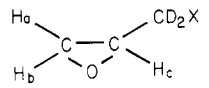

part, 2 H, CH_2), 3.11–3.66 (ABC type m, C part with FCCH coupling, 1 H, $CHCD_2F$). **9b**: ^1H NMR ($CDCl_3$) δ 2.65 (dd, 1 H, H_b, J_1 = 5.0 Hz, J_2 = 2.6 Hz), 2.84 (dd, 1 H, H_a, J_1 = 5.0 Hz, J_2 = 4.0 Hz), 3.25 (dd, 1 H, $CHCD_2Cl$, J_1 = 4.0 Hz, J_2 = 2.6 Hz). **9c** (X = Br) ^1H NMR ($CDCl_3$) δ 2.69 (dd, 1 H, H_b, J_1 = 5.0 Hz, J_2 = 2.1 Hz), 2.97 (dd, 1 H, H_a, J_1 = 5.0 Hz, J_2 = 4.0 Hz), 3.30 (dd, 1 H, $CHCD_2Br$, J_1 = 4.0 Hz, J_2 = 2.1 Hz). **9d** (X = I) ^1H NMR ($CDCl_3$) δ 2.63 (dd, 1 H, H_b, J_1 = 5.0 Hz, J_2 = 1.9 Hz, 3.00 (dd, 1 H, H_a, J_1 = 4.0 Hz, J_2 = 5.0 Hz), 3.37 (dd, 1 H, $CHCD_2I$, J_1 = 4.0 Hz, J_2 = 1.9 Hz).

(*S*)-Glycerol 1,2-Acetonide ((*S*)-2). This compound was synthesized by the reported procedures[6,8,19] from D-mannitol: $[\alpha]^{25}_D$ +11.7° (6.42, MeOH).

(*R*)-3-(Mesyloxy)-1,2-propanediol Acetonide (14) and (*R*)-3-Halogeno-1,2-propanediol Acetonide (15a–d). (*S*)-2 was transformed into **14**, **15a,c,d**, and **15b** similarly to the procedure used for **6**-Ms, **10a,c,d**, and **10b**, respectively. **14**: 88% yield; bp 127 °C (0.22 mm); $[\alpha]^{27}_D$ −3.43° (6.42, Bz); ^1H NMR ($CDCl_3$) δ 1.34 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 3.03 (s, 3 H, CH_3SO_3), 3.63–4.66 (overlapped 2 ABC type m, 5 H, CH_2CHCH_2). **15a**: 40% yield by KF, 80% by Bu_4NF; bp 124 °C; $[\alpha]^{16}_D$ +12.7° (2.44, Bz); ^1H NMR ($CDCl_3$) δ 1.37 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 3.65–4.65 (ABC type m with FCCH coupling at methine, 3 H, CH_2CH), 4.49 (q, 2 H, CH_2F, J_{FCH} = 46.8 Hz, J_{HCCH} = 4.8 Hz). **15b**: 80% yield; bp 63 °C (37 mm); $[\alpha]^{25}_D$ +35.9° (5.03, Bz); ^1H NMR ($CDCl_3$) δ 1.36 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_2), 3.35–3.62 (ABC type BC part q, 2 H, CH_2Cl), 3.66–4.45 (ABC type m with complicated pattern at methine, 3 H, $CHCH_2CH_2Cl$). **15c**: 70% yield; bp 63 °C (15 mm); $[\alpha]^{25}_D$ +36.4° (5.80, Bz); ^1H NMR ($CDCl_3$) δ 1.36 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 3.30–3.47 (ABC type BC part q, 2 H, CH_2Br), 3.68–4.57 (ABC type m with complicated pattern at methine CH_2CHCH_2Br). **15d**: 75% yield; bp 50 °C (7 mm); $[\alpha]^{26}_D$ +34.5 (5.94, Bz); ^1H NMR ($CDCl_3$) δ 1.37 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 3.15–3.33 (ABB′ type BB′ q, 2 H, CH_2I), 3.66–4.56 (ABC type m with complicated pattern at methine, 3 H, CH_2CHCH_2I).

