Chemo-, Regio-, and Stereoselective Hydroalumination of 7,8-Epoxy-2,3,5,6-tetramethylenebicyclo[2.2.2]octane

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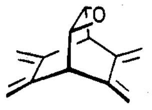
Received December 18, 1981

The oxirane ring of 7,8-epoxy-2,3,5,6-tetramethylenebicyclo[2.2.2]octane (**1**) was not reduced by $NaAlH_2(OCH_2CH_2OCH_3)_2$. Hydroalumination of the syn diene occurred instead with the formation of a η^1-allylaluminate **5**, which yielded selectively 1,2- or 1,4-hydrogenated products, depending upon the protic quenching conditions. **5** added to acetaldehyde, giving the alcohol **10**, whose structure was determined by single-crystal X-ray diffraction studies on its *p*-bromobenzoate **11**. The *re* (or *si*) face of the electrophile attacked the endo *si* (or *re*) face of the allylaluminate at the disubstituted rather than the less crowded and nonsubstituted carbon.

7,8-Epoxy-2,3,5,6-tetramethylenebicyclo[2.2.2]octane (**1**)



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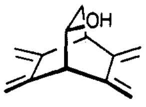

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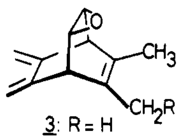
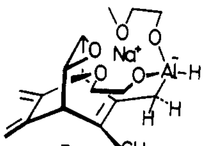


3: R = H
4: R = D

has been prepared recently in our laboratory.[2] Attempts to reduce the epoxide **1** to the corresponding alcohol **2** with $LiAlH_4$ or $LiEt_3BH$ in tetrahydrofuran (THF) yielded complex mixtures of rearranged[3] and polymerized products. Sodium bis(methoxyethoxy)aluminium hydride[4] (Vitride) is a highly valuable reducing agent for carbonyl,[5] carboxyl,[6] and epoxide functions.[7] Hydrogenations of double bonds conjugated with aromatic[8] and carbonyl groups may occur under forcing conditions.[5a,6b] Dienes were found to resist the hydrogenation, although the polymerization of butadiene catalyzed by $NaAlH_2(OCH_2CH_2OCH_3)_2$ has been reported.[9] We report the room-temperature hydroalumination of an exocyclic diene by Vitride. Assistance of the homoconjugated oxirane ring[10,11] (which is not reduced!) gives a relatively stable 3,3-disubstituted allylaluminate, **5**. Quenching with water results in protonation at the primary center, whereas attack by electrophilic carbonyls occurs at the tertiary allylic center giving a quaternary substituted carbon.



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Results

When epoxy tetraene **1** was added to a 70% solution of Vitride (1.1 mol equiv) in toluene at 20 °C, a yellow solution was formed with complete disappearance of **1** after 5–10 min (^1H NMR). Quenching with an excess of ice/water furnished *syn*-2,3-epoxy-5,6-dimethyl-7,8-dimethylenebicyclo[2.2.2]oct-5-ene (**3**) in good yield (80–85%). No trace of alcohol **2** could be detected. The structure of **3** was deduced from its spectral characteristics and by comparison with those of other related dienes.[2,14] $Eu(dpm)_3$-induced shifts on δ_H as well as $Yb(dpm)_3$-induced shifts on δ_C allowed unambigous determination of the configuration of the epoxide ring in **3** (see Experimental Section). Quenching with D_2O led to the incorporation of one deuterium atom (>97% d_1 by MS). ^1H and ^{13}C NMR spectra were consistent with structure **4**, where the deuterium atom substitutes exclusively one of the methyl groups. **3** furnished the expected Diels–Alder adduct with tetracyanoethylene (TCNE).

The high regioselectivity of the Vitride/H_2O hydrogenation of **1** → **3**, coupled with the relatively facile hydroalumination of the conjugated diene as well as the absence of reduction of the epoxide function, suggested a direct, quantitative coordination of the Na^+ cation of Vitride by

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(1) (a) Institute of Organic Chemistry. (b) Institute of Crystallography of the University of Lausanne.

