Preparation and Properties of Monosulfoxides of Dithioethers

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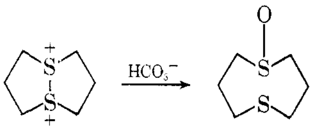
A study of the synthesis and properties of a series of acyclic and mesocyclic monosulfoxides of dithioethers with various oxidizing agents (MCPA, $NaIO_4$, Me_2SO) is reported. The results of this study are compared with monosulfoxide formation by the hydrolysis of dithioether dications. ^{13}C and ^1H NMR are used to identify the monosulfoxides. ^{13}C NMR is especially useful in confirming the structure of 2,5-dithiahexane monosulfoxide, where the ^1H NMR spectrum in $CDCl_3$ shows three singlets. Although $NaIO_4$ is the reagent of choice, small amounts of the disulfoxide (3–4%) are always present even though 1 equiv of oxidizing agent is used. Likewise with MCPA small amounts of disulfoxides are always present, and in certain compounds (1,4-dithiacycloheptane, 2,4-dithiahexane, and 2,7-dithiaoctane) the disulfoxide is formed in 25% yield. The influence of the S–O dipole on the reactivity of the remaining thioether group is discussed.

We recently reported that dithioether dications react with aqueous bicarbonate to give high yields of monosulfoxides, uncontaminated by sulfones and disulfoxides.[1] To confirm the identity of these monosulfoxides, we felt that it was necessary to synthesize authentic samples of monosulfoxides of dithioethers by another route. However, there were no established procedures in the literature for preparing these monosulfoxides, so a study of this reaction was initiated. The names and abbreviations of the dithioethers are as follows: 1,4-dithiane (1,4-DT); 1,4-dithiacycloheptane (1,4-DTCH); 1,5-dithiacyclooctane (1,5-DTCO); 1,5-dithiacyclononane (1,5-DTCN); 1,6-dithiacyclodecane (1,6-DTCD); 2,5-dithiahexane (2,5-DTH); 2,6-dithiaheptane (2,6-DTHP); and 2,7-dithiaoctane (2,7-DTO).



Background. In devising methods for the preparation of sulfoxides, the usual problem is overoxidation to sulfones. Several methods for the preparation of sulfoxides which have been used successfully include hydrogen peroxide in acetic acid in the presence of a catalytic amount of strong acid,[2] sodium periodate,[3] *m*-chloroperbenzoic acid, and oxygen exchange with dimethyl sulfoxide.[4] However, in the oxidation of dithioethers to monosulfoxides, not only overoxidation to sulfone but also formation of disulfoxide must be avoided. Attempts to oxidize dithioethers to monosulfoxides often result in the formation of one or both of the isomeric disulfoxides even though 1 equiv of oxidizing agent is used. An example of this problem is found in the oxidation of 1,4-dithiane with hydrogen peroxide. Although 1,4-dithiane 1-oxide would be expected in the reaction, only 1,4-dithiane and 1,4-dithiane 1,4-dioxide were detected in equal amounts.[5] 1,4-Dithiane 1-oxide can be prepared by treatment of 1,4-dithiane with 0.5 equiv of hydrogen peroxide.[6]

Even though hydrogen peroxide can cause difficulties, this reagent is still used extensively in the oxidation of dithioethers. Ogura and Tsuchihashi oxidized 2,4-dithiapentane and its derivatives using from 1 to 3 equiv of hydrogen peroxide and only reported monosulfoxide formation.[7] However, these dithioethers are thioacetals and may behave quite differently from the dithioethers under investigation. 3,6-Dithiaoctane was oxidized to the disulfoxide using slightly more than 2 equiv of hydrogen peroxide. The monosulfoxide of 3,6-dithiaoctane had to be synthesized in an unusual manner. Ethyl 2-chloroethyl sulfide was oxidized with hydrogen peroxide to make the sulfoxide, which was then treated with sodium ethanethiolate. No attempt was made to oxidize 3,6-dithiaoctane directly to the monosulfoxide.[8]