(*R*)-3-Halogeno-1,2-propanediol (16a–d) and (*R*)-3-Halogeno-1,2-epoxypropane (18a–d). Compounds **15a–d** were converted to **18a–d** through **16a–d** and **17a–d** similarly to the conversion through **11a–d** and **12a–d**. **16a**: 60% yield; 73 °C (2.8 mm); $[\alpha]^{11}_D$ −17.4° (3.05, EtOH); ^1H NMR (CD_3OD) δ 3.00–3.90 (ABC type m, 3 H, CH_2CH), 4.35 (q, 2 H, CH_2F, J_{JCH} = 48.0 Hz, J_{HCCH} = 5.6 Hz). **16b**: 86% yield; bp 95 °C (7 mm); $[\alpha]^{26}_D$ +3.85° (5.56, $CHCl_3$); ^1H NMR (CD_3OD) δ 3.50–4.17 (overlapped 2 ABC type m, 5 H, CH_2CHCH_2). **16c**: 80% yield; bp 102 °C (7 mm); $[\alpha]^{25}_D$ −3.94° (5.07, $CHCl_3$); ^1H NMR (CD_3OD) δ 3.42, 3.52 (ABC type ($J/_{\Delta\nu} \simeq 0.1$) 2 broad s, 2 H, $BrCH_2$), 3.66, 3.72, 3.76, 3.78 (ABC type ($J/_{\Delta\nu} \simeq 0.2$) q, 2 H, OCH_2), 3.65–4.35 (m, 1 H, CH). **16d**: 80% yield; mp 46–48 °C; $[\alpha]^{23}_D$ −4.2° (5.10, EtOH); ^1H NMR (CD_3OD) δ 3.25 (d, 2 H, CH_2I, J = 4.5 Hz), 3.67 (br s, 3 H, $CHCH_2$).

Diethyl Bis(methoxymethyl)malonate (20).[21] To small pieces of Na wire (11.5 g, 0.50 mol) in Et_2O (1 L) was added diethyl malonate (**19**; 40 g, 0.25 mol) dropwise with vigorous stirring, and the mixture was allowed to react until all the Na was consumed (about 5 h). To this reaction mixture was added chloromethyl methyl ether (40.25 g, 0.50 mol) [**caution**: chloromethyl methyl ether is a cancer suspect agent; handle in a hood; all the apparatus should be washed with aqueous alkaline to decompose the remaining agent] dropwise with stirring with ice cooling. The reaction mixture was then refluxed for 10 h and set aside overnight. The formed salt was filtered off and washed with ether (200 mL). After the removal of the solvent, fractional distillation under reduced pressure gave 30 g of the product with a boiling range of 81–100 °C (3 mm). Redistillation gave pure **20** (25.1 g, 40%), bp 85–86 °C (3.5 mm).

4,4-Bis(hydroxymethyl-d_2)-2,6-dioxaheptane (21). **20** (24.8 g, 0.10 mol) in Et_2O (50 mL) was reduced similarly to the procedure used for **5** with LAD (4.2 g, 0.10 mol) in Et_2O (300 mL). The crude **21** was proved to be sufficiently pure by gas chromatography and NMR analyses and was used for the following synthesis without further purification: 15.2 g (90%) yield; ^1H NMR ($CDCl_3$) δ 3.26 (br s, 2 H, OH), 3.37 (s, 6 H, CH_3), 3.45 (s, 4 H, CH_2). Corresponding nondeuterated compound absorbs at δ 3.24 (br s, 2 H, OH), 3.37 (s, 6 H, CH_3), 3.45 (s, 4 H, CH_2), 3.70 (s, 4 H, CH_2OH).

4,4-Bis(chloromethyl-d_2)-2,6-dioxaheptane (22). To an ice-cooled solution of **21** (15.2 g, 0.09 mol) in Py (15.9 g, 0.20 mol) was added dropwise $SOCl_2$ (23.8 g, 0.20 mol). The reaction mixture was gradually heated to 100 °C in 4 h, maintained for 2 h at 100 °C, diluted with CH_2Cl_2 (100 mL) after cooling to room temperature, and washed with 1 H HCl (100 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic solution was dried (Na_2SO_4), concentrated, and distilled under reduced pressure to give **22** (16.1 g) as a colorless liquid: 89% yield; bp 78.5 °C (10 mm); ^1H NMR ($CDCl_3$) δ 3.37 (s, 6 H, CH_3), 3.42 (s, 4 H, CH_2). Nondeuterated compound absorbs at δ 3.37 (s, 6 H, CH_3), 3.42 (s, 4 H, CH_2), 3.60 (s, 4 H, CH_2Cl). Anal. Calcd for $C_7H_{10}D_4Cl_2O_2$: C, 40.99; H, 4.91, D, 3.92; Cl, 34.63. Found: C, 40.91; H + D, 8.93; Cl, 34.57.

