mass spectrometry laboratory and Mr. William Garrison of the University of Missouri—St. Louis mass spectrometry laboratory for obtaining the mass spectral data used in this study. The high-resolution mass spectrometer and data processing equipment at the University of Illinois—Urbana employed in this study were provided by National Institutes of Health Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively.

Supplementary Material Available. Full spectral, chromatographic and analytical data for all new alkyl alkanethiolsulfinates and alkanethiolsulfonates prepared in this study (as well as some new data on previously prepared compounds) will appear as Tables I and II following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-3921.

The Chemistry of Alkyl Thiolsulfinate Esters. VII. Mechanistic Studies and Synthetic Applications

Eric Block* and John O'Connor

Contribution from the Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121. *Received December 28, 1973*

Abstract: The pyrolysis of alkyl thiolsulfinates is shown to afford alkanesulfenic or alkanethiosulfoxylic acids which may be trapped in good yields with acetylenes giving α,β-unsaturated sulfoxides or thiolsulfinates, respectively. In the absence of trapping agents the sulfenic acids can undergo a variety of reactions including dehydration to thiolsulfinate and exchange (*via* nucleophilic displacement) with thiolsulfinate leading to a scrambling process if two different thiolsulfinates are involved. The sulfenic acids can initiate more complicated sequences leading to formation of thiolsulfonate and disulfide (disproportionation) or to α-alkanesulfinyl and α-alkanesulfonyl disulfides (Pummerer rearrangement). Mechanisms are proposed for the various thermal reactions of thiolsulfinates based on detailed product studies and study of substituent, solvent, and catalyst effects. The mechanisms advanced bear on the mode of antioxidant action of thiolsulfinates and provide a possible explanation for the unusually low optical stability of optically active thiolsulfinates. Photochemical reactions of dialkyl thiolsulfinates are also discussed. A number of typical reactions for the α-alkanesulfinyl disulfide, 2,3,5-trithiahexane 5-oxide, are presented including selective deoxygenation without S–S scission, Pummerer rearrangement with acetic anhydride, and selective sulfinyl sulfur–carbon bond cleavage. Evidence is presented for the facile formation of the first known example of a discrete α-disulfide carbanion.

Dialkyl thiolsulfinates, RS(O)SR, are a readily available class of organic sulfur compounds whose fundamental chemistry has not been systematically explored, this despite possible advantages which may be realized from similarities in chemical behavior between alkyl thiolsulfinates and alkyl sulfoxides, compounds of great and varied synthetic utility.[1] Presumably the reputation of the lower dialkyl thiolsulfinates as malodorous, unstable substances is responsible for the neglect of this class of compounds. In the accompanying paper[2] we have discussed aspects of the synthesis and properties of dialkyl thiolsulfinates. In this paper we present details of several synthetically useful reactions of alkyl thiolsulfinates and provide evidence concerning the mechanisms of these reactions.[3] Some novel aspects of the chemistry of several new classes of organic sulfur compounds, discovered during the course of this research, will also be discussed. Finally, since we have found alkyl thiolsulfinates to be useful precursors of alkanesulfenic (and related) acids, some new features of the chemistry of these latter elusive sulfur acids will be described.

Preparation and Reactions of Alkanesulfenic Acids; a Convenient Synthesis of α,β-Unsaturated Sulfoxides. A limited number of reports in the literature provide evidence for the similarity in chemical behavior of thiolsulfinates and sulfoxides. For example the reaction in eq 1[4] is analogous to the allyl sulfoxide–allyl sulfenate interconversion,[5] that in eq 2[6] to the Pummerer reaction of sulfoxides,[1] and that in eq 3[7] to the reduction of sulfoxides to sulfides under analogous conditions.[8]

Examples are known from sulfoxide chemistry of both C–S homolysis[9] and cycloelimination[10] reactions

* Visiting Professor, Harvard University, 1974.

(1) For recent references, see E. Block, *J. Chem. Educ.*, **48**, 814 (1971); L. Field, *Synthesis*, **4**, 101 (1972).

(2) E. Block and J. O'Connor, *J. Amer. Chem. Soc.*, **96**, 3921 (1974).

(3) Portions of this work have been reported in preliminary form: (a) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972); (b) *ibid.*, **94**, 644 (1972); (c) E. Block and S. W. Weidman, *ibid.*, **95**, 5046 (1973); (d) E. Block and J. O'Connor, *ibid.*, **95**, 5048 (1973).

(4) J. E. Baldwin, G. Höfle, and S. C. Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971).

(5) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968).

(6) I. Saito and S. Fukui, *J. Vitaminol. (Kyoto)*, **12**, 244 (1966).

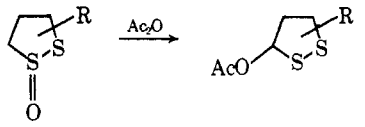
(7) H. Bretschneider and W. Klötzer, *Monatsh. Chem.*, **81**, 589 (1950).

(8) C. R. Johnson, C. C. Bacon, and J. J. Rigau, *J. Org. Chem.*, **37**, 919 (1972).

(9) D. J. Abbott and C. J. M. Stirling, *Chem. Commun.*, 165 (1968); E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4861 (1968).

(10) D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, **34**, 4115 (1969); D. N. Jones, E. Helmy, and A. C. F. Edmonds, *J. Chem. Soc. C*, 833 (1970), and references therein.

(1)



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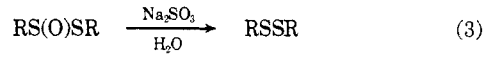
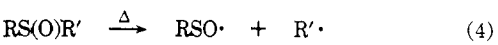


(3)

on pyrolysis (eq 4 and 5, respectively).[11] Recent studies



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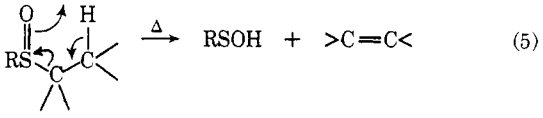
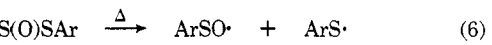
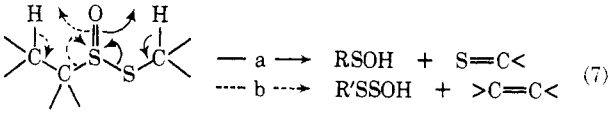


(5)

by Fava and coworkers[12] have demonstrated that, at moderate temperatures, diaryl thiolsulfinates decompose by S–S homolysis (eq 6), a process facilitated by the unusually weak S–S bond (bond strength ~35 kcal[12]). On the other hand, mass spectral studies of dialkyl thiolsulfinates[2] suggested the possibility of two thermal cycloelimination pathways, as shown in eq 7. Path 7a



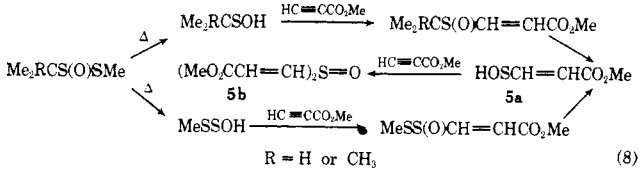
(6)



(7)

should be favored in view of the weakness of the thiolsulfinate S–S linkage and the enhanced acidity of the α-sulfenyl protons. Indeed, pyrolysis of a number of alkyl thiolsulfinates bearing α-sulfenyl C–H bonds generates sulfenic acids which may be trapped in excellent yield with acetylenes, providing a synthetically useful approach to α,β-unsaturated sulfoxides (see Table I)[3a,13] The thiocarbonyl compounds give polymer which on cracking at 200° affords 1,3,5-trithiane or derivatives. In support of the mechanism of eq 7a, we find that pyrolysis of hexadeuteriothiolsulfinate **3** (Table I, entry 3) in methyl propiolate gave methyl *trans*-β-(β',β',β'-trideuterioethylsulfinyl)acrylate with no evidence for tetradeuterated material or material with vinylic C–D bonds. The formation of β,β'-bis(*trans*-carbomethoxy)divinyl sulfoxide **5b** from methyl 2-propanethiolsulfinate and methyl 2-methyl-2-propanethiolsulfinate can be explained in terms of trapping of the α,β-unsaturated sulfenic acid **5a** formed either from the α,β-unsaturated sulfoxides or from α,β-unsaturated thiolsulfinates (*cf.* eq 8).[14]

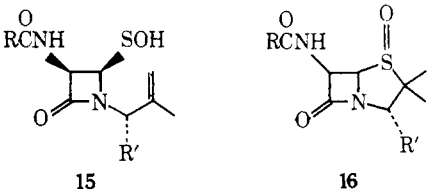
2-Methyl-2-propyl 2-methyl-2-propanethiolsulfinate



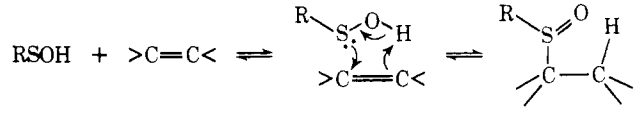
(8)

(7), which lacks α-sulfenyl protons but does have β-sulfinyl protons, undergoes elimination of type b, eq 7, generating isobutylene and a representative of a previously unknown class of sulfur acids, alkanethiosulfoxylic acids (alternatively named as alkyl hydrogen thiosulfoxylates), RSSOH, which may be trapped with acetylenes affording α,β-unsaturated thiolsulfinates in a regio- and stereospecific process (*cf.* Table I).[3b,15] As will be discussed below, the thermal stability of dialkyl thiolsulfinates is determined both by the ease of formation of sulfenic (or thiolsulfoxylic) acids from the former compounds as well as the facility with which subsequent processes involving sulfenic and related acids occur. Particular stability results when neither α-sulfenyl nor β-sulfinyl protons are available for the β-elimination processes of eq 7, as in the case of thiolsulfinates **8** and **14** (Table II).

Sulfenic acids can also be trapped with activated olefins although simple olefins are unreactive in the absence of unusual proximity effects (see the case of the intramolecular cyclization of the penicillin sulfenic acid discussed below). Thus, methanesulfenic acid, generated from MeS(O)SMe, can be trapped with ethyl acrylate affording ethyl β-methylsulfinylpropionate in 90% yield;[18] under similar reaction conditions cyclohexene gave no adduct. Penicillin sulfenic acid **15**, which has recently been isolated as a crystalline solid,[19a] is reported to give adducts with norbornadiene, 4-methyleneoxetan-2-one, and acrolein;[19b] in the absence of external trapping agents the sulfenic acid group adds to the internal double bond to generate a penicillin sulfoxide, **16**.[20] Mechanistically, sulfenic acid addition to unsaturates and its converse, sulfoxide pyrolysis giving sulfenic acid,



15 **16**



(9)

(11) Some sulfoxides, such as episulfoxides, are capable of decomposition by both pathways: *cf.* ref 4 and K. Kondo, M. Matsumato, and A. Negishi, *Tetrahedron Lett.*, 2131 (1972); D. M. Lemal and P. Chao, *J. Amer. Chem. Soc.*, **95**, 922 (1973).

(12) P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 5971 (1970).

(13) For recent syntheses of α,β-unsaturated sulfoxides, see F. A. Carey and O. Hernandez, *J. Org. Chem.*, **38**, 2670 (1973), D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Amer. Chem. Soc.*, **94**, 2891 (1972), D. J. Abbott, S. Collona, and C. J. M. Stirling, *Chem. Commun.*, 471 (1971), G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3624 (1969), and J. Almog and B. A. Weissman, *Synthesis*, **5**, 164 (1973).

(14) Adduct **5b** is also formed on pyrolysis of $(t\text{-Bu})_2SO$ in methyl propiolate: J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967).

(15) (a) It has been recently alleged that *n*-butanesulfoxylic acid, *n*-BuOSOH, adds to ethyl acrylate at 130–140° in a *nonregiospecific* fashion: F. Mathey and J.-P. Lampin, *Tetrahedron Lett.*, 3121 (1972). (b) For a discussion of thiosulfoxylic acids as possible reaction intermediates, see N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 236 (1962). (c) For an example of a thiosulfoxylate ester, see ref 4. (d) Somewhat analogous intramolecular cycloelimination reactions have been described for ylides derived from the reaction of carbenes[16] or nitrenes[17] with *t*-BuSS-*t*-Bu.

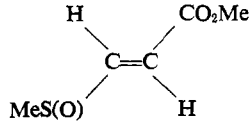
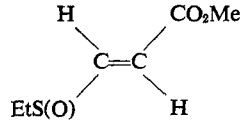
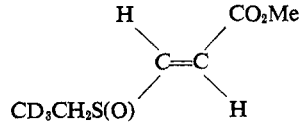
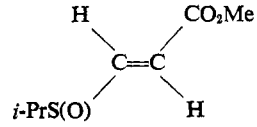
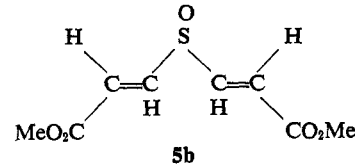
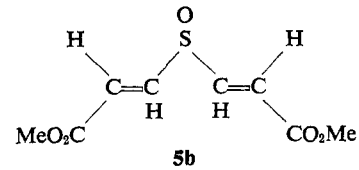
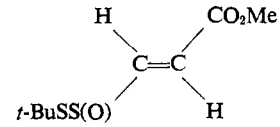
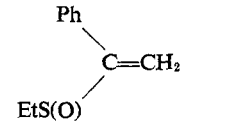
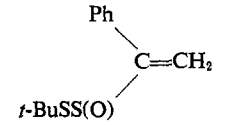
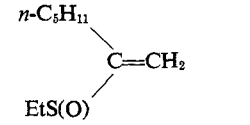
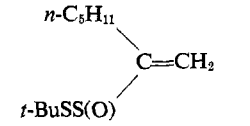
(16) S. Searles, Jr., and R. E. Wann, *Tetrahedron Lett.*, 2899 (1965).

(17) W. Ando, H. Fujii, and T. Migita, *Int. J. Sulfur Chem., Part A*, **2**, 143 (1972).

(18) Shelton[14] has reported the trapping of 2-methyl-2-propanesulfenic acid with ethyl acrylate.

(19) (a) T. S. Chou, J. R. Burgtorf, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, *J. Amer. Chem. Soc.*, **96**, 1609 (1974). (b) D. H. R. Barton, *et al.*, *J. Chem. Soc. Perkin Trans. 1*, 1187 (1973).

Table I. α,β-Unsaturated Sulfoxides and Thiolsulfinates through Reaction of Alkyl Thiolsulfinates with Alkynes

Thiolsulfinate	Alkyne	Product (isolated yield, %)	
1. MeS(O)SMe (**1**), methyl methanethiolsulfinate	$HC{\equiv}CCO_2Me$		(65)
2. EtS(O)SEt (**2**), ethyl ethanethiolsulfinate	$HC{\equiv}CCO_2Me$		(76)
3. $CD_3CH_2S(O)SCH_2CD_3$ (**3**), ethyl-*2,2,2-d*$_3$ ethane-*2′,2′,2′-d*$_3$-thiolsulfinate	$HC{\equiv}CCO_2Me$		(27)
4. *i*-PrS(O)SMe (**4**), methyl 2-propanethiolsulfinate	$HC{\equiv}CCO_2Me$		(49)
		 **5b**	(7)
5. *t*-BuS(O)SMe (**6**), methyl 2-methyl-2-propanethiolsulfinate	$HC{\equiv}CCO_2Me$	 **5b**	(46)
6. *t*-BuS(O)S-*t*-Bu (**7**), 2-methyl-2-propyl 2-methyl-2-propanethiolsulfinate	$HC{\equiv}CCO_2Me$		(56)
7. MeS(O)S-*t*-Bu (**8**), 2-methyl-2-propyl methanethiolsulfinate	$HC{\equiv}CCO_2Me$	No reaction	
8. EtS(O)SEt (**2**)	$HC{\equiv}CPh$		(91)
9. *t*-BuS(O)S-*t*-Bu (**7**)	$HC{\equiv}CPh$		(30)
10. EtS(O)SEt (**2**)	$HC{\equiv}CC_5H_{11}$-*n*		(33)
11. *t*-BuS(O)S-*t*-Bu (**7**)	$HC{\equiv}CC_5H_{11}$-*n*		(21)

can be viewed as a reversible six-electron sigmatropic rearrangement (eq 9).[20] However, proton transfer and C–S bond formation *via* the sulfur lone pair (in sulfenic acid addition) may not be entirely synchronous (*e.g.*, to explain the direction of addition to phenylacetylene, it can be argued that proton transfer is slightly advanced over C–S bond formation[21]).