Sodium periodate has become well known as the reagent of choice to oxidize monothioethers to sulfoxides.[3] Isolated yields greater than 90% are reported. The disulfoxides of 2,4-dithiapentane and 2,5-dithiahexane have been synthesized using 2 equiv of sodium periodate. Louw and co-workers reported the synthesis of 2,5-dithiahexane 2-oxide using sodium periodate, but no synthetic details or physical properties were given.[9] Apparently, disulfoxide was also formed in the reaction, and, as expected, the monosulfoxide was hard to separate from the disulfoxide. In 1968, Kleinar prepared 1,5-dithiacyclooctane 1-oxide and 2,6-dithiaheptane 2-oxide using sodium periodate, but this research has not been published.[10]

The only study of the electronic effects which lead to sulfoxide formation in a system with two interacting thioether groups was carried out on substituted 1,3-dithianes.[11] In 1,3-dithiane, where the two sulfur atoms are separated by only one methylene group, there is a strong interaction between the two sulfur atoms. The lone pair orbitals can combine to give filled bonding and antibonding orbitals. The filled σ^* orbital possesses electron density localized away from the sulfur atoms and interacts with electrophilic oxidizing agents. This interaction leads to the formation of a sulfoxide which contains an equatorial oxygen. In the reaction of 4,6-dimethyl-1,3-dithiane with hydrogen peroxide, a nucleophilic attack on the peroxide oxygen by the thioether gives the monosulfoxide(s) having equatorial oxygen to axial oxygen in a ratio of 98:2.[11]

Although the mechanism for the oxidation by sodium periodate is unknown,[12] it has been proposed to proceed via a cyclic intermediate.[13] Due to the proximity of the two sulfur atoms in 1,3-dithiane, the lone pair on the thioether is polarized toward the positively charged sulfur in the periodate complex. In the oxidation of 2-*tert*-butyl-1,3-dithiane with sodium periodate, the monosulfoxide with equatorial oxygen was found to be the most favored product of kinetic control by a ratio of 90:10 and of thermodynamic control by 70:30.[14]

m-Chloroperbenzoic acid (MCPA) is also used to oxidize thioethers to sulfoxides. When thiiranes were oxidized with MCPA,[15] higher yields and purer sulfoxides were obtained than when either sodium periodate[16] or hydrogen peroxide[17] was used.

Another method for making disulfoxides from dithioethers involves oxygen exchange with dimethyl sulfoxide (Me_2SO). Since a large excess of Me_2SO must be used in the reaction, it is not possible to synthesize monosulfoxides of dithioethers by this method.[4]

Results and Discussion

When this study began, there were no detailed procedures in the literature for the synthesis of monosulfoxides of di-

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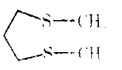
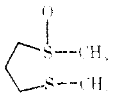
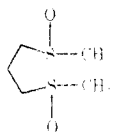
Table I. ¹H NMR Data for 2,6-Dithiaheptane, 2,6-Dithiaheptane 2-Oxide, and 2,6-Dithiaheptane 2,6-Dioxide[a,b]

	2.3 (m, 4, -CH_2-S) 1.8 (s, 6, CH_3-S) 1.6 (m, 2, -CH_2-)
	2.6 (m, 2, -CH_2-SO) 2.4 (m, 2, -CH_2-S) 2.3 (s, 3, CH_3-SO) 1.8 (s, 3, CH_3-S) 1.8 (m, 2, -CH_2-)
	2.6 (m, 4, -CH_2-SO) 2.3 (s, 6, CH_3-SO) 2.0 (m, 2, -CH_2-)

[a] Spectra were obtained in $CDCl_3$. [b] In parts per million (δ) relative to Me_4Si (multiplicity, number of hydrogens, assignment).

thioethers. In our laboratory, Gorewit synthesized 1,5-dithiacyclooctane 1-oxide in a straightforward reaction by combining equal molar amounts of 1,5-dithiacyclooctane and MCPA.[18] The products consisted of 89% 1,5-dithiacyclooctane 1-oxide and 3% 1,5-dithiacyclooctane 1,5-dioxide.