2,2-Bis(chloromethyl-d_2)-1,3-propanediol (23). **22** (16.1 g, 0.080 mol) was heated with Me_3SiI (36.0 g, 0.18 mol) at 100 °C for 5 days in dry chlorobenzene (50 mL) in a reaction tube sealed under vacuum. The contents were poured into 2 N methanolic HCl (200 mL), and the mixture was refluxed for 2 h. The volatile components were removed at reduced pressure, and the residue was purified by sublimation, after treatment with sodium thiosulfate, if necessary, in order to remove liberated I_2 (94%): mp 79.0–80.0 °C; ^1H NMR (CD_3OD) δ 3.61 (s, 4 H, CH_2OH). Anal. Calcd for $C_5H_6D_4Cl_2O_2$: C, 33.92; H, 3.42; D, 4.55; Cl, 40.05. Found: C, 34.10; H + D, 8.10; Cl, 39.96. Nondeuterated **17**: ^1H NMR (CD_3OD) δ 3.63 (s, 4 H, CH_2OH), 3.67 (s, 4 H, CH_2Cl); mp 76.0–76.2 °C.

2,2-Bis(chloromethyl-d_2)-3-(tosyloxy)propanol (24). To a solution of **23** (14.2 g, 0.080 mol) in Py (60 mL) was added portionwise TsCl (15.1 g, 0.080 mol) with efficient stirring during 30 min at 20 °C. After being stirred for 30 min, the reaction mixture was maintained for 20 h at room temperature, diluted with CH_2Cl_2 (100 mL), and washed with 2 N HCl until the aqueous washings became acidic. The H_2O layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extract was dried (Na_2SO_4), concentrated, and finally evacuated at 0.2 mm for 18 h at 25 °C. The resulting material was used without further purification. **23** was similarly converted to the mesylate and *p*-bromobenzenesulfonate by treating with MsCl or BroCl, respectively, in Py. **23** was also treated with an equimolar amount of TFAA. The mixture was used in the subsequent reaction after evaporating off the volatile material at ambient temperature (0.2 mm).

3,3-Bis(chloromethyl-d_2)oxetane (25). The crude tosylate above was dissolved in THF (100 mL), and NaH (3.2 g, 60% in oil) was added at 0 °C in small portions. After the addition, the reaction system was refluxed for 1 h, and the salt that formed was filtered off after cooling. The filtrate was concentrated and fractionally distilled to yield 4.69 g of **25**: 85.2% yield; bp 81.5–81.7 °C (10 mm); ^1H NMR ($CDCl_3$) δ 4.47 (s, 4 H, OCH_2). Anal. Calcd for $C_5H_4D_4Cl_2O$: C, 37.76; H, 2.54; D, 5.07; Cl, 44.58. Found: C, 37.68; H + D, 7.74; Cl, 44.33.

Cyclization of *N*-(2-Biphenylyl)hydroxylamine Derivatives to N-Substituted Carbazoles[1]

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Received November 19, 1981

The cyclization of *N*-(2-biphenylyl)hydroxylamine (**1a**) to carbazole (**2a**) has been the subject of many reports.[3-7]

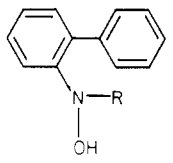
(1) Taken in part from the Ph.D. dissertation of G.T.B., University of Connecticut, 1978.

(2) Beacon Research Laboratories, Texaco, Inc., Beacon, NY.

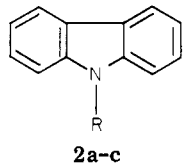
0022-3263/82/1947-3585$01.25/0

We have now studied the behavior of the *N*-benzoyl- and *N*-tosyl-*N*-(2-biphenylyl)hydroxylamines (**1b** and **1c**) to examine whether these hydroxylamines could cyclize to an *N*-substituted carbazole with retention of the N substituent, thereby eliminating a nitrene mechanism for this special case. This was demonstrated by the successful cyclizations of **1b** and **1c** to *N*-benzoylcarbazole (**2b**) and *N*-tosylcarbazole (**2c**) as described below.

