different in diethyl ether solvent as well as in THF.

Experimental Section

Materials. Lithium aluminum hydride (Ventron) was used without further purification. Solutions of $LiAlH_4$ were analyzed for total hydride concentration by the Felkin iodine titration method.[15] A quantity of sample was injected into 0.4 N iodine in benzene. Water, ethanol, and acetic acid were added, and the solution was back-titrated with standard 0.1 N sodium thiosulfate.

3,3,5-Trimethylcyclohexanone (1) was prepared by the catalytic hydrogenation of isophorone as described elsewhere.[4] *tert*-Butyl alcohol (Baker) was dried by passage through a 40-cm column of Linde 4-Å molecular sieves, followed by distillation. 2-Methyl-2,4-pentanediol (3, Eastman) was dried over 4-Å molecular sieves. 2,3-Dimethyl-2,3-butanediol (4, Aldrich) and 2,2-dimethyl-1,3-propanediol (5, Aldrich) were dissolved in anhydrous ether, and the solutions were dried over 4-Å molecular sieves. The sieves were filtered off over a pad of glass wool in a nitrogen-filled glovebag, and solvents were removed on a rotary evaporator. The rotary evaporator was vented with dry nitrogen.

Solutions. Solutions of lithium aluminum hydride were prepared in an all-glass, grease-free Schlenk apparatus. The system was dried under vacuum and purged with argon several times prior to use. All manipulations were carried out under positive argon pressure. Residual oxygen was scavenged from Linde high-purity argon by passage through a 30 cm × 5 cm diameter column of BASF Corp. BTS catalyst. The argon was then passed through a similar column of Linde 4-Å molecular sieves to remove H_2O.

Reagent grade diethyl ether (Mallinckrodt) was distilled from $LiAlH_4$ through a 20-cm Vigreux column onto $LiAlH_4$. The solution was stirred for 30 min, and then after being allowed to settle it was filtered twice through sintered glass and was delivered to silicone rubber-serum-capped bottles. All $LiAlH_4$ solutions were clear and colorless.

Solutions of 3,3,5-trimethylcyclohexanone were prepared by injecting a weighed amount of ketone into vacuum-dried bottles of diethyl ether distilled from $LiAlH_4$. The volume of solvent was calculated from its weight.

Alkoxyaluminohydride solutions were prepared in one of two fashions. In the case of liquid alcohols, a weighed amount of alcohol was injected slowly into a known volume of standardized $LiAlH_4$ solution. Solutions with [*t*-BuOH]:[$LiAlH_4$] ratios greater than ca. 2.5 formed white $LiAlH(O\text{-}t\text{-}Bu)_3$ precipitates. All solutions of 2-methyl-2,4-pentanediol (3) were clear and colorless. Solid alcohols 4 and 5 were dissolved in a minimum amount of diethyl ether distilled from sodium benzophenone ketyl. A weighed amount of a solution of known concentration was injected into a known volume of standardized $LiAlH_4$. Both of these solutions formed precipitates at [diol]:[$LiAlH_4$] ratios greater than ca. 1.25.

Reduction Products. Equal volumes of ketone and hydride solutions were mixed at 25.0 °C by using an ultraviolet stopped-flow spectrophotometer described previously.[16] Hydride concentrations were 0.027–0.055 M, and the concentration of ketone 1 was ca. 0.005 M. After being allowed to stand approximately 1 min, the effluent from the instrument was quenched in 0.1 M aqueous phosphate buffer (75 mL; pH = 7) at 0 °C. The organic layer was removed. The aqueous layer was acidified with 1 N H_2SO_4 to dissolve the salts, followed by extraction with ether (2 × 25 mL). The ethereal layers were combined, washed with 10% aqueous $NaHCO_3$ (1 × 30 mL), and dried over $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator or by fractional distillation. The residue was analyzed by gas chromatography on a F&M Model 700 gas chromatograph equipped with a thermal conductivity detector. Peak areas were measured by disk integration.

Products of the reduction of 1 using *tert*-butyl alcohol or 3 were separated on a 12 ft × 0.125 in., 15% Carbowax 20M on 60/80 Chromosorb W (DMCS) column, with an oven temperature of 150 °C and a helium flow rate of 20 mL/min. The following compounds are listed in order of increasing retention times: *tert*-butyl alcohol, **1**, **2t**, **2c**, **3**. Compounds **2t** and **2c** were isolated by preparative gas chromatography, and the structural assignments were confirmed by comparing their melting points with those reported in the literature.[17]

Products of the reduction of 1 using 4 or 5 were separated on a 12 ft × 0.125 in., 15% FFAP on 60/80 Chromosorb W (DMCS) column, with an oven temperature of 110 °C and a helium flow rate of 25 mL/min. Mesitylene was used as an internal standard. The retention time of **2c** was 40 min. The following compounds are listed in order of increasing retention times: mesitylene, **1**, **5**, **2t**, **2c**. Compound 4 was very highly retained and occasionally bled off the column, causing base-line interference.

Analyses of product mixtures containing any one of the diols sometimes showed early peaks of significant size in the gas chromatograms, which were presumed, on the basis of absolute yield calculations, to be diol elimination products.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1**, 873-94-9; **2c**, 933-48-2; **2t**, 767-54-4; **3**, 107-41-5; **4**, 126-30-7; **5**, 76-09-5; diethyl ether, 60-29-7; $LiAlH_4$, 16853-85-3; *t*-BuOH, 75-65-0; $LiAlH(O\text{-}t\text{-}Bu)_3$, 17476-04-9; $LiAlH_3(O\text{-}t\text{-}Bu)$, 24507-64-0; $LiAlH_2(O\text{-}t\text{-}Bu)_2$, 24315-46-6.

