at room temperature saturated aqueous sodium bicarbonate and ether were added. The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. Concentration followed by flash chromatography (eluant, hexane–ethyl acetate, 9:1) gave the alcohol **46** (80%): IR (neat) 3630, 1589, and 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 1.23–1.45 (m, 8 H), 1.42 (broad s, 1 H, exchangeable with D_2O), 1.50–1.63 (m, 4 H), 3.64 (t, 2 H, J = 6.5 Hz), 3.65 (t, 2 H, J = 6.5 Hz), 7.34–7.46 (m, 6 H), 7.64–7.70 (m, 4 H). Anal. Calcd for $C_{24}H_{36}O_2Si$: C, 74.94; H, 9.46. Found: C, 74.76; H, 9.62.

Selective Removal of *tert*-Butyldimethylsilyl Ether 38. A solution of the bis(silyl ether) **38** (0.5 mmol) in 4.5 mL tetrahydrofuran was treated with 0.1 N $HClO_4$ (0.5 mL) and stirred at room temperature for 24 h. Normal workup gave after flash chromatography (eluant, hexane–ethyl acetate, 9:1) pure alcohol **45**: ^1H NMR ($CDCl_3$) δ 1.21–1.38 (m, 9 H), 1.28 (s, 9 H), 1.47–1.63 (m, 4 H), 3.61 (t, 2 H, J = 6.5 Hz), 3.71 (t, 2 H, J = 6.5 Hz), 7.28–7.42 (m, 6 H), 7.61–7.66 (m, 4 H). Anal. Calcd for $C_{24}H_{36}O_3Si$: C, 71.95; H, 9.06. Found: C, 71.84; H, 9.01.

Chemical Compatibility: Preparation of *tert*-Butoxydiphenylsilyl Ether 37 from Diol 22. (a) Selective Silylation of Diol 22. Following the representative procedure outlined above a mixture of 1,5-hexanediol (16.8 mmol) and triethylamine (25.1 mmol) in 87 mL of dry methylene chloride, under nitrogen, was treated at 0 °C with *tert*-butoxydiphenylsilyl chloride (22.7 mmol). The cooling bath was removed and the resulting mixture stirred for an additional period of 20 h and then quenched with saturated aqueous sodium bicarbonate. Normal workup (ether) gave after flash chromatography (eluant, hexane–ethyl acetate, 8:2) the monosilyl alcohol **29** (82%): IR (neat) 3360, 3068, 1591, 1365, and 1051 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (d, 3 H, J = 7.5 Hz), 1.21 (s, 9 H), 1.40–1.50 (m, 4 H), 1.52–1.66 (m, 2 H), 3.70–3.81 (m, 1 H), 3.75 (t, 2 H, J = 6.0 Hz), 7.29–7.43 (m, 6 H), 7.62–7.68 (m, 4 H). Anal. Calcd for $C_{22}H_{32}O_3Si$: C, 70.92; H, 8.66. Found: C, 70.61; H, 8.71.

(b) Oxidation of Alcohol 29. A cold (−78 °C) stirred solution of oxalyl chloride (6.0 mmol) in 10 mL of dry methylene chloride, under nitrogen, was treated with a solution of DMSO (7.0 mmol) in 2 mL of the same solvent. After 10 min a solution of alcohol **29** (4.7 mmol) in 6 mL of dry methylene chloride was added dropwise and the reaction mixture aged for 50 min. Triethylamine (14.0 mmol) was then added and the resultant mixture allowed to warm to room temperature. After 1 h water and ether were added. The organic layer was separated and washed with 10% aqueous sodium hydrogen sulfate, water, and brine. Drying ($MgSO_4$) and concentration gave a yellow oil, which was purified by flash chromatography (eluant, hexane–ethyl acetate, 85:15) to yield ketone **36** (83%): IR (neat) 3055, 1710, 1583, 1367, and 1042 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 1.54–1.72 (m, 4 H), 2.10 (s, 3 H), 2.42 (br t, 2 H, J = 7.0 Hz), 3.73 (t, 2 H, J = 6.0 Hz), 7.29–7.42 (m, 6 H), 7.61–7.66 (m, 4 H). Anal. Calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16. Found: C, 70.32; H, 8.12.

(c) Butyllithium Addition of Ketone 36. A cold (−78 °C) stirred solution of ketone **36** (0.3 mmol) in 1.6 mL dry ether was treated with a 1.6 M solution of butyllithium (0.24 mL) in hexanes. After 1 h the reaction mixture was quenched with saturated aqueous ammonium chloride and diluted with ether. The ether layer was separated, washed with water and brine, and dried over sodium sulfate. Concentration followed by purification (silica gel, 9:1 hexane–ethyl acetate) gave the tertiary alcohol **37**: IR (neat) 3350, 3058, 1365, and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86–0.94 (br t, 3 H), 1.12 (s, 3 H), 1.20–1.48 (m, 9 H), 1.31 (s, 9 H), 1.50–1.70, (m, 4 H), 3.70–3.78 (br t, 2 H), 7.29–7.42 (m, 6 H), 7.6–7.69 (m, 4 H).[23]