Benzoate **1b** was synthesized from *N*-(2-biphenylyl)-hydroxylamine (**1a**) and benzoyl chloride. The hydroxylamine **1a** was prepared by sodium borohydride reduction of 2-nitrosobiphenyl (**5**)[4] which was prepared by MCPBA oxidation of 2-aminobiphenyl.[8] Attempted preparation of **1a** by zinc amalgam reduction of 2-nitrobiphenyl[5] was unsuccessful. The *N*-(4-toluenesulfonyl) derivative **1c** was prepared from 2-nitrosobiphenyl and 4-toluenesulfinic acid.[9]



1a-c



2a-c

a, R = H; b, R = $C_6H_5C(O)$; c, R = 4-$CH_3C_6H_4SO_2$

When **1b** was treated with P_4O_{10} in refluxing benzene, a 70% yield of *N*-benzoylcarbazole (**2b**) was produced. The tosylhydroxylamine **1c** cyclized to *N*-tosylcarbazole (**2c**) in 55% yield under similar conditions. Hot polyphosphoric acid (PPA) was also effective: **1c** in hot PPA gave **2c** in 46% yield. Hot PPA was not useful for the cyclization of **1b** since the product, *N*-benzoylcarbazole (**2b**), was unstable in hot PPA. A separate experiment showed that **2b** decomposed to 3,6-dibenzoylcarbazole (**6**), carbazole (**2a**), and a monobenzoylcarbazole under these reaction conditions.[10] Since the hydroxylamine **1b** gave, in hot PPA, a similar mixture of products, it is likely that *N*-benzoylcarbazole (**2b**) was produced under these conditions and subsequently decomposed.

The successful cyclizations, with retention of the N substituent, show that the reactions do not involve a nitrene. The initial step of the reaction is most likely the formation of a polyphosphate ester from the hydroxylamine **1a**. The reaction can then proceed either by loss of polyphosphate ion and formation of a nitrenium ion or by displacement of the polyphosphate ion by the phenyl ring.

In addition to mechanistic considerations, these reactions illustrate a useful approach to carbazole synthesis. **1b** and **1c** give the N-substituted carbazoles in 46–70g yield whereas the underivatized hydroxylamine **1a** leads to carbazole itself in 0–20% yield.[3-5] This improvement may find utility in the synthesis of unsymmtrically substituted carbazoles or natural products.

Experimental Section

Microanalyses were performed by Baron Consulting Co., Orange, CT. Melting points were measured on a Mel-Temp apparatus or a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ^1H NMR spectra were recorded with a Varian EM360A or a Bruker WH-90 high-resolution FT spectrometer. IR spectra were of substances in KBr disks except where noted and were taken with a Perkin-Elmer 137 instrument.

2-Nitrosobiphenyl (5) was prepared from 2-aminobiphenyl;[12] mp 109.5–110 °C (lit.[12] mp 111–112 °C).

4-Toluenesulfinic acid was prepared by an adaptation of the method of Kulka:[13] 80% yield; mp 78–82 °C (lit.[14] mp 84 °C).

***N*-(2-Biphenylyl)-*N*-hydroxy-4-toluenesulfonamide (1c).** A solution of 1.52 g (5.46 mmol) of 4-toluenesulfinic acid in 10 mL of $CHCl_3$ at 10 °C was added to a solution of 1.78 g (5.46 mmol) of 2-nitrosobiphenyl (**5**) in 60 mL of $CHCl_3$ at 10 °C, and the mixture was stirred for 3 h and then slowly added to 600 mL of hexane; 1.58 g (48%) of **1c** precipitated as a pink solid, mp 140–143 °C. Reprecipitation from benzene with hexane gave the analytical sample: mp 144.2–145.5 °C; IR 3370 (OH), 1350, 1150 cm^{-1} (SO_2); NMR (Me_2SO-d_6) δ 2.12 (s, 3 H, CH_3), 4.22 (s, 1 H, OH), 7.20–7.65 (complex, 13 H, Ar H). Anal. Calcd for $C_{19}H_{17}NO_3S$: C, 67.24; H, 5.05; N, 4.13. Found: C, 67.02; H, 4.97; N, 3.94.