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(3) See the hydride reductions of *exo*-2,3-epoxy-5,6-dimethylenenorbornane: Chollet, A.; Vogel, P. *Helv. Chim. Acta* **1978**, *61*, 732.

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(11) If not assisted by a function that can bind to the aluminium,[12] hydroaluminations of olefins and acetylenes are slow reactions.[13] Nevertheless, they can be catalyzed by transition-metal derivatives, e.g.: Sato, F.; Sato, S.; Kodama, M.; Sato, M. *J. Organomet. Chem.* **1977**, *142*, 71. Ashby, E. C.; Noding, S. A., *Tetrahedron Lett.* **1977**, 4579. Ashby, E. C.; Lin, J. J.; Goel, A. B. *J. Org. Chem.* **1978**, *43*, 258. Ashby, E. C.; Noding, S. A. *Ibid.* **1979**, *44*, 4364; **1980**, *45*, 1035. Boireau, G.; Abenhaim, D.; Henry-Basch, E. *Tetrahedron* **1980**, *36*, 3061. See also: Schwartz, J.; Carr, D. B.; Hansen, R. T.; Dayrit, F. M. *J. Org. Chem.* **1980**, *45*, 3053.

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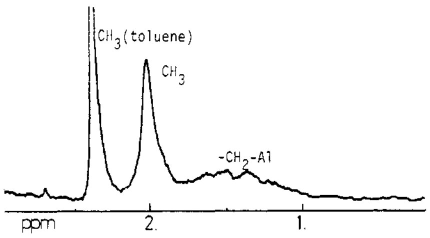
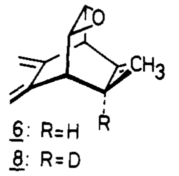


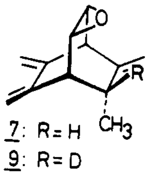
Figure 1. ^1H NMR of **5** (80 MHz, toluene, benzene, 30 °C).

the oxygen atom of the epoxide function of **1**. The ^1H NMR spectrum (see Figure 1) and the ^{13}C NMR spectrum of the solution obtained by mixing **1** with Vitride in toluene and benzene were consistent with the formation of the η^1-allylaluminate **5**.[15] Typically broad signals due to the quadrupolar moment of ^{27}Al ($I = {}^5/_2$)[15,16] were observed at δ_H 1.8–1.0 (see Figure 1) and $\delta_C \simeq 32$ ($Al-CH_2$). Both the ease and the specificity of the hydroalumination **1** → **5** are noteworthy.[11]

When 2 mol equiv of acetic acid was added to a solution of **5** (25 °C, 3 h) followed by quenching with water, a mixture of **3** (25–30%) and the two isomeric 1,2-hydrogenated products **6** (40–45%) and **7** (20–25%) was isolated (VPC). With a large excess of acetic acid and subsequent workup with water, **3** was the major product isolated (78%). Control experiments showed that **3**, **6**, and **7** were stable under the conditions used above. When 1 equiv of HCl in acetic anhydride was added followed by quenching with water, **3** was not formed; only the dienes **6**/**7** (3:2, 66%) were isolated. With DCl/acetic anhydride the monodeuterated trienes **8** and **9** were obtained.



6: R=H
8: R=D

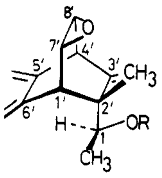


7: R=H
9: R=D

The structures of **6**(**8**) and **7**(**9**) (easily separated by preparative VPC) were deduced from their microanalyses and their spectral data. Distinction between **6** and **7** was based on Eu(dpm)$_3$-induced shifts on δ_H.

Attempts to alkylate **5** with a 1–20-fold excess of CH_3I or $(CH_3)_2SO_4$ failed, even in the presence of $Pd(Ph_3P)_4$, $NiCl_2$, or $CoCl_3$. Quenching of the reaction mixtures with H_2O gave polymers and the triene **3** (20–40 °C, 1–48 h). When a concentrated solution of **5** was allowed to react with acetaldehyde, a relatively slow addition giving the alcohol **10** (37%) occurred competitively with the polymerization of **5**. The same product was isolated (25–35%) when 1–2 equiv of acetyl chloride as electrophile is used (CH_3COCl is reduced by **5**, generating CH_3CHO, which seems to add faster than CH_3COCl). Under all conditions investigated besides **10** only polymers were found. This suggests a high regio- and stereoselective addition of the allylaluminate intermediate to the carbonyl electrophile.