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Registry No. **5**, 53668-78-3; **6**, 114058-14-9; **7**, 114058-15-0; **8**, 17922-24-6; **9**, 90101-29-4; **11**, 114058-16-1; **12**, 114058-17-2; **13**, 114058-18-3; **14**, 114058-19-4; **15**, 114058-20-7; **16**, 114058-21-8; **17**, 94124-59-1; **18**, 114058-22-9; **19**, 114058-23-0; **20**, 112-66-3; **21**, 114058-24-1; **22**, 928-40-5; **23**, 94-96-2; **24**, 96720-08-0; **25**, 1490-04-6; **26**, 123-96-6; **27**, 590-67-0; **28**, 98-55-5; **29**, 114058-25-2; **30**, 114094-30-3; **31**, 114058-26-3; **32**, 114058-27-4; **33**, 114058-28-5; **34**, 114058-29-6; **35**, 114058-30-9; **36**, 114058-31-0; **37**, 114058-32-1; **38**, 114058-33-2; **39**, 114058-34-3; **40**, 114058-35-4; **41**, 114058-36-5; **42**, 114058-37-6; **43**, 94124-43-3; **44**, 91898-32-7; **45**, 114058-38-7; **46**, 94124-45-5; **47**, 114058-39-8; **48**, 114058-40-1; **49**, 94124-47-7; Ph_2SiCl_2, 80-10-4; t-Bu_2SiCl_2, 18395-90-9; MeOH, 67-56-1; i-PrOH, 67-63-0; 2,6-$Me_2C_6H_3OH$, 576-26-1; t-BuOH, 75-65-0; Me_2SiCl_2, 75-78-5; $CH_3(CH_2)_{11}OH$, 112-53-8; HSi(Bu-t)$_2$(OMe), 56310-21-5; t-Bu_2SiBr_2, 94403-14-2; i-BuMgBr, 926-62-5; (i-Bu)Si(Ph)$_2$Cl, 81851-76-5; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0.

(23) This compound was not submitted for elemental analysis.

Organic Disulfides and Related Substances. 49. Preparation of Cyclic Thiosulfinates and Reactions with Thiols[1]

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The four stereoisomers of 1,2-dithiane-4,5-diol 1-oxide were prepared by oxidizing the corresponding dithianes with H_2O_2 in MeOH/H_2O by using tungstic acid as a catalyst, MnO_2 to destroy excess H_2O_2, and chromatography to separate products. These cyclic thiosulfinates (**8**, **9**, **12**, and **13**), together with 1,4-dihydro-2,3-benzodithin 2-oxide (**2**), were converted to bisunsymmetrical disulfides, $R^a(SSR^b)_2$ with *p*-toluenethiol and 3-mercaptopropanediol as models respectively for arene- and alkanethiols. 1,5-Dihydro-2,3,4-benzotrithiepin 2-oxide (**5**) gave the disulfide trisulfides **6a** and **6b**, $R^a(SSR^b)(SSSR^b)$, with these thiols but **6a** and **6b** were quite unstable. Mass spectra are discussed; tetramethylene sulfone may provide a useful matrix for both positive- and negative-ion FAB spectra of organosulfur compounds.

Relatively little attention has been given to thiosulfinates, RS(O)SR.[2] In particular, reactions of thiosulfinates with thiols seem to have been studied preparatively in a fairly general way only by Schöberl and Gräfje[3]

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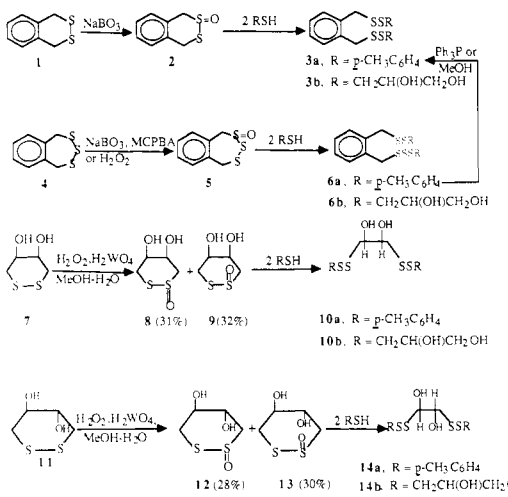
Scheme I[a]



[a] **15**, RSH = p-$CH_3C_6H_4SH$; **16**, RSH = $HOCH_2CH(OH)CH_2SH$.

and mechanistically by Kice and co-workers,[4] although others have studied reactions closely related to cysteine or cystine.[5] A particularly intriguing feature of such reactions is that one molecule of the thiosulfinate reacts with two of a thiol (eq 1),[3a,4a,b,5e] in marked contrast to the 1:1 relationship seen with thiosulfonates (eq 2).[6]

$$RS(O)SR + 2R'SH \rightarrow 2RSSR' + H_2O \quad (1)$$

$$RS(O)_2SR + R'SH \rightarrow RSO_2H + RSSR' \quad (2)$$

Recent interest led us to several cyclic thiosulfinates that afforded an opportunity to expand the even more limited knowledge about the chemistry of the cyclic class (Scheme I). Reactions of cyclic thiosulfinates with thiols seem to have been studied only by Schöberl and Gräfje,[3a] who investigated some reactions with cysteine but did not report yields or analyses,[3a] and by Boduszek and Kice who studied kinetics but did not report isolations.[4d]

Synthesis of Cyclic Thiosulfinates. The cyclic thiosulfinates **2** and **5** were prepared as starting materials without problems, by perborate oxidation as reported earlier (Scheme I).[1a] On the other hand, oxidation of the 1,2-dithiane-4,5-diols **7** and **11** to the thiosulfinates proved to be considerably more of a problem, and several oxidations with conventional oxidants and solvents led only to complex strongly acidic mixtures, in common with earlier efforts to oxidize **11** to the 1,1-dioxide.[7] Ultimately, however, oxidation of **7** led successfully to a mixture of 1,2-dithiane-*t*-4,*t*-5-diol *r*-1-oxide (**8**) and 1,2-dithiane-*c*-4,*c*-5-diol *r*-1-oxide (**9**),[8] which could be separated to give **8** and **9** in yields of 31–32% (Scheme I). Similar oxidation of **11** gave **12** and **13** in yields of 28–30%. The keys to success were these: (a) oxidation with H_2O_2 in ca. 3.3–3.9:1 ratio to **7** and **11** (cleaner, and better yields than ca. 1:1, 2:1, or 4.5:1), with use of a neutral but polar solvent system (3:1 MeOH–H_2O), and with tungstic acid as a catalyst; (b) destruction of excess H_2O_2 with MnO_2 immediately after TLC showed disappearance of **7** or **11** (along with appearance of new spots for the two products, of about equal intensity), otherwise further oxidation makes separation very difficult; and (c), separation of the two products by chromatography on silica gel.