***N*-(2-Biphenylyl)-*N*-hydroxybenzamide (1b).** A solution of *N*-(2-biphenylyl)hydroxylamine (**1a**) was prepared by the method of Patrick and Schield[4] modified in the following manner: a mixture of 2.5 g (13.5 mmol) of 2-nitrosobiphenyl (**5**) and 0.2 g (5.0 mmol) of $NaBH_4$ in 150 mL of anhydrous ether and 10 mL of absolute ethanol at 0 °C under N_2 was stirred for 6 h, after which time the green color of the nitroso compound had changed to pale yellow. The solution of the unstable *N*-(2-biphenylyl)-hydroxylamine (**1a**) was next treated with 1.7 g (12.0 mmol) of benzoyl chloride and 1.0 mL (12.0 mmol) of pyridine and stirred for 4 h. The solution was then extracted with 50 mL of 3 N NaOH which was added dropwise to 75 mL of ice-cold 3 N HCl; 3.2 g (88%) of **1b** precipitated as a white solid, mp 139–142 °C. Recrystallization from ethanol–water gave an analytical sample: mp 143.5–144.5 °C; IR 3100 (OH), 1640 cm^{-1} (CO); NMR (Me_2SO-d_6) δ 6.70–7.80 (complex). Anal. Calcd for $C_{19}H_{15}NO_2S$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.50; H, 5.18; N, 4.92.

Cyclization of *N*-(2-Biphenylyl)-*N*-hydroxybenzamide (1b) to *N*-Benzoylcarbazole (2b). (1) In P_4O_{10}. A mixture of 0.48 g (1.6 mmol) of *N*-(2-biphenylyl)-*N*-hydroxybenzamide (**1b**) and 2 g of P_4O_{10} in 100 mL of benzene was refluxed for 20 min and filtered hot; the black residue was combined with water and extracted with benzene. The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated to dryness to give 0.30 g (70%) of ***N*-benzoylcarbazole (2b)** as a light yellow solid, mp 93–95 °C (lit.[15] mp 98 °C).

(2) In PPA. A suspension of 0.48 g (1.6 mmol) of *N*-(2-biphenylyl)-*N*-hydroxybenzamide (**1b**) in 15 g of PPA was stirred at 95 °C. After 30 min the mixture was poured into 100 mL of ice-cold water to give 0.37 g of a green solid, which TLC ($CHCl_3$) analysis showed to be a mixture of at least five compounds. The TLC of the mixture was identical with that of the reaction products of N-benzoylcarbazole (**2b**) in PPA at 95 °C for 30 min.

Cyclization of *N*-(2-Biphenylyl)-*N*-hydroxy-4-toluenesulfonamide (1c) to *N*-(4-Toluenesulfonyl)carbazole (2c). (1) In P_4O_{10}. A mixture of 1.0 g (3.0 mmol) of *N*-(2-biphenylyl)-*N*-hydroxy-4-toluenesulfonamide (**1c**) and 3 g P_4O_{10} in 100 mL of benzene was refluxed for 10 min and filtered hot, the black residue was combined with water and extracted with benzene, the combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated to dryness to give 0.68 g of a tan solid (mp 110–125 °C) which when recrystallized from ethanol–water gave 0.52 g (55%) of ***N*-(4-toluenesulfonyl)carbazole (2c)** as a white solid, mp 129–129.5 °C (lit.[16] mp 133 °C).

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(2) In PPA. A suspension of 0.32 g (1.0 mmol) of *N*-(2-biphenylyl)-*N*-hydroxy-4-toluenesulfonamide (**1c**) in 40 g of PPA was stirred at 105 °C for 30 min and poured into 200 mL of cold water to give 0.18 g of a green solid. The solid was extracted with 25 mL of acetone which was evaporated under reduced pressure to give 0.14 g (46%) of *N*-(4-toluenesulfonyl)carbazole (**2c**) as a white solid, mp 128.5–130 °C (lit.[16] mp 133 °C).

Reaction of *N*-Benzoylcarbazole (2b) in PPA. A suspension of 1.0 g (3.7 mmol) of *N*-benzoylcarbazole (**2b**) in 20 g of PPA was stirred at 95 °C for 30 min and poured into 150 mL cold water to give 0.85 g of a green solid. Analysis by preparative TLC ($CHCl_3$) identified the major products, in increasing R_f value, as follows: 3,6-dibenzoylcarbazole (**6**), 31%, mp 252–254 °C (lit.[17] mp 258 °C); 28% of a monosubstituted carbazole, IR 1660 cm^{-1} (CO); carbazole (**2a**), 29%, mp 233–235 °C (lit.[18] mp 238 °C); small amounts (5–7%) of minor products.

Acknowledgment. We thank the University of Connecticut Foundation for financial assistance (to G.T.B.).