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Lithium Aluminum Hydride–Aluminum Hydride Reduction of Sultones

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Received July 7, 1980

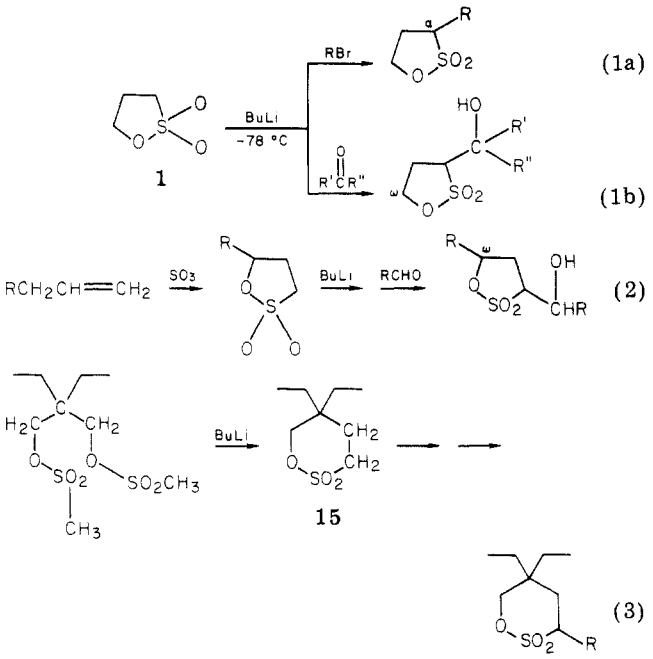
Lithium aluminum hydride–aluminum hydride reduction of secondary and tertiary (C–O) substituted γ-sultones or α-alkyl-β′-hydroxy γ-sultones yields mercapto alcohols and mercapto diols, respectively, in fair to good yield. These products result from S–O cleavage of the sultone ring. Primary sultones and α-dialkyl-β′-hydroxy γ-sultones give predominantly C–O cleavage to form sulfonic acid derivatives. δ-Sultones are much less reactive toward the mixed hydride, and refluxing in dioxane is required for their reduction.

Dithianes,[1] sulfides,[2] sulfoxides[3] and sulfones[4] have found extensive and practical use as activating and masking groups in synthetic organic chemistry.[5] The comparable use of sultones[6] has been severely limited by

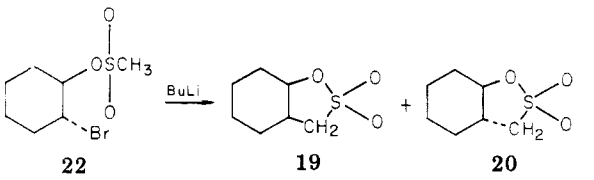
0022-3263/81/1946-0101$01.00/0

the lack of a general procedure for desulfurization of sultone intermediates. In this publication we examine the scope and limitations of the lithium aluminum hydride–aluminum chloride reduction of γ- and δ-sultones, a reaction which in certain instances offers a practical solution to the problem of sultone desulfurization.

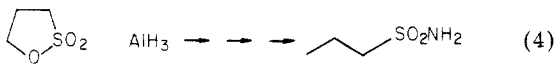
Synthesis of Sultones. The sultones used in this study were prepared by (a) the alkylation[7] of commercially available propane sultone **1** (eq 1), (b) the sulfonation[8] of 1-tetradecene followed by alkylation (eq 2), and (c) the cyclization[9] of the dimesylates of 1,2- and 1,3-diols (eq 3).



The dimesylate of *trans*-1,2-cyclohexanediol (**21**) was largely recovered following treatment with butyllithium.[9] The only product isolated after chromatography was the trans sultone (**20**) in a scant 2% yield. Cyclization of the mesylate of *trans*-2-bromocyclohexanol (**22**)[9] afforded, following chromatography on silica gel, a 39% yield of cis sultone **19** contaminated by 10–20% of the trans sultone **20**. It is likely that the cis sultone **19** partially isomerizes to the trans sultone **20** during the reaction workup or during chromatography.



Reduction of Sultones. Results for the lithium aluminum hydride–aluminum hydride reduction of sultones are displayed in Table I. The data suggest a competition between hydride attack at sulfur[10,11] leading to S–O bond cleavage vs. hydride displacement at the C–O carbon (ω-carbon) resulting in C–O bond cleavage.[12] Attack at sulfur eventually results in further reduction to a mercaptide and some subsequent desulfurization. Displacement at the ω-carbon yields sulfonic acid derivatives which are difficult to isolate from the reaction mixture and generally are lost in the reaction workup. The competition is largely determined by the steric environment of the ω-carbon. This is seen in the case of sultones **1–5** where the ω-carbon is primary and where aluminum hydride leads to complete destruction of the sultone and the failure to recover organic products by employing the usual workup procedure. In the case of propane sultone **1**, a modified and tedious isolation procedure followed by derivatization led to propanesulfonamide (**44**), demonstrating the validity of the assumption of hydride displacement at the ω-carbon and C–O bond cleavage (eq 4).



Reduction of sultones **6**, **7**, **9**, and **20** where the ω-carbon is secondary or tertiary affords products (50–80%) derived from attack at sulfur with concomitant S–O bond rupture.

δ-Sultones are stable to the mixed hydride under conditions which destroy γ-sultones.[13] Forcing conditions, using refluxing dioxane, are required to bring about reduction. Sulfur attack and desulfurization seem to compete on an equal basis with reaction at the ω-carbon in the case of the primary but hindered δ-sultone **16**. Increasing the bulk around sulfur by introducing an α-methyl group seriously impedes attack at sulfur resulting in ω-carbon attack and the formation of nonrecoverable products.