Since 1,5-dithiacyclooctane 1-oxide had been synthesized in good yield using 1 equiv of MCPA, no problems were anticipated in the synthesis of other monosulfoxides. However, when 1,4-dithiacycloheptane was treated with MCPA under the same conditions, only unreacted 1,4-dithiacycloheptane and small amounts of several other products, apparently the isomeric disulfoxides, were found in the reaction mixture. Thus, it appears that 1,4-dithiacycloheptane 1-oxide is oxidized more rapidly than the dithioether itself.

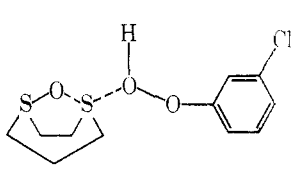
Because of this difficulty with MCPA, the oxidation of 1,4-dithiacycloheptane was carried out using 1 equiv of $NaIO_4$. With this reagent, a 58% yield of the monosulfoxide was obtained with only a small amount (~4%) of the disulfoxide.

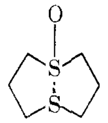
In all of the reactions using either sodium periodate or MCPA as the oxidizing agent, at least 2–4% of the disulfoxide is always formed in addition to the desired monosulfoxide. In several of the oxidations with MCPA (1,4-dithiacycloheptane, 2,5-dithiahexane, 2,7-dithiaoctane), a larger amount, approximately 25%, of the disulfoxide and an equal amount of unreacted dithioether are obtained along with the monosulfoxide. Therefore, of the literature procedures, sodium periodate is the reagent of choice. However, monosulfoxides of the dithioethers are obtained by hydrolysis of the dithioether dications[1] in high yield and free from *all* traces of disulfoxide.

A comparison of the reactivity of the various dithioethers with MCPA shows that little disulfoxide is formed when a trimethylene chain spans the two sulfur atoms. However, except for 1,4-dithiane, an appreciable amount of disulfoxide always forms when two or four methylene groups separate the two sulfur atoms. These observations can be explained by a consideration of the structure of the monosulfoxides and the transition state leading to disulfoxide formation.

The mechanism of the oxidation of thioethers by MCPA involves a nucleophilic attack on the peroxide oxygen by the thioether.[20] Little steric effect should be observed in this reaction, and the charge distribution in the activated complex depends on the polarization of the thioether lone pair by the electrophile. Thus, in the oxidation of a monosulfoxide to a disulfoxide the relative orientation of the polar S–O group of the sulfoxide with respect to the thioether group will influence the course of the reaction.

If the S–O dipole of the sulfoxide can be aligned with the forming S–O dipole in the activated complex, disulfoxide formation would be more favorable than monosulfoxide formation. This interaction should be most important when a five-membered ring can form, and it would account for the high yield of disulfoxide formation in 1,4-dithiacycloheptane and 2,5-dithiahexane. However, in cases where three methylene groups separate the thioether from the sulfoxide groups, a *sulfur–sulfur* interaction in the ground state reduces the nucleophilicity of the thioether group and prevents disulfoxide formation. This interaction would account for dominant monosulfoxide formation in 1,5-dithiacyclooctane, 1,5-dithiacyclononane, and 2,6-dithiaheptane.





In cases where more than three methylenes separate the thioether and sulfoxide groups, such as in 2,7-dithiooctane, the groups should function independently and disulfoxide formation should compete favorably with monosulfoxide formation. 1,4-Dithiane is a special case where through-bond rather than through-space interactions occur. In this situation the nucleophilicity of the free thioether group is reduced in the monosulfoxide, and disulfoxide formation becomes unfavorable.