Registry No. 1a, 16169-17-8; **1b**, 82390-31-6; **1c**, 82390-32-7; **2b**, 19264-68-7; **2c**, 3165-71-7; **5**, 21711-71-7; **6**, 78901-33-4.

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Reductions of Diterpene Epoxides. A Partial Synthesis of 8β-Hydroxyisopimar-15-ene

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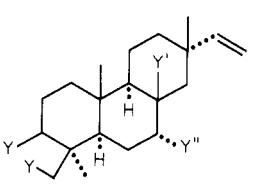
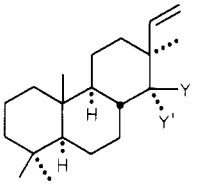
Received December 29, 1981

In connection with a study of rearrangements of diterpene epoxides, several pimaradienic monoepoxides had to be prepared. On treatment with *m*-chloroperbenzoic acid,[1] the sandaracopimaradienic substance **1a**[2] was converted into its 8β,14β-epoxide (**1b**),[4,5] and pimaradiene (**2a**)[6,7] was converted into its 8α,14α-epoxide (**2b**).[8] With these epoxides and the 7,8-epoxide pairs **1e** and **1g**, as well as **1f** and **1h**,[10] derived from the isopimaradienic substances virescenol B diacetate (**1c**)[9] and isopimaradiene (**1d**),[7] respectively, it became of interest to investigate their behavior on reduction with a metal and hydrogen source. Whereas previous reductions of such epoxides with lithium in ethylamine[11,12] had led to products in which both the epoxide unit and the vinyl group had been reduced,[13] the following study reveals that lithium–ammonia reduction furnishes alcohols in which the vinyl group remains intact.

Reduction of the 8β,14β-epoxide diacetate **1b** with lithium in liquid ammonia yielded triol **3a**, indicating that

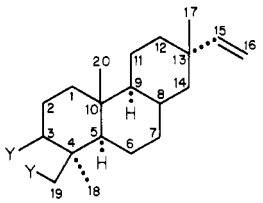


3a, Y = Y′ = OH; Y″ = H
b, Y = OAc; Y′ = OH; Y″ = H
c, Y = Y″ = H; Y′ = OH
d, Y = Y″ = OH; Y′ = H
e, Y = Y′ = H; Y″ = OH

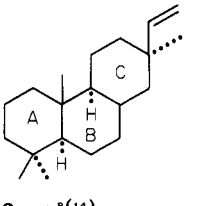


4a, Y = H; Y′ = OH
b, Y = H; Y′ = OAc
c, Y + Y′ = O
d, Y = OH; Y′ = H

it had taken place expectedly at the secondary carbon–oxygen site and had followed the usual steric course of trans diaxial ring opening of an epoxide. Reduction of the 8α,14α-epoxide **2b**, on the other hand, produced two alcohols, **2c** and **4a**. The latter alcohol functioned as a stereochemical point of reference of itself as well as its precursor in view of its ready conversion into ketone **4c** on Jones oxidation, the lack of change of this substance on base-catalyzed equilibration, and its transformation into the starting alcohol (**4a**) and its isomer (**4d**) on reduction with lithium aluminum hydride. The formation of two products in the reduction of the α-epoxide is unusual. Whereas each product is an axial alcohol (with respect to ring C), each substance represents epoxide ring opening at a different carbon–oxygen bond center. This anomaly may be attributable to the greater steric interfernce with chemical activity at C(8), the expected reaction site, than at C(14) and to a lowering of the usual, conformational



1a, Y = OAc; $\Delta^{8(14)}$
b, Y = OAc; 8β,14β-epoxy
c, Y = OAc; $\Delta^{7(8)}$
d, Y = H; $\Delta^{7(8)}$
e, Y = OAc; 7α,8α-epoxy
f, Y = H; 7α,8α-epoxy
g, Y = OAc; 7β,8β-epoxy
h, Y = H; 7β,8β-epoxy



2a, $\Delta^{8(14)}$
b, 8α,14α-epoxy
c, 8α-hydroxy

(1) M. Curini, P. Ceccherelli, R. Pellicciari, and E. Sisani, *Gazz. Chim. Ital.*, **110**, 621 (1980).

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(13) Vinyl group reductions: ref 4a; P. Ceccherelli, M. Curini, R. Pellicciari, and R. Coccia, unpublished observations.

0022-3263/82/1947-3587$01.25/0