In contrast with the regioselective trapping of a proton from water by the nonsubstituted allylaluminate carbon, the condensation with acetaldehyde occurred at the more crowded, disubstituted center, the endo face being preferred by the electrophile. ^1H and ^{13}C NMR confirmed

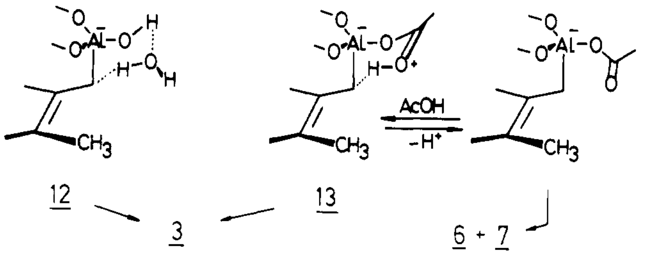


R = H : 10
R = p-Br-C$_6$H$_4$CO : 11

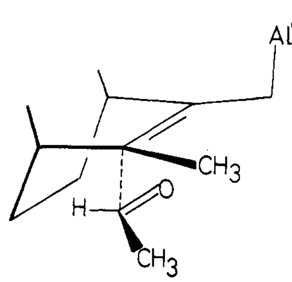
the regioselectivity of the reaction **1** → **10**. The configurations ($1'S^*,2'R^*,1S^*$) of the centers of the newly formed carbon–carbon bond were determined by single-crystal X-ray diffraction studies of the *p*-bromobenzoate derivative **11** (see supplementary material).

Discussion

No simple explanation can be given for the selective 1,4- and 1,2-hydrogenations reported here. It is possible that the acidic treatment of **5** destroys its conformational rigidity (formation of H_2 and precipitation of sodium salts was detected) and yields various intermediates (including those of metal allylic migrations) leading competitively to 1,2- and 1,4-hydrogenation products upon protonation with acetic acid. The relatively high 1,4-selectivity observed when **5** is quenched with water or a larger excess of acetic acid could also be explained by invoking intramolecular proton transfer in allylaluminate intermediates such as **12** and **13**, leading to the "abnormal" quenching product **3**.



The failure of **5** to react with CH_3I, $(CH_3)_2SO_4$, CH_3COCl, and $(CH_3CO)_2O$ is probably due to steric hindrance of the approach of the bulky electrophiles onto the endo face of the allylaluminate, the polymerization of **5** being a faster process. The smaller CH_3CHO reacts to give **10** in reasonable yield. The exo face of **5** is blocked by the epoxide-coordinated sodium aluminate; only the endo face is available for the condensation reaction, the transition state of which tends to minimize steric repulsions and imposes the observed configuration at the alcoholic center of **10**.



The reactions **5** + H^+ → **6** + **7** and **5** + CH_3CHO → **10** follow the path expected (S_Ei' and S_E2' mechanisms) for allylmetal compounds.[17] As long as the rigidity of the internally solvated sodium aluminate **5** is maintained,

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[15] Equilibrium with η^3-allylaluminate intermediates cannot be excluded; see, e.g.: Lehmkuhl, H.; Ziegler, K.; Gellert, H.-G. In "Methoden der Organischen Chemie (Houben-Weyl)"; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1970; XIII/4, p 144 and references therein.

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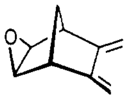
[17] Organoallylboranes: Mehrotra, I.; Devaprabhakara, D. *J. Organomet. Chem.* **1973**, *51*, 93. Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 1977 and references therein. Allylic boron "ate" complexes: Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969. Allylalanes: Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1 and references therein.

metal allylic migration[15,18] does not occur, and highly regioselective and stereoselective electrophilic quenching is observed.