The presence of an alcohol function β to the sulfur atom has a dramatic effect on the course of the hydride reduction. Apparently the hydride reacts initially with the alcohol group, affording an alkoxy hydride which permits hydride to be selectively directed to the more proximate sulfur atom. Thus even with a nonhindered primary ω-carbon the presence of a monoalkylcarbinol at the α pos-

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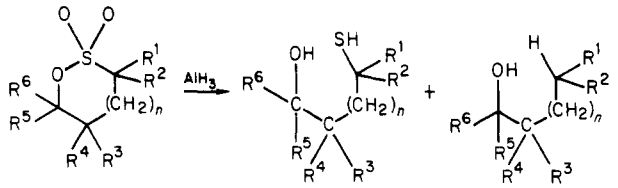
Table I. Sultones and Their Reduction Products



no.	n	R^1	R^2	R^3	R^4	R^5	R^6	mercapto alcohol	alcohol
1	0	H	H	H	H	H	H	0	0
2	0	CH_3	H	H	H	H	H	0	0
3	0	$CH_2CH{=}CH_2$	H	H	H	H	H	0	0
4	0	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	H	H	H	H		
5	0	$CH_2C_6H_5$	H	H	H	H	H	0	0
6	0	H	H	H	H	$C_{11}H_{23}$	H	47,[a] 37[b]	5,[a] 35[b]
7	0	H	H	CH_3	C_6H_5	CH_3	CH_3	58[a]	7[a]
8	0	$CH(OH)C_8H_{17}$	H	H	H	H	H	30,[a] 44[b]	16,[a] 15[b]
9	0	CH(OH)(*i*-Pr)	H	H	H	H	H	45[a]	5[a]
10	0	$CH(OH)C_6H_5$	H	H	H	$C_{11}H_{23}$	H	52[a]	27[a]
11	0	$CH(OH)(CH_3)_2$	H	H	H	H	H	22[a]	0
12	0	$\llcorner C(OH)(CH_2)_5 \lrcorner$	H	H	H	H	H	3[a]	0
13	0	$C(OH(C_6H_5)_2$	H	H	H	H	H	0	17[a,c]
14	1	H	H	H	H	CH_3	H		
15	1	H	H	C_2H_5	C_2H_5	H	H		35,[a] 45[b]
16	1	CH_3	H	C_2H_5	C_2H_5	H	H		5[b]
17	1	$C(OH)(CH_3)_2$	H	C_2H_5	C_2H_5	H	H	37[b]	12[b]
18	1	$\llcorner C(OH)(CH_2)_5 \lrcorner$	H	H	H	CH_3	H	0	0
19	0	H	H	H	$\blacktriangleright CH_2CH_2CH_2CH_2 \blacktriangleleft$		H	68[a]	0
20	0	H	H	H	$\blacktriangleright CH_2CH_2CH_2CH_2 \blacktriangleleft$		H	76[a]	0

[a] Refluxing ether. [b] Refluxing dioxane. [c] Refluxing dioxane plus 17% of 36.

ition leads in compounds 8 and 9 to at least 50% attack at sulfur. Combining the hindrance at the ω-carbon with the presence of an α-alkylcarbinol group in sultone 10 leads to products derived from sulfur attack in up to 80% isolated yield.

When the carbinol carbon at the α position is fully substituted, neighboring-group assistance of attack at sulfur falls off, and ω-carbon attack and C–O cleavage once again take over when the ω-carbon is primary as seen in the reductions of 11–13.

From the foregoing it is apparent that the mixed-hydride reduction of sultones is somewhat limited in scope. The reduction should prove useful in cases where the ω-carbon is substituted or where an alkylcarbinol group is located at the α position. Although complete desulfurization was not observed with the compounds examined in this study, this is not a serious problem since final removal of sulfur from the mercaptan can be achieved by stirring with Raney nickel.

Experimental Section

All boiling and melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord, Model 137-B. All NMR spectra were measured in $CDCl_3$ with Varian Associates A-60 and Perkin-Elmer R-32 spectrometers. Mass spectra were determined by the Purdue University Mass Spectral Service employing a Hitachi RMU-6A spectrometer. Microanalyses were performed by Dr. C. S. Yeh and associates.

General Procedure for Alkylation of Sultones.[9] A solution of 1 equiv of *n*-butyllithium in hexane was added dropwise under nitrogen to a mechanically stirred solution of 1 equiv of a sultone in THF at −78 °C. After stirring for 15–30 min, the alkyl halide, ketone, or aldehyde was added dropwise (neat if a liquid or in THF if a solid) to the vigorously stirred solution. The mixture was stirred at −78 °C for 2 h, allowed to warm to 0 °C and was then treated with 0.2 L of water. The organic phase was washed with water and saturated salt solution and dried ($MgSO_4$), and the solvents were removed by using a rotatory evaporator. The crude sultone was washed through a short 60–200-mesh silica gel column with pentane–ether to remove polymeric material which was generally a byproduct of the reaction. Data on the sultones prepared by this procedure are collected in Table II.

5-Undecyl-1,2-oxathiolane 2,2-Dioxide (6). Liquid SO_3 (8.3 mL) was added to a solution of 40.9 g (0.209 mol) of 1-tetradecene in 2 L of CH_2Cl_2 under nitrogen at −78 °C. The solution was allowed to warm to ambient temperature over a period of 4 h, and the solvent was removed to leave a red-brown solid. Recrystallization from pentane gave 7.9 g (13.8%) of **6** as white granules: mp 59–61 °C (lit.[14] mp 61.3–62.5 °C); NMR 0.88 (t, 3), 1.28 (br s, 20), 2.0–2.8 (m, 2), 3.17–3.45 (m, 2), 4.38–4.87 ppm (m, 1); mass spectrum, *m/e* (relative intensity) 276 (10), 166 (22), 121 (38), 112 (21), 98 (27), 97 (31), 96 (24), 95 (24), 84 (45), 83 (41), 82 (31), 81 (33), 70 (55), 69 (59), 68 (31), 67 (39), 57 (54), 55 (100), 54 (26).

