(1*S*,2*S*,3*S*,4*R*,7*S*,8*R*,9*R*,10*S*)-3,4:9,10-Bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-5,11-diene (5) from 4a. To a solution of **4a** (0.119 g, 0.257 mmol) in toluene (2.5 mL) was added Bu_3SnH (0.600 g, 2.06 mmol) followed by AIBN (0.042 g, 0.256 mmol), and the solution was refluxed under an argon atmosphere for 26 h. The reaction mixture was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel eluting with 15% EtOAc/hexanes to provide pure **5** as white crystals (0.071 g, 0.233 mmol, 91% yield): mp 150–151 °C; ^1H NMR δ 5.96 (2 H, m), 5.58 (1 H, ddd, J = 10.2, 3.6, 1.4), 5.48 (1 H, ddd, J = 10.2, 3.0, 1.5), 4.30 (1 H, dd, J = 7.3, 3.1), 4.25 (1 H, dd, J = 7.3, 3.0), 4.18 (1 H, ddd, J = 4.9, 3.6, 1.4), 4.13 (1 H, br d, J = 4.9), 2.85 (2 H, m), 2.34 (1 H, m), 2.20 (1 H, br d, J = 9.0), 1.33 (3 H, s), 1.31 (3 H, s), 1.29 (3 H, s), 1.26 (3 H, s); ^{13}C NMR δ 132.4 (CH), 129.3 (CH), 128.8 (CH), 126.6 (CH), 108.6 (C), 107.6 (C), 78.6 (CH), 78.4 (CH), 77.6 (CH), 70.9 (CH), 41.0 (CH), 40.7 (CH), 34.3 (CH), 33.1 (CH), 28.3 (CH_3), 26.8 (CH_3), 25.4 (CH_3), 25.0 (CH_3). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.89; H, 8.02.

(1*R*,2*S*,5*S*,6*S*,7*S*,8*S*,9*S*,10*R*)-4-Chloro-5,6:9,10-bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-3,11-diene (7) from 4b. To a solution of **4b** (72.3 mg, 0.194 mmol) and AIBN (cat. quantity) in toluene (3 mL) was added Bu_3SnH (225 mg, 0.775 mmol), and the reaction mixture was refluxed under an argon atmosphere for 3 h. The mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel eluting with 20% EtOAc/hexanes to afford pure **7** as white crystals (65.5 mg, 0.194 mmol, 100% yield): mp 148–150 °C; $[\alpha]_D$ = +114° (c 0.6, $CHCl_3$); IR ν 3040, 2981, 1664, 1371, 1208, 1062, 876 cm^{-1}; ^1H NMR δ 6.03 (2 H, m), 5.71 (1 H, d, J = 4.3), 4.27 (1 H, m), 4.14 (1 H, d, J = 4.6), 2.86 (2 H, m), 2.53 (1 H, m), 2.23 (1 H, d, J = 9.0), 1.37 (3 H, s), 1.34 (3 H, s), 1.29 (3 H, s), 1.25 (3 H, s); ^{13}C NMR δ 132.5 (CH), 131.3 (CH), 128.8 (C), 127.9 (CH), 108.9 (C), 108.5 (C), 79.5 (CH), 78.6 (CH), 77.9 (CH), 72.7 (CH), 41.2 (CH), 40.4 (CH), 35.7 (CH), 34.3 (CH), 27.8 (CH_3), 26.6 (CH_3), 25.4 (CH_3), 25.0 (CH_3). Anal. Calcd for $C_{18}H_{23}ClO_4$: C, 63.81; H, 6.84. Found: C, 63.84; H, 6.89.

(1*S*,2*S*,3*S*,4*R*,7*S*,8*R*,9*R*,10*S*)-3,4:9,10-Bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-5,11-diene (5) from 4b. A solution of **4b** (80 mg, 0.214 mmol) in absolute ethanol (2 ml) was heated to reflux, and finely divided sodium metal (130 mg, 5.65 mmol) was added in ca. 10-mg portions over a period of 1.25 h while monitoring the progress of the reaction by TLC. When the reaction was complete, the mixture was cooled to rt and quenched with H_2O (0.5 mL). The ethanol was removed in vacuo, and the aqueous mixture was extracted with CH_2Cl_2 (4 × 8 mL). The combined organic layers were washed with H_2O (1 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to provide 66 mg of crude brown oil. Flash chromatography through a small pipet eluting with a solvent gradient of 0 → 25% EtOAc/hexanes provided pure **5** as a white solid (31 mg, 0.101 mmol, 48% yield). The spectral data were identical to that shown for **5** above.