This work demonstrates the role that a neighboring epoxide function can play (without formation of an Al alcoholate) in facilitating and orienting the direct hydroalumination of a diene by Vitride. The distance between the oxygen and the olefinic functions is critical. Under the conditions of the reaction **1** → **5**, Vitride did not add to epoxydiene **14**[19] or to tetraenes **15**[20] and **16**.[21] Under forcing conditions (high concentrations, 80 °C) only polymerization was observed.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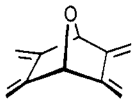
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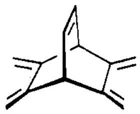
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Experimental Section

Melting points (mp) were not corrected and were taken with a Tottoli apparatus; UV spectra were taken with a Pye Unicam SP 1800 instrument (λ_{max} (nm) (ϵ), sh = shoulder); IR spectra are given in ν (cm^{-1}; s = strong, m = medium, w = weak); ^{1}H NMR spectra were taken on a Bruker WP 80 CW instrument (δ, apparent multiplicity, apparent coupling constants $J_{H,H}$ (Hz), number of protons or tentative attributions) with s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad, and δ_{Me_4Si} 0.0; ^{13}C NMR spectra were taken with a Bruker WP 60 spectrometer (15.08 MHz, spectrum width 3750 Hz, 4096 points, FT mode; δ, multiplicity, $^1J_{C,H}$). Mass spectra (MS) were taken on a Hewlett-Packard HP 5980 A spectrometer (*m/z* (amu) (% base peak)) in electron ionization mode. Elementary analysis were performed by the microanalytical laboratory of the University of Geneva (Dr. K. Eder). Analytical gas chromatography was performed on a Hewlett-Packard 5710 A, preparative gas chromatography on a Carlo Erba Fractovap 2400 V Chromatograph.

***syn*-7,8-Epoxy-2,3-dimethyl-5,6-dimethylenebicyclo[2.2.2]oct-2-ene (3).** Epoxy tetraene **1**[2] (0.5 g, 2.9 mmol) was added portionwise to a stirred solution of Vitride (sodium bis(2-methoxyethoxy)aluminium hydride–70% toluene solution) (0.93 g, 3.2 mmol) in 3–4 mL of anhydrous toluene. After stirring at 20 °C for 1 h, the mixture was cooled to 0 °C and 0.15 mL of water was added dropwise. The salts were filtered off and washed with toluene. The organic solution was dried ($MgSO_4$) and evaporated to dryness under vacuum. The crude triene **3** was recrystallized from pentane (−15 °C) with a yield of 0.43 g (85%) of colorless crystals: mp 50–51 °C; UV (EtOH 96%) 242 (9050), UV (dioxane) 224 (9000); IR (CH_2Cl_2) 3090 (w), 3020 (m), 2960 (s), 2920 (s), 2860 (s), 1790 (m), 1620 (s), 1440 (s), 1390 (s), 1230 (m), 1185 (s), 1150 (w), 1125 (m), 1050 (w), 1015 (w), 990 (m), 950 (s), 940 (s), 880 (s); ^{1}H NMR ($CDCl_3$ [relative slope of the induced chemical shift by added Eu(dpm)$_3$]) δ 5.3 (s, 2 H [0.14]), 4.9 (s, 2 H [0.15]), 3.22 (m, H–C (1, 4) [0.39]), 3.2 (m, H–C (7, 8) [1.0]), 1.7 (s, H_3C–C (2, 3) [0.30]); ^{13}C NMR ($CDCl_3$, [LIS with Yb(dpm)$_3$]) δ 142.9 (s, C(5, 6) [0.22]), 126.9 (s, C(2, 3) [0.31]), 104.9 (t, $^1J_{CH}$ = 158 Hz, $H_2C{=}C$(5, 6) [0.12]), 50.5 (d, 143, C(1, 4) [0.37]), 48.8 (d, 189, C(7, 8) [1.0]), 15.9 (q, 127, CH_3–C(2, 3) [0.14]); MS (70 eV) 175 (7), 174 (M$^+$, 39), 161 (7), 159 (28), 146 (25), 145 (100), 131 (66), 130 (66), 129 (76), 128 (66), 127 (25), 117 (28), 116 (45), 115 (10), 105 (48), 103 (21), 91 (100). Anal. Calcd for $C_{12}H_{14}O$ (174.24): C, 82.72; H, 8.10. Found: C, 82.86; H, 8.10.