4,5,5-Trimethyl-4-phenyl-1,2-oxathiolane 2,2-Dioxide (7). From 25.5 g (0.159 mol) of 3,3-dimethyl-2-phenyl-1-butene and 6.6 mL of SO_3 there was obtained after recrystallization from CH_2Cl_2 30.7 g (81%) of sultone **7** as white granules: mp 125–126 °C; NMR 1.22 (s, 3), 1.66 (s, 3), 1.77 (s, 3), 3.31–4.39 (AB q, 2), 7.28 ppm (s, 5); mass spectrum, *m/e* (relative intensity) no parent, 119 (43), 118 (100), 117 (58), 103 (35), 91 (28), 78 (24), 77 (22).

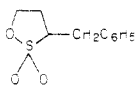
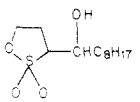
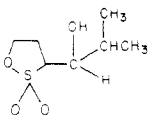
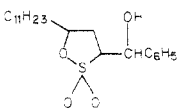
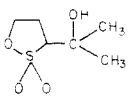
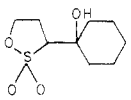
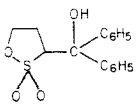
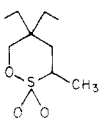
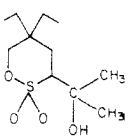
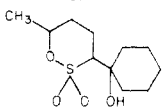
5,5-Diethyl-1,2-oxathiane 2,2-Dioxide (15). To a stirred solution of 109.8 g (0.381 mol) of the dimesylate of 3,3-diethyl-1,3-propandiol (mp 92.5–94.5 °C) in 1.8 L of THF at −78 °C under nitrogen was added dropwise over a period of 45 min 221 mL of 1.9 M *n*-butyllithium. The solution was stirred at −78 °C for 2 h, warmed to room temperature, and allowed to stand for 47 h. After the addition of 0.2 L of water, the organic phase was washed with water and saturated salt solution and dried ($MgSO_4$), and the solvents were removed to give 78.3 g of an oil. Chromatography on silica gel and elution with 50:50 pentane–ether afforded 52.6 g (71.8%) of sultone **15** as a clear oil: bp 98 °C (0.06 mm); n^{20}_D 1.4705; NMR 0.84 (t, 6, J = 7 Hz), 1.41 (q, 4, J = 7 Hz), 2.01 (t, 2), 3.5 (AB q, 2), 4.24 ppm (s, 2); mass spectrum, *m/e* (relative intensity) 192 (2), 162 (12), 110 (16), 98 (26), 97 (100), 96 (43), 83 (25).

Anal. Calcd for $C_8H_{16}O_2S$: C, 49.97; H, 8.39; S, 16.68. Found: C, 49.86; H, 8.38; S, 16.49.

6-Methyl-1,2-oxathiane 2,2-dioxide (14) was prepared in 90% yield as described by Durst:[9] bp 121–123 °C (2 mm); NMR 1.39

(14) F. Püschel and C. Kaiser, *Chem. Ber.*, **97**, 2917 (1964).

Table II. Preparation and Properties of γ- and δ-Sultones

compd	no.	yield, %	bp (mm) or [mp], °C	n_D	mass spectrum,[c] m/e	^{1}H NMR[b]
	2	39	79.5 (0.2)		136 (0.5), 72 (12), 55 (32)	1.46 (d, 3, J = 6.8), 2.0-3.6 (m, 3), 4.42 (dd, 2, J = 5.8)
	3	47	oil[a,d]	1.4755	162 (0.1), 80 (16), 79 (15), 78 (12)	2.1-3.0 (m, 4), 3.0-3.7 (m, 1), 4.43 (dd, 2, J = 8.5), 5.0-6.2 (m, 3)
	4	6	oil[a,d]	1.4900	none, 120 (11), 118 (12), 117 (16), 105 (26), 93 (201), 92 (21), 91 (55)	2.28-2.78 (m, 6), 4.37 (t, 2, J = 7.1), 5.05-6.30 (m, 6)
	5	60	[54.5-58.5]		212 (10), 131 (14), 130 (100), 129 (14), 118 (21), 117 (93), 115 (26)	2.06 (m, 5), 4.09-4.38 (m, 2), 7.22 (s, 5)
	8	58	[29.5-34.5][a]		264 (4), 246 (4), 181 (8), 164 (18), 151 (62), 143 (26), 122 (43)	0.87 (dist t, 3), 1.10-1.7 (16), 2.55 (m, 1), 3.35 (m, 1), 4.40 (m, 2)
	9	35	84 (0.05)[a]	1.4777	194 (3), 151 (100), 123 (12), 122 (44)	0.92, 1.03 (dd, 6, J = 6.2), 1.85 (hept, 1), 2.65 (qd, 2, J = 2), 3.89 (dd, 1, J = 6.3), 4.42 (t, J = 7.5)
	10	68	[53-55][a]		382 (13), 300 (15), 282 (13), 108 (51), 107 (100)	2.0-2.5 (m, 2), 3.42 (s, 1), 3.4-3.7 (m, 1), 4.3-4.8 (m, 1), 5.36 (dd, 1), 7.34 (s, 5)
	11	50	[53.5-55]		none, 165 (48), 83 (19), 71 (27), 53 (100)	1.3 (s, 3), 1.57 (s, 3), 2.40-2.9 (m, 2), 2.97 (s, 1), 3.35 (t, 1, J = 9.5 Hz), 4.38 (t, 2)
	12	42	[98-101]		220 (12), 177 (43), 156 (16), 138 (32), 99 (100), 95 (16)	1.2-2.1 (m, 10), 2.3-3.0 (m, 2), 2.81 (s, 1), 3.40 (t, 1, J = 9.5), 4.40 (td, 2, J = 8 Hz)
	13	49	[193-194]		304 (14), 286 (11), 184 (16), 183 (100), 105 (16)	2.49 (m, 2), 4.34 (m, 1), 4.79 (s, 1), 5.09 (t, 2, J = 9 Hz), 7.1-7.7 (m, 10)
	16	90	105 (0.05)[a]	1.4692	206 (3), 141 (33), 127 (20), 113 (11), 112 (45), 111 (33), 110 (34), 83 (100)	0.89 (t, 6), 1.41 (d, 3, J = 6.9 Hz), 1.0-1.7 (m, 4), 1.81 (d, 2), 4.28 (AB q, 2)
	17	68	125 (0.05)[a]	1.4831	250 (0.81), 235 (16)	0.88 (t, 6), 2.9 (s, 1), 3.05-3.40 (m, 1), 4.20 (AB q, 2)
	18	69	[95-97][a]		248 (9), 166 (15), 128 (11), 125 (13), 123 (27), 99 (100)	1.44 (d, 3), 1.3-2.0 (m, 12), 2.0-2.45 (m, 2), 2.96-3.2 (dd, 1), 4.75 (m, 1)