NMR Spectra of Monosulfoxides. In an acyclic monosulfoxide the NMR spectrum was expected to look like a combination of the spectrum of the dithioether and the disulfoxide, and perhaps the spectrum of the monosulfoxide would be difficult to distinguish from a mixture of dithioether and disulfoxide. To test this potential problem, an equal molar amount of 2,6-dithiaheptane and 2,6-dithiaheptane 2,6-dioxide was mixed, and the NMR spectrum was compared to that of authentic 2,6-dithiaheptane 1-oxide.

In 2,6-dithiaheptane the methyl group is a singlet at δ 1.8, whereas in 2,6-dithiaheptane 2,6-dioxide the methyl group is shifted downfield to δ 2.3. Since the monosulfoxide has one methyl group α to a thioether and the other methyl group α to a sulfoxide, its NMR spectrum shows two methyl singlets, which are in the same locations as those of 2,6-dithiaheptane and 2,6-dithiaheptane 2,6-dioxide. The main difference between the spectrum of 2,6-dithiaheptane 2-oxide and the spectrum of an equal molar mixture of 2,6-dithiaheptane and 2,6-dithiaheptane 2,6-dioxide occurs in the α methylene region. In the mixture, the resonance due to the α methylenes of 2,6-dithiaheptane 2,6-dioxide occurs at δ 2.6 and is a triplet. The triplet due to the α methylenes of 2,6-dithiaheptane is at δ 2.3 and is partly overlapped by the methyl singlet of the disulfoxide. The monosulfoxide has peaks between δ 2.3 and 2.7 as well; however, they form a complex multiplet which is quite distinct from the peaks of the mixture. Hence, a comparison of the NMR spectrum in the δ 2.3–2.7 region indicates whether the monosulfoxide or a mixture containing dithioether and disulfoxide is present (Table I). The spectra of 2,7-dithiaoctane and its mono- and disulfoxides are similar to those of 2,6-dithiaheptane and its sulfoxides, except that the additional β methylene group in the 2,7-dithiaoctane compounds increases the intensity in that δ region. However, the region in the NMR due to the β methylene is not as indicative of whether a monosulfoxide or a mixture is present.

The NMR spectra of all monosulfoxides, except 2,5-dithiahexane 2-oxide, were as expected. The spectrum of 2,5-dithiahexane 2-oxide in deuterated chloroform has three singlets

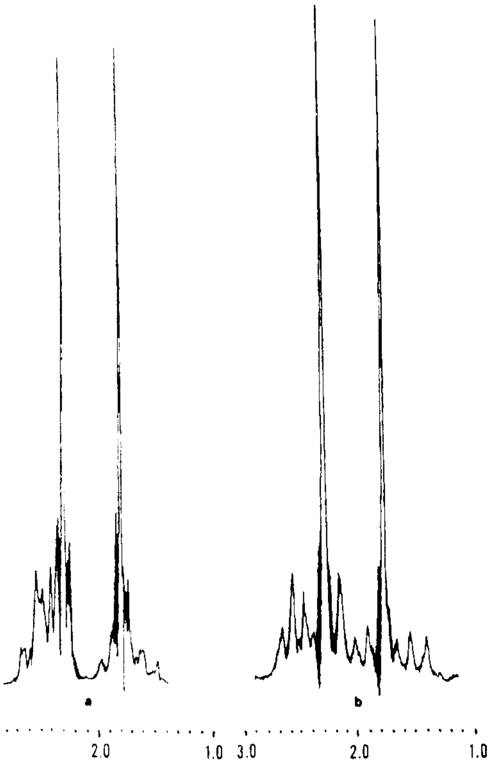


Figure 1. ^{1}H NMR spectra of (a) 2,6-dithiaheptane monosulfoxide and (b) an equal molar mixture of 2,6-dithiaheptane and 2,6-dithiaheptane disulfoxide.