***syn*-2-Deuteriomethyl-7,8-epoxy-3-methyl-5,6-dimethylenebicyclo[2.2.2]oct-2-ene (4)** was made by using the procedure as above, except that D_2O was used to hydrolyze the allylaluminate **5**. The ^{1}H NMR ($CDCl_3$) spectrum is the same as for **3**, except at δ 1.7 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.9 (q, 127, CH_3–C(3)), 15.6 (tt, $^1J_{CH}$ = 127, $^1J_{CD}$ = 19 Hz, CH_2D–C(2)); MS (70 eV) 97% monodeuteration. Anal. Calcd. for $C_{12}H_{13}DO$ (175.25): C, 82.24; H, 8.62. Found: C, 82.17; H, 8.48.

Allylaluminate 5. When the above reaction was done in benzene-d_6 instead of toluene, the following spectra were recorded before the hydrolysis: ^{1}H NMR (C_6D_6 + toluene) δ 5.5, 5.45, 5.15, 5.0 (br s), 4.3–1.3 (m, H–C(1, 4, 7, 8), 2.03 (s, CH_3), 1.8–1.0 (br m, Al–CH_2); ^{13}C NMR (C_6D_6 + toluene) δ 144.6, 137.3, 121.8 (s), 103.7, 102.5 (t, 160), 76.4 (q, 140), 60.7, 58.0 (t, 138), 52.4, 50.1 (d, 145), 50.7 (br d, 190), 32 (very br), 16.4 (q, 125).

***anti*-7,8-Epoxy-6-*exo*-methyl- (6) and *anti*-7,8-Epoxy-6-*endo*-methyl-2,3,5-trimethylenebicyclo[2.2.2]octane (7).** Epoxy tetraene **1**[2] (0.5 g, 2.9 mmol) was added portionwise to a stirred solution of Vitride (0.93 g, 3.2 mmol) in 4–5 mL of anhydrous toluene. After stirring at 20 °C for 1 h, the mixture was cooled to 0 °C, and a solution of gaseous HCl (100 mg) in Ac_2O (2 mL) was added. In a few seconds, the mixture became very viscous, and water (0.2 mL) was added at once. The precipitate was filtered off and washed with toluene. The organic solution was dried ($MgSO_4$), concentrated under vacuum, and purified by column chromatography (20 g SiO_2, CH_2Cl_2) to yield 0.33 g (66%) of a 3:2 mixture of **6**/**7** that was separated by preparative VPC (OV-225, 10%, Chromosorb WAW 60/80 mesh; 3 m Pyrex column, 8 mm i.d., 150 °C, 240 mL/min H_2). **6**: colorless oil (24%); UV (EtOH 96%) 241 (7500), 247 (7400), 255 (sh, 4900); UV (dioxane) 241 (7500), 248 (7350), 257 (sh, 4800); IR (CH_2Cl_2) 3080 (w), 3020 (w), 2960 (s), 2920 (s), 2880 (s), 1660 (m), 1640 (m), 1460 (m), 1400 (w), 1370 (w), 1210 (w), 1190 (m), 1120 (m), 1090 (m), 1070 (m), 1030 (m), 1015 (m), 990 (w), 950 (w), 920 (m), 890 (s), 840 (s); ^{1}H NMR ($CDCl_3$) δ 5.36 (s), 5.31 (s), 4.9 (s), 4.87 (s), 4.86 (d, *J* = 3 Hz), 4.66 (d, *J* = 3 Hz, $H_2C{=}C$(5)), 3.3 (m, H–C(7, 8)), 3.3 (m, H–C(4)), 2.63 (m, H–C(1)), 2.19 (m, H–C(6-endo) less deshielded than in **7**), 1.22 (d, *J* = 7 Hz, H_3C–C(6-exo) more deshielded than in **7** because of the anisotropy of the epoxide ring); MS (70 eV) 175 (2), 174 (M$^+$, 28), 159 (15), 145 (22), 131 (46), 91 (100). Anal. Calcd for $C_{12}H_{14}O$ (174.24): C, 82.72; H, 8.10. Found: C, 82.95; H, 8.15.