(20) R. D. G. Cooper, *J. Amer. Chem. Soc.*, **92**, 5010 (1970); D. H. R. Barton, *et al.*, *J. Chem. Soc. C*, 3540 (1971).

If the unsaturated trapping agent is omitted, other reactions of sulfenic acids are seen. Thus in the pyrolysis of unsymmetrical dialkyl thiolsulfinates MeS(O)SEt and EtS(O)SMe, the formation of low concentrations (~4%) of the symmetrical thiolsulfinates MeS(O)-

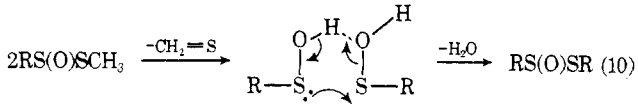
(21) Similar arguments have been advanced by Shelton and Davis (*Int. J. Sulfur Chem.*, in press). These authors have also rigorously established the cis stereochemistry of sulfenic acid addition to phenyl acetylene through the use of deuterium labeling. We thank Professor Shelton for a preprint.

Table II. Relative Thermal Stability of *Neat* Dialkyl Thiolsulfinate Esters

Thiolsulfinate	$t_{1/2}$ at 96° (min)
MeS(O)SMe (**1**)	7
MeS(O)SEt (**9**), ethyl methanethiolsulfinate	11
MeS(O)S-*i*-Pr (**10**), 2-propyl methanethiolsulfinate	32
EtS(O)SMe (**11**), methyl ethanethiolsulfinate	40
n-$C_{12}H_{25}$S(O)S-*n*-$C_{12}H_{25}$ (**12**), *n*-dodecyl dodecanethiolsulfinate	52
i-PrS(O)S-*i*-Pr (**13**), 2-propyl 2-propanethiolsulfinate	66
t-BuS(O)S-*t*-Bu (**7**)	148
MeS(O)S-*t*-Bu (**8**)	~10^3
1-AdS(O)S-1-Ad (**14**), 1-adamantyl 1-adamantanethiolsulfinate	>10^5 [a]

[a] After 1.2×10^5 min, >70% remaining thiolsulfinate.

SMe and EtS(O)SEt, respectively, can be unambiguously established. When a more stable symmetrical thiolsulfinate results, as in the formation of *t*-BuS(O)S-*t*-Bu during pyrolysis of *t*-BuS(O)SMe, yields as high as 52% may be isolated. In thiolsulfinate formation from dehydration of sulfenic acids, the sulfenic acids (possibly associated by hydrogen bonding as shown in eq 10)



may be functioning as both S nucleophiles and S electrophiles.[22,23,26]

Our demonstration of the formation of sulfenic or thiosulfoxylic acids and thiocarbonyl compounds from the thermal decomposition of alkyl thiolsulfinates is of interest not only as a new method for generating these several species but also because it serves to explain the known antioxidant activity of the parent thiolsulfinate esters.[27] It has been shown[28] that sulfenic acids (produced thermally from dialkyl sulfoxides) are extremely active radical scavengers, reacting with peroxy radicals with a rate constant at 60° of at least 10^7 l. mol^{-1} sec^{-1} (similar in scavenging ability to a hindered phenoxy radical), presumably giving the sulfinyl radicals of low reactivity[12] (eq 11). It is likely that thiosulfoxylic

$$R\cdot + R'SOH \longrightarrow R\text{-}H + R'SO\cdot \quad (11)$$

acids would also be efficient radical scavengers. In addition, thiocarbonyl componds have also been found to be effective radical traps.[29] Among the compounds claimed to be particularly effective inhibitors of olefin autoxidation are sulfoxides **17** and **18** and thiolsulfinate **7** and close relatives of **11**. Table III indicates the rate

Table III. Rate Constants for Unimolecular Thermal Decomposition of Several Sulfoxides and Thiosulfinates of Known Antioxidant Activity

Compd	Retardation ratio[a]	10^5 *k* dec, sec^{-1} 75°	96°	Ref
t-BuS(O)-*t*-Bu (**17**)	144	7	68[b]	*f*
$(MeO_2CCH_2CH_2)_2SO$ (**18**)		5.8	37[b]	*g*
t-BuS(O)S-*t*-Bu (**7**)	140	1.4	19	This work
EtS(O)SMe (**11**)	145,[c] 248[d]		~0.5[e]	This work

[a] Defined[27a] as the ratio of the times taken for 0.1% (w/w) of oxygen to be absorbed by squalene plus additive and by pure squalene, respectively. The larger the ratio, the better the performance of the additive as a retarder of oxidation. The concentrations of the sulfur compounds are 0.004–0.01 *M*. [b] Extrapolated from data at other temperatures. [c] Ethyl ethanethiolsulfinate (**2**). [d] *n*-Butyl butanethiolsulfinate. [e] Estimated for a benzene solution 0.016 *M* in EtS(O)SMe. [f] J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, in press. [g] C. Armstrong and G. Scott, *J. Chem. Soc. B*, 1747 (1971).

constants for unimolecular thermal decomposition at 96° to sulfenic (or thiosulfoxylic) acids for these four compounds. The similarity of the rate constants in Table III provides support for our suggestion that the antioxidant activity of alkyl thiolsulfinates is due to the formation of sulfenic and thiosulfoxylic acids.[3b]

Another possible instance in which the sulfenic acid functions as a nucleophile is seen when a pair of *different* thiolsulfinate esters are mixed in the dark either neat or in benzene solution. Under these conditions a rapid equilibrium is established resulting in the complete scrambling of the sulfinyl and sulfenyl fragments (eq 12). On the time scale of this scrambling process there

$$MeS(O)SMe + EtS(O)SEt \rightleftharpoons MeS(O)SEt + EtS(O)SMe \quad (12)$$

is no significant thiolsulfinate disproportionation. Surprisingly, in the thiolsulfinate concentration range 0.0005–0.05 *M* (each) the scrambling reaction shows *first-order kinetics* (at 96° the rate of disappearance of EtS(O)SEt is 37, 25, and 31 $\times 10^{-5}$ sec^{-1} for thiolsulfinate concentrations of 0.05, 0.005, and 0.0005 *M*, respectively; similar rate constants are obtained for the disappearance of MeS(O)SMe) and a low activation enthalpy (−16 kcal/mol, calculated from the first-order rate constants determined at 96, 85, 75, and 65°). The scrambling reaction did not occur on ultraviolet irradiation of a pentane solution of the pair of thiolsulfinates. In an effort to determine if the species responsible for thiolsulfinate scrambling could also scramble a mixture of disulfides, a benzene solution *ca.* 5×10^{-3} *M* each in EtS(O)SEt, MeS(O)Me, EtSSEt, and MeSSMe was heated at 96° for 80 min with periodic analysis by quantitative vpc. Although complete thiolsulfinate scrambling had occurred, there was no significant disulfide scrambling.

In order to compare the ease of the thiolsulfinate scrambling process with similar processes for pairs of different disulfides or thiolsulfonates, carefully purified samples of mixed disulfides or alkyl thiolsulfonates were

(22) Kinetic evidence for the substantial nucleophilicity of sulfenic acids toward sulfenyl sulfur has been presented by Kice and Cleveland: J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **95**, 104 (1973).

(23) The importance of intramolecular hydrogen bonding in the stabilization of 1-anthraquinonesulfenic acid[24] and pyrimidinesulfenic acids[25] has been discussed.[24,25] Sulfenic acid **15** may also derive stability from an internal hydrogen bond. It is perhaps significant that in these internally hydrogen bonded sulfenic acids, thiolsulfinate formation does not seem to occur.

(24) T. C. Bruice and A. B. Sayigh, *J. Amer. Chem. Soc.*, **81**, 3416 (1959).

(25) B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *J. Amer. Chem. Soc.*, **91**, 3634 (1969).

(26) For an example of nucleophilic substitution at *sulfinyl* sulfur *via* a five-membered cyclic transition state, see F. Wudl and T. B. K. Lee, *J. Amer. Chem. Soc.*, **95**, 6349 (1973).

(27) (a) D. Barnard, L. Bateman, M. E. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 5339 (1961); (b) L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *ibid.*, 3570 (1962); (c) A. Rahman and A. Williams, *J. Chem. Soc. B*, 1391 (1970); (d) also see ref 15b; (e) D. Barnard and J. I. Cunneen, British Patent 889,112 (1962); (f) J. I. Cunneen and D. F. Lee, *J. Appl. Polym. Sci.*, **8**, 699 (1964).

(28) P. Koelewijn and H. Berger, *Recl. Trav. Chim. Pays-Bas*, **91**, 1275 (1972).

(29) N. Kito and A. Ohno, *Bull. Chem. Soc. Jap.*, **46**, 2487 (1973).

Table IV. Thermal Scrambling Reactions of Pairs of Disulfides, Alkyl Thiolsulfinates, and Alkyl Thiolsulfonates

Reactants[a] (molar ratio)	Conditions[b]	Products (mol %)
EtS(O)SMe + MeS(O)SEt (1:1)	25°, 11 hr	MeS(O)SMe (16), MeS(O)SEt (36), EtS(O)SMe (37), EtS(O)SEt (11)
EtSSEt + MeSSMe (1.5:1)	25°, 240 hr	EtSSEt (61.8), EtSSMe (0.6), MeSSMe (37.7)
	96°, 1.25 hr	EtSSEt (61), EgSSMe (1), MeSSMe (38)
$EtSO_2SEt$ + $MeSO_2SMe$ (1.4:1)	96°, 6 hr	$EtSO_2SEt$ (57), $MeSO_2SMe$ (35), $EtSO_2SMe$ (4), $MeSO_2SEt$ (5)

[a] Freshly distilled. [b] Neat compounds reacted in the absence of light.

kept at 96° in the dark and periodically analyzed by vpc with the results shown in Table IV. A parallel experiment involving alkyl thiolsulfinates (neat) had to be carried out at 25° since scrambling occurred almost instantaneously at 96°.

While the results of the above experiments argue against the involvement of free radicals in the *thiolsulfinate* scrambling process (mixtures of disulfide are known to be readily scrambled by radicals[30]), a further search for radicals was made under conditions of pyrolysis of alkyl thiolsulfinates neat or in solution at temperatures up to 140° in an esr spectrometer,[31] using a spin trap, or using CIDNP techniques (see Experimental Section). In none of these experiments was there any evidence for the production of free radicals. On the other hand, the scrambling reaction was promoted by added acid, retarded by added 2,6-lutidine, and inhibited by added methyl acrylate. The scrambling reaction can best be interpreted in terms of parallel chain reactions involving a cyclic sulfenic acid–thiolsulfinate exchange process as the chain-propagating step (see Scheme I and **10**).

Scheme I. Proposed Mechanism for Thiolsulfinate Scrambling

$$MeS(O)SMe \xrightarrow{k_1} MeSOH + CH_2{=}S \qquad \text{Initiation}$$

$$EtS(O)SEt \xrightarrow{k_1'} EtSOH + CH_3CH{=}S$$

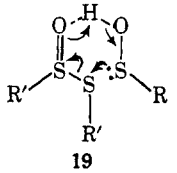
$$MeSOH + EtS(O)SEt \underset{}{\overset{k_2}{\rightleftharpoons}} EtSOH + MeS(O)SEt \qquad \text{Propagation}$$

$$EtSOH + MeS(O)SMe \overset{k_2'}{\rightleftharpoons} MeSOH + EtS(O)SMe$$

$$RSOH + RS(O)SR \xrightarrow{k_3} RSO_2H + RSSR \qquad \text{Termination}$$

Applying the steady-state expression for the sulfenic acid concentration and the additional assumptions that $k_1 \simeq k_1'$, $k_2 \simeq k_2'$, and $k_2 \gg k_3$, first-order kinetics can be obtained for the initial stages of the scrambling process with a rate constant, k_s, approximated by $k_1k_2/2k_3$. Using a value of $k_s = 30 \times 10^{-5}$ sec^{-1} (see above) and an approximate value of $k_1 = 0.5 \times 10^{-5}$ sec^{-1} (both at 96°; k_1 taken from estimated k_1 for EtS(O)SMe given in Table III) it is seen that $k_2/k_3 \simeq 120$.

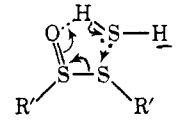
Concerted transition state **19** involves frontside



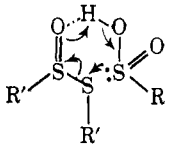
$\xrightarrow{\text{fast}}$ R'SOH + RS(O)SR'

19

nucleophilic displacement at sulfur aided by a "push–pull" weakening of the S–S bond;[32,33] similar transition states have been proposed to describe the reaction of thiolsulfinates with thiols[34,35] (eq 13) and with sulfinic acids[3c] (eq 14). The ability of dialkyl thiolsulfinates to



$\longrightarrow$ R'SOH + R'SSR (13)



$\longrightarrow$ R'SOH + RSO_2SR' (14)

form hydrogen bonds (a key feature of the transition states depicted in **19** and eq 13 and 14) is intermediate between the hydrogen bonding abilities of dialkyl sulfoxides and dialkyl sulfinates, as determined through a study of the frequency shift of the phenol OH stretching vibration band in the infrared (see Experimental Section).

There are some intriguing implications of this thiolsulfinate scrambling reaction in connection with the mechanism of racemization of optically active thiolsulfinates. All attempts to prepare simple optically active dialkyl thiolsulfinates have thus far been unsuccessful,[36,37] a consequence that we attribute to the occurrence of the above described scrambling process. Fava and coworkers have reported the unusually facile thermal racemization of aryl arenethiolsulfinates, obtaining first-order rate constants ranging from $\sim 2 \times 10^{-5}$ sec^{-1} (in acetic acid or in benzene saturated with water) to 46×10^{-5} sec^{-1} (in dry benzene) at 50° (the aryl groups

Table V. Product Distribution (Mol %) in the Disproportionation of EtS(O)SMe at Room Temperature as a Function of Time

Product	Time, weeks: 4	7	10	12	16
MeSSMe	4	5	10	13	6
MeSSEt	7	13	17	19	14
EtSSEt	0.7	3	4	5	5
EtS(O)SMe, **11**	77	49	21	7	2
EtS(O)SEt	2	4	6	3	1
$EtSO_2SMe$	10	24	37	47	54
$EtSO_2SEt$	0.6	2	4	6	9
$EtSO_2SMe/EtSO_2SEt$	16	13	9.6	8.4	5.8

(30) See E. Block, *Quart. Rep. Sulfur Chem.*, 4(4), 237 (1969), and references therein.

(31) For esr studies of alkanesulfinyl radicals, see T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Lett.*, 4075 (1972).

(32) For a review of electrophile/nucleophile assisted S–S bond scission, see J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).

(33) For somewhat analogous cyclic six-membered intermediates for substitution at sulfinyl sulfur, see F. G. Yamagishi, D. R. Rayner, E. T. Zwicker, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 1916 (1973).

(34) J. M. Shreeve, *Accounts Chem. Res.*, **6**, 387 (1973).

(35) G. Tsukamoto, T. Watanabe, and I. Utsumi, *Bull. Chem. Soc. Jap.*, **42**, 2566 (1969).

(36) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965).

(37) The separation of the diastereomers of the S-monoxide of L-cystine has been reported: W. E. Savige, J. Eager, J. A. Maclaren, and C. M. Roxburgh, *Tetrahedron Lett.*, 3289 (1964).