at δ 2.9, 2.6, and 2.1 which integrate to 4:3:3. It appears that the methylene protons α to the sulfoxide and those α to the thioether coincidentally occur at the same frequency. When the NMR spectrum of 2,5-dithiahexane 2-oxide is obtained in deuterium oxide, the singlet at δ 2.9 is split into multiplets because the methylene protons α to the sulfoxide shift downfield slightly. The ^{13}C NMR spectrum of 2,5-dithiahexane 2-oxide in deuterated chloroform shows four different carbons. Off-resonance decoupling identifies the carbon at 25.6 ppm as the methylene α to the thioether and the carbon at 52.8 ppm as the methylene α to the sulfoxide. Both methylenes have hydrogen absorptions at δ 2.9, as shown in Table II.

Summary

The synthesis of monosulfoxides of dithioethers using *m*-chloroperbenzoic acid and sodium periodate results in variable yields of monosulfoxide which are always contaminated by at least small amounts of disulfoxides. With MCPA, often a large fraction of the product is the disulfoxide. Oxygen exchange between dithioethers and Me$_2$SO would seem to be the favored method for synthesis of disulfoxides.

It appears that the best method for synthesizing pure monosulfoxides of dithioethers involves treatment of the dithioether dications with water. The monosulfoxides are formed in greater than 70% yield, and no disulfoxides or sulfones can be impurities. The major limitation of the method is that the dithioether dications must have the two dicationic sulfur atoms in close proximity to one another so that one group influences the other. When the two positively charged atoms are isolated from one another, a mixture of dithioether, monosulfoxide, and disulfoxide would be expected.

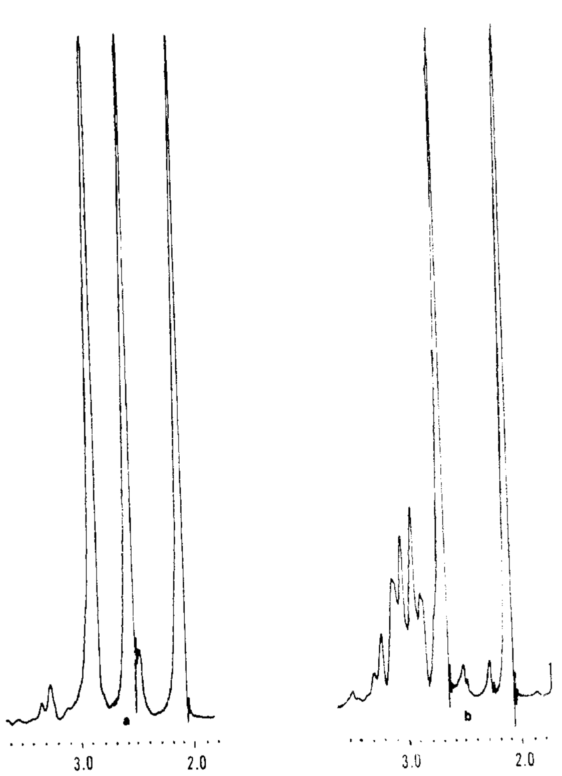
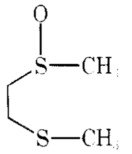


Figure 2. ^{1}H NMR spectra of 2,5-dithiahexane monosulfoxide (a) in deuterated chloroform and (b) in deuterium oxide.

Table II. ^{13}C and ^{1}H NMR Data for 2,5-Dithiahexane 2-Oxide[a]



^{13}C NMR, δ	assignment	^{1}H NMR, δ
52.8	CH$_2$ α to S–O	2.9
37.4	CH$_3$ α to S–O	2.6
25.4	CH$_2$ α to S	2.9
14.6	CH$_3$ α to S	2.1

[a] Spectrum was taken in CDCl$_3$; in parts per million (δ) relative to Me$_4$Si.