Evidence that **8** and **9** were geometrical isomers, as were **12** and **13**, was afforded by reaction of a thiol with either of the pairs **8**, **9** or **12**, **13** to give the same bis(disulfide) (Scheme I; vide infra). The sterochemistry shown in Scheme I was assigned on the presumption that because of hydrogen bonding the 5-hydroxyl group (that nearer the S=O function) would result in broader IR bands at lower frequency when cis to the S=O function than when trans to it. Hence the two isomers that showed relatively broad bands in the range of ca. 3400–3150 cm^{-1} were presumed to be the *c*-5 isomers **9** and **12**, and the two that showed relatively sharp bands at higher frequency were considered to be the *t*-5 isomers (**8**, 3350 cm^{-1}; **13**, 3430 and 3300 cm^{-1}).

Synthesis and Stability of Di- and Trisulfides. In order to assess the generality of reactions of cyclic thiosulfinates with thiols, we first used **2** and **5** as model thiosulfinates, with *p*-toluenethiol (**15**) as a model arenethiol and 3-mercapto-1,2-propanediol (**16**) as a model alkanethiol (these thiols were chosen as models because the radioprotective activities of the disulfides **17**[9] and **18**[10] made variants such as those in Scheme I seem attractive candidates as antiradiation drugs; the cyclic hydroxy thiosulfinates **8**, **9**, **12**, and **13** were chosen as synthons because of the radioprotective activity of the bis(disulfide) **19**, along with that of the dihydroxy disulfide **18**).[10]

p-$CH_3C_6H_4SS(CH_2)_4SO_2Na$
17

$HOCH_2CH(OH)CH_2SS(CH_2)_4SO_2Na$
18

$[NaO_2S(CH_2)_4SS(CH_2)_2]_2$
19

The reaction of the thiosulfinates **2** and **5** with *p*-toluenethiol (**15**) gave the disulfide **3a** and trisulfide **6a** in

(1) (a) Paper 48: Singh, P. K.; Field, L. *Phosphorus Sulfur*, in press. (b) This investigation was supported by the U.S. Army Medical Research and Development Command, Department of the Army, under Contract No. DAMD17-85-C-5181; this paper has been designated as Contribution No. 1833 to the U.S. Army Drug Development Program. Additional support from GM-31304 and GM-15431 is acknowledged (B.J.S.), along with PHS Grant ES00267 to the Vanderbilt Center in Molecular Toxicology.

(2) Cf., for example, the following reviews: (a) Schöberl, A.; Wagner, A. In *Methoden der Organischen Chemie (Houben-Weyl)*, vierte auflage; Müller, E., Ed; Georg Thieme Verlag: Stuttgart, 1955; Vol IX, pp 691–693. (b) Krauthausen, E. In *Methoden der Organischen Chemie (Houben-Weyl)*, vierte auflage (extension); Klamann, D., Ed.; Georg Thieme Verlag: Stuttgart, 1985; Vol E11, pp 651–655. (c) Hogg, D. R. in *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon Press: New York; Vol. 3, pp 294–299. (d) Field, L. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; pp 325, 349–350. (e) Oae, S.; Kunieda, N., in ref 2d, pp 620–624.

(3) (a) Schöberl, A.; Gräfje, H. *Justus Liebigs Ann. Chem* **1958**, *617*, 71. (b) Schöberl, A.; Gräfje, H. *Proc. Int. Wool Text. Res. Conf., 1955* **1956**, 157, 477; *Chem. Abstr.* **1958**, *52*, 302.

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(7) Field, L.; Khim, Y. H. *J. Org. Chem.* **1972**, *37*, 2710.

(8) This nomenclature is based on IUPAC Rule B-1.52 (p 55), by which the sulfur atoms in the heterocycle are numbered 1 and 2, and on Rule E-2.3.3 (p 478), by which the configurations of the OH groups at C-4 and C-5 are denoted cis (*c*) or trans (*t*) with reference to the *S*-oxide at position 1 (*r*-1). [Rigaudy, J.; Klesney, S. P.; Eds. *IUPAC Nomenclature of Organic Chemistry. Sections A, B, C, D, E, F and H*; Pergamon: Elmsford, NY, 1979]. We thank Professor Howard E. Smith for calling our attention to Rule E-2.3.3.

(9) Bowman, G. T.; Clement, J. J.; Davidson, D. E., Jr.; Eswarakrishnan, V.; Field, L.; Hoch, J. M.; Musallam, H. A.; Pick, R. O.; Ravichandran, R.; Srivastava, P. K. *Chem.-Biol. Interact.* **1986**, *57*, 161.

(10) Macke, J. D.; Field, L. *Phosphorus Sulfur*, in press.

Scheme II[a]

$$R^a(SSR^b)_2 \rightarrow R^bSSR^b + R^aSS + R^a$$

$$R^a(SSR^b)(SSSR^b) \rightarrow R^bSSR^b + R^bSSSR^b + R^aSS + R^a$$

[a] R^a is seen only for o-$C_6H_4(CH_2)_2$.

44–45% yield. A reviewer suggested (and we concur) that the reasonably high yield of **6a** obtained from the reaction of **5** and **15** indicates that the thiol **15** attacks the dicoordinate sulfur of **5** adjacent to the S=O group; attack at the other dicoordinate sulfur seems likely to lead to a complex mixture and is very unlikely to produce **6a**. The trisulfide (**6a**) was much less stable than the disulfide, however, and disproportionation precluded elemental analysis. As Scheme I shows, the identity of **6a** was confirmed by desulfurization to the disulfide **3a** (24% yield; desulfurization also occurred to a considerable extent in methanol during ca. 5 h, even at ca. 25 °C); furthermore, the single TLC spot from **6a** gave a fast atom bombardment (FAB) mass spectrum appropriate for **6a**.