[a] Satisfactory elemental analyses obtained for this compound. [b] Given as δ values; J values are in hertz. ^{13}C NMR spectra for these compounds will be reported elsewhere. [c] Relative intensity is given in parentheses. Only most abundant ions are recorded. The first m/e value is for the parent ion. [d] Purified by column chromatography using a silica gel column.

(d, 3, J = 6.2 Hz), 1.5–2.42 (m, 4), 2.87–3.85 (m, 2), 4.8 ppm (m, 1); mass spectrum, m/e (relative intensity) 150 (0.6) 107 (10), 71 (60).

***trans*-3,4,5,6,7-Octahydro-1,2-benzoxathiole 2,2-Dioxide (20).** Slow addition of 209 mL of 2.2 M *n*-butyllithium to a solution of 113.6 g (0.42 mol) of the dimesylate of *trans*-1,2-cyclohexanediol in 1.8 L of THF under nitrogen at −78 °C was followed by stirring at −78 °C for 1 h. The mixture was allowed to warm to room temperature and to stand for 42 h. The usual workup gave a crude yellow oil which solidified on being allowed to stand and proved to be largely the starting dimesylate of *trans*-1,2-cyclohexanediol. The crude product was chromatographed on an alumina column by elution with methylene chloride followed by ether to give, after recrystallization from pentane–ether, 1.4 g (1.9%) of the trans sultone **20** as white needles: mp 65.5–67.4 °C; NMR 1.1–2.7 (m, 9), 2.8–3.68 (m, 2), 3.95–4.42 ppm (dt, 1); mass spectrum, m/e (relative intensity) 176 (2), 112 (47), 95 (20), 94 (91), 84 (44), 83 (48), 81 (26), 79 (74), 71 (28), 70 (65), 69 (42), 68 (100), 67 (33), 66 (20), 57 (60), 56 (55), 55 (73), 54 (49), 53 (41).

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.71; H, 6.86; S, 18.19. Found: C, 47.89; H, 6.89; S, 17.98.

***cis*-3,4,5,6,7-Octahydro-1,2-benzoxathiole 2,2-Dioxide (19).** Treatment of bromomesylate **22**[9] as described above gave a yellow oil. Chromatography on 60–200-mesh silica gel by eluting with 4 L of CH_2Cl_2 and 2 L of ether and collecting 25-mL fractions afforded 31.2 g of product (fractions 33–55) whose NMR spectrum indicated the presence of a mixture of 68% cis sultone **19** and

32% of the starting bromomesylate **22**. Fractions 56–90 contained 5.48 g of a yellow oil which proved to be sultone **19** contaminated, as indicated by its ^{13}C NMR spectrum, with a small amount of the trans sultone **20**. The NMR of **19** showed signals at 1.15–2.35 (m, 9), 3.0–3.7 (8 lines, 2), and 4.68–4.88 ppm (m, 1).

General Method for Lithium Aluminum Hydride–Aluminum Hydride Reduction of Sultones. The sultone (0.5 equiv) was added to a stirred slurry of sublimed $AlCl_3$ (1 equiv) and lithium aluminum hydride (4 equiv) in ether or dioxane (distilled from calcium hydride) at ambient temperature. The mixture was refluxed, generally for 20 h, and cooled, and 10% hydrochloric acid was added cautiously. The aluminum salts were removed by filtration and dissolved in 0.2 L of 10% hydrochloric acid, and the solution was extracted twice with ether and once with methylene chloride. The organic phases were combined and dried ($MgSO_4$) and the solvents removed in vacuo.

Reduction of Sultone 6. Reduction of 1.013 g (3.66 mmol) of **6** in refluxing ether for 42 h and recrystallization of the crude product from pentane gave 0.42 g (46.6%) of 1-mercapto-3-tetradecanol (**23**): mp 32–33 °C; IR (melt) 3.0, 3.9, 13.91 μm; NMR 0.88–1.01 (dist t, 3), 1.12–1.58 (br s, 20), 1.58–1.92 (m, 2), 2.67 (q, 2), 3.45–3.99 ppm (br m, 1).

Anal. Calcd for $C_{14}H_{30}OS$: C, 68.33; H, 12.27; S, 13.01. Found: C, 68.22; H, 12.41; S, 12.82.

Reduction of 1.033 g (3.74 mmol) of **6** in refluxing dioxane for 20 h followed by chromatography on silica gel gave 0.252 g (31%) of 3-tetradecanol (**24**) as a clear oil:[15] NMR 0.78–1.08 (m, 6), 1.14–1.65 (br s, 22), 2.58 (s, 1) and 3.26–3.67 ppm (br s, 1).

A slower moving fraction contained 0.344 g (37.4%) of **23**.