7 was separated as a colorless oil (12%): UV (EtOH 96%) 235 (7600), 241 (sh, 7250), 256 (sh, 5650), UV (dioxane) 237 (7600), 243 (sh, 7250), 257 (sh, 5000); IR (CH_2Cl_2) 3020 (w), 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1470 (m), 1380 (m), 1185 (w), 1120 (w), 1080 (m), 1030 (w), 1020 (m), 990 (w), 950 (w), 920 (w), 890 (w), 840 (m); ^{1}H NMR ($CDCl_3$) δ 5.46, 5.30, 4.87, 4.86 (s, $H_2C{=}C$(2, 3)), 4.8, 4.65 (d, *J* = 2.5 Hz, $H_2C{=}C$(5)), 3.3 (m, H–C(4)), 3.28 (m, H–C(7, 8)), 2.63 (m, H–C(1)), 2.62 (m, H–C(6-exo)), 0.86 (d, *J* = 7 Hz, H_3C–C(6-endo)) (Eu(dpm)$_3$ added to a mixture of **6** + **7** led to induced chemical shifts, confirming the above attributions and structures) MS (70 eV) 174 (M$^+$, 2), 159 (8), 145 (14), 131 (28), 115 (64), 90 (100). Anal. Calcd for $C_{12}H_{14}O$ (174.24): C, 82.72; H, 8.10. Found: C, 82.88; H, 8.18.

Monodeuterated Trienes 8 and 9. The same procedure as for the preparation of **6** + **7** was used, with AcCl/D_2O instead of Ac_2O/HCl; workup was with D_2O. **8**: ^{1}H NMR ($CDCl_3$) same as that of **6**, except for the absence of the signal at 2.16 ppm and the br s at 1.22 ppm. **9**: ^{1}H NMR ($CDCl_3$) same as that of **7**, except for the absence of the signal at 2.62 ppm and the br s at 0.86 ppm. Anal. Calcd for $C_{12}H_{13}DO$ (175.25): C, 82.24; H, 8.26. Found: C, 82.36; H, 8.57 (mixture of **8** + **9**).

Tetracyanoethylene Adduct with 3. Triene **3** (0.2 g, 1.1 mmol) and tetracyanoethylene (0.15 g, 1.1 mmol) were stirred in benzene (8 mL) at 20 °C for 5 h. After removal of the solvent under vacuum, the residue was recrystallized from CH_2Cl_2/pentane, with a yield of 0.34 g (100%) of colorless crystals: mp 173–174 °C; UV (EtOH) final absorption ϵ^{210} 4000; IR (KBr) 3020 (w), 2980 (m), 2960 (s), 2930 (s), 2920 (m), 2860 (m), 2250 (w), 1440 (s), 1400 (s), 1380 (w), 1330 (w), 1285 (w), 1265 (w), 1250 (w), 1230 (s), 1190 (s), 1150 (m), 1110 (w), 1050 (w), 1010 (w), 970 (w), 950 (m), 920 (s), 890 (w), 845 (s), 830 (m); ^{1}H NMR (acetone-d_6) δ 3.58–3.38 (m, 8 H), 1.72 (s, 6 H); MS (70 eV) 302 (M$^+$, 14), 273 (78), 208 (62), 207 (51), 193 (35), 182 (30), 159 (62), 140 (41), 129 (41), 128 (41), 115 (100), 91 (76). Anal. Calcd for $C_{18}H_{14}ON_4$ (302.34): C, 71.51; H, 4.67. Found: C, 71.61; H, 4.67.

***syn*-1-[7′,8′-Epoxy-3′,5′,6′-trimethylene-2′-*endo*-bicyclo[2.2.2]octyl]ethanol (10).** Tetraene **1**[2] (0.5 g, 2.9 mmol) was added protionwise to a stirred solution of Vitride, 70% in toluene (3 mL). After stirring at 20 °C for 30 min, the mixture was cooled to 0 °C, and acetaldehyde (0.255 g, 5.8 mmol) was added dropwise

