperature (18 °C) for the two compounds.

(14*R*)-*ent*-3β,14,15-Triacetoxy-8,13β-epoxylabdane (4b). Acetylation of compound **4a** gave compound **4b**: mp 199–200 °C (MeOH); $[\alpha]^{25}_D$ +7.4° (*c* 0.39, $CHCl_3$); IR (KBr) 1750, 1740, 1735 (OAc) cm^{-1}; ^1H NMR δ 5.05 (1 H, dd, X part of an ABX system, J_{XA} = 9 Hz, J_{XB} = 2.5 Hz, H-14), 4.53 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 4.47 (1 H, dd, B part of an ABX system, J_{BA} = 11.5 Hz, H-15), 4.07 (1 H, dd, A part of an ABX system, H′-15), 2.10, 2.04, and 2.01 (3 H each, singlets, 3 OAc), CMe singlets at 1.23 (6 H), 0.87 (3 H), 0.85 (3 H), and 0.82 (3 H); mass spectrum (75 eV, direct inlet), m/z (relative intensity) M^+ absent, 451 ($M^+ - 15$, 3), 407 (2), 391 (2), 331 (1), 321 (34), 261 (100), 243 (65), 203 (15), 201 (21), 135 (62). Anal. Calcd. for $C_{26}H_{42}O_7$: C, 66.92; H, 9.07. Found: C, 66.98; H, 8.96.

(14*R*)-*ent*-8,13β-Epoxylabdane-3β,14,15-triol (4c). Alkaline hydrolysis of compound **4b** gave compound **4c**: mp 132–134 °C (Me_2CO–*n*-hexane); $[\alpha]^{18}_D$ –13.0° (*c* 0.115, MeOH); IR (KBr) 3450, 3200 (br, OH) cm^{-1}; ^1H NMR ($CDCl_3$–C_5D_5N, 9:1) δ 3.80–3.40 (3 H, complex singal, H-14 and 2 H-15), 3.27 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), CMe singlets at 1.29 (3 H), 1.17 (3 H), 1.07 (3 H), 0.85 (3 H), and 0.79 (3 H); mass spectrum (75 eV, direct inlet), m/z (relative intensty) M^+ absent, 325 ($M^+ - 15$, 8), 291 (6), 279 (34), 261 (40), 243 (62), 203 (26), 135 (100), 121 (61), 95 (68), 81 (72), 69 (83). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.43; H, 10.46.

(14*R*)-*ent*-8,13β-Epoxy-14,15-(isopropylidenedioxy)labdan-3β-ol (4d). Obtained from compound **4c** as prevously described for the preparation of compound **3d**. Compound **4d** had mp 72–75 °C (*n*-hexane): $[\alpha]^{18}_D$ –9.6° (*c* 0.42, $CHCl_3$); IR (KBr) 3350 (OH) cm^{-1}; ^1H NMR δ 4.20–3.70 (3 H, complex signal, H-14 and 2 H-15), 3.23 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), CMe singlets at 1.47 and 1.37 (acetonide), 1.30 (3 H), 1.18 (3 H), 1.00 (3 H), 0.83 (3 H), and 0.78 (3 H); mass spectrum (75 eV, direct inlet), m/z (relative intensity) M^+ absent, 365 ($M^+ - 15$, 6), 347 (2), 307 (2), 289 (2), 279 (46), 261 (52), 243 (71), 203 (15), 135 (81), 121 (42), 95 (53), 81 (59), 69 (62), 55 (76), 43 (100). Anal. Calcd for $C_{23}H_{40}O_4$: C, 72.59; H, 10.60. Found: C, 72.62; N, 10.57.

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Registry No. 1, 42895-91-0; 2, 82398-41-2; 3a, 82351-54-0; 3b, 82351-55-1; 3c, 82351-56-2; 3d, 82351-57-3; 3e, 82351-58-4; 3f, 82351-59-5; 3g, 82351-60-8; 3h, 82351-61-9; 4a, 82398-42-3; 4b, 82398-43-4; 4c, 82398-44-5; 4d, 82398-45-6; 5, 76549-11-6; 6, 52591-03-4.

Epoxidation of Olefins by a Polymeric Reagent Electrochemically Generated and Recycled in Situ

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Recently we have developed a novel method of oxidation of alcohols by a polymeric reagent of electrochemically generated and recycled in situ (Scheme I).[1] Cross-linked poly(4-vinylpyridine) hydrobromide is an excellent precursor of the polymeric reagent. This method does not consume any chemical oxidant and does not produce any contaminating reduced product. Since oxidation of olefins is also an essential reaction in synthetic organic chemistry, we have directed our attention to the oxidation of olefins[2,3] using this methodology. During the investigation, we were somewhat surprised to find that the use of polymeric quaternary ammonium bromide as a precursor of the polymeric reagent resulted in a facile epoxidation of olefins,

(1) Yoshida, J.; Nakai, R.; Kawabata, N. *J. Org. Chem.* **1980**, *45*, 5269.

(2) Epoxidation of olefins by polymeric reagent (polymeric peroxy acid) has been reported: (a) Harrison, C. R.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1974**, 1009. (b) Harrison, C. R.; Hodge, P. *J. Chem. Soc., Perkin Trans. 1* **1976**, 605. (c) Frēchet, J. M. J.; Haque, K. E. *Macromolecules* **1975**, *8*, 130.

(3) An elegant indirect electrochemical epoxidation of olefins with bromide ion as mediator has been reported: (a) Torii, S.; Uneyama, K.; Ono, M.; Tazawa, H.; Matsunami, S. *Tetrahedron Lett.* **1979**, 4661. (b) Torii, S.; Uneyama, K.; Matsunami, S. *J. Org. Chem.* **1980**, *45*, 16. (c) Torii, S.; Uneyama, K.; Tanaka, H.; Yamanaka, T.; Yasuda, T.; Ono, M.; Kohmoto, Y. *Ibid.* **1981**, *46*, 3312. Indirect electrochemical epoxidation of propylene with chloride ion as mediator has also been developed: (d) Rifi, M. R.; Covitz, F. H. "Introduction to Organic Electrochemistry"; Marcel Dekker: New York, 1974; Chapter 5.

0022-3263/82/1947-3575$01.25/0