Reduction of Sultone 7. Reduction of 2.013 g (8.38 mmol) of **7** followed by chromatography on silica gel gave 1.015 g (58%) of 1-mercapto-2,3-dimethyl-2-phenyl-3-butanol (**25**) as a pale yellow oil: IR 2.85, 3.87, 6.67 μm; NMR 1.05 (s, 3) 1.18 (s, 3), 1.1–1.6 (m, 2), 1.49 (s, 3), 2.7 and 3.6 (AB q, 2, S–CH_2), 7.3 ppm (s, 5); mass spectrum, *m/e* (relative intensity) 176 (P – 34, 14), 119 (64), 118 (100), 117 (30), 91 (33), 59 (74).

Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63; S, 15.24. Found: C, 68.75; H, 8.73; S, 15.01.

Reduction of Sultone 8. Reduction of 3.19 g (12 mmol) of **8** in refluxing ether for 21 h gave 1.74 g of an oil. Chromatography on silica gel afforded the following. (a) 2-Octyltetrahydrofuran (**26**):[16] oil; 0.111 g (5%); IR 3.4, 3.49, 9.4 μm; NMR 0.91 (dist t, 3), 1.1–2.1 (m, 18), 3.5–4.05 ppm (m, 3); mass spectrum, *m/e* (relative intensity) 184 (1) and 71 (100). (b) 1,4-Dodecanediol (**27**):[16] 0.9 g (25%); IR 2.99, 8.45, 9.55 μm; NMR ($CDCl_3$) 0.88 (dist t, 3), 1.15–1.8 (m, 20), 3.52–3.8 ppm (m, 3). (c) 3-Mercapto-1,4-dodecanediol (**28**): 0.39 g (14%); IR 3.03, 3.93, 9.54 μm; NMR 0.89 (dist t, 3), 1.2–2.1 (m, 16), 2.89–3.34 (m, 1), 3.6–4.05 (m, 6); mass spectrum, *m/e* (relative intensity) 216 (P – 18, 5), 92 (41), 74 (100).

Anal. Calcd for $C_{12}H_{26}O_2S$: C, 61.49; H, 11.18; S, 13.68. Found: C, 61.73; H, 10.95; S, 13.4.

Reduction of Sultone 9. Reduction of 3 g (15.42 mmol) of **9** in 30 mL of refluxing ether for 20 h gave 1.14 g (45%) of 3-mercapto-5-methyl-1,4-hexanediol (**29**): bp 98 °C (0.07 mm); IR 2.99, 3.9, 9.46, 12.57 μm; NMR 0.82–1.1 (dd, 6), 1.2–2.3 (m, 3), 3.12–3.4 (m, 4), 3.56 (s, 1), 3.8–3.98 ppm (td, 2); mass spectrum, *m/e* (relative intensity) 146 (56), 84 (43), 69 (100), 59 (29), 57 (45), 56 (28), 55 (75), 45 (36), 43 (50), 41 (95), 39 (48).

Anal. Calcd for $C_7H_{16}O_2S$: C, 51.18; H, 9.82; S, 19.52. Found: C, 50.97; H, 10.08; S, 19.61.

When the reduction was carried out by adding $AlCl_3$ to a mixture of sultone **9** and $LiAlH_4$ in 300 mL of ether and refluxing the mixture for 20 h, there was obtained 0.72 g (48%) of 2,2,4-trimethyl-1,5-pentanediol [**30**; bp 79.5 °C (0.06 mm)] which solidified on standing. Recrystallization from ether–pentane gave white needles, mp 51.5–53.5 °C (lit.[17] mp 51.8–52.2 °C).

Reduction of Sultone 10. Reduction of 2.05 g (5.36 mmol) of sultone **10** in 0.3 L of refluxing ether for 22.5 h and chromatography on silica gel gave the following. (a) 1-Phenyl-4-pentadecanol (**31**): oil; 0.343 g (21%); IR 2.93 μm; NMR ($CDCl_3$) 0.98 (dist t, 3), 1.1–1.9 (m, 26), 2.27 (s, 1), 3.5–3.8 (br m, 1), 4.54 (m, 1), 7.34 ppm (br s, 5). (b) 1-Phenyl-1,5-pentadecanediol (**32**): 0.11 g (6%); mp 49.5–51 °C (after recrystallization from ether–pentane); IR 2.93 μm; NMR 0.89 (dist t, 3), 1.12–1.9 (m, 26), 3.4–4.0 (br m, 2), 4.4–4.6 (m, 1), 7.34 ppm (m, 5). (c) 2-Mercapto-1-phenyl-1,4-pentadecanediol (**33**): 1.005 g (53%); mp 80–81.3 °C after recrystallization from ether–pentane; IR 3.0, 3.88, 6.7 μm; NMR 0.9 (dist t, 3), 1.14–1.9 (m, 21), 3.15–4.05 (m, 5), 4.68 (t, 1, J = 5 Hz), 7.34 ppm (s, 5); mass spectrum, *m/e* (relative intensity) 352 (1), 228 (36), 120 (26), 118 (70), 117 (23), 107 (100), 105 (33), 79 (30), 60 (37), 56 (32), 55 (41), 43 (49), 41 (43).

Anal. Calcd for $C_{21}H_{36}O_2S$: C, 71.54; H, 10.39; S, 9.09. Found: C, 71.44; H, 10.48; S, 9.22.

Reduction of Sultone 11. Reduction of 2.22 g (12.29 mmol) of **11** in refluxing ether for 20 h and distillation gave 0.4 g (22%) of 3-mercapto-4-methyl-1,4-pentanediol (**34**): oil; bp 83–84 °C (0.07 mm); IR 2.99, 8.81, 9.56, 10.43 μm; NMR 1.28 (s, 6), 1.4–2.4 (m, 2), 2.75–3.2 (m, 1), 3.7–4.01 ppm (m, 5); mass spectrum, *m/e* (relative intensity) 132 (P – 18, 63), 101 (45), 99 (24), 88 (100), 81 (35), 74 (72), 73 (22), 70 (45), 69 (32), 59 (80), 55 (24), 45 (20), 43 (80), 41 (53).