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with stirring. After 3 h at 20 °C, water (1 mL) was added. The precipitate was filtered off and washed with toluene. The organic solution was dried ($MgSO_4$) and evaporated to dryness under vacuum. The residue was purified by column chromatography on silica gel (25 g, AcOEt). The yield was 0.235 g (37%) of **10** after recrystallization from hexane/CH_2Cl_2 (3:1) as colorless crystals: mp 85–86 °C (there was less than 5% of the trienes **3**, **6**, and **7** isolated by chromatography); UV (EtOH 95%) 243 (8000), UV (isooctane) 243 (8000); IR ($CHCl_3$) 3580 (w), 3460 (w), 3080 (m), 2980 (s), 2950 (s), 2920 (m), 2880 (w), 1800 (w), 1710 (w), 1640 (m), 1620 (m), 1450 (m), 1390 (s), 1370 (s), 1295 (m), 1260 (s), 1230 (m), 1105 (s), 1095 (s), 1035 (m), 1005 (w), 985 (w), 950 (s), 900 (s), 860 (s), 845 (s); ^1H NMR ($CDCl_3$) δ 5.44, 5.43, 4.99, 4.94, 4.88 and 4.81 (s, $H_2C{=}C(3', 5', 6')$), 3.45 (dd, J = 4.0, 4.5 Hz, H(4′)), 3.33 (m, H(7′, 8′)), 3.22 (q, J = 6.5 Hz, H–C(OH)Me), 2.63 (dd, J = 4.0, 4.5 Hz, H(1′)), 2.02 (br s, OH), 1.20 (s, CH_3), 1.07 (d, J = 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$ [relative slope of the induced chemical shift by added $Yb(dpm)_3$]) δ 153.1 (s, C(3′) [36.2]), 142.6 (s, C(6′) [21.9]), 141.8 (s, C(5′) [19.3]), 108.8 (t, $^1J_{CH}$ = 158 Hz, $CH_2{=}C(3')$ [28.7]), 108.33 (t, $^1J_{CH}$ = 158 Hz, $CH_2{=}C(5')$ [10.3]), 108.28 (t, $^1J_{CH}$ = 158 Hz, $CH_2{=}C(6')$ [12.9]), 69.8 (d, $^1J_{CH}$ = 146 Hz, C(OH) [100]), 53.1 (d, $^1J_{CH}$ = 188 Hz, C(7′) [36.7]), 52.7 (d, $^1J_{CH}$ = 188 Hz, C(8′) [23.8]), 52.5 (d, $^1J_{CH}$ = 139 Hz, C(1′) [39.1]), 49.0 (d, $^1J_{CH}$ = 139 Hz, C(4′) [30.7]), 45.6 (s, C(2′) [48.9]), 16.1 (q, $^1J_{CH}$ = 128 Hz, $CH_3C(2')$ [35.9]), 15.6 (q, $^1J_{CH}$ = 126 Hz, CH_3 [55.3]); MS (70 eV) 174 (38 [$M^+ - 44$]), 159 (46) 145 (100), 131 (67), 130 (42), 129 (46), 128 (42), 117 (25), 116 (23), 115 (56), 105 (41), 91 (75). Anal. Calcd for $C_{14}H_{18}O_2$ (218.3): C, 77.03; H, 8.31. Found: C, 76.79; H, 8.47%.

***p*-Bromobenzoate of Alcohol 10 (11).** A mixture of **10** (0.15 g, 0.68 mmol), *p*-bromobenzoyl chloride (0.17 g, 0.77 mmol), and anhydrous pyridine (2.5 mL) was heated until complete dissolution. After stirring at 20 °C for 5 h, the reaction mixture was poured onto ice (25 g) and $NaHCO_3$ (1 g). The mixture was extracted with CH_2Cl_2 (25 mL, 3×) and dried ($MgSO_4$). The solvent was evaporated under vacuum and the residue recrystallized from CH_2Cl_2/hexane (1:2) with a yield of 0.215 g (78%): mp 187–189 °C; UV (EtOH 95%) 245 (7800); IR (KBr) 2990, 1710, 1590, 1480, 1450, 1395, 1370, 1340, 1300, 1270, 1250, 1170, 1115; ^1H NMR (CD_3COCD_3) δ 7.95, 7.71 (4 H, aromatic), 5.62, 5.55, 5.08, 5.02, 4.70, 4.69 (s, $H_2C{=}C(3', 5', 6')$), 4.78 (q, J = 6.5 Hz, H–C(OAr)), 3.46 (d, J = 4–5 Hz, H(4′)), 3.35 (t, J = 4–5 Hz, H(7′)), 3.31 (t, J = 4–5 Hz, H(8′)), 2.85 (d, J = 4–5 Hz, H(1′)), 1.45 (s, CH_3), 1.25 (d, J = 6.5 Hz, CH_3); MS (70 eV) 402 (1), 400 (1), 358 (13), 356 (13), 343 (10), 341 (10), 330 (23), 329 (23), 328 (23), 327 (23), 315 (10), 313 (15), 312 (15), 310 (12), 229 (15), 227 (17), 221 (18), 200 (82), 157 (100), 155 (85). Anal. Calcd for $C_{21}H_{21}O_3Br$ (401.3): C, 62.85; H, 5.27. Found: C, 62.78; H, 5.32%.