Table VI. Product Distribution from Pyrolysis of Alkyl Thiolsulfinate Esters

No.	Thiolsulfinate (% converted)	Conditions	Products (mol % in product)			
			Thiolsulfonates	Disulfides	α-Sulfinyl and α-sulfonyl disulfides	Other
1	MeS(O)SMe (**1**) (100)	Neat, 25° or 96°; 1 *M* in C_7H_{16}, 19 hr, 96°	$MeSO_2SMe$ (50)	MeSSMe (50)		
2	MeS(O)SMe (**1**) (~100)	1.1 *M* in C_6H_6, 6 hr at 96°	$MeSO_2SMe$ (26)	MeSSMe (35)	$MeSCH_2SSMe$ (8), $MeS(O)CH_2SSMe$ (14), $MeSO_2CH_2SSMe$ (3)	H_2O, MeS_3Me (14), $MeSO_2H$, $MeSO_3H$
3	MeS(O)SMe (**1**) (~100)	~1.5 *M* in C_6H_6 + 1 equiv of H_2O, reflux 52 hr	$MeSO_2SMe$ (tr)	MeSSMe (tr)	$MeS(O)CH_2SSMe$ (84% yield), $MeSO_2CH_2SSMe$ (tr)	MeS_3Me(tr), $MeSCH(MeSO_2)SSMe$ (tr)
4	MeS(O)SEt (**9**) (34)	Neat, 25°, 4 days	$MeSO_2SEt$ (14), $MeSO_2SMe$ (3)	MeSSMe, MeSSEt (9), EtSSEt (3)		MeS(O)SMe (5)
5	MeS(O)SEt (**9**) (~100)	Neat, 96°, 1 hr	$MeSO_2SEt$ (29), $MeSO_2SMe$ (11), $EtSO_2SEt$ (upper limit, <0.1%)	MeSSMe (10), MeSSEt (33), EtSSEt (11)		MeS_3Me (2), MeS_3Et (3), EtS_3Et (1)
6	MeS(O)S-*i*-Pr (**10**) (~100)	Neat, 96°, 75 min	$MeSO_2S$-*i*-Pr (10) $MeSO_2SMe$ (22)	MeSSMe, MeSS-*i*-Pr (32)		H_2O (15), *i*-PrS_3-*i*-Pr (2)
7	MeS(O)S-*t*-Bu (**8**) (~40)	Neat (tr H_2O), 96°, 166 min	$MeSO_2SMe$ (23) $MeSO_2S$-*t*-Bu (10)	MeSS-*t*-Bu (9), *t*-BuSS-*t*-Bu, *t*-BuS_3-*t*-Bu (1)		$MeSO_2SS$-*t*-Bu, MeOH (~6)
8	EtS(O)SMe (**11**) (~27)	Neat, 25°, 4 wk	$EtSO_2SMe$ (9.5), $EtSO_2SEt$ (0.6)	MeSSMe (4), MeSSEt (6.4), EtSSEt (0.7)	$EtS(O)CH_2SSMe$ (4)	EtS(O)SEt (2)
9	EtS(O)SMe (**11**) (~100)	Neat, 96°, 5 hr	$EtSO_2SMe$ (33), $EtSO_2SEt$ (5)	MeSSMe (3), MeSSEt (19), EtSSEt (11)	$EtS(O)CH_2SSMe$ (22), $EtS(O)CH_2SSEt$ (4)	MeS_3Me (1), MeS_3Et (2)
10	EtS(O)SMe (**11**) (~77)	0.033 *M* in C_7H_{16}, 96°, 21 hr	$EtSO_2SMe$ (25), $EtSO_2SEt$ (7)	Not determined		EtS(O)SEt (6)
11	EtS(O)SMe (**11**) (~100)	~2 *M* in C_6H_6 + 1 equiv of H_2O, reflux 23 hr	$EtSO_2SMe$ (24), $EtSO_2SEt$ (10)	MeSSMe (32), MeSSEt (7), EtSSEt (2)	$EtS(O)CH_2SSMe$ (66.5), $EtS(O)CH_2SSEt$ (22.2), $EtS(O)CHMeSSMe$ (3.1), $EtSO_2CHMeSSMe$ (5.8), $EtSO_2CH_2SSMe$ (1.5), $EtSO_2CHMeSSEt$ (0.7), $EtSO_2CH_2SSEt$ (0.2) [a]	(14)
12	EtS(O)SMe (**11**) (100)	0.905 *M* in C_6H_6 + CF_3COOH + Et_2S, 25°, 1 min	$EtSO_2SMe$ (35), $EtSO_2SEt$ (10)	MeSSMe, MeSSEt (42), EtSSEt (13)		
13	EtS(O)SEt (**2**) (~100)	~2 *M* in C_6H_6, 96°, 4 hr			$EtS(O)CHMeSSEt$ (~15% yield)	
14	*i*-PrS(O)SMe (**4**) (~100)	Neat, 96°, 9.3 hr	*i*-$PrSO_2SMe$ (10), *i*-$PrSO_2S$-*i*-Pr (4.5)	*i*-PrSSMe (22) (other R_2S_n)	*i*-$PrS(O)CH_2SSMe$ (6) (12% yield)	H_2O (57)
15	*t*-BuS(O)SMe (**6**) (~100)	Neat, 96°, 5.5 hr	*t*-$BuSO_2SMe$ (9), *t*-$BuSO_2S$-*t*-Bu (?; <0.2)	*t*-BuSSMe *t*-BuSS-*t*-Bu (29)	*t*-$BuS(O)CH_2SSMe$ (17) (27% yield)	H_2O, isobutylene (tr), *t*-BuS_3-*t*-Bu (2), *t*-BuS(O)S-*t*-Bu (39), *t*-BuS_4-*t*-Bu (1), *t*-$BuSO_2SSMe$ (1), *t*-$BuSO_2SS$-*t*-Bu (2)

16	*t*-BuS(O)SMe (6) (~100)	With equal wt H_2O, 96°, 5.5 hr, Ar atmosphere	*t*-$BuSO_2SMe$ (26)	*t*-BuSSMe (5), *t*-BuSS-*t*-Bu (9)	*t*-$BuS(O)CH_2SSMe$ (24) (41% yield)	*t*-BuS(O)S-*t*-Bu (36)
17	*t*-BuS(O)SMe (6) (~100)	Neat + 0.2 equiv CaH_2, 96°, 5.5 mm, 5.5 hr	*t*-$BuSO_2SMe$ (7)	*t*-BuSS-*t*-Bu (13)	*t*-$BuS(O)CH_2SSMe$ (7) (11% yield) *t*-$BuSO_2CH_2SSMe$ (19) (29% yield)	*t*-BuS(O)S-*t*-Bu (52), *t*-BuS_3-*t*-Bu (3)
18	*t*-BuS(O)S-*t*-Bu (7) (100)	Neat, 96°, 12 hr		*t*-BuSS-*t*-Bu (4)		H_2O, isobutylene (49), *t*-Bu_2S_3 (21), *t*-$BuSO_2SS$-*t*-Bu, (7), *t*-Bu_2S_4 (19)
19	MeS(O)SMe (1) (~100)	2.3:1 molar ratio $EtSO_2SEt$:MeS(O)SMe, 96°, 1 hr	$MeSO_2SMe$ (13.5), $MeSO_2SEt$ (1.5), $EtSO_2SMe$ (3), $EtSO_2SEt$ (82)			
20	EtS(O)SEt (2) (~100)	2.7:1 molar ratio Me_2S_2:EtS(O)SEt, 96°, 3 hr	$EtSO_2SMe$ (1.5), $EtSO_2SEt$ (6)	MeSSMe (53), MeSSEt (34), EtSSEt (5)		MeSSSMe (0.4), EtSSSMe (1)
21	None	3.2:1 molar ratio Et_2S_2:$MeSO_2SMe$, 96°, 6 hr	$MeSO_2SMe$ (25), $MeSO_2SEt$ (1)	EtSSEt (74)		

[a] Relative amounts.

are *p*-chlorophenyl or *p*-tolyl) with $\Delta H^{\ddagger} = 23$ kcal/mol.[36,38] The similarity of Fava's rate constants with the extrapolated rate constant for the scrambling reaction at 50° of 1.1×10^{-5} sec^{-1} and the estimated activation enthalpy (16 kcal/mol) for this latter process suggests an alternative explanation from that offered by Fava for the racemization, namely the facile reaction of arenesulfenic acid (perhaps generated from the thiolsulfinate through reaction with traces of water) with optically active thiolsulfinate. This explanation removes the puzzling inconsistency between the hypothesis offered by Fava for rapid racemization of diaryl thiolsulfinates and the observation by Padwa[39] that cyclic thiolsulfinate **20** is configurationally stable up to

20

166°. A coplanar Cope elimination of the type indicated in eq 7a is impossible for **20** as is the chain-type scrambling of Scheme I. The decreased rate of racemization of aryl thiolsulfinates in protic compared to aprotic solvents reported by Fava[36] may possibly be due to hydrogen bonding effects by the protic solvent which interfere with transition state **19**.

Further Reactions of Alkyl Thiolsulfinate Esters. The Disproportionation Reaction. In the accompanying paper[2] we provide evidence from deuterium labeling for the overall disproportionation process shown in eq 15.

$$\mathrm{RS(O)SR'} \longrightarrow \underset{\text{major}}{\mathrm{RSO_2SR'}} + \underset{\text{minor}}{\mathrm{RSO_2SR}} + \mathrm{RSSR} + \mathrm{RSSR'} + \mathrm{R'SSR'} \quad (15)$$

In order to ascertain the detailed mechanism of this reaction, we have examined the variation in product distribution with time from a variety of unsymmetrical dialkyl thiolsulfinates. One consequence of this mechanistic study was the discovery of syntheses of representatives of several new classes of organosulfur compounds, as will be described in the next section.

Table V provides a summary of data obtained from a detailed vpc study of the thermal disproportionation of EtS(O)SMe (**11**) at room temperature in the dark over a period of weeks while Table VI provides more exhaustive details on the products from pyrolysis of a variety of dialkyl thiolsulfinates under a number of reaction conditions. Some salient observations with regard to EtS(O)SMe are (1) unsymmetrical thiolsulfonate $EtSO_2SMe$ predominates over symmetrical thiolsulfonate $EtSO_2SEt$, most dramatically early during the course of the reaction; (2) formation of $EtSO_2SEt$ lags behind the build up of a low but easily detectable concentration of symmetrical thiolsulfinate EtS(O)SEt; (3) the presence of isomeric thiolsulfonates $MeSO_2SEt$ and $MeSO_2SMe$ can be rigorously excluded by both vpc and ir analysis; (4) additional products include trisulfides, water, and α-sulfinyl and α-sulfonyl disulfides. Control experiments carried out under conditions somewhat more drastic than those used for the pyrolyses of neat thiol-

(38) P. Koch and A. Fava, *J. Amer. Chem. Soc.*, **90**, 3867 (1968).
(39) F. Wudl, R. Gruber, and A. Padwa, *Tetrahedron Lett.*, 2133 (1969).

sulfinates indicate that exchange processes involving thiolsulfinates (or intermediates derived therefrom) and disulfides or thiolsulfonates do not significantly affect the thiolsulfinate-derived thiolsulfonate distribution (*cf.* entries 19–21, Table VI) but substantially modify the disulfide distribution. A study of the pyrolysis of a variety of unsymmetrical dialkyl thiolsulfinates either neat or in solution as summarized in Table VI generalizes the trends seen with EtS(O)SMe with respect to disproportionation. An important conclusion from these studies is the complete absence of any thermal pathway for interconversion of unsymmetrical isomeric thiolsulfinates, whether by dissociative or migration pathways (eq 16), in contrast to the situation with

$$RS(O)SR' \not\rightleftharpoons RSS(O)R' \qquad (16)$$

diaryl thiolsulfinates.[12] This conclusion also requires that the sulfenic acid dehydration reaction, eq 17, be

$$2RSOH \longrightarrow RS(O)SR + H_2O \qquad (17)$$

irreversible (at least where R is an alkyl group[40]); if this were not true, a facile pathway would exist for thiolsulfinate interconversion (see eq 18).[41]

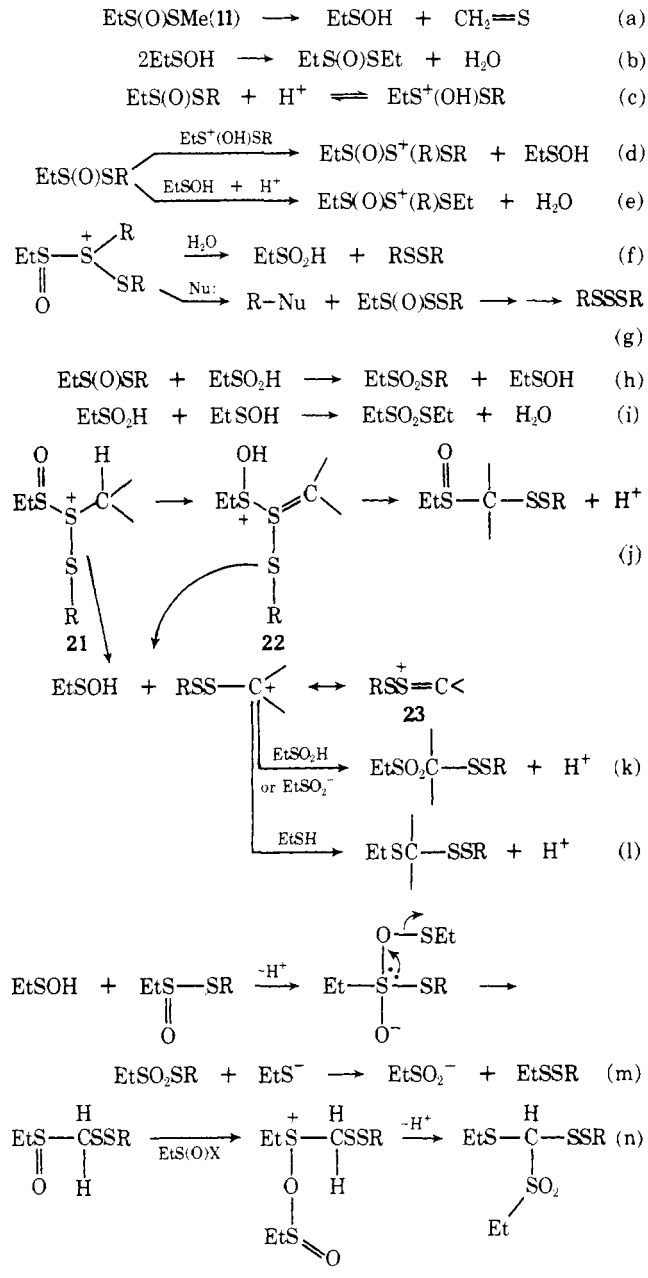
$$RS(O)SR' + H_2O \rightleftharpoons RSOH + R'SOH \rightleftharpoons RSS(O)R' + H_2O \qquad (18)$$

Scheme II accommodates all of our observations on the pyrolysis of dialkyl thiolsulfinates. The great predominance of unsymmetrical thiolsulfonate during the early stages of disproportionation of EtS(O)SMe follows from eq f (and h) because the predominant thiolsulfinate at this time is the unsymmetrical one (R = Me). Only as the concentration of symmetrical thiolsulfinate builds up from eq b are significant quantities of symmetrical thiolsulfonate produced (eq f, R = Et). The minor quantities of trisulfides (unequivocally identified by gc–ms) may possibly be formed through nucleophilic displacement at the activated alkyl group of the sulfinyl thioalkyl sulfonium ion followed by decomposition of the presumably highly reactive trisulfide monoxide (eq g). The studies involving the disproportionation of specifically deuterated dimethyl and diethyl thiolsulfinates described in the accompanying paper[2] indicate that, in the absence of factors associated with different alkyl groups, unsymmetrical thiolsulfonate predominates over symmetrical thiolsulfonate by a ratio of about 2.5:1. In the pyrolysis of unsymmetrically alkyl substituted thiolsulfinates, steric (and inductive) effects associated with the different alkyl substituents influence the relative facility with which the unsymmetrical thiolsulfinate and the symmetrical thiolsulfinate, formed in step b, progress through the several steps of Scheme II and therefore influence the ratio of unsymmetric to symmetric thiolsulfonate as well as the overall rate of disproportionation as indicated in Table II. For example, in the pyrolysis of MeS(O)S-*i*-Pr, steric factors may retard the rate of reaction of methanesulfinic acid with this unsymmetrical thiolsulfinate (*cf.* eq 14) relative to the rate of reaction of methanesulfinic acid with MeS(O)SMe (whose formation *via* steps a and b may take on increased importance because of the diminished

(40) Kice has suggested[22] that reaction 17 (R = phenyl) is favored over its reversal by an equilibrium constant of at least 10^6.