Anal. Calcd for $C_6H_{14}O_2S$: C, 47.97; H, 9.39; S, 21.34. Found: C, 48.21; H, 9.12; S, 21.04.

Reduction of Sultone 12. Reduction of 3.2 g (14.52 mmol) of sultone **12** in refluxing ether for 20 h gave an oil after distillation. Preparative TLC using 4:1 pentane–ether gave 0.66 g (2.8%) of 4-mercapto-1-oxaspiro[4.5]decane (**35**): IR 3.9, 8.73, 9.47, 9.65, 10.42, 10.75 μm; NMR 1.38–1.77 (br s and m, 10), 1.77–3.28 (m, 4), 3.68–4.02 ppm (m, 2).

Anal. Calcd for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61. Found: C, 62.90; H, 9.51; S, 18.51.

Reduction of Sultone 13. Reduction of 1.01 g (3.33 mmol) of **13** in refluxing ether for 21 h followed by preparative TLC gave the following. (a) 2,2-Diphenyltetrahydrofuran (**36**): 0.127 g (17%); R_f 0–0.16; IR 6.25, 6.7, 9.44, 9.69 μm; NMR 1.52–2.06 (m, 2), 2.47 (td, 2), 3.93 (t, 2, J = 7 Hz), 7.0–7.5 ppm (m, 10); mass spectrum, *m/e* (relative intensity) 224 (42), 147 (100), 105 (77), 77 (32). (b) 1,1-Diphenyl-1-butene (**37**):[18] 0.13 g (19%); IR 6.23, 6.7 μm; NMR 1.0 (t, 3, J = 7.4 Hz), 2.12 (pentet, 2), 6.09 (t, 1, J = 7.7 Hz), 7.21 ppm (m, 10); mass spectrum, *m/e* (relative intensity) 208 (100), 207 (23), 193 (67), 179 (25), 178 (28), 165 (27), 130 (40), 115 (76), 91 (40).

Reduction of Sultone 15. Reduction of 1 g (5.19 mmol) of **15** in refluxing ether for 41 h gave 0.235 g (35%) of 2,2-diethyl-1-butanol (**38**):[19] bp 65 °C (18 mm); NMR 0.79 (dist t, 9), 1.2 (qd, 6), 2.11 (s, 1), 3.35 ppm (s, 2).

Reduction of 2.9 g of **15** in refluxing dioxane for 65.5 h gave 0.88 g (45%) of alcohol **38**.

Reduction of Sultone 16. Reduction of 1.07 g (5.17 mmol) of **16** in refluxing ether for 114.5 h gave 0.167 g of an oil, bp 92–98 °C (22 mm). Preparative TLC gave 0.03 g (4%) of 2,2-diethyl-1-pentanol (**39**): IR 2.92, 9.66, 9.79, 10.76 μm; NMR 0.8 (br t, 9), 1.05–1.8 (m, 8), 3.35–3.6 (m, 3). Two other fractions were isolated in insufficient amounts to permit identification.

Reduction of Sultone 17. Reduction of 1.06 g (4.25 mmol) of **17** in refluxing ether for 117.5 h and chromatography on silica gel gave 0.094 g (12%) of what appeared to be 2,2-diethyl-5-methyl-1,5-hexanediol (**40**) which was not fully characterized: NMR 0.8–2.2 (m, 22), 3.38 (s, 2). A second fraction contained 0.345 g (37%) of 2,2-diethyl-4-mercapto-5-methyl-1,5-hexanediol (**41**): IR 2.95, 3.89, 8.92, 9.54, 9.76 μm; NMR 0.69–1.0 (m, 6), 1.26 (d, 6), 1.0–1.55 (m, 5), 1.73 (d, 2), 2.82 (t, 1), 3.38 (d, 2), 3.78 ppm (br s, 2).

Anal. Calcd for $C_{11}H_{24}O_2S$: C, 59.95; H, 10.98; S, 14.55. Found: C, 60.01; H, 10.74; S, 14.30.

Reduction of Trans Sultone 20. Reduction of 1.01 g (5.73 mmol) of trans sultone **20** in refluxing ether for 21 h gave after chromatography on silica gel, 0.64 g (76%) of *trans*-2-(mercaptomethyl)cyclohexanol (**42**): IR 2.99, 3.9, 9.48, 9.71, 10.29 μm; NMR 0.95–2.35 (m, 9), 2.52–2.9 (m, 2), 2.97 (s, 2), 3.1–3.7 ppm (m, 1).

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Anal. Calcd for $C_7H_{14}OS$: C, 57.49; H, 9.72; S, 21.92. Found: C, 57.24; H, 9.53; S, 22.20.

Stirring **42** in methanol with Raney nickel afforded *trans*-2-methylcyclohexanol whose infrared spectrum was identical with that of an authentic sample.[20]

Reduction of Cis Sultone 19. Reduction of 2.167 g (12.29 mmol) of cis sultone **19**, contaminated with some trans sultone **20**, gave, after chromatography on silica gel, 1.06 g (56%) of *cis*-2-(mercaptomethyl)cyclohexanol (**43**): IR 2.92, 3.89, 8.54, 10.34 μm; NMR 1.04–1.95 (m, 9), 2.25–2.9 (m, 4), 4.1 ppm (br s, 1); mass spectrum, *m/e* (relative intensity) 146 (15), 128 (42), 95 (81), 94 (53), 81 (100), 79 (45), 69 (21), 68 (35), 67 (52), 57 (45), 55 (39), 41 (83).

Column fractions which eluted later contained 0.21 g (12%) of trans mercapto alcohol **42**.