Experimental Section

Physical Measurements. Melting points are uncorrected and were determined on a Thomas-Hoover Unimelt. ^{1}H NMR spectra were measured on a Varian Model EM-360 spectrometer; ^{13}C NMR spectra were measured at 25.14 MHz on a Nicolet TT-23 spectrometer. Ultraviolet and visible spectra were determined on a Cary-17 recording spectrometer. Infrared spectra were measured on a Beckman IR8 or IR12 infrared spectrometer. Gas chromatograms were obtained on a Varian Aerograph Model 90-P chromatograph. Thin-layer chromatograms were run on Eastman Kodak silica gel TLC plates or Merck silica gel TLC plates. Column chromatography was run on Merck silica gel. Microanalyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley, Calif.

One analytical procedure is described for a typical synthesis of a monosulfoxide of a dithioether. The yield and experimental data for other monosulfoxides prepared by the same procedure are then listed.

Use of MCPA. The sulfoxides were synthesized by a modification of the procedure of Kondo.[15] To a rapidly stirring solution of 2.63 g (17.7 mmol) of 1,5-dithiacyclooctane in 100 mL of chloroform maintained at −20 °C under nitrogen was added 3.59 g (17.7 mmol) of 85% *m*-chloroperbenzoic acid in 90 mL of chloroform over 30 min. The solution was stirred for 30 min longer at −20 °C and then allowed to warm to room temperature over 45 min. Anhydrous ammonia was bubbled into the reaction mixture. Immediately the mixture became cloudy and ammonium *m*-chlorobenzoate precipitated. The mixture was filtered through a bed of Celite and treated once more with ammonia. The filtrate was concentrated to a yellow oil under vacuum. The oil was dissolved in 1:1 ethanol–ether and cooled overnight. Filtration of the white crystals gave 66.2 mg (2%) of **1,5-dithiacyclooctane 1,5-dioxide:** mp 150–151 °C; IR (CH_2Cl_2) 1020 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 3.33 (m, 8, $-CH_2S{=}O$), 2.60 (m, 4, $-CH_2-$).

The remaining oil was dissolved in ether–dichloromethane (5:1) and cooled overnight. The flask containing the crystals and supernatant liquid was placed in liquid nitrogen and transferred to a drybox. The crystals were filtered rapidly and then dried under vacuum to give 1.78 g (62%) of very hygroscopic **1,5-dithiacyclooctane 1-oxide:** mp 27–29 °C; IR (CH_2Cl_2) 1010 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 3.12 (m, 4, $CH_2S{=}O$), 2.64 (m, 4, CH_2S), 2.29 (m, 4, $-CH_2-$); ^{13}C NMR ($CDCl_3$) δ 56.6, 30.2, 23.7; mass spectrum (70 eV), *m/e* (relative intensity) 164 (10), 148 (40), 106 (78), 45 (100). Precise mass for $C_6H_{12}S_2O$: found, 164.0357 and 164.0327.[18]

2,6-Dithiaheptane 2-Oxide: 2.95 g (96%);[23] IR (CH_2Cl_2) 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.6 (m, 2, $-CH_2SO$), 2.4 (m, 2, CH_2S), 2.3 (s, 3, CH_3SO), 1.8 (s, 3, CH_3S), 1.8 (m, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 54.2, 37.8, 32.1, 21.0, 14.3; mass spectrum (70 eV), *m/e* (relative intensity) 136 (83), 121 (82), 73 (79), 61 (100), 45 (87). Anal. Calcd for $C_5H_{12}OS_2$: C, 39.44; H, 7.94. Found: C, 39.43; H, 7.83.

1,4-Dithiane 1-Oxide: 0.55 g (68%); mp 119–122 °C (lit.[16] mp 125 °C); IR (Nujol) 1050 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 2.1–3.7 (m, 8); mass spectrum (70 eV), *m/e* (relative intensity) 120 (100), 84 (95), 61 (76), 46 (71).