(41) Note that even in the presence of substantial amounts of water (Table VI, entry 11) the thiolsulfinate-derived thiolsulfonate distribution remains the same.

Scheme II. Summary of Proposed Thermal Reactions of Unsymmetrical Alkyl Thiolsulfinates



reactivity of MeS(O)S-*i*-Pr (**10**) toward displacement processes) accounting for the predominance of symmetrical over unsymmetrical thiolsulfonate by a factor of 2.2:1 (Table VI, entry 6). On the other hand, in the case of pyrolysis of *t*-BuS(O)SMe (**6**), a very considerable amount of the relatively unreactive *t*-BuS(O)S-*t*-Bu (**7**) accumulates in the reaction and practically no symmetrical thiolsulfonate (*t*-$BuSO_2S$-*t*-Bu) is formed (Table VI, entry 15). In this case steps f and h are made difficult by steric factors and rearrangement processes (*cf.* step j) become dominant. Anhydrous MeS(O)S-*t*-Bu (**8**) is quite resistant to disproportionation (*cf.* Table II) since elimination processes such as step a (Scheme II) are impossible. However, if traces of water are present, disproportionation does occur and symmetrical thiolsulfonate ($MeSO_2SMe$) is found to predominate over unsymmetrical thiolsulfonate (Me-SO_2S-*t*-Bu) by a ratio varying from 5.2:1 at ~10% reaction to 2.3:1 after ~40% reaction (*cf.* entry 7,

Table VII. Product Distribution from Ultraviolet Irradiation of Alkyl Thiolsulfinate Esters

No.	Thiolsulfinate (% converted)	Conditions[a]	Products (mol % in product) Thiolsulfonates	Disulfides
1	MeS(O)SMe (variable)	1–2 *M* in CH_2Cl_2 or C_6H_6, −40° or +40°	$MeSO_2SMe$ (50)	MeSSMe (50)
2	EtS(O)SMe (75)	0.005 *M* in CF_3Cl, −10° argon atmosphere	$EtSO_2SEt$ (17), $EtSO_2SMe$ (3)	MeSSMe, MeSSEt (46), EtSSEt (1)
3	EtS(O)SMe (100)	0.004 *M* in CF_3Cl, −70° argon atmosphere	$EtSO_2SEt$ (17), $EtSO_2SMe$ (9), $MeSO_2SEt$ (3)[b]	MeSSMe (26), MeSSEt (38), EtSSEt (7)
4	EtS(O)SMe (39)	0.163 *M* in C_6H_6 at 25°	$EtSO_2SEt$ (10), $EtSO_2SMe$ (5), $MeSO_2SEt$ (<0.2)	MeSSMe (16), MeSSEt (7)

[a] Wavelength of irradiation was 254 nm using either a low- or medium-pressure mercury arc lamp with appropriate filters. [b] The presence of this compound was confirmed by ir analysis; irradiation of MeS(O)SEt gave similar results.

Table VI). Presumably the thiolsulfinate reacts with traces of water to give methanesulfinic acid which then initiates a number of the reactions shown in Scheme II.

While we have not attempted a full kinetic analysis of the various reactions occurring on thermal decomposition of unsymmetrical alkyl thiolsulfinates, the following observations support the proposals of Scheme II.[42] In the concentration range 1–2 *M* in benzene, the initial rate of disappearance of EtS(O)SMe follows second-order kinetics with $k = 3.05 \times 10^{-5}$ l. mol^{-1} sec^{-1} at 96°; a substantial rate increase was seen with added trifluoroacetic acid and an even more dramatic increase noted with the added pair trifluoroacetic–diethyl sulfide. In all of these studies involving decomposition of EtS(O)SMe, as well as in additional studies involving decomposition of EtS(O)SMe in water–benzene, in dilute heptane solution and neat at various temperatures, similar product distributions are seen (*cf.* Table V and entires 8–12, Table VI) arguing for a common mechanism for decomposition under all of these conditions.

We have found that ultraviolet irradiation of dialkyl thiolsulfinates in several solvents also leads to disproportionation,[44] although there apparently are significant differences between the intermediates involved and products produced in the photochemical and thermal processes. As we have previously mentioned, irradiation of a pentane solution of a pair of different thiolsulfinates failed to lead to scrambling (eq 12) although disproportionation was observed; furthermore there was no evidence for the formation of $MeS(O)CH_2SSMe$ from irradiation of a benzene solution of MeS(O)SMe (*cf.* Table VII, entry 1). In addition, in the photolysis of unsymmetrical alkyl thiolsulfinates EtS(O)SMe and MeS(O)SEt in various solvents, *symmetrical* thiolsulfonate predominated over unsymmetrical thiolsulfonate by a ratio ranging from 5:1 to 2:1 (*cf.* Table VII). In some experiments, *e.g.*, low temperature irradiation of a thoroughly degassed solution of an unsymmetrical thiolsulfinate in CF_3Cl, isomeric thiolsulfinates, and thiolsulfonates could be detected (*e.g.*, RSS(O)R′ and $RSSO_2R'$ from RS(O)SR′) although in concentrations rarely exceeding ~15% of total thiolsulfinate or thiolsulfonate. We suggest that photolysis of dialkyl thiolsulfinates gives rise to thiyl and alkanesulfinyl radicals which may undergo reactions similar to those proposed by Fava[12] as shown in Scheme III. It

Scheme III. Proposed Photochemical Reactions of Unsymmetrical Alkyl Thiolsulfinates

$$RS(O)SR' \xrightarrow{h\nu} RSO\cdot + R'S\cdot \quad (a)$$

$$RSO\cdot + RS(O)SR' \longrightarrow RS(O)OSR + R'S\cdot \quad (b)$$

$$RS(O)OSR \longrightarrow RSO_2SR \text{ or } RSO_2\cdot + RS\cdot \quad (c)$$

$$R'S\cdot \text{ (or } RS\cdot) + RS(O)SR' \longrightarrow R'SSR' \text{ (or RSSR')} + RSO\cdot \quad (d)$$

$$R'S\cdot \text{ (or } RS\cdot) + RSO_2SR \longrightarrow R'SSR \text{ (or RSSR)} + RSO_2\cdot \quad (e)$$

$$RSO_2\cdot + RS(O)SR' \longrightarrow RSO_2SR' + RSO\cdot \quad (f)$$

$$RSO\cdot + R'S\cdot \rightleftharpoons RS{-}O{-}SR' \rightarrow RS\cdot + R'SO\cdot \quad (g)$$

$$RS(O)SR' \xrightarrow{h\nu} RS{-}O{-}SR' \rightarrow RSS(O)R'$$

should, however, be noted that irradiation of solutions of dialkyl thiolsulfinates in the cavity of an esr spectrometer did not give rise to observable alkanesulfinyl radical absorption.[45] Furthermore, low temperature nmr examination of samples of MeS(O)SMe irradiated in CH_2Cl_2 at low temperature for various time periods showed the presence of $MeSO_2SMe$ and MeSSMe with no additional peaks such as might be attributable to MeS–O–SMe or MeS–O–S(O)Me.

Alkyl Thiolsulfinates as Precursors to α-Heteroatom Substituted Disulfides. Certainly the most novel consequence of our study of thiolsulfinate chemistry was the discovery of derivatives of α-alkylthiyl disulfides as pyrolysis products of dialkyl thiolsulfinate esters. This discovery prompted a careful study of reactions affording these unusual α-heteroatom substituted disulfides with the aim of maximizing their yields and understanding their origin. We have suggested[3d] that structures of general formula **24** are formed *via* a Pummerer re-

$$RSO_nCR'R''SSR'''$$
24

arrangement of our postulated sulfinyl sulfonium ion intermediate **21** as depicted in Scheme II. The α-alkylsulfinyl disulfides may result from a direct rearrangement of an ylide such as **22** or else from rapid recombination of alkylidene sulfonium ion **23** with the quite nucleophilic alkanesulfenic acid.[46] The α-alkylsulfonyl

(42) Scheme II parallels in a number of important ways the mechanism proposed by Kice to explain the concomitant acid/nucleophile catalyzed disproportionation of aryl thiolsulfinates.[43] In our case the divalent sulfur of one thiolsulfinate is the nucleophile (rather than an external agent) promoting S–S scission of a second thiolsulfinate molecule. The rate of disproportionation is greatly increased by the addition of a substance such as a sulfide which contains a much more nucleophilic sulfur atom than found in thiolsulfinates.

(43) J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **95**, 109 (1973).

(44) (a) For another report of photochemically induced disproportionation, see ref 36. (b) For a report of γ-radiation induced disproportionation, see P. J. Berner, Ph.D. Thesis, Stevens Institute of Technology, 1964.

(45) J. K. Kochi, unpublished results.

(46) For some related studies, see J. L. Kice and E. H. Morkved, *J. Amer. Chem. Soc.*, **85**, 3472 (1963).

and α-alkylthiyl disulfides may be postulated to result from attack of alkanesulfinic acid (or alkanesulfinate anion) and thiol (or thiolate anion) on the sulfonium ions **23**, processes with precedence in Pummerer rearrangements.[47]

The distribution of α-alkylsulfinyl and α-alkylsulfonyl disulfides from pyrolysis of EtS(O)SMe (**11**) (Table VI, entry 11), provides some support for the proposed mechanism. In this pyrolysis all four possible sulfinyl sulfonium ions **25–28** are presumably formed

$$\underset{\textbf{25}}{EtS(O)\overset{+}{S}MeSMe} > \underset{\textbf{26}}{EtS(O)\overset{+}{S}MeSEt} \simeq \underset{\textbf{27}}{EtS(O)\overset{+}{S}EtSMe} > \underset{\textbf{28}}{EtS(O)\overset{+}{S}EtSEt}$$

and can be postulated to have the relative order of abundance shown (based on the assumption that precursor EtS(O)SMe is much more abundant than precursor EtS(O)SEt, **2**). We have shown elsewhere that α-disulfide carbonium ions are considerably less stable than the corresponding α-alkylthiyl carbonium ions[48] (thus the rate of SN1 hydrolysis of chloromethyl methyl disulfide is *ca.* 7000 times slower than SN1 hydrolysis of chloromethyl methyl sulfide). We suggest that alkyl substituted carbonium ions **29** and **30** (derived from ions **27** and **28**, respectively), because of their enhanced stability compared to ions **31** and **32** (derived from ions

$$\underset{\textbf{29}}{CH_3\overset{+}{C}HSSMe} \quad \underset{\textbf{30}}{CH_3\overset{+}{C}HSSEt} \quad \underset{\textbf{31}}{\overset{+}{C}H_2SSMe} \quad \underset{\textbf{32}}{\overset{+}{C}H_2SSEt}$$

25 and **26**, respectively), are better able to escape from their sulfenic acid partner (*cf.* steps j and k, Scheme II) to be trapped by sulfinic acid (or sulfinate anion). A combination of arguments based on the relative abundance of ions **25–28**, on the relative stabilities of carbonium ions **29–32**, and the predominance of a direct rearrangement of ylide **22** (or predominance of processes involving cage recombination) can reasonably explain the observed distribution of α-alkylsulfinyl and α-alkylsulfonyl disulfides produced in this particular reaction.

We may briefly consider several alternative mechanisms to account for the formation of these α-heteroatom substituted disulfides. Neither mechanism I nor II accounts satisfactorily for α-alkylsulfonyl disulfide

$$\text{I} \quad RS(O)SCH_3 + R'\cdot \longrightarrow RS(O)SCH_2\cdot + R'H$$

$$RS(O)SCH_2\cdot \rightarrow \underset{\displaystyle CH_2}{R{-}S(O\cdot){-}S} \rightarrow RS(O)CH_2S\cdot \qquad (19)$$

$$RS(O)CH_2S\cdot + RS(O)SCH_3 \longrightarrow RS(O)CH_2SSCH_3 + RSO\cdot$$

$$\text{II} \quad RS(O)SCH_3 \longrightarrow RSOH + S{=}CH_2 \longrightarrow RS(O)CH_2SH$$

$$RS(O)CH_2SH + RS(O)SCH_3 \longrightarrow RS(O)CH_2SSCH_3 + RSOH \qquad (20)$$

formation (alkyl thiolsulfonates RSO_2SCH_3 are unreactive under the conditions used in these studies). Mechanism I (eq 19) is also unlikely in view of our failure to detect free radicals. Furthermore, under conditions which presumably generate radicals, namely irradiation of a benzene solution of MeS(O)SMe, no $MeS(O)CH_2SSMe$ could be detected. Mechanism II (eq 20) is made unlikely by the known high reactivity of thioformaldehyde toward self-reaction[49] coupled with the efficient trapping of sulfenic acids (in yields in some cases in excess of 90%) realized with acetylenes, with no evidence of the formation of adducts of the type $RS(O)CH_2SCR'{=}CHR''$. A third alternative mechanism involving a direct Pummerer rearrangement of a thiolsulfinate (*cf.* eq 2) is of course precluded by the experimental results obtained for EtS(O)SMe and *t*-BuS(O)SMe.

Consideration of the mechanism proposed in Scheme II suggested that α-alkylsulfinyl disulfide formation might be made to predominate over thiolsulfonate formation if attack by water on the sulfinyl sulfur of ions such as **21** (Scheme II) could be suppressed. One solution to this problem was achieved through the use of an aromatic solvent in the pyrolyses. Thus, while pyrolysis of MeS(O)SMe (**1**) neat or in heptane solution at 96° led almost exclusively to an equimolar mixture of MeSSMe and $MeSO_2SMe$, pyrolysis of **1** (at 96°) in anhydrous C_6F_6, benzene, and 1,3,5-trimethylbenzene afforded 2,3,5-trithiahexane 5-oxide, $MeS(O)CH_2SSMe$ (**33**) in 24, 40, and 52% yields, respectively, in addition to the disproportionation products. A π complex involving the aromatic nucleus and the electrophilic sulfur centers of the sulfonium ion of type **21** can be invoked. Such a complex would be more efficiently formed from 1,3,5-trimethylbenzene than the electron-poor hexafluorobenzene. It is interesting to note that while disulfide and thiolsulfonate formation from MeS(O)SMe are substantially reduced through the use of benzene as a solvent, the yield of trisulfide is actually increased (Table VI, entry 2). This observation is consistent with a reaction sequence such as that shown in eq 21. Complexation with benzene would not be expected to substantially hinder nucleophilic attack at carbon.[50]

$$CH_3S(O)\overset{+}{S}(SCH_3)CH_3 + Nu: \longrightarrow CH_3{-}\overset{+}{N}u + CH_3S(O)SSCH_3$$

$$CH_3S(O)SSCH_3 + H_2O \longrightarrow CH_3SO_2H + CH_3SSH \qquad (21)$$

$$CH_3SSH + CH_3S(O)SCH_3 \longrightarrow CH_3SSSCH_3 + CH_3SOH$$

The yield of **33** from MeS(O)SMe could be substantially increased by the use of a refluxing two-phase system of water–benzene as solvent. In this manner 30 g of pure **33** could be routinely prepared in 84% yield (yield based on distilled material) as in eq 22. Attack

$$\underset{\textbf{1}}{3MeS(O)SMe} \xrightarrow[\text{reflux}]{C_6H_6{-}H_2O} \underset{\textbf{33}\ (84\%)}{2MeS(O)CH_2SSMe} + H_2O \qquad (22)$$

by water at the sulfinyl sulfur of sulfonium ion **34**, derived from pyrolysis of *t*-BuS(O)SMe, **6**, is also hindered and in this case substantial quantities of the nicely crystalline Pummerer product, 2,2-dimethyl-3,5,6-trithiaheptane 3-oxide (**35**), are formed without the use of benzene as solvent. The maximum yield of **35** is obtained when thiolsulfinate **6** is pyrolyzed in the presence of an equal weight of water (yield of **35** with water

(47) See, for example, G. A. Russell and E. T. Sabourin, *J. Org. Chem.*, **34**, 2336 (1969).