Stirring cis mercapto alcohol **43** with Raney nickel afforded *cis*-2-methylcyclohexanol whose infrared spectrum was identical with that of an authentic sample.[20]

Reduction of Propane Sultone 1. Reduction of 1.71 g (14 mmol) of propane sultone **1** in refluxing ether for 22 h was carried out and the reaction mixture worked up in the usual manner. The aluminum salts were removed by filtration, and examination of the filtrate indicated the absence of organic products. The aluminum salts were dissolved in 200 mL of 25% sulfuric acid, and KOH was added to bring the pH to 10–12, resulting in a thick white precipitate. The solid was removed by filtration, and the filtrate was neutralized to a light phenolthalein pink. The resulting solution was evaporated to dryness, and the solid was dried at 100 °C for 12 h. The solid was treated with 25 g of PCl_5 at ambient temperature for 5 h and at 150 °C for 30 min. The mixture was stirred with hot benzene for 15 min and filtered, and the salts were washed with benzene. The benzene solution was cautiously washed with water, dried ($MgSO_4$), and concentrated to about 50 mL. The solution was cooled to 0 °C and added to 200 mL of concentrated ammonium hydroxide. After being allowed to stand at ambient temperature for 30 min, the aqueous phase was extracted with benzene and methylene chloride. The combined organic phases were dried ($MgSO_4$) and evaporated to leave a yellow oil. Recrystallization from ether–pentane gave 0.1 g (6%) of 1-propanesulfonamide (**44**) as white needles: mp 46.8–47.5 °C (lit.[21] mp 52 °C); NMR 1.1 (t, 3, J = 7.9 Hz), 1.68–2.14 (m, 2), 3.12 (t, 2), 5.07 ppm (br s, 2).

Registry No. **1**, 1120-71-4; **2**, 1121-03-5; **3**, 69873-07-0; **4**, 75732-42-2; **5**, 75732-43-3; **6**, 5981-19-1; **7**, 75732-44-4; **8**, 75732-45-5; **9**, 75732-46-6; **10**, 75732-47-7; **11**, 75732-48-8; **12**, 75732-49-9; **13**, 75732-50-2; **14**, 4362-71-4; **15**, 75732-51-3; **16**, 75732-52-4; **17**, 75732-53-5; **18**, 75732-54-6; **19**, 27304-60-5; **20**, 75732-55-7; **21**, 38932-04-6; **22**, 27304-57-0; **23**, 75732-56-8; **24**, 1653-32-3; **25**, 75732-57-9; **26**, 5921-92-6; **27**, 38146-95-1; **28**, 75751-06-3; **29**, 75732-58-0; **30**, 3465-14-3; **31**, 75732-59-1; **32**, 75732-60-4; **33**, 75732-61-5; **34**, 75732-62-6; **35**, 75732-63-7; **36**, 887-15-0; **37**, 1726-14-3; **38**, 13023-60-4; **39**, 14202-62-1; **40**, 75732-64-8; **41**, 75732-65-9; **42**, 75732-66-0; **43**, 75732-67-1; **44**, 24243-71-8; 2,3-dimethyl-3-phenyl-2-butanol, 2371-91-7; 5-methyl-1,4-hexanediol, 38624-36-1; 1,1-diphenyl-1,4-butanediol, 1023-94-5; SO_3, 7446-11-9; 1-tetradecene, 1120-36-1; 3,3-dimethyl-2-phenyl-1-butene, 5676-29-9; 3,3-diethyl-1,3-propandiol dimesylate, 75732-68-2; 1-(3-hydroxy-1-mercaptopropan-1-yl)cyclohexanol, 75732-69-3.

(20) "Sadtler Infrared Prism Spectra", Spectra No. 13370 and 13371.

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Synthesis and Absolute Configuration of the First Optically Active Organic Molecule with *T* Symmetry: (-)-1,3,5,7-Tetrakis[[(2-(1*S*,3*S*,5*R*,6*S*,8*R*,10*R*)-D_3-trishomocubanyl)acetoxy]methyl]adamantane

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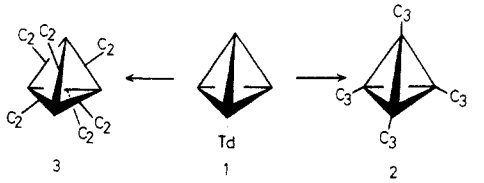
Received June 15, 1980

By starting from the Diels–Alder adduct **12** between 2-(methoxycarbonyl)-1,4-benzoquinone (**11**) and cyclopentadiene, the modified Barborak synthesis of D_3-trishomocubane afforded (-)-2-(1*S*,3*S*,5*R*,6*S*,8*R*,10*R*)-D_3-trishomocubaneacetic acid (**19**) whose esterification with 1,3,5,7-tetrakis(hydroxymethyl)adamantane (**27**) gave (-)-**28**, the first *T* symmetric organic molecule with known absolute configuration.

Among the gyrochiral[1] organic molecules so far synthesized, ones with the highest symmetry have been D_3 molecules with symmetry number 6. In a preceding paper,[2] we have reported the preparation and absolute configuration determination of (+)-D_3-trishomocubane (**7**), a typical cage-shaped molecule with this symmetry, and this prompted us to explore possible synthetic routes to organic molecules of polyhedral *T* symmetry. The inherent symmetry number 12 for the *T* point group demands 12 asymmetric units with same chirality to be arranged around the axes of rotation of a regular tetrahedron.[3]

Scheme I



One way to achieve this is that first we prepare a chiral molecular component with C_3 symmetry by arranging these

(1) This name has been given to describe the symmetry of a shape which is chiral but not asymmetric. Nakazaki, M.; Naemura, K.; Yoshihara, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3278.

(2) Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Org. Chem.* **1978**, *43*, 689. For other syntheses of optically active D_3-trishomocubane see: Helmchen, G.; Staiger, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 116; Eaton, P. E.; Leipzig, B. *J. Org. Chem.* **1978**, *43*, 2483.

(3) Farina, M.; Morandi, C. *Tetrahedron* **1974**, *30*, 1819.

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