The mercaptopropanediol **16** gave much poorer yields than **15** with both thiosulfinates **2** and **5**. Thus the disulfide **3b** was obtained in only 5% yield and, although the trisulfide **6b** was obtained in ca. 8% yield, facile loss of sulfur and then disproportionation to the two symmetrical disulfides precluded characterization of **6b**.

In summary, the trisulfides (**6a,b**) were much less stable than the disulfides (**3a,b**), and the hydroxyalkyl products (**3b, 6b**) were less stable than the tolyl products (**3a, 6a**). The decreasing order of stability was **3a** > **3b** ≫ **6a** ≫ **6b**; the relative stabilities of **3a** and **3b** are discussed in ref 1a).

In view of the relative instability even of the disulfides **3a** and **3b**,[1a] the good yields and stabilities of **10a, 10b** and **14a,14b** came as refreshing surprises. All four products were obtained in yields of 67–81%, and all were nice crystalline solids with discrete melting points, in the range of 71–108 °C. The stabilities of all four were roughly comparable and, in marked contrast to **3a, 3b** and **6a, 6b**, methanolic solutions of each showed no indication of disproportionation by TLC or NMR even after at least 2 days under ambient conditions (**3a**, the most stable of the previous group, in methanol began to disproportionate in 10–12 h).[1a] As mentioned, after separation of **8** and **9**, reaction of each with the thiol **15** (or **16**) led to the same disulfide **10a** (or **10b**). Similarly, **14a** or **14b** produced from **12** was the same as that obtained from **13**.

Mass Spectra of the Di- and Trisulfides. Mass spectrometry was used extensively to provide confirmatory evidence for the structures proposed for the foregoing compounds. It permitted a number of general and specific conclusions. In general, the EI mass spectra of the polysulfur compounds **3b**,[1a] **6b, 10a, 10b, 14a,** and **14b** provided no evidence for molecular ions or ions arising by minimal fragmentation of molecular ions (although **10a** did show $M^{\bullet+}$ at a relative abundance of 0.2%). However, in general the spectra did show extensive structure-related fragment ions associated with fissions of the disulfide bonds, under electron impact conditions. A strong tendency was observed for the bisdisulfide or disulfide–trisulfide structures to generate ions characteristic of the corresponding symmetrical disulfides, as summarized in Scheme II. It is not clear whether these disproportionations occur as the result of thermal processes on the probe or as a result of electron impact. These assignments were supported in most instances by the exact masses of the corresponding ^{34}S satellite peaks. An exception to Scheme II was seen in the spectra of the bisdisulfides **10a** and **14a**, which showed intense peaks corresponding to the unsymmetrical disulfide ions formed by the loss of the elements of one $(S)C_6H_4$-(CH_3) from the molecular ion.

Because of our inability to detect molecular ions under electron impact conditions for most of these molecules, we also explored the possibility that the "soft" ionization technique of fast atom bombardment (FAB) mass spectrometry might generate useful structural information. However, attempts to obtain FAB spectra for **5** or **6a** as representative compounds failed when using matrices such as glycerol, thioglycerol, *m*-nitrobenzyl alcohol, tetraethylene glycol, dibutyl phthalate, and 3-amino-1,2-propanediol. This negative result is interpreted as being a consequence of the inability to ionize these relatively apolar molecules in these matrices. Lloyd and Cotter have reported recently the use of tetramethylene sulfone (TS) as a suitable matrix for obtaining negative ion FAB spectra of nonpolar compounds such as coenzyme Q_6 and vitamin K_1, which fail to yield spectra in a variety of other FAB matrices.[11] They propose that $[M]^{\bullet-}$ ions are formed from these molecules by charge transfer from $[SO_2]^{\bullet-}$, which is an intense matrix ion apparently formed by collisions with the xenon fast atoms. By contrast, **5** and **6a** in TS gave intense *both* positive and negative ion FAB spectra which showed both molecular ion ($[M]^{\bullet-}$ and $[MH^+]$) and fragment-ion information. Clearly, the molecular radical anions are formed by a charge-transfer mechanism similar to that reported by Lloyd and Cotter.[11] The formation of $[MH]^+$ ions is interesting and probably arises by protonation of the organosulfur compound by a matrix species such as $[(CH_2)_4SOH]^+$, which is a dominant fragment ion in the positive ion FAB spectrum of TS. We have encountered many similar instances where TS proved to be the only matrix which would yield spectra of organosulfur compounds. The matrix has excellent solvent properties for many of these molecules. Therefore it would seem that the use of TS as matrix may have some general utility in the structural characterization of labile, apolar organosulfur compounds having appropriate proton and/or electron affinities. Spectra using TS tend to be short-lived, however, owing to relatively high matrix volatility. In an attempt to produce longer lived spectra, pentamethylene sulfone (PS) was used with a view to exploring the possible use of a eutectic TS–PS mixture, or a mixture of PS and another matrix. Unfortunately, PS proved to have a surprisingly high melting point (95–96 °C) and conditions could not be found where a PS–TS mixture would remain liquid under ambient conditions; PS would not dissolve in other commonly used matrices. The use of a TS–PS matrix might nonetheless have merit in systems equipped for mild heating of the FAB target. Similarly, mild target cooling might lengthen spectral duration when TS alone is used.