(48) E. Block, *J. Org. Chem.*, **39**, 734 (1974); E. Block, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **19**, 205 (1974).

(49) The half-life of thioformaldehyde is *ca.* 6 min at 10^{-5} mm: D. R. Johnson, F. Y. Powell, and W. H. Kirchoff, *J. Mol. Spectrosc.*, **39**, 136 (1971).

(50) The formation of **33** from **1** could also be favored through the use of 2-butanone as a solvent. Here, too, an association between **1** and the solvent can be invoked. (See S. Oae, *Quart. Rep. Sulfur Chem.*, **5**, 53 (1970), for evidence for the association of dimethyl sulfoxide and ketones.)

is 41%; in the absence of added water the yield of **35** is only 27%). Only poor yields of **35** are obtained on pyrolysis of thiosulfinate **6** in benzene. If water is

$$4t\text{-BuS(O)SCH}_3 \xrightarrow{\Delta} 2t\text{-BuS(O)}\overset{+}{\text{S}}\text{(CH}_3\text{)SCH}_3 + 2t\text{-BuSO}^-$$
6 **34**

$$2t\text{-BuSO}^- \xrightarrow{+2H^+} H_2O + t\text{-BuS(O)S-}t\text{-Bu}$$

$$\mathbf{34} \xrightarrow{-2H^+} 2t\text{-BuS(O)CH}_2\text{SSCH}_3$$
35

rigorously excluded during the pyrolysis of **6** through use of various basic dehydrating agents (CaC_2, CaH_2) coupled with a vacuum of 5.5 mm (sufficient to cause **6** to gently reflux at 96°), the reaction takes a surprising turn. Under these conditions the major crystalline product is the α-sulfonyl disulfide 2,2-dimethyl-3,5,6-trithiaheptane 3,3-dioxide (**36**) obtained in 29% yield, in addition to an 11% yield of **35**. The basic reagent may promote the conversion of sulfenic acid to sulfinate anion as indicated in step m, Scheme II.[51] The sulfinate anion would then afford the α-sulfonyl disulfide through interaction with carbonium ion **23**. The precise role of water in all of these above described reactions remains to be explained.

Reactions of α-Alkylsulfinyl and α-Alkylsulfonyl Disulfides. Detection of an α-Disulfide Carbanion. We have shown that representatives of two new classes of organic sulfur compounds, α-alkylsulfinyl and α-alkylsulfonyl disulfides, may be prepared in moderate to good yields from readily available thiolsulfinate precursors. Of particular interest in the chemistry of these new compounds is the extent to which the normal reactions of the isolated disulfide group and the isolated alkylsulfinyl or alkylsulfonyl groups are modified by each other's presence. For example, it is known that disulfides bearing α protons are susceptible to base-induced α-elimination reactions, as illustrated by the formation of thiobenzophenone and arylthiolate from disulfide **37**.[52a] It is interesting to note that if this elimination reaction is carried out with isopropyl [^{3}H]-alcohol as solvent and allowed to proceed to about 50% completion, there is no tritium incorporated into the recovered disulfide. This observation rules out the intermediacy of carbanion **38** and indicates a concerted

$$\underset{\mathbf{37}}{\underset{\text{H}}{\text{Ph}_2\text{C—S—S—Ar}}} \xrightarrow{\text{NaOCHMe}_2} \text{Ph}_2\text{C=S} + \text{ArS}^- \qquad \underset{\mathbf{38}}{\text{Ph}_2\overset{-}{\text{C}}\text{—S—S—Ar}}$$

E2 elimination process.[52a] Indeed, in searching the literature on the reactions of disulfide with base,[52b] we find no definitive evidence for the existence of discrete α-disulfide carbanions. α-Alkylsulfinyl and α-alkylsulfonyl disulfides are particularly interesting candidates for α-disulfide carbanion formation in view of the well-known carbanion-stabilizing effect of the sulfinyl and sulfonyl groups and the anticipated instability (on dipole–dipole repulsion grounds) of thiocarbonyl compounds of type **39**. We have found that brief exposure

$$\underset{\mathbf{39}}{\text{RSO}_n\text{—CH=S}}$$

of t-$BuSO_2CH_2SSCH_3$, **36**, to methanol-d_4 in the presence of a trace of sodium methoxide-d_3 gave rapid exchange of the methylene protons affording the 4,4-dideuterio derivative **36b** (85% d_2, 13% d_1, 1.5% d_0) in 82% isolated yield.[53] This experiment provides the first unequivocal evidence for the existence of a discrete α-disulfide carbanion (**36a**). Efforts to trap this inter-

$$\underset{\mathbf{36}}{t\text{-BuSO}_2\text{CH}_2\text{SSCH}_3} \xrightarrow[\text{CD}_3\text{ONa}]{\text{CD}_3\text{OD}} \underset{\mathbf{36a}}{t\text{-BuSO}_2\overset{-}{\text{C}}\text{HSSCH}_3} \longrightarrow \longrightarrow \underset{\mathbf{36b}}{t\text{-BuSO}_2\text{CD}_2\text{SSCH}_3}$$

mediate carbanion and related α-disulfide carbanions with other electrophiles in a synthetically useful manner are in progress.

Among other reactions, dialkyl sulfoxides are known to undergo ready O-alkylation, reduction (both of the S–O bond and, in suitable cases, of a C–S bond), and Pummerer rearrangement.[1] While a variety of reducing agents are available for reduction of sulfoxide to sulfide,[54] most of these agents would also be expected to readily reduce the S–S linkage. Indeed, in a recent report dealing in part with reduction of S=O in the presence of S–S, the desired selectivity was achieved only in poor yield (6% yield) using triphenylphosphine as reducing agent.[55] In our hands, 2,3,5-trithiahexane was isolated in 8% yield and triphenyl phosphate in 65% yield from reaction of MeS(O)CH_2SSMe, **33**, and triphenyl phosphite (eq 23). A much more satisfactory

$$\underset{\mathbf{33}}{\text{MeS(O)CH}_2\text{SSMe}} + (\text{PhO})_3\text{P} \longrightarrow \underset{8\%}{\text{MeSCH}_2\text{SSMe}} + (\text{PhO})_3\text{P=O} \quad (23)$$

procedure for selective S=O reduction was developed based on the report of Johnson[8] that the rate of reduction of sulfoxides by bisulfite is greatly enhanced if the sulfoxides are first O-alkylated. Thus, sequential treatment of **33** with triethyloxonium fluoroborate in methylene chloride followed by brief exposure to ice cold aqueous sodium bisulfite afforded an 86% yield (after distillation) of $MeSCH_2SSMe$ as a pale yellow, thermally unstable oil (eq 24). The mass spectrum of

$$\underset{\mathbf{33}}{\text{MeS(O)CH}_2\text{SSMe}} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{Et}_3\text{O}^+} \text{MeS}\overset{+}{\text{(OEt)}}\text{CH}_2\text{SSMe} \xrightarrow{\text{NaHSO}_3} \underset{86\%}{\text{MeSCH}_2\text{SSMe}} \quad (24)$$

this compound indicates a preference for elimination of the alkyldithiyl radical (base peak is $MeSCH_2^+$, m/e 61) rather than the alkylthiyl radical (relative abundance of m/e 93, $MeSSCH_2^+$, is 3%), an observation consistent with the greater stability of the right-hand pair of products in eq 25 compared to the left-hand pair of products.

$$\text{MeS}\cdot + \text{MeSSCH}_2^+ \longleftarrow \text{MeSCH}_2\text{SSMe}\cdot^+ \longrightarrow \text{MeSCH}_2^+ + \text{MeSS}\cdot \quad (25)$$

Selective cleavage of the sulfinyl sulfur–methylene carbon bond in **33** could be effected with aluminum

(51) We thank Professor John Kice for this suggestion.

(52) (a) U. Miotti, U. Tonellato, and A. Ceccon, *J. Chem. Soc. B*, 325 (1970). (b) For a general review of the reactions of disulfides with base, see J. P. Danehy, *Int. J. Sulfur Chem., Part B*, 6(2), 103 (1971).

(53) Similar studies with various α-alkylsulfinyl disulfides have thus far led only to extensive decomposition.

(54) G. M. Gurria and G. H. Posner, *J. Org. Chem.*, **38**, 2419 (1973), and references therein.

(55) R. G. Hiskey and M. A. Harpold, *J. Org. Chem.*, **32**, 3191 (1967).

amalgam to give dimethyl disulfide in a nonoptimized yield of 30%. Treatment of **33** with acetic anhydride led to a Pummerer rearrangement giving 3-acetoxy-2,3,5-trithiahexane in 47% yield (eq 26). A Pummerer

$$\underset{\mathbf{33}}{\mathrm{MeS(O)CH_2SSMe}} \xrightarrow{\mathrm{Ac_2O}} \underset{47\%}{\mathrm{MeSCH(OAc)SSMe}} \qquad (26)$$

rearrangement of **33** is also presumably responsible for the formation of 3-methanesulfonyl-2,3,5-trithiahexane as a minor product from pyrolysis of MeS(O)SMe (**1**) in aqueous benzene (see step n, Scheme II).

Experimental Section

The melting points are corrected. The ir spectra, unless otherwise noted, were determined as a thin film on either a Perkin–Elmer 137 or 337 infrared spectrophotometer. The uv spectra were determined in 95% ethanol on a Perkin–Elmer 202 or 450 uv spectrophotometer. Analyses were carried out by Chemalytics, Tempe, Ariz., and by Mr. J. Nemeth and his associates (University of Illinois—Urbana). Satisfactory analyses were obtained for all new compounds. Nmr spectra were obtained with a Varian T-60 instrument using tetramethylsilane as an internal standard. Mass spectra were determined on an A.E.I. MS-12 mass spectrometer operating at 70 eV and source temperatures of 50° or lower (for thermally unstable substrates). Exact mass measurements were made on a Varian MAT 731 high-resolution double focusing mass spectrometer by the staff of the mass spectrometry laboratory at the University of Illinois—Urbana. Vapor phase chromatography (vpc) was accomplished on a Hewlett Packard Model 5750 gas chromatograph (flame ionization detector) equipped with a Hewlett Packard Model 3370A digital integrator. A $^1/_8$ in. × 6 ft column of 10% silicone rubber UCW-98 on 80–100 mesh Chromosorb W was used for analytical purposes. For vpc analysis of the most thermally labile thiolsulfinates, a column temperature of 70–75° and an injection port temperature of 80° was employed. Under these conditions, pure samples of MeS(O)SMe (injected as 1% solutions in ether) showed only a single peak (retention time 4 min) corresponding to the thiolsulfinate (peaks corresponding to the disproportionation products, MeSSMe and $MeSO_2SMe$, were absent).[56] Vpc retention times for all thiolsulfinates and thiolsulfonates studied are given in Tables I and II in the supplementary material for the accompanying paper. Mass analyses for thiolsulfinate pyrolysis products were accomplished, either in conjunction with or without prior fractionation by preparative tlc, by quantitative vpc using *ca.* 1% solutions containing known weights of dodecane or cyclododecane as internal standards (after calibration with authentic samples of the various components). Coupled gas chromatography–mass spectrometry (gc–ms) was accomplished using the described vpc facilities coupled *via* an all-glass Watson–Biemann separator to the source of the MS-12 mass spectrometer. A number of mass spectra were also obtained under gc–ms conditions using an LKB Model 9000 integrated gc–ms system through the courtesy of Professor William Sherman (Washington University School of Medicine). Under the mild gc–ms operating conditions, even the most thermally labile thiolsulfinates studied gave excellent reproducible mass spectra. Preparative tlc was performed on Merck PF_{254} silica gel plates 1.5 mm thick. Esr studies were performed by Professor M. T. Jones on a Varian E-12 esr spectrometer.

α-Ethylsulfinylstyrene. A solution of EtS(O)SEt[1,57] (**2**) (0.372 g, 2.7 mmol) in phenylacetylene (3.315 g, 32 mmol) was heated overnight at 96° in an argon atmosphere. Distillation of the yellow product gave 2.953 g of phenylacetylene (97% recovery of unreacted material), collected in a trap chilled with liquid nitrogen, and 0.440 g of the title compound (91% yield) as a practically colorless oil: bp 80–85° (0.01 mm); nmr (CCl_4) δ 1.07 (t, J = 7.5 Hz, 3 H), 2.35 (dectet, 2 H), 5.90 and 5.94 (s, total area 2 H), and 7.35 (s, 5 H). In 1:1 C_6D_6/CCl_4 the δ 5.9 singlets appeared at δ 5.80 and 6.04 with individual areas of 1 H each and shoulders suggesting coupling constants of <1 Hz. The ir spectrum (neat film) had bands at 9.44 (S=O), 9.73, 10.83, 12.85, 13.93, and 14.30 μ. The mass spectrum had *m/e* 180 ($C_{10}H_{12}SO$, M^+) with major peaks at *m/e* 103 ($M - C_6H_5$, base peak) and 77 ($C_6H_5^+$).

Ethyl β-Methylsulfinylpropionate. A solution of 0.220 g of MeS(O)SMe[58] (**1**) (2 mmol), and 1.66 g (16.6 mmol) of ethyl acrylate was heated at 96° for 8 hr, filtered, and then concentrated *in vacuo* to afford 0.271 g of ethyl β-methylsulfinylpropionate (82% yield) as a slightly colored liquid. A colorless sample of this product (purified by preparative tlc with ether as developing solvent) had ir (neat) 5.80 (s, C=O of ester) and 9.52 μ (s, S=O), nmr (benzene) δ 1.01 (t, 3 H), 2.10 (s, 3 H), 2.45–2.90 (mult., 4 H) and 3.95 (q, 2 H) and was spectrally and chromatographically identical with a sample of ethyl β-methylsulfinylpropionate prepared by oxidation of ethyl β-methylthiopropionate.[58]

Methyl *trans*-β-Ethylsulfinylacrylate. A solution of 0.343 g (2.5 mmol) of **2** in 2.4 g (29 mmol) of methyl propiolate was heated at 96° for 20 hr, concentrated *in vacuo*, and the yellow oil subjected to preparative tlc (ethyl acetate) to give as the main component 0.306 g (76% yield) of a yellow oil: ir (neat) 5.80 (C=O), 6.16 (C=C), 9.46 and 9.71 μ (S=O), nmr (CCl_4) δ 1.28 (t, J = 7 Hz, 3H), 2.84 (m, 2 H), 3.79 (s, 3 H), 6.46 (d, J = 15 Hz, 1 H), 7.72 (d, J = 15 Hz, 1 H). Irradiation of the δ 1.28 triplet simplified the multiplet at δ 2.84 to a pair of doublets. The mass spectrum showed peaks at *m/e* 162 (M^+, $C_6H_{10}SO_3$), 102 (base). An analytical sample was prepared by recrystallization twice from hexane; the colorless crystalline solid had mp 59.5–61°.

Methyl *trans*-β-Methylsulfinylacrylate. A solution of 0.239 g (2.2 mmol) of **1** in 2.2 ml (30.6 mmol) of methyl propiolate was heated at 96° for 10.5 hr, filtered, and concentrated *in vacuo*, and the yellow oil subjected to preparative tlc (ethyl acetate as developing solvent) to give 0.213 g (65% yield) of a pale yellow oil: ir (neat) 5.80 (s, C=O), 6.16 (m, C=C), 9.35–9.50 (s, S=O); nmr ($CDCl_3$) 2.73 (s, 3 H), 3.80 (s, 3 H), 6.60 (d, J = 15 Hz, 1 H), 7.72 (d, J = 15 Hz, 1 H), mass spectrum *m/e* 148 (M^+, $C_5H_8SO_3$), 101 ($M^+ - CH_3S\cdot$, base).