1,5-Dithiacyclononane 1-Oxide: 0.40 g (83%); mp 65–70 °C; IR (Nujol) 1010 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 3.2 (m, 4, $-CH_2SO$), 2.7 (m, 4, $-CH_2S$), 2.0 (m, 6, $-CH_2-$); ^{13}C NMR ($CDCl_3$) δ 47.8, 46.5, 31.8, 29.4, 26.5, 19.3, 17.4; mass spectrum (70 eV), *m/e* (relative intensity) 162 (53), 161 (21), 120 (31), 88 (60), 87 (93), 55 (100). Anal. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91. Found: C, 46.92; H, 7.66.

1,4-Dithiacycloheptane 1,4-Dioxide: 38.2 mg;[24,25] mp 143–145 °C; IR (Nujol) 1040 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 3.3 (broad s, 4, CH_2SO), 2.5 (m, 2, CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 138 (39), 89 (88), 76 (65), 63 (74), 45 (69), 41 (100). Anal. Calcd for $C_5H_{10}O_2S_2$: C, 36.12; H, 6.06. Found: C, 36.10; H, 6.05.

2,7-Dithiaoctane 2-Oxide: 1.50 g (23%);[24] IR (neat) 1020 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 2.3–2.8 (m, 4, CH_2S and CH_2SO), 2.4 (s, 3, CH_3SO), 2.0 (s, 3, CH_3S), 1.7 (m, 4, CH_2); ^{13}C NMR ($CDCl_3$) δ 52.6, 37.2, 32.4, 26.9, 20.5, 14.2; mass spectrum (70 eV), *m/e* (relative intensity) 166 (12), 150 (10), 103 (30), 61 (82), 55 (100). Anal. Calcd for $C_6H_{14}OS_2$: C, 43.33; H, 8.49. Found: C, 43.44; H, 8.28.

2,5-Dithiahexane 2,5-Dioxide: 0.42 g (25%); α mp 169–171 °C (lit. mp 169–170[4] and 163–164 °C[19]); α and β mmp 136–142 °C (lit.[21] 128–130 °C); IR (Nujol) 1040 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 3.1 (m, 4, CH_2SO), 2.6 (s, 6, CH_3SO); mass spectrum (70 eV), *m/e* (relative intensity) 139 (8), 126 (5), 91 (50), 64 (35), 63 (100).

Use of Sodium Periodate. Sulfoxides were synthesized by a modification of the procedure of Leonard and Johnson[3] and Carlson and Helquist.[22] To a solution of 1.20 g (10.0 mmol) of 2,5-dithiahexane in 125 mL of methyl alcohol was added 2.25 g (10.5 mmol) of sodium periodate in 50 mL of water at room temperature over 30 min. The mixture was stirred for 20 h. The resulting mixture was filtered to remove sodium iodate. The filtrate was concentrated under vacuum to a yellow oil containing a white solid. The mixture was treated with water and extracted three times with chloroform. The combined organic phase was washed with aqueous sodium thiosulfate, dried over Na_2SO_4, filtered, and concentrated under vacuum to give 0.67 g (42%) of **2,5-dithiahexane 2-oxide:** IR (CH_2Cl_2) 1052 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 2.9 (s, 4, $-CH_2-$), 2.5 (s, 3, CH_3SO), 2.1 (s, 3, CH_3S); ^{13}C NMR ($CDCl_3$) δ 52.8, 37.4, 25.6, 14.6; mass spectrum (70 eV), *m/e* (relative intensity) 138 (11), 126 (6), 122 (2), 91 (70), 64 (72), 63 (100). Anal. Calcd for $C_4H_{10}OS_2$: C, 35.01; H, 7.29. Found: C, 35.14; H, 7.14.

2,7-Dithiaoctane 2-Oxide: 1.60 g (32%).