Experimental Section

Melting points were determined by using a Thomas-Hoover stirred-liquid apparatus and are corrected. Solvents were removed by using a Rotavapor-R and then an oil pump at 0.1 Torr. Eastman Chromagram (catalog no. 13181) or Whatman K6F silica gel 250-μm plates (catalog no. 4861-620) were used for TLC, with visualization by UV or I_2 vapor. Baker 7024 silica gel (40-μm average particle size) was used for flash column chromatography, which was done with gel columns of ca. 17 × 200 mm in size, unless otherwise specified; crude samples were loaded as described previously.[1a] Preparative TLC was performed on Whatman PLK 5F silica gel 1000-μm plates (catalog no. W406). ^1H NMR spectra were recorded on a IBM NR/300 FT NMR (300 MHz) spectrometer in deuteriated solvents; chemical shifts are reported in ppm (δ); solvent peaks were used as standards, e.g. δ 7.24 (s) for $CDCl_3$, 4.63 (s) for D_2O, or 3.3 (quintet) for CD_3OD; our views

(11) Lloyd, J. R.; Cotter, M. L. *Biomed. Mass Spectrom.* **1986**, *13*, 447.

as to assignments are illustrated for the typical products **6a**, **8** (numbering proceeds from S(O) = 1, through S = 2, then around the ring in sequence), **10a**, and **10b**. Mass spectra were obtained on a VG 70-250 GC-MS instrument equipped for electron impact (EI) and fast atom bombardment (FAB) mass spectrometry. EI-MS was carried out in the exact mass mode with the instrument set to a resolving power of 10 000 and scanned at 10 s/decade. Sample introduction was via direct introduction probe. Reported data were obtained by spectral averaging of sequential spectra. Exact masses reported are on the basis of ^{12}C. Funding for the mass spectrometric studies was provided by the NIH, Division of Research Resources Grant RR01688. IR spectra (neat liquids or Nujol mulls for solids) were obtained on a Perkin-Elmer Model 727 spectrometer and are reported in cm^{-1}; strong peaks are indicated as s (others were medium or weak). Elemental analyses were done for **3a** and **9** by Galbraith Laboratories, Knoxville, TN, and the remainder in the Department of Chemistry, Vanderbilt University; samples were dried over P_2O_5 at ca. 25 °C for 18–24 h before submission.

Hydrogen peroxide was a 30% commercial solution, which was used as received (density stated to be 1.110). The following were prepared essentially as reported: **1,4-dihydro-2,3-benzodithiin (1) and 1,5-dihydro-2,3,4-benzotrithiepin (4)** by procedures of Milligan and Swan,[1a,12] with some modifications that improved the yield of **4**;[1a] ***cis*** **(7)** and ***trans*****-4,5-dihydroxy-1,2-dithiane (11)**,[13] with MeOH instead of EtOH for extraction of **7** and **11** because of greater effectiveness and less problem with bumping (**7**, 86% yield, mp 130–132 °C, lit.[13] mp 132 °C; **11**, 81% yield, mp 128–130 °C, lit.[13] mp 132 °C); the *S*-oxides **2** and **5** were obtained from **1** and **4**, respectively.[1a] Pentamethylene sulfone was prepared by oxidizing the sulfide (0.102 g, 1.00 mmol) in AcOH (13 mL) by stirring with $NaBO_3 \cdot 4H_2O$ (0.62 g, 4.03 mmol) for 60 h, removing solvent, and extracting into boiling EtOAc; the filtrate, washed (brine, aqueous $NaHCO_3$, H_2O) and dried ($MgSO_4$), gave 0.070 g (52%), mp 95–96 °C (lit.[14] mp 97–98 °C). Other materials used were commercial, unless otherwise specified.

Oxidation of *cis*-1,2-Dithiane-4,5-diol (7) to 1,2-Dithiane-*t*-4,*t*-5-diol *r*-1-Oxide (8) and 1,2-Dithiane-*c*-4,*c*-5-diol *r*-1-Oxide (9). A solution of H_2O_2 (11.0 mmol, ca. 1.12 mL of 30% solution) in H_2O (10 mL) was added (15 min) to a stirred solution of the cis diol **7** (0.500 g, 3.28 mmol) in MeOH (30 mL) containing H_2WO_4 (0.070 g, 0.28 mmol) as catalyst at 0 °C. After 4 h of stirring, TLC (using 7% MeOH in CH_2Cl_2) first indicated complete disappearance of **7** (and appearance of two new spots of almost equal intensity with very close R_f values below **7**). After filtration through Celite, the filtrate was stirred overnight with a pinch of MnO_2 to decompose the excess of H_2O_2 (negative test with KI–starch paper); *CAUTION*.[15] Excess MnO_2 was removed, and the clear filtrate was concentrated below 35 °C and then was subjected to freeze-drying at 0.1 Torr. Chromatographic separation of the resulting semisolid on a silica gel column (25 × 200 mm) using 3–5% MeOH in CH_2Cl_2 furnished the *t*-4,*t*-5-oxide **8** as fraction I (0.173 g; 31% yield) as a white crystalline solid: mp 156–158 °C; TLC R_f 0.45 (10% MeOH in CH_2Cl_2); IR (Nujol) 3350 s, 1405, 1290, 1270, 1140, 1070 s, 1050 s, 1030 s, 1000 s, 965, 910 s, 900, 865, 810, 710, 670 cm^{-1}; ^1H NMR (D_2O) δ 4.27 (s, br, 1 H at C_5), 4.00–3.97 (2t, J = 11.1 and 2.6 Hz, 1 H at C_4), 3.83–3.78 (dd, J = 14.6 and 2.4 Hz, 1 H) and 3.63–3.55 (m, 1 H) at C_6, 3.29–3.24 (dd, J = 14.6 and 2.3 Hz, 1 H) and 2.76–2.71 (dd, J = 13.7 and 3.2 Hz, 1 H) at C_3; MS(EI), exact mass found 167.9910 (40), $C_4H_8O_3S_2$ requires 167.9915; *m/z* (relative intensity) 134 (49), 132 (13), 120 (30), 119 (30), 108 (28), 106 (8) and 101 (68). Anal. Calcd for $C_4H_8O_3S_2$: C, 28.56; H, 4.79; S; 38.12. Found: C, 28.38; H, 4.81; S, 37.46.