Methyl *trans*-β-(β′,β′,β′-Trideuterioethylsulfinyl)acrylate. A solution of 0.125 g (0.87 mmol) of $CD_3CH_2S(O)SCH_2CD_3$ (**3**) in 1.2 g (14 mmol) of methyl propiolate was heated at 96° for 18 hr and then worked up as above to afford 0.039 g (27% yield) of the title compound as a colorless crystalline solid: mp 55.5–58° (uncorr.); ir (KBr pellet) 4.50 and 4.80 (C–D), 5.81 (C=O), 6.15 (C=C), and 9.58 μ (S=O), nmr ($CDCl_3$) δ 2.80 (br m, 2 H), 3.83 (s, 3 H), 6.61 (d, J = 15 Hz, 1 H), 7.55 (d, J = 15 Hz, 1 H). The mass spectrum at 10 eV showed peaks in the parent region at *m/e* 164, 165, 166, and 167 with relative intensities of 7.7, 100.0, 10, and 6.2%, respectively. The calculated intensities for the parent region peaks, assuming a 7.7:100 ratio of $C_6H_8D_2SO_3$ (*m/e* 164; starting material **1** actually consists of 87.4% d_6 and 12.6% d_5 material) to $C_6H_7D_3SO_3$, are 100, 8.2, and 5.3 for *m/e* 165, 166, and 167, respectively, allowing a maximum ratio of $C_6H_6D_4SO_3/C_6H_7D_3SO_3$ of 1.8:100 (within estimated experimental error of zero).

Reaction of MeS(O)S-*t*-Bu (8) with Methyl Propiolate. Heating a mixture of 0.029 g of **8**[2] (0.2 mmol) with 0.176 g of methyl propiolate (2.1 mmol) at 96° for 25 hr in a sealed tube did not lead to any significant reaction as determined by vpc, ir, and nmr analysis.

Methyl *trans*-β-2-Propanesulfinylacrylate. A solution of 0.364 g of *i*-PrS(O)SMe (**4**)[2] (2.6 mmol) and 2.64 g of methyl propiolate (31 mmol) was heated at 96° for 10 hr to give a yellow solution and a colorless precipitate. The colorless precipitate (0.053 g) was isolated by filtration, washed with methylene chloride, and sublimed at 200–210° to give a colorless sublimate whose ir spectrum (KBr pellet) was superimposable with the ir spectrum of authentic 1,3,5-trithiane in the region 2.5–25 μ. Since the original, highly insoluble precipitate was different from 1,3,5-trithiane (vpc, nmr) but was converted to 1,3,5-trithiane on sublimation, it is presumed to be polythioformaldehyde (isolated in 44% yield). Concentration of the filtrate followed by recrystallization of the residue from carbon tetrachloride afforded 0.042 g (7% yield) of a colorless solid, mp 107.6–108.3°, whose ir and nmr spectra were identical with the spectra reported by Shelton and Davis for **5b** (β,β′-bis(*trans*-carbomethoxy)divinyl sulfoxide)[14] (lit. mp 105–106°). The concentrated mother liquor from this recrystallization was subjected to preparative tlc (ethyl acetate) to afford 0.220 g (49% yield) of the title compound as a slightly yellow oil: ir (neat) 5.79 (C=O), 6.17 (C=C), 9.40 and 9.70 μ (S=O); nmr (CCl_4) δ 1.18 and 1.32 (pair of doublets, J = 7 Hz, 6 H), 2.92 (septet, J = 7 Hz, 1 H), 3.75 (s, 3 H), 6.47

(56) The isolation of pure samples of MeS(O)SMe, **1**, by preparative vpc has been described: T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, **31**, 3587 (1966). We thank these authors for a discussion of their vpc conditions.

(57) L. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Amer. Chem. Soc.*, **69**, 1710 (1947).

(58) J. L. Szabo and E. T. Stiller, *J. Amer. Chem. Soc.*, **70**, 3667 (1948).

(d, J = 15 Hz, 1 H), and 7.55 (d, J = 15 Hz, 1 H). Irradiation of the septet at δ 2.92 transformed the δ 1.8 and 1.32 peaks to singlets (diastereotopic methyl groups) at δ 1.18 and 1.32. The high-resolution mass spectrum indicated a parent peak at m/e 176.05074 (calcd for $C_7H_{12}SO_3$, 176.0507).

Reaction of *t*-BuS(O)SMe (6) with Methyl Propiolate. Heating a solution of 0.506 g of **6**[2] (3.3 mmol) and 5.52 g (66 mmol) of methyl propiolate at 100° for 15 hr gave 0.332 g (46% yield) of **5b**, mp 107.6–108.3°.

2-Ethylsulfinyl-1-heptene. A solution of 0.394 g (2.9 mmol) of **2** in 21.5 g of 1-heptyne (0.224 mol) was refluxed under argon for 4.5 hr. The unreacted 1-heptyne was then recovered by distillation (at 20 Torr) and the residue subjected to dry column chromatography[59] on a 30 × 1.18 in. silica gel column (ethyl acetate as eluent) to give 0.162 g of the title compound as a yellow oil (33% yield). Molecular distillation at 55–60° (0.01 Torr) afforded a colorless liquid: ir (neat) 6.17 (C=C) and 9.40–9.57 μ (S=O); nmr (CCl_4) δ 0.8–1.9 (m, 12 H), 1.9–2.3 (m, 2 H, allylic protons), 2.62 (m, 2 H, $CH_3CH_2S(O)$) 5.56 (t, J = 1.3 Hz, 1 H), 5.72 (t, J = 0.8 Hz, 1 H). High-resolution mass spectrometry indicated a parent at m/e 174.1079 (calcd for $C_9H_{18}SO$, 174.1078); the base peak in the mass spectrum was at m/e 55 ($C_4H_7^+$).

Runs using a high initial concentration of thiolsulfinate showed evidence of reactions involving the thiolsulfinate and the 2-ethylsulfinyl-1-heptene.

2-Methyl-2-propyl α-Styrenethiolsulfinate. A solution of 0.406 g (2.1 mmol) of *t*-BuS(O)S-*t*-Bu, in 2.028 g (20 mmol) of phenylacetylene was heated at 96° for 7 hr. A gas-phase ir spectrum of the gaseous reaction product was superimposable on that of authentic isobutylene. Preparative tlc of the product afforded 0.151 g (30% yield) of the title compound which after additional purification by molecular distillation at temperatures below 50° was a colorless liquid: nmr (CCl_4) δ 1.50 (s, 9 H), 6.00 and 6.16 (AB q, J = 0.6 Hz, 2 H), 7.30 (s, 6 H); ir 9.10 (S=O) and 10.75 μ (C=CH_2), mass spectrum showed parent at m/e 240 ($C_{12}H_{16}S_2O$).

***t*-BuS(O)S-*t*-Bu(7)-Methyl Propiolate Adduct.** A solution of 0.409 g (2.1 mmol) of **7** in 1.91 g (23 mmol) of methyl propiolate was heated at 96° for 6 hr and then concentrated *in vacuo* to afford 0.264 g (56% yield) of the adduct, *trans*-*t*-BuSS(O)CH=$CHCO_2$Me. Additional purification of this material by molecular distillation at 52° (0.02 mm) gave a product with nmr (CCl_4) δ 1.58 (s, 9 H), 3.75 (s, 3 H), 6.58 and 7.67 (AB q, J = 15 Hz, 2 H); ir 5.79 (C=O), 6.20 (C=C), 9.06 (S=O), and 10.45 μ (trans CH=CH); mass spectrum m/e 222 ($C_8H_{14}S_2O_3$, M^+).

2-Methyl-2-propyl 2-Hept-1-enethiolsulfinate. A solution of 0.613 g of **7** (3.2 mmol) in 30 ml (32 g, 0.31 mol) of 1-heptyne was refluxed for 8 hr, excess alkyne was distilled off *in vacuo*, and the residue was subjected to dry column chromatography[59] (silica gel–CH_2Cl_2) to give 0.152 g (21% yield) of the title compound which, after further purification by molecular distillation at 70° (0.01 mm), was a colorless liquid showing nmr (CCl_4) δ 0.70–1.90 (m with s at 1.60, 18 H), 2.1–2.4 (m, 2 H), 5.64 (m, 1 H), 5.95 (d, J = 0.6 Hz); ir 6.10 (C=C), 9.15 (S=O), 10.8 μ (C=CH_2); uv λ_{max} 261 (ϵ 2960).

Scrambling Reaction of EtS(O)SEt and MeS(O)SMe. Equimolar quantities of the title compounds and a known weight of *n*-dodecane as an internal standard were made up to various volumes with anhydrous benzene (dried over P_4O_{10}). The scrambling reaction was monitored by quantitative vpc by observing the disappearance of the symmetrical thiolsulfinate peaks. The rate of the scrambling process was *independent* of thiolsulfinate concentration in the range 5×10^{-2}–5×10^{-4} M in each thiolsulfinate ($k_{0.05\ M}$ = 3.74×10^{-4} sec^{-1}, $k_{0.005\ M}$ = 3.10×10^{-4} sec^{-1}, $k_{0.0005\ M}$ = 3.10×10^{-4} sec^{-1} at 96°). On the time scale of the scrambling reaction very little disproportionation occurred (the half-life for disproportionation of $C_2H_5S(O)SCH_3$, 0.016 M in benzene, at 96° is *ca.* 2000 min while the half-life for the scrambling process, as determined above, is approximately 33 min at 96°).

Irradiation of a pentane solution 5×10^{-3} M each in $CH_3S(O)SCH_3$ and $C_2H_5S(O)SC_2H_5$ at 254 nm gave no indication of thiolsulfinate scrambling although some disproportionation products were produced. A modest retardation in the rate of scrambling of a mixture of $CH_3S(O)SCH_3$ and $C_2H_5S(O)SC_2H_5$ (0.05 M, each, in benzene) was produced when the solution was 1 M in 2,6-dimethylpyridine while a significant acceleration in rate of scrambling was produced when the solution was made 0.02 M in methanesulfonic acid.

Search for Free Radicals from Thiolsulfinate Decomposition. Neat samples of MeS(O)SMe (**1**) and *i*-PrS(O)SMe and sample of **1** in heptane and dodecane solution were examined at high sensitivity both at room temperature and at elevated temperatures (up to 140°) using a variable temperature probe in an esr spectrometer. There was no indication, under any of the conditions used, of the presence of free radicals.

An attempt was made to capture free radicals to form a spin adduct: a solution of 0.1 M in α-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone[60] and 0.01 M in **1** in benzene was degassed by a freeze–thaw cycle and then heated to 95°. No esr signal could be detected after 3 days at 96°.

Study of Hydrogen Bonding Ability of Alkyl Thiolsulfinates. A solution 4.82×10^{-3} M in phenol in CCl_4 showed a "free" O–H stretch in the ir at 3607 cm^{-1}. When this solution was made 0.01 M in MeS(O)SMe, EtS(O)SEt, or dimethyl sulfoxide, a hydrogen bonded OH band appeared at 3329, 3300, and 3241 cm^{-1}, respectively, corresponding to respective shifts of 278, 307, and 366 cm^{-1} (compare the literature[61] value for the shift with dimethyl sulfoxide of 360 cm^{-1}). The above results indicate[61] that the thiolsulfinate oxygen (in dialkyl thiolsulfinates) is somewhat less basic than the oxygen in dialkyl sulfoxides but more basic than the sulfinyl oxygen in methyl methanesulfinate (OH shift = 243 cm^{-1}).[61]

Decomposition Studies on Neat, Unsymmetrical Thiolsulfinates. General Procedures. The thiolsulfinate was carefully purified, generally by distillation twice just prior to use. In all cases quantitative vpc analysis indicated only trace amounts of disulfide and thiolsulfonates while ir analysis indicated only traces of water or other hydroxylic contaminants; no effort was made, unless specifically indicated, to rigorously exclude traces of water. Samples for pyrolysis at elevated temperatures (generally 96°, using a constant-temperature oil bath) were sealed in glass tubes (often melting point capillaries) and held beneath the surface of the bath liquid by wiring them to wooden sticks. Other samples were simply placed under argon and maintained at room temperature in the dark with occasional sampling. The progress of the disproportionation was best determined by quantitative vpc or ir spectroscopy, while product analysis often involved infrared analysis in the 15–25 μ region (where isomeric thiolsulfonates show characteristic differences), coupled gc–ms analysis, or preparative tlc followed by spectroscopic and vpc analysis of the fractions. Direct quantitative vpc analysis of the pyrolysis product was used only if other evidence indicated no significant peak overlap.

Kinetic Measurements on Thiolsulfinate Decomposition. Measurements on neat samples were made using the above described capillary tube method. Samples were pyrolyzed (generally in a large bath maintained at 96.0 ± 0.1°) for varying time periods and then placed in an ice bath. Weighed amounts of pyrolysis products in volumetric flasks were diluted with CCl_4 for analysis by quantitative ir (at the S=O band at 1100 cm^{-1}; Beer's law was demonstrated by dilution studies), or after addition of a known weight of dodecane, the samples were diluted with ether and analyzed by quantitative vpc (multiple analyses were made for each point). In the case of *t*-BuS(O)S-*t*-Bu, **7**, decomposition could also be followed through measurement of rate of gas evolution (the half-life as determined by this method was ~70% as large as that determined by quantitative ir). The decomposition of **7** in anhydrous heptane (concentration of thiolsulfinate was 0.01 M) as followed by quantitative ir gave good first-order kinetics with $k = 19 \times 10^{-3}$ sec^{-1} at 96° and 1.4×10^{-5} sec^{-1} at 75°.

Decomposition of EtS(O)SMe, 11. (A) Neat; 25°. Results summarized in Table V.

(B) Neat, 96°, 5 hr. See Table VI, entry 9. The absence of $CH_3SO_2SCH_3$ and $CH_3SO_2SC_2H_5$ was confirmed by striking experiments. The identity of the trisulfide components was established by gc–ms analysis (LKB-9000) with comparison of the mass spectra so obtained with those of authentic samples of dimethyl and diethyl trisulfide; vpc spiking experiments also supported the presence of the several trisulfides. A portion of the pyrolysate was rapidly distilled at 90° (bath temperature) and 0.05 Torr. A detailed spectroscopic examination of the pot residue (including preparative tlc followed by spectral analysis) indicated that the higher boiling component was identical with the mixture of higher boiling products obtained by refluxing methyl ethanethiolsulfinate with benzene and water (see below).

(59) B. Loev and M. M. Goodman, *Intra-Sci. Chem. Rep.*, 4(4), 283 (1970).

(60) J. G. Pacifici and H. L. Browning, Jr., *J. Amer. Chem. Soc.*, 92, 5231 (1970); we thank Dr. Pacifici for a sample of this compound.

(61) J. B. F. N. Engberts and G. Zuidema, *Recl. Trav. Chim. Pays-Bas*, 89, 1202 (1970).

(C) In Heptane. A 0.033 *M* solution of **11** in heptane (dried over P_4O_{10}) was kept at 96° in an argon atmosphere. Samples were periodically taken, concentrated down, and analyzed by quantitative vpc with the results indicated in Table VI, entry 10.

The presence of EtS(O)SEt (**2**) was verified in this and other runs involving pyrolysis of neat **11** by mass spectrometric analysis at 11 eV (as well as vpc methods): the peak at *m/e* 138 (**2**) increased in intensity relative to the *m/e* 140 peak ($C_2H_5SO_2SCH_3$) with decreasing electron beam energy. The upper limit on $CH_3SO_2SC_2H_5$ concentration could be set (by quantitative vpc analysis) at 0.4%; ir analysis indicated the absence of the CH_3SO_2S group (both $CH_3SO_2SCH_3$ and $CH_3SO_2SC_2H_5$ as well as other compounds possessing the CH_3SO_2 group show strong ir absorption at 750 cm^{-1}).