(1*S*,2*S*,3*S*,4*R*,7*S*,8*R*,9*R*,10*S*)-9,10-(Isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-5,11-diene-3,4-diol (6). A solution of **5** (28 mg, 0.092 mmol) in glacial acetic acid (1 mL) and H_2O (0.2 mL) was stirred at rt for 18 h. The solution was saturated with NaCl and extracted with EtOAc (4 × 2 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 × 1 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was recrystallized from a mixture of EtOAc/hexanes to provide the pure diol (**6**) as a white crystalline solid (15 mg, 0.0567 mmol, 63% yield): mp 123–125 °C; $[\alpha]_D$ = −78° synthesized from **4a** (c 0.72, $CHCl_3$), $[\alpha]_D$ = −83° synthesized from **4b** (c 0.93, $CHCl_3$); IR ($CHCl_3$) ν 3580, 3440, 3005, 2960, 2920, 1380, 1205, 1065 cm^{-1}; ^1H NMR δ 6.05 (2 H, m), 5.72 (2 H, m), 4.26 (2 H, m), 4.04 (1 H, br s), 3.54 (1 H, br s), 3.05 (1 H, m), 2.84 (1 H, m), 2.35 (1 H, br d, J = 8.8), 2.01 (3 H, m), 1.31 (3 H, s), 1.26 (3 H, s); ^{13}C NMR δ 134.1 (CH), 130.8 (CH), 130.7 (CH), 127.3 (CH), 108.6 (C), 78.7 (CH), 78.6 (CH), 71.7 (CH), 66.6 (CH), 40.4 (CH), 38.5 (CH), 38.0 (CH), 35.1 (CH), 25.4 (CH_3), 25.0 (CH_3).

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Note Added in Proof. A paper describing the dimer **4a** appeared while this manuscript was being processed: Ley, S. V.; Redgrave, A. J.; Taylor, S. C.; Abmed, S.; Ribbons, D. W. *Synlett* **1991**, 741.

Registry No. 2a, 130792-45-9; **3a**, 130669-75-9; **3b**, 127666-06-2; **4a**, 137769-14-3; **4b**, 137792-30-4; **5**, 137769-15-4; **6**, 137792-31-5; **7**, 137769-16-5.

Supplementary Material Available: X-ray crystallographic data for compound **4a** and ^1H and ^{13}C NMR spectra for compounds **4a**, **4b**, **5**, **6**, and **7** (17 pages). Ordering information is given on any current masthead page.

Reductive Cleavage of *tert*-Butyldimethylsilyl Ethers by Diisobutylaluminum Hydride

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The utility of the *tert*-butyldimethylsilyl (Tbs) group for the protection of hydroxyl groups[1,2] has been enhanced by the availability of diverse methods for its introduction[1,3] and removal (especially fluoride ion,[1] aqueous acid,[1,2] and aqueous HF–CH_3CN[4]). We report herein a new method for the cleavage of Tbs ethers under reductive and near-neutral conditions using diisobutylaluminum hydride (DIBAL-H). In the original research on protection of the hydroxyl function by Tbs it was found that the conversion of a γ-lactone to the corresponding lactol could be carried out selectively with DIBAL-H (1.2 equiv) in toluene at −78 °C in the presence of the Tbs ether function which remained unchanged,[1] and many instances of such reactions are now known. Nonetheless, Tbs ethers react with DIBAL-H in methylene chloride solution at 23 °C in 1–2 h to yield desilylated alcohols (1) according to the following equation.

$$\underset{\mathbf{1}}{\mathrm{ROSiMe_2}t\text{-Bu}} + i\text{-Bu}_2\mathrm{AlH} \rightarrow \underset{\mathbf{3}}{\mathrm{ROAl}i\text{-Bu}_2} + \underset{\mathbf{2}}{\mathrm{HSiMe_2}t\text{-Bu}}$$

The formation of *tert*-butyldimethylsilane (**2**) was established by 500-MHz ^1H NMR analysis of the cleavage reaction in carbon tetrachloride or deuteriochloroform solution which revealed the simultaneous development of peaks due to **2**[5] and **3**. The cleavage reaction was clean and complete with a series of test cases which gave pure alcohols simply by extractive isolation in the indicated isolated yields (in parentheses): 1-hexanol (93%), benzyl alcohol (91%), phenol (84%), *trans*-4-*tert*-butylcyclohexanol (87%). The mildness of the method is indicated by the deprotection of the chiral 1,2-propadienyl ether **4**

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to form the very acid-sensitive chiral carbinol 5[6] in 95% isolated yield.