The *c*-4,*c*-5 oxide **9** appeared as fraction II (0.176 g, 32% yield): white crystals, mp 168–169 °C; TLC R_f 0.43 (10% MeOH in CH_2Cl_2); IR (Nujol) 3400–3200 s (br), 1405, 1340, 1225, 1205, 1130, 1085, 1045 s, 1020 s, 980, 905, 810, 715 cm^{-1}; ^1H NMR (D_2O) δ 4.25–4.21 (m, 2 H), 3.74 (d, J = 14.9 Hz, 1 H), 3.31–3.12 (m, 3 H); MS(EI), exact mass found 167.9914, $C_4H_8O_3S_2$ requires 167.9915. Anal. Calcd for $C_4H_8O_3S_2$: C, 28.56; H, 4.79; S, 38.12. Found: C, 28.31; H, 4.82; S, 38.28.

Oxidation of *trans*-1,2-Dithiane-4,5-diol (11) to 1,2-Dithiane-*t*-4,*c*-5-diol *r*-1-Oxide (12) and 1,2-Dithiane-*c*-4,*t*-5-diol *r*-1-Oxide (13). The oxides **12** and **13** were prepared essentially by the procedure used for **8** and **9** from **7**, except that stirring was done for 6 h. From 1.00 g (6.57 mmol) of the trans diol **11**, 2.23 mL of 30% H_2O_2 (21.8 mmol), and 0.14 g (0.56 mmol) of H_2WO_4 in 3:1 MeOH–H_2O (80 mL) after usual workup (*CAUTION*)[15] and separation of the crude semisolid on a silica gel column 40 × 200 mm) using 3–5% MeOH in CH_2Cl_2, the *t*-4,*c*-5 oxide **12** was obtained as fraction I in a yield of 0.311 g (28%): mp 135–137.5 °C; TLC R_f 0.49 (7% MeOH in CH_2Cl_2); IR (Nujol) 3400–3150 s (br), 1410, 1390, 1340, 1260, 1160, 1130, 1065 s, 1020 s, 950, 900, 885, 820, 780, 745, 720 cm^{-1}; ^1H NMR (D_2O) δ 4.01–3.99 (m, 2 H), 3.86 (d, J = 15 Hz, 1 H), 3.31 (d, J = 3 Hz, 2 H), 2.85–2.80 (dd, J = 3.8 Hz, 1 H); MS(EI), exact mass found 167.9915, $C_4H_8O_3S_2$ requires 167.9915. Anal. Calcd for $C_4H_8O_3S_2$: C, 28.56; H, 4.79; S, 38.12. Found: C, 27.99; H, 4.73; S, 38.59.

The *c*-4,*t*-5 oxide **13** was obtained as fraction II (0.330 g, 30% yield): mp 147–149 °C; TLC R_f 0.41 (7% MeOH in CH_2Cl_2); IR (Nujol) 3430, 3300 s, 1415, 1375 s, 1320, 1275, 1230, 1215, 1180, 1130, 1085, 1050 s, 990 s, 865, 740, 715 cm^{-1}; ^1H NMR (D_2O) δ 4.14–4.05 (m, 1 H), 3.86–3.78 (m, 1 H), 3.68–3.64 (dd, J = 3.7 Hz, 1 H), 3.39–3.34 (dd, J = 11 Hz, 1 H), 3.14–3.04 (m, 2 H); MS(EI), exact mass found 167.9925, $C_4H_8O_3S_2$ requires 167.9915. Anal. Calcd for $C_4H_8O_3S_2$: C, 28.56; H, 4.79; S, 38.12, Found: C, 28.11; H, 4.92; S, 38.00.

General Procedure for the Preparation of 3ab and 6ab. In a typical experiment, a methanolic solution (ca. 5 mL of MeOH/mmol) of two molar proportions of *p*-toluenethiol (**15**) or 3-mercapto-1,2-propanediol (**16**) was added (10 min) to the stirred methanolic solution of the monooxide **2** or **5** (ca. 20 mL of MeOH/mmol) at 0–5 °C in the dark under Ar. After a stirring period of 40–60 min more at 25 °C, solvent was removed and the crude product was chromatographed on a silica gel column with 5–7% CH_2Cl_2 in hexane (for **3a** and **6a**) or 5% MeOH in CH_2Cl_2 (for **3b** and **6b**) as eluant. Variations and details were as follows.

1,2-Bis[(*p*-tolyldithio)methyl]benzene (3a). Reaction of 0.100 g (0.54 mmol) of the monooxide **2** and 0.135 g (1.09 mmol) of **15** yielded 0.098 g (44%) of **3a** as slightly yellow viscous liquid: TLC R_f 0.45 (10% CH_2Cl_2 in hexane); the IR and ^1H NMR spectra were identical with those of **3a** obtained previously.[1a]

1,2-Bis[[(2,3-dihydroxypropyl)dithio]methyl]benzene (3b). 3-Mercapto-1,2-propanediol (**16**; 0.117 g, 1.08 mmol) and **2** (0.100 g, 0.54 mmol) gave 0.010 g (5% yield) of **3b** as a semisolid: TLC R_f 0.38 (10% MeOH in CH_2Cl_2). The IR and NMR spectra were identical with those of authentic **3b**.[1a]

1-[(*p*-Tolyldithio)methyl]-2-[(*p*-tolyltrithio)methyl]benzene (6a). The general procedure gave with **15** (0.362 g, 2.91 mmol) and the trisulfide monooxide **5** (0.300 g, 1.39 mmol), 0.280 g (45% yield) of **6a** as oil: TLC R_f 0.48 (10% CH_2Cl_2 in hexane): IR (neat) 3100–2925, 1600, 1490 s, 1450, 1305, 1185, 1020, 805 s, 765, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51–7.07 (m, 12 H, Ar), 4.08 (d, J = 10 Hz, 2 H, CH_aH_b), 4.05 (d, J = 10 Hz, 2 H, CH_aH_b), 2.34 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3).