(D) In Benzene–Water. Results summarized in Table VI, entry 11. Following pyrolysis under the conditions indicated in Table VI, entry 11, the reaction mixture was dried ($MgSO_4$), concentrated *in vacuo*, the volatile components removed by distillation (maximum head temperature of 50° at 0.03 Torr), and the pot residue subjected to preparative tlc with ether as eluent to give three fractions of R_f values 0.1, 0.75, and 0.9, all yellow oils.

The first fraction (R_f 0.1) had an ir spectrum (neat) very similar to that of 2,3,5-trithiahexane 5-oxide with strong bands at 9.50 and 9.75 μ (S=O) but having additional bands at 6.85 and 7.20 μ (–CH_2–, CH_3C). Vpc analysis indicated three closely spaced long retention time components of relative areas 21:1:7 (in order of retention time). Coupled gc–ms analysis indicated a parent peak for the first (and largest) component of *m/e* 170 ($C_4H_{10}S_3O$) with a base peak at *m/e* 93 ($CH_3SSCH_2^+$); the third had a parent of *m/e* 184 ($C_5H_{12}S_3O$) and a major fragment peak at *m/e* 107 ($C_2H_5SSCH_2^+$ or $CH_2SSCH(CH_3)^+$).[62] A mass spectrum of the mixture of components had *no* peak at *m/e* 198 ($C_6H_{14}S_3O$). High-resolution mass spectrometry on the mixture indicated exact masses of 169.9895 (calcd for $C_4H_{10}S_3O$, 169.9894) and 184.0049 (calcd for $C_5H_{12}S_3O$, 184.0050). A low eV (8.8 eV) spectrum of the mixture showed the disappearance of the lower mass (fragment) peaks and the persistence of the *m/e* 170 and 184 peaks (relative intensities 3.3:1, respectively, at 8.8 eV) indicating that these two peaks are parent peaks. An nmr ($CDCl_3$) spectrum of the mixture showed peaks at δ 1.37 (t, rel area 25.5., CH_3CH_2), 2.55 (s, rel area *ca.* 16.5, CHSS), 2.4–3.2 (m, rel area 17.5, CH_2CH_3), 3.97 (br s, rel area 10, S(O)-CH_2SSCH$_3$), 4.06 (s, rel area 3, S(O)CH_2SSC_2H_5). Irradiation of the δ 1.37 triplet collapsed the δ 2.7–3.2 multiplets to a δ 2.85 singlet without significantly sharpening the peaks at δ 3.97 and 4.06.

The evidence presented is consistent with this component being a mixture of 2,3,5-trithiaheptane 5-oxide ($C_2H_5S(O)CH_2SSCH_3$; 73%), 3,4,6-trithiaoctane 6-oxide ($C_2H_5S(O)CH_2SSC_2H_5$; 34%), and 4-methyl-2,3,5-trithiaheptane 5-oxide ($C_2H_5S(O)CH(CH_3)$-$SSCH_3$; 3%).

The second fraction (R_f 0.75) was found to be a mixture of methyl ethanethiolsulfonate, ethyl ethanethiolsulfonate, and products of much longer retention time so it was resubjected to preparative tlc, this time using methylene chloride as eluent. The higher boiling components were present exclusively in a band of R_f 0.1 while the thiolsulfonates were found in a band of R_f 0.4. This R_f 0.1 band had ir (CCl_4) absorption at 7.57 and 8.8 μ (vs, $-SO_2-$); vpc analysis indicated a mixture of four closely spaced long retention time peaks of relative areas 17:72:2:9 (in order of retention time). Coupled gc–ms analysis indicated a parent peak for the major (second) component at *m/e* 200 ($C_5H_{12}S_3O_2$) and a base peak at *m/e* 107 (CH_3-$SSCH(CH_3)^+$ or $C_2H_5SSCH_2^+$) with metastable support for a direct 200→107 fragmentation. The mass spectrum of the mixture had significant peaks, on high-resolution analysis, at *m/e* 214.0157 (calcd for $C_6H_{14}S_3O_2$, 214.0156), 200.0000 (calcd for $C_5H_{12}S_3O_2$, 200.0000) and 185.9844 (calcd for $C_4H_{10}S_3O_2$, 185.9843). A low eV (8.8 eV) spectrum of the mixture showed the disappearance of the lower mass (fragment) peaks and the persistence of the *m/e* 186, 200, and 214 peaks (rel intensities, 8:15:2, respectively) indicating that the latter peaks are parent peaks. In the 70 eV mass spectrum of the mixture other significant peaks appeared at 121 ($C_4H_9S_2^+$; 13%) 107 ($C_3H_7S_2^+$; base) and 93 ($C_2H_5S_2^+$; 34%) with a metastable corresponding to the process 214→121. The nmr spectrum ($CDCl_3$) revealed peaks at δ 1.38 (t, J = 8 Hz, area 36.5, CH_3CH_2), 1.72 (d, J = 7 Hz, area 24, CH_3CH), 2.51 (s, area 21, $CH_3SSCH(CH_3)$), 2.56 (s, area 5, CH_3SSCH_2), 3.14 (q, J = 8 Hz, area *ca.* 5.5, CH_3-CH_2), 3.17 (q, J = 8, area *ca.* 16.5, CH_3CH_2), 3.94 (q, J = 7 Hz, area 8, $CH_3CH<$), and 4.05 (s, area 4, $-SO_2CH_2SS-$). Irradiation of the δ 1.38 and 1.72 multiplets collapsed the δ 3.17 and 3.94 quartets, respectively, to singlets. The data are consistent with this tlc fraction having the composition 72% 4-methyl-2,3,5-trithiaheptane 5,5-dioxide ($C_2H_5SO_2CH(CH_3)SSCH_3$), 17% 2,3,5-trithiaheptane 5,5-dioxide ($C_2H_5SO_2CH_2SSCH_3$), 9% 5-methyl-3,4,-6-trithiaoctane 6,6-dioxide ($C_2H_5SO_2CH(CH_3)SSC_2H_5$), and 2% 3,-4,6-trithiaoctane 6,6-dioxide ($C_2H_5SO_2CH_2SSC_2H_5$).

The third fraction (R_f 0.9) appeared to be a complex mixture of polysulfides; however, insufficient material was present for characterization of the individual components.

From quantitative vpc analysis of the original thiolsulfinate pyrolysis product, a ratio of 8.82:1 for $C_2H_5S(O)CH_2SSCH_3$/$C_2H_5SO_2CH(CH_3)SSCH_3$ could be determined, and from this ratio the per cent composition of the higher boiling fraction of the pyrolysate was determined as: $C_2H_5S(O)CH_2SSCH_3$, 66.5%, $C_2H_5S(O)$-$CH_2SSC_2H_5$, 22.2%, $C_2H_5S(O)CH(CH_3)SSCH_3$, 3.1%, $C_2H_5SO_2$-$CH(CH_3)SSCH_3$, 5.8%, $C_2H_5SO_2CH_2SSCH_3$, 1.5%, $C_2H_5SO_2CH_2$-SSC_2H_5, 0.2%, and $C_2H_5SO_2CH(CH_3)SSC_2H_5$, 0.7%.

Pyrolysis of MeS(O)S-*t*-Bu (8) (See Table VI, Entry 7). A sample of **8**[2] distilled at 95° (8 Torr) from one half of its weight of calcium carbide (after stirring under argon at 90° over CaC_2 for 1 hr), gave a half-life of decomposition at 96.0° of *ca.* 1020 min. If the thiolsulfinate was purified only by distillation, without the use of calcium carbide, a half-life at 96° of 290 min was obtained (both using quantitative ir). Portions of this latter sample of **8** were pyrolyzed (neat) for varying periods of time and analyzed by quantitative vpc before and after preparative tlc; the tlc fractions were analyzed by ir, nmr, and mass spectral methods as well. In addition to a rather complex mixture of polysulfides (CH_3SSCH_3, *t*-Bu-S_n-Bu-*t*, with n = 2, 3, 4, and *t*-BuS_nCH_3, with n = 2, 3, 4), the major product was a mixture of $MeSO_2SMe$ and $MeSO_2SBu$-*t* in a molar ratio varying from 5:1 hr at 96° to 3:1 after 12 hr at 96°. A minor component of the thiolsulfonate fraction (isolated by preparative vpc) was tentatively identified as CH_3SO_2SSBu-*t* on the basis of its mass spectrum (*m/e* 200, M^+, $C_5H_{12}S_3O_2$, supported by relative size of 202 and 204 isotope peaks; base peak *m/e* 57), its ir and nmr spectrum (very similar to that of $MeSO_2SBu$-*t*) and its vpc properties (a single peak of retention time three times as long as that of $MeSO_2$-SBu-*t*).

Pyrolysis of *i*-PrS(O)SMe (4). A pure sample of **4**[2] was heated in a sealed, evacuated tube at 96° for 9.3 hr. The pyrolysate was centrifuged to separate a small upper layer of water (identified by chemical and spectral means). Preparative tlc of the centrifugate followed by vpc, ir, and nmr analysis of each fraction allowed the makeup of the original pyrolysate to be determined as indicated in Table VI, entry 14. The characterization of 6-methyl-2,3,5-trithiaheptane 5-oxide was based on ir (neat) 9.50 and 9.78 μ (S=O), nmr δ 1.22 and 1.32 (singlets, 7 H), 2.55 (s, 3 H), 2.89 (m, 1 H), 3.81 (s, 2 H), and the fact that this tlc fraction was quite polar based on its R_f values.

After pyrolysis of **4** at 96° for 2.2 hr, the molar ratio of *i*-$PrSO_2$-SMe to *i*-$PrSO_2SPr$-*i* was determined (by vpc analysis) to be *ca.* 6.4:1.

2,3,5-Trithiahexane 5-Oxide (33). MeS(O)SMe (**1**) was prepared by peracetic acid oxidation of a chloroform solution of dimethyl disulfide according to the method of Moore and O'Connor[56] and was used, after removal of chloroform *in vacuo*, without further purification to remove minor amounts of MeSSMe and $MeSO_2SMe$. A mixture of 200 ml of benzene, 0.348 mol of **1**, and 8 ml of water (0.445 mol) was refluxed under argon for 52 hr. The reaction mixture was then extracted seven times with 60-ml portions of 1 *N* H_2SO_4; the acidic extract was neutralized to litmus with sodium bicarbonate, saturated with ammonium sulfate, and extracted with four 100-ml portions of chloroform. The chloroform solution was dried ($MgSO_4$), filtered, stirred overnight with 2 g of calcium hydride, filtered after the addition of Celite 545, concentrated *in vacuo*, and distilled to give a main fraction of bp 98° (0.04 Torr); the overall yield of pure **33** was 30.2 g (84% yield; including a small amount of pure product obtained by distillation of the concentrated benzene layer from the extraction). The product is a colorless, water soluble oil with ir (neat) 9.58 μ (s, S=O), nmr ($CDCl_3$) δ 2.55 (s, 3 H), 2.68 (s, 3 H), 3.97 (AB quartet, J = 6 Hz, 2 H), mass spectrum *m/e* 156 (M^+, $C_3H_8S_3O$), 93 ($CH_3SSCH_2^+$, base peak), 63 (CH_3SO^+, 12%), 45 (CHS^+, 93%).

Preparative tlc of a portion of the pot residue from distillation using ether as developing solvent gave fractions of R_f 0.68 and 0.5 in addition to material of R_f <0.1.

From the fraction of R_f 0.68 there was obtained colorless needles (from hexane), mp 89.5–90.0°, showing in its ir (KBr pellet) spectrum strong, sharp bands at 7.68, 7.72, and 8.85 μ ($-SO_2-$) and nmr

(62) The direct transitions 170 → 93 and 184 → 107 are supported by metastable peaks.

($CDCl_3$) spectrum with peaks at δ 2.45 (s, 3 H), 2.62 (s, 3 H), 3.13 (s, 3 H), and 4.76 (s, 1 H). The mass spectrum showed *m/e* 218 (M^+, $C_4H_{10}S_4O_2$), 47 (CH_3S, 74%), and 45 (CHS^+, base), among others. The product had a vpc retention time *ca.* 3.7 times as great as 2,3,5-trithiahexane 5-oxide.

The proposed structure for this product is 4-methylsulfonyl-2,3,-5-trithiahexane, $CH_3SCH(CH_3SO_2)SSCH_3$.

The fraction of R_f 0.5, a slightly yellow oil, had ir (neat or CCl_4) 7.65 and 8.65 μ (vs, $-SO_2-$), nmr ($CDCl_3$) δ 2.60 (s, 3 H), 3.03 (s, 3 H), and 4.10 (s, 3 H). The mass spectrum had a parent at *m/e* 171.9687 (calcd for $C_3H_8S_3O_2$, 171.9687) with other peaks at *m/e* 93 (CH_3SSCH_2+, 36%), 47 (CH_3S+, 80%), and 45 (CHS+, base). This fraction showed a single vpc peak of retention time 1.1 times that of 2,3,5-trithiahexane 5-oxide; the proposed structure is $CH_3SO_2CH_2SSCH_3$, 2,3,5-trithiahexane 5,5-dioxide.

Pyrolysis of MeS(O)SMe (1) in Anhydrous Benzene. A 1 *M* solution of **1** in anhydrous benzene was heated at 96° in a sealed tube for 6 hr and then analyzed by vpc and coupled gc–ms. After 6 hr at 96° practically all thiolsulfinate had been consumed. In addition to moderate amounts of $MeS(O)CH_2SSMe$ (**33**) and $MeSO_2CH_2SSMe$ (vpc analysis only), gc–ms analysis indicated the presence of significant quantities of MeSSSMe, $MeSO_2SMe$, and $MeSCH_2SSMe$ (all characterized by the identity of their mass spectra with those of authentic samples as well as by vpc retention time).

In a separate experiment it was shown that for **1** solutions in benzene of equal concentration the addition of water significantly *retards* the disappearance of thiolsulfinate while at the same time significantly increases the yield of **33**.

From pyrolysis of **1** in *anhydrous* benzene (*ca.* 1.5 *M* solution heated at 96° for 12 hr) a 13% yield of **33** and a 72% yield of water could be isolated (according to the stoichiometry $3CH_3S(O)SCH_3 \rightarrow 2CH_3S(O)CH_2SSCH_3 + H_2O$). The nmr spectrum of the acidic aqueous phase had peaks corresponding to CH_3SO_2H and CH_3SO_3H as verified by analysis of an authentic mixture.

More dilute solutions of **1** (*i.e.*, 0.02 *M*) in benzene decompose much more slowly than more concentrated solutions; the yields of **33** is also decreased compared to more concentrated runs.

The addition of catalytic amounts of methanesulfonic acid greatly accelerated the rate of decomposition of 1 *M* benzene solutions of the thiolsulfinate; the ratio of $MeSO_2SMe$ to **33** was larger than the ratio obtained by pyrolysis in the absence of acid.

Pyrolysis of 1 under Other Conditions. (A) Neat at 96°. Neat pyrolysis of **1** gave equimolar amounts of MeSSMe and $MeSO_2SMe$ with only traces of **33**.

(B) In Other Aromatic Solvents at 96°. Pyrolysis of *ca.* 1 *M* solutions of **1** in benzene, hexafluorobenzene, and 1,3,5-trimethylbenzene was conducted at 96° while monitoring the progress of the reactions by quantitative vpc (known weights of dodecane were present in each solution). The *maximum* yields of **33** in these three solutions was determined to be 40, 24, and 52%, respectively (corrected for unconsumed thiolsulfinate).

(C) Other Solvents (Pyrolysis at 96°). Results similar to those obtained with *anhydrous* benzene was observed with 1,2-dimethoxyethane, ethyl acetate, and methyl ethyl ketone. Significant quantities of 2,3,5-trithiahexane appeared to be formed with carbon tetrachloride and 1,2-dichloromethane while primarily thiolsulfonate and disulfide were formed with nitromethane or heptane.