Acknowledgment. We thank Hoffmann-La Roche & Co (Basel), the Swiss National Science Foundation, and the Fonds Herbette (Lausanne) for generous financial support. We are grateful to F. Berchier and C. Debonneville for the technical assistance and to Dr. R. Hunston for correcting the manuscript.

Registry No. 1, 75073-80-2; 3, 82149-54-0; 3 tetracyanoethylene adduct, 82134-65-4; 4, 82134-61-0; 5, 82149-56-2; 6, 82189-06-8; 7, 82134-62-1; 8, 82134-63-2; 9, 82188-44-1; 10, 82149-55-1; 11, 82134-64-3; acetaldehyde, 75-07-0; acetyl chloride, 75-36-5; vitride, 22722-98-1; tetracyanoethylene, 670-54-2.

Supplementary Material Available: Crystal structure of $C_{21}H_{21}O_3Br$ (**11**) with a summary of the crystal data and refinement information (Table I), interatomic distances (Table 2), bond angles (Table 3), torsion angles and information on least-squares planes (Table 4), shortest intermolecular contacts (Table 5), atomic parameters and anisotropic temperature factors (Table 6), and an ORTEP drawing (Figure 2) (7 pages). Ordering information is given on any current masthead page.

Synthesis of Sulfides and Mercaptans from Thioketals

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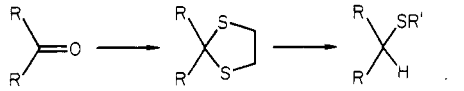
Received September 9, 1981

The treatment of ketone thioketals with excess *n*-butyllithium in ether at 25 °C leads to fragmentation to intermediate thioketones, which in most cases are further reduced to mercaptans via β-hydrogen transfer from *n*-butyllithium. Mercaptide anions formed in the reaction can be quenched with electrophiles to produce sulfides. Mercaptans, methyl sulfides, and allyl sulfides have been prepared from adamantanone, menthone, and cyclooctanone by using this approach. Camphor thioketal, however, cleaves to give thiocamphor which because of steric hindrance enolizes with *n*-butyllithium rather than reduces. Thiocamphor is isolated after quenching in 62% yield.

A recent publication from this laboratory[1] described a new method for the synthesis of secondary mercaptans and sulfides from 1,3-dithiolanes (eq 1). A fragmentation mechanism involving a thiocarbonyl intermediate has been proposed to account for the products. The following describes the synthesis of various sulfides and mercaptans and provides specific evidence for the proposed thiocarbonyl intermediate. Our mechanism for the cleavage/reduction process we proposed is shown in eq 2.



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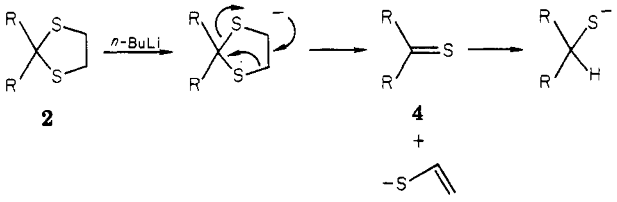

(2)

2 4 5

While our original paper put forward no direct evidence for the intermediate thioketone **4** and thioacetaldehyde

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