Because **6a** was found to be unstable under ambient conditions, elemental analysis was not feasible. Since a single spot in TLC suggested the presence of a single compound, the TLC spot was extracted and examined immediately by using the "soft" ionization technique of FAB-MS. The positive ion FAB mass spectrum obtained by using tetramethylene sulfone as matrix showed all major peaks consistent with the structure **6a**. These included (*m/z*, relative intensity) 447 (0.2) (MH^+?), 355 (2.5) (M – C_7H_7), 323 (5) (355 – S), 291 (25) (323 – S), 278 (2) ($C_{14}H_{14}S_3$), 259 (30) (291 – S), 246 (6) (M – $CH_2S_3C_7H_7$ + H), 167 (36) ($C_8H_7S_2$), 155 (20) ($C_7H_7S_2$), 135 (100) (C_8H_7S), 123 (15) (C_7H_7S), 104 (7) (C_8H_8), and 91 (18) (C_7H_7).

Sulfur Abstraction from 6a To Give 3a. In accordance with a procedure of Harpp et al.,[16] a solution of triphenylphosphine (0.029 g, 0.11 mmol) in benzene (2 mL) was added during 5 min to the stirred solution of **6a** (0.045 g, 0.10 mmol) in benzene (3 mL) at 25 °C. Stirring was continued for 30 min until TLC (10%

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CH_2Cl_2 in hexane) showed no spot for Ph_3P at R_f 0.54, along with the appearance of a new spot near the origin (R_f 0.04); the R_f values of **6a** and **3a** were too close to provide useful guides to completion of the reaction. Removal of solvent and preparative TLC gave 0.010 g (24% yield) of **3a** (R_f, IR, and NMR spectra identical with those of authentic **3a**),[1a] together with 0.024 g (82% yield) of triphenylphosphine sulfide (mp 159–161.5 °C; lit.[16] mp 159–162 °C).

1-[[(2,3-Dihydroxypropyl)dithio]methyl]-2-[[(2,3-dihydroxypropyl)trithio]methyl]benzene (6b). The general method gave 0.019 g (8%) of **6b**, from **5** (0.117 g, 0.54 mmol) and **16** (0.117 g, 1.08 mmol), as thick oil: TLC R_f 0.36 (10% MeOH in CH_2Cl_2; the single spot when removed and rechromatographed gave three spots). By the time the ^1H NMR spectrum could be obtained, it showed the material to be almost entirely **3b**, with quite small reasonably placed peaks attributed to **6b**. The disulfide **6b** thus was much less stable than the tolyl derivative **6a**, and attempts to purify it by TLC led only to loss of sulfur and disproportionation.

***erythro*-1,4-Bis(*p*-tolyldithio)-2,3-butanediol (10a). (a) From the *c*-4,*c*-5-Diol *r*-1-Oxide 9.** A solution of *p*-toluenethiol (**15**, 0.066 g, 0.53 mmol) in MeOH (2 mL) was added (5 min) to the stirred solution of **9** (0.035 g, 0.21 mmol) in MeOH (2 mL) under Ar in the dark at 15 °C. After 25 min, TLC (5% MeOH–CH_2Cl_2) showed a new spot and no **9**. Removal of MeOH and chromatography on a silica gel column using 100% CH_2Cl_2 as eluant gave 0.067 g (80%) of **10a** as a white crystalline solid: mp 91–93 °C; TLC R_f 0.50 (1.5% MeOH in CH_2Cl_2); IR (Nujol) 3350–3275 s, 1600, 1490 s, 1300, 1120, 1090, 1060 s, 1025, 1015, 1000, 900, 850, 800 s, 755, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41 (d, J = 8.1 Hz, 4 H, Ar), 7.12 (d, J = 8.1 Hz, 4 H, Ar), 3.94–3.86 (m, 2 H, CH), 3.02–2.97 (dd, J = 13.9 and 3.7 Hz, 2 H), and 2.77–2.74 (dd, J = 13.9 and 8.5 Hz, 2 H) CH_2, 2.41 (d, J = 3.6 Hz, 2 H, OH), 2.32 (s, 6 H, CH_3); MS(EI), exact mass found 398.0479 (0.2), $C_{18}H_{22}O_2S_4$ requires 398.0503; 275.0231 (91) (M – C_7H_7S requires 275.0234) and 246.0547 (100) ($C_{14}H_{14}S_2$ requires 246.0537). Anal. Calcd for $C_{18}H_{22}O_2S_4$: C, 54.24; H, 5.56; S, 32.17. Found: C, 53.87; H, 5.62; S, 32.58.

(b) From the *t*-4,*t*-5-Diol *r*-1-Oxide 8. The procedure for **10a** used with monooxide **8** (0.076 g, 0.45 mmol) and thiol **15** (0.140 g, 1.13 mmol) furnished 0.145 g (81%) of **10a**: mp and mmp 91–93 °C; the R_f, IR, and NMR data were identical with those of **10a** obtained from **9**.