Pyrolysis of *t*-BuS(O)S-*t*-Bu (7). A sample of 0.780 g of **7** (4.02 mmol) was heated for 8 hr at 96° in a small tube connected to a gas buret. A total of 1.83 mmol of a gas was collected over water; the ir spectrum of a dried sample of the gas was identical with the ir spectrum of an authentic sample of 2-methylpropene. The residual liquid, which contained a few droplets of water, was subjected to preparative tlc on silica gel with methylene chloride as eluent to give 0.100 g of a waxy solid of R_f 0.72 and 0.405 g of a liquid of R_f 0.98. The foul smelling waxy solid, after sublimation at 45° (0.01 mm) had: mp 56.5–62.5°; ir (KBr pellet) 7.64 and 9.00 ($-SO_2-$, vs); nmr (CCl_4) δ 1.42 and 1.47 (s of equal area); mass spectrum *m/e* 242 ($C_8H_{18}S_3O_2$, parent), and was identified as *t*-$BuSO_2$-SS-*t*-Bu. The liquid tlc fraction was identified by glc and mass spectrometry as a mixture of *t*-BuSS-*t*-Bu, *t*-BuS_3-*t*-Bu, *t*-BuS_4-*t*-Bu (0.13, 0.80, and 0.72 mmol, respectively). The molar composition of the pyrolysate was estimated to be: isobutylene, 49%, *t*-Bu_2S_2, 3.5%, *t*-Bu_2S_3, 21.4%, *t*-Bu_2S_4, 19.3%, *t*-$BuSO_2SS$-*t*-Bu, 7% H_2O (not determined quantitatively).

Pyrolysis of EtS(O)SEt (2) in Benzene. A solution of 0.700 g of **2** (5.1 mmol) in 2.5 ml of benzene was heated at 96° in a sealed tube for ~4 hr and then concentrated *in vacuo* and the concentrate subjected to preparative tlc (silical gel, ethyl acetate). The band of R_f 0.44, characterized as 5-methyl-3,4,6-trithiaoctane 6-oxide, was obtained in 15% yield (0.086 g) and after molecular distillation at 80° (0.08 mm) was a colorless liquid showing a single peak on vpc analysis and having nmr ($CDCl_3$) δ 0.90–1.20 (m, overlapping ethyl CH_3 protons, 6 H), 1.33 and 1.51 (d, J = 7 Hz, 3 H, CH_3 protons in diastereomers), 2.26 and 2.42 (pair of overlapping quartets (J = 7 Hz) with further couplings, $-CH_2-$ protons, 4 H), 3.31 and 3.47 (pair of overlapping quartets, J = 7 Hz, 1 H, tertiary protons in diastereomers); double resonance studies indicated that the quartet at δ 3.47 is coupled to the doublet at δ 1.33 and that the quartet at δ 3.31 is coupled to the doublet at δ 1.51. The ir spectrum had bands at 9.47 and 9.80 μ in CCl_4 solution; mass spectrum showed *m/e* 198 ($C_6H_{14}S_3O$, M^+), 121 ($EtSSCHCH_3^+$, 82% base).

2,2-Dimethyl-3,5,6-trithiaheptane 3-Oxide (35). Run 1. Pyrolysis with an Equal Weight of Water. A mixture of 6.00 g (39.5 mmol) of *t*-BuS(O)SMe (**6**) and 6.0 g of water was vigorously stirred at 96° in an argon atmosphere for 5.5 hr. The reaction product was then diluted with a small quantity of methylene chloride, the layers were separated, the aqueous layer (after saturation with ammonium sulfate) was extracted with several small portions of methylene chloride, and the combined, dried ($MgSO_4$) organic phase was treated with pentane and chilled to precipitate 1.59 g (8 mmol = 41% yield) of the title compound as a colorless crystalline solid. Recrystallization of the solid from boiling hexane gave colorless needles which were sublimed at 60° (0.01 Torr) to give an analytical sample: mp 98.0–99.5°; ir (KBr pellet) 9.68 and 9.74 μ (vs, S=O), nmr ($CDCl_3$), δ 1.30 (s, 9 H), 2.60 (s, 3 H), 3.60 (d, 1 H, J = 14 Hz), 4.01 (d, 1 H, J = 14 Hz), uv max (95% ethanol) 246 (ϵ 443), mass spectrum *m/e* 198 (M^+, $C_6H_{14}S_3O$), 93 ($CH_3SSCH_2^+$, 30%), 119 (*t*-$BuS(O)CH_2^+$, 8%), 142 ($MeSSCH_2SOH\cdot^+$, 3%) and 41 ($C_3H_7^+$, base). The cryoscopically determined molecular weight was 186.

Analysis by quantitative vpc of the original pyrolysis mixture before recrystallization indicated the composition (given as mol %): MeSS-*t*-Bu, 5%, *t*-BuSS-*t*-Bu, 9%, *t*-$BuSO_2SMe$, 26%, *t*-BuS(O)S-*t*-Bu, 36%, *t*-$BuS(O)CH_2SSMe$, 24%. The identity of the various pyrolysis products was confirmed by separation using preparative tlc followed by spectral and chromatographic analysis of the individual fractions. The following minor (<2% mol fraction) products were also detected: isobutylene (trace), *t*-BuS_n-*t*-Bu (n = 3 and 4), *t*-$BuSO_2SSMe$, *t*-$BuSO_2SS$-*t*-Bu.

Run 2. Pyrolysis in the Absence of Added Water. From the pyrolysis of 20 mmol of **6** (96° for 5 hr) there was isolated 0.53 g (2.7 mmol, 27% yield) of **35** along with a mixture of liquid products similar in composition to that obtained with added water.

2,2-Dimethyl-3,5,6-trithiaheptane 3,3-Dioxide (36). A mixture of **6** (3.27 g, 21.5 mmol) and 0.16 g of calcium hydride was refluxed with vigorous stirring at 96° and 5.5 mm pressure under a small West condenser for 6.5 hr. At the completion of the reaction, quantitative vpc analysis indicated the composition by weight: *t*-BuS(O)S-*t*-Bu, 52%, *t*-$BuSO_2CH_2SSMe$, 19%, *t*-BuSS-*t*-Bu, 13% *t*-$BuS(O)CH_2SSMe$, 7%, *t*-$BuSO_2SMe$, *t*-$BuSO_2SMe$, 7%, *t*-BuSSS-*t*-Bu, 3%. The reaction product was diluted with methylene chloride, filtered, reconcentrated, chilled, and treated with ether–pentane to yield 0.911 g of slightly yellow crystals indicated by nmr to consist of 0.237 g of *t*-$BuS(O)CH_2SSMe$ (11% yield) and 0.675 g of *t*-$BuSO_2CH_2SSMe$ (29% yield). The two crystalline components could be readily separated by preparative tlc (silica gel, methylene chloride) giving *t*-$BuS(O)CH_2SSMe$ as the more polar component (R_f 0.28) and *t*-$BuSO_2CH_2SSMe$ as the less polar component (R_f 0.55). Recrystallization of the latter compound from boiling hexane followed by sublimation at 60° (0.01 mm) gave a colorless solid: mp 56.0–58.0°; nmr ($CDCl_3$) δ 1.45 (s, 9 H), 2.60 (s, 3 H), and 4.13 (s, 2 H), ir (KBr pellet) 7.78 and 9.03 μ ($-SO_2-$), and mass spectrum *m/e* 214 ($C_6H_{14}S_3O_2$, M^+), 93 ($CH_3SSCH_2^+$, 37% base), 57 ($C_4H_9^+$, base).

Irradiation of EtS(O)SMe (11). (1) In CF_3Cl Solution. A CF_3Cl solution 4×10^{-3} *M* in **11** and 2×10^{-4} *M* in dodecane was placed in a long quartz tube containing a quartz cold finger. Argon was bubbled through the solution as it was chilled to ~−70° using methanol as circulating coolant in the cold finger and a slow stream of ethanol at −70° as an external rinse (to prevent icing of the apparatus). While argon bubbling was continued, the apparatus was irradiated at 254 nm with a bank of low-pressure mercury lamps. Quantitative vpc analysis after 11 min indicated the composition (in mol %) MeSSMe, 26; EtSSMe, 38; EtSSEt, 7; $MeSO_2SEt$, 3; $EtSO_2SMe$, 9; $EtSO_2SEt$, 17; after 15 min the composition was MeSSMe, 28; EtSSMe, 35; EtSSEt, 7; $MeSO_2SEt$, 2; $EtSO_2SMe$, 9; $EtSO_2SEt$, 18. Longer irradiation caused extensive decomposition. Comparison of the 3–25 μ ir spectrum of the concentrated 15-min photoproduct with that of an authentic mixture of $MeSO_2SEt$ + $EtSO_2SMe$ + $EtSO_2SEt$ (ratio 2:9:18) and with an authentic

2:1 mixture of $EtSO_2SEt$ + $EtSO_2SMe$ verified the presence of $MeSO_2SEt$ as indicated by vpc analysis of the photoproduct.

(2) In Benzene Solution. A benzene solution 1.63×10^{-1} *M* in **11** and 1.9×10^{-2} *M* in dodecane was irradiated at 25° for 11 min with light of wavelength 254 nm from a low-pressure mercury lamp. Quantitative vpc analysis indicated the composition MeSSMe, 16; MeSSEt, 7; EtS(O)SMe, 61; $EtSO_2SMe$, 5; $EtSO_2SEt$, 10; $MeSO_2SEt$, less than 0.2%. There was no evidence of the formation of α-alkanesulfinyl or α-alkanesulfonyl disulfides.

Irradiation of MeS(O)SMe (1). A 1 *M* solution of **1** in CH_2Cl_2 was irradiated in a thin walled nmr tube using a 450-W Hanovia medium-pressure mercury lamp equipped with a Corex filter. Irradiation at 0° for varying time periods showed the formation of equal amounts of MeSSMe and $MeSO_2SMe$ (as indicated by nmr analysis by a singlet for the former at δ 2.41 and a pair of singlets for the latter at δ 2.69 and 3.32). Irradiation of a portion of this solution for 100 min at −40° (the nmr tube was refrigerated and irradiated in an unsilvered quartz dewar) followed by nmr analysis at −40° indicated ~20% disproportionation. The nmr spectrum remained unchanged on warming the sample to room temperature; there was no indication of nmr peaks other than those attributable to thiolsulfinate, thiolsulfonate, and disulfide. Very similar results were obtained on irradiation at 254 or 300 nm of a benzene solution 2 *M* in **1**. $MeS(O)CH_2SSMe$ could not be detected by vpc.

Deuterium Exchange Study with *t*-$BuSO_2CH_2SSMe$ (36). A solution of 0.0427 g of recrystallized **36** (0.2 mmol) in 0.4 ml of CD_3OD in an nmr tube was treated with 0.001 mmol of CH_3ONa (in CH_3OD) at room temperature. The nmr spectrum taken immediately following the addition of base indicated the complete disappearance of the $-CH_2-$ band (which appeared at δ 4.33 in CD_3OD) without any other changes in the nmr spectrum. The sample was then concentrated *in vacuo* and the residue recrystallized from boiling hexane to give 0.0355 g (82% yield) of colorless crystals, mp 55.6–56.7°, characterized as *t*-$BuSO_2CD_2SSMe$ (**35b**). Mass spectral analysis (corrected for isotopic contributions other than that of deuterium) indicated the isotopic distribution $C_6H_{12}D_2S_3O_2$, 85.2%, $C_6H_{13}DS_3O_2$, 13.3%, and $C_6H_{14}S_3O_2$, 1.5%. The significant peak at *m/e* 93 ($CH_3SSCH_2^+$) in the mass spectrum of undeuterated material was substantially shifted to *m/e* 95 ($CH_3SSCD_2^+$). The nmr spectrum ($CDCl_3$) indicated singlets at δ 1.47 (9 H) and 2.62 (3 H) (essentially the same peak positions for these two peaks as in undeuterated material); by integration the maximum level of monodeuterated material was estimated as *ca.* 10% of the amount of dideuterated material. The ir spectra (KBr pellets) of the deuterated and undeuterated compounds were identical with the exception of the appearance of bands in the spectra of the former compound at 4.44 and 4.63 μ (C-D) and the presence of a single strong band in the former at 14.3 μ instead of two weaker bands in the spectrum of the latter at 13.3 and 14.2–14.4 μ. A mixture melting point of **36** and the 4,4-dideuterio derivative **36b** showed no depression.

2,3,5-Trithiahexane. To 3.92 g (25 mmol) of distilled $MeS(O)CH_2SSMe$ (**33**) was added 32.5 ml of 0.8 *M* triethyloxonium fluoroborate in methylene chloride (26 mmol). The homogeneous solution was stirred under a drying tube at 25° for 1 hr and then diluted with 75 ml of methylene chloride and chilled in an ice bath. With vigorous stirring, 75 ml of ice cold saturated sodium bisulfite solution was added. Vigorous agitation of the heterogeneous solution was continued at 0° for 30 min whereupon 200 ml of pentane was added, the organic layer was separated, washed successively with water, 1 *N* H_2SO_4 and several times again with water, and dried ($MgSO_4$). Solvent removal *in vacuo* gave 3.17 g (86%) of 2,3,5-trithiahexane as a slightly yellow liquid of 95% purity. Vacuum distillation gave 2.58 g of a very slightly yellow, odorous liquid: bp 32° (<0.01 mm); λ max 236 (ε 1140); nmr ($CDCl_3$) δ 2.23 (s, 3 H), 2.50 (s, 3 H), 3.86 (s, 2 H); mass spectrum (gc–ms) *m/e* (rel intensity) 142 ($C_3H_8S_3$, M^+, 15%), 93 ($M^+ - CH_3S\cdot$; 4%), 79 ($M^+ - CH_3SCH_2\cdot$; 4%), 61 ($M^+ - CH_3SS\cdot$; base).

As this compound readily disproportionates to dimethyl disulfide and 2,4,5,7-tetrathiaoctane, it is best stored protected from light in a freezer.

Heating an equimolar mixture of **33** and triphenyl phosphite under argon at 65° for 24 hr gave 2,3,5-trithiahexane in 8% yield and triphenyl phosphate in 65% yield.

4-Acetoxy-2,3,5-trithiahexane. A mixture of 5.00 g of $MeS(O)CH_2SSMe$ (**33**) (32 mmol), 9 ml of acetic anhydride (96 mmol), and 60 ml of benzene was refluxed for 114 hr. The yellow product was then concentrated *in vacuo* and distilled giving 3.0 g (47% yield) of the title compound as a yellow liquid: bp 66–68° (0.01 mm); nmr ($CDCl_3$) 2.18 (s, 3 H), 2.28 (s, 3 H), 2.48 (s, 3 H), 6.80 (s, 1 H); ir (neat film) 5.78 (vs, C=O), 8.28 (vs, COC), and 9.80 (s, ester band); mass spectrum *m/e* 198 (M^+, $C_5H_{10}S_3O_2$), 151 (0.1% base, $MeSSCHOAc^+$), 139 (8% base, $MeSSCHSMe^+$), 119 (70% base $MeSCHOAc^+$), 44 (base, $MeCO^+$).

Reduction of $MeS(O)CH_2SSMe$ (33) with Aluminum Amalgam. A solution of 0.161 g of **33** (1.03 mmol) in 90% tetrahydrofuran–10% water at 0° was treated with 0.0285 g (1.06 mmol) of aluminum foil amalgamated according to the procedure of Corey and Chaykovsky[63] just prior to use. The reaction was maintained at 0° with stirring for 3 hr, at which time all of the aluminum had dissolved and all of the starting material had been consumed (as indicated by vpc analysis). Quantitative vpc analysis indicated a 30% yield of dimethyl disulfide. The presence of dimethyl disulfide was also established by work-up followed by nmr analysis (singlet in CCl_4 at δ 2.39).

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