4 5

The reactivity of Tbs ethers toward DIBAL-H at room temperature should be kept in mind when reductions are carried out with this reagent on O-silylated substrates.[7]

Experimental Section

The following experimental procedure is representative.

Desilylation of *trans*-4-*tert*-Butylcyclohexyl *tert*-Butyldimethylsilyl Ether by Diisobutylaluminum Hydride. A solution of 17 mg (0.063 mmol) of the Tbs ether of *trans*-4-*tert*-butylcyclohexanol in methylene chloride (3 mL) was treated at 0 °C with a 1.0 M solution of diisobutylaluminum hydride in toluene (0.18 mL, 0.18 mmol) under nitrogen with stirring. After 2 h at 23 °C, 0.5 g of crushed ice was added, and the mixture was washed with 1 mL of 0.5 M hydrochloric acid. The organic layer was dried (K_2CO_3), filtered through a small plug of silica gel, and concentrated under reduced pressure to give 9 mg of *trans*-4-*tert*-butylcyclohexanol (87%) which was identified and shown to be pure by 500-MHz ^1H NMR and TLC analyses and comparison with an authentic sample.[5,7]

Registry No. 1 (R = hexyl), 80033-60-9; 1 (R = benzyl), 21862-63-5; 1 (R = Ph), 18052-27-2; 1 (R = 4-*tert*-butylcyclohexyl), 71009-16-0; 2, 29681-57-0; 4, 137655-10-8; 5, 124563-11-7; hexanol, 111-27-3; phenol, 108-95-2; benzyl alcohol, 100-51-6; diisobutylaluminum hydride, 1191-15-7.

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Reactions of α,β-Epoxy Carbonyl Compounds with Methanethiolate: Regioselectivity and Rate

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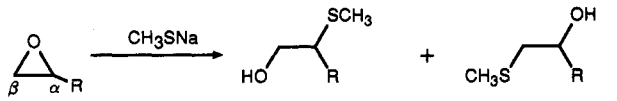
Reactions between epoxides and biogenic thiols are biologically important in several respects.[1] Potentially toxic xenobiotic epoxides[2] and endogenous epoxides[3] form adducts with glutathione. Epoxides alkylate active-site cysteine residues of certain enzymes.[4] Potent enzyme inhibitors, known to alkylate cysteine residues, include structurally diverse α,β-epoxy carbonyl and related compounds.[5]

Under physiological conditions, the thiolate of cysteine (pK_a 8.2) is actually the significant nucleophile.[1] As a nonpeptidic model, we were therefore interested in the reactivity of α,β-epoxy carbonyl compounds (i.e. **1a–c,e**) toward simple thiolate anions to afford β-hydroxy-α-thio carbonyl compounds (**2**) and α-hydroxy-β-thio carbonyl compounds (**3**). A primary question was whether the carbonyl would increase the reactivity of these epoxides. Although reactions of epoxides[6] including α,β-epoxy ketones,[7] α,β-epoxy esters,[2c,8] α,β-epoxy carboxylic acids,[9] and α,β-epoxy amides[10] with thiols and (occasionally) thiolates have been reported, reaction rates have not been measured and a comprehensive understanding of regioselectivity and relative reactivity does not emerge from the literature due to differences in the reagents, solvents, and temperatures employed. Retro-aldol reactions of the β-hydroxy-α-thio carbonyl regioisomers (i.e. **2**) also complicate comparisons. Catalysis by Lewis acids and mineral acids provides dif-

Table I. Pseudo-First-Order Rates and Regioselectivities in Reactions of CH_3S^- with Epoxides (1) at pD 9.84[a]

epoxide	R	k (min^{-1})	2:3	k_α (min^{-1})	k_β (min^{-1})
1a	$COCH_3$	1.45[b]	>95:5	1.45[b]	
1b	CO_2CH_3	0.44	57:43	0.25	0.19
1c	$CONH_2$	0.166	22:78	0.037	0.13
1d	CH_2CH_3	0.086	<5:95		0.086
1e	CO_2^-	0.010	36:64	0.0036	0.0064

[a] Reactions of 1 (0.097 M) with CH_3S^- (0.0145 M) were conducted in D_2O at 19.4 °C. [b] Extrapolated from rate at pD 9.21.



1 2 3

a; R = $COCH_3$
b; R = CO_2CH_3
c; R = $CONH_2$
d; R = CH_2CH_3
e; R = CO_2^-

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