***threo*-1,4-Bis(*p*-tolyldithio)-2,3-butanediol (14a). (a) From the *t*-4,*c*-5-Diol *r*-1-Oxide 12.** The procedure for **10a** used with monooxide **12** (0.040 g, 0.24 mmol) and thiol **15** (0.060 g, 0.48 mmol) gave 0.064 g (67% yield) of **14a** as a white crystalline solid: mp 103–105 °C; TLC R_f 0.75 (5% MeOH in CH_2Cl_2); IR (Nujol) 3350 s (br), 1600, 1490 s, 1400, 1300, 1275, 1160, 1110, 1090 s, 1050, 1015, 915, 890, 850, 835, 810, 800 s, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41, (d, J = 8.1 Hz, 4 H, Ar), 7.11 (d, J = 8.1 Hz, 4 H, Ar), 3.90–3.83 (m, 2 H), 2.87–2.85 (dd, J = 3.4 Hz, 4 H), 2.35 (d, J = 6.0 Hz, 2 H), 2.31 (s, 6 H); MS(EI), exact masses found were similar to those of **10a** above; exact masses found m/z (relative intensity), mmu error were 275 (85), 0.2 and 246 (100), 1.1. Anal. Calcd for $C_{18}H_{22}O_2S_4$: C, 54.24; H, 5.56; S, 32.17. Found: C, 54.20; H, 5.64; S, 32.23.

(b) From the *c*-4,*t*-5-Diol *r*-1-Oxide 13. From monooxide **13** (0.400 g, 2.38 mmol) and thiol **15** (0.739 g, 5.95 mmol), 0.750 g (79% yield) of **14a** was obtained: mp and mmp 103–105 °C; R_f, IR, and NMR data were identical with those of **14a** from **12**.

***erythro*-1,4-Bis[(2,3-dihydroxypropyl)dithio]-2,3-butanediol (10b). (a) From the *c*-4,*c*-5-Diol *r*-1-Oxide 9.** Essentially as described for **10a**, except for 1 h of stirring, **9** (0.040 g, 0.24 mmol) and 3-mercapto-1,2-propanediol (**16**; 0.052 g, 0.48 mmol) gave 0.064 g (73% yield) of **10b** after chromatographic separation on a silica gel column with 7–10% MeOH in CH_2Cl_2, as white crystalline solid: mp 71–73 °C; TLC R_f 0.30 (15% MeOH in CH_2Cl_2); IR (Nujol) 3300 s (br), 1400, 1320, 1220, 1130, 1100 s, 1070 s, 1050 s, 1020 s, 970, 925, 905, 880, 850 cm^{-1}; ^1H NMR (D_2O) δ 3.92–3.77 (m, 4 H, CH), 3.58–3.54 (dd, J = 15.8 and 4.1 Hz, 2 H) and 3.47–3.43 (dd, J = 11.8 and 6.1 Hz, 2 H) terminal CH_2 of side chain, 3.01–2.82 (4 t, 4 H, CH_2 of center), 2.74–2.59 (m, 4 H, $SSCH_2$ of side chain) (the solution was unchanged after 10 days); MS(EI), exact mass found 273.9834 (2.6), $C_7H_{14}O_3S_4$ (M – $C_3H_6O_2$ – H_2O) requires 273.9826; 214.0334 (37), $C_6H_{14}O_4S_2$ requires 214.0334; 165.0045 (100), $C_5H_9O_2S_2$ requires 165.0044; 151.9966 (60), $C_4H_8O_2S_2$ requires 151.9966; and 107.9694 (68), $C_2H_4OS_2$ requires 107.9703. Anal. Calcd for $C_{10}H_{22}O_6S_4$: C, 32.77; H, 6.05; S, 34.99. Found: C, 32.52; H, 6.12; S, 34.87.

(b) From the *t*-4,*t*-5-Diol *r*-1-Oxide 8. The procedure for **10b** from **9** gave 0.102 g (77%) of **10b** from **8** (0.061 g, 0.36 mmol) and the thiol **16** (0.078 g, 0.72 mmol): mp 71–73 °C; the R_f, IR, and NMR data of **10b** were identical with those of authentic **10b**.

***threo*-1,4-Bis[(2,3-dihydroxypropyl)dithio]-2,3-butanediol (14b). (a) From the *t*-4,*c*-5-Diol *r*-1-Oxide 12.** The procedure for **10b** with monooxide **12** (0.071 g, 0.42 mmol) and thiol **16** (0.091 g, 0.84 mmol) afforded 0.107 g (69%) of **14b** as white solid: mp 108–110 °C; TLC R_f 0.30 (15% MeOH in CH_2Cl_2); IR (Nujol) 3275 s (br), 1415, 1400, 1330, 1245, 1155, 1085 s, 1030 s, 935, 910, 885, 870, 850, 815 cm^{-1}; ^1H NMR (D_2O) δ 3.93–3.81 (m, br, 4 H), 3.56–3.43 (4 d, 8 lines, 4 H), 2.93–2.82 (3 d, 6 lines, 4 H), 2.81–2.61 (sharp m, 10 lines, 4 H) (the solution was unchanged after 10 days); MS(EI) similar to **10b**; exact masses found m/z (relative intensity), mmu error were 214 (61), 0.0; 165 (10), 0.5; 152 (100), 0.2 and 108 (61), 0.2. Anal. Calcd for $C_{10}H_{22}O_6S_4$: C, 32.77; H, 6.05; S, 34.99. Found: C, 32.37; H, 6.07; S, 34.47.

(b) From the *c*-4,*t*-5-Diol *r*-1-Oxide 13. The procedure for **10b** with 0.051 g (0.30 mmol) of **13** and 0.065 g (0.60 mmol) of thiol **16** furnished 0.078 g (71% yield) of **14b**: mp 108–110 °C; the R_f, IR and NMR data were identical with those of **14b** from **12**.

Notes

Laser-Driven Thermolysis of Spirohexane

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There is continuing research interest in chemistry of strained organic molecules.[2-4] Spiropentanes are, however, the only members of spiroalkanes whose thermal behavior has been studied thus far.[5-7] Although the thermolysis of three-membered rings is expected[2] to yield ethylene and carbenes, both cyclopropane[8] and spiropentane[5-7] deriva-

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