1,4-Dithiacycloheptane 1-Oxide: 3.47 g (58%); IR (CH_2Cl_2) 1040 cm^{-1} ($S \rightarrow O$); ^{1}H NMR ($CDCl_3$) δ 3.0–3.5 (m, 4, $CH_2S(-O)CH_3$), 2.5–2.9 (m, 4, CH_2SCH_3), 1.8–2.4 (m, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 55.5, 48.7, 31.9, 24.7, 21.2; mass spectrum (70 eV), *m/e* (relative intensity) 150 (65), 133 (15), 106 (10), 90 (42), 87 (23), 45 (100). Anal. Calcd for $C_5H_{10}OS_2$: C, 39.97; H, 6.71. Found: C, 39.82; H, 6.68.

1,5-Dithiacyclooctane 1-Oxide: 1.67 g (85%).

1,5-Dithiacyclononane 1-Oxide: 0.20 g (72%).

1,6-Dithiacyclodecane 1-Oxide: 0.19 g (85%); ^{1}H NMR ($CDCl_3$) δ 2.7–3.7 (m, 4, CH_2SO), 2.4–2.7 (m, 4, CH_2S), 1.4–2.2 (m, 8, CH_2).

2,6-Dithiaheptane 2-Oxide: 0.64 g (40%).

Use of Me_2SO. 2,7-Dithiaoctane 2,7-dioxide was synthesized by the method of Hull and Bargar.[4] To 3.00 g (20 mmol) of 2,7-dithiaoctane was added 4.5 mL of Me_2SO and 14.5 μL of 12 N hydrochloric acid. The mixture was heated overnight on a steam bath. Upon cooling to room temperature, white crystals precipitated. The crystals were collected by suction filtration and recrystallized from ethyl acetate to give 2.51 g (69%) of **2,7-dithiaoctane 2,7-dioxide:** mp 100–105 °C (lit.[4] mp 110–111 and 120–122 °C); IR (Nujol) 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.8 (m, 4, CH_2SO), 2.5 (s, 6, CH_3SO), 1.8 (m, 4, CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 167 (52), 149 (12), 119 (38), 103 (43), 63 (70), 61 (50), 55 (100).

2,6-Dithiaheptane 2,6-Dioxide: 2.46 g (74%) recrystallized from tetrahydrofuran; mp 109–111 °C (lit.[4] mp 117–118 °C); IR (CH_2Cl_2) 1054 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.7 (t, 4, CH_2SO), 2.4 (s, 6, CH_3SO), 2.2 (m, 2, CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 153 (44), 105 (50), 89 (78), 77 (64), 63 (100).

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Registry No.—1,5-DTCO, 6572-95-8; 1,5-DTCO 1,5-dioxide, 67463-83-6; 1,5-DTCO 1-oxide, 61358-15-4; 2,6-DTHP, 24949-35-7; 2,6-DTHP 2-oxide, 67217-05-4; 1,4-DT, 505-29-3; 1,4-DT 1-oxide, 19087-70-8; 1,5-DTCN, 6573-48-4; 1,5-DTCN 1-oxide, 67463-84-7; 1,4-DTCH, 6008-55-5; 1,4-DTCH 1,4-dioxide, 67463-85-8; 2,7-DTO, 15394-33-9; 2,7-DTO 2-oxide, 67463-86-9; 2,5-DTH, 6628-18-8; 2,5-DTH 2,5-dioxide, 10349-04-9; 2,5-DTH 2-oxide, 67463-87-0; 1,4-DTCH 1-oxide, 67463-88-1; 1,6-DTCD, 51472-64-1; 1,6-DTCD 1-oxide, 67463-89-2; 2,7-DTO 2,7-dioxide, 56348-36-8; 2,6-DTHP 2,6-dioxide, 56348-35-7.

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(23) Crude weight; a small sample was purified by preparative gas chromatography.
(24) Purified by column chromatography on silica gel with chloroform as eluent.
(25) Recrystallized from dichloromethane–heptane.