Electron Impact Induced Processes of Thermally and Photochemically Labile Organic Sulfur Compounds. A Mass Spectral Study of Dialkyl Thiolsulfonates, Disulfides, Trisulfides, and α-Disulfones

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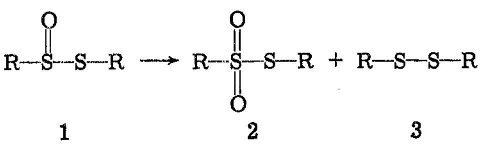
The mass spectral fragmentation patterns of various dialkyl thiolsulfonates, diethyl disulfide and trisulfide, and dimethyl α-disulfone have been studied, using deuterium labeling and defocusing techniques to clarify the mechanisms of a number of novel rearrangement processes. Among the more interesting processes seen are a fragmentation occurring via an apparently unprecedented 2,2,1-bicyclic transition state (or its stepwise counterpart), the electron impact induced rearrangement of thiolsulfonates to sulfenyl sulfinates, nonspecific hydrogen transfer in the formation of HSSH from diethyl disulfide, and the formation of H_2S_3 and EtSSSH from diethyl trisulfide. Where information is available, electron impact induced processes for the compounds studied are compared with thermal and photochemical pathways.

We recently reported a detailed study of the mass spectra of dialkyl thiolsulfinates (1) and indicated the considerable utility of mass spectrometry in clarifying the mechanism of thermal disproportionation of these unstable compounds to thiolsulfonates (2) and disulfides (3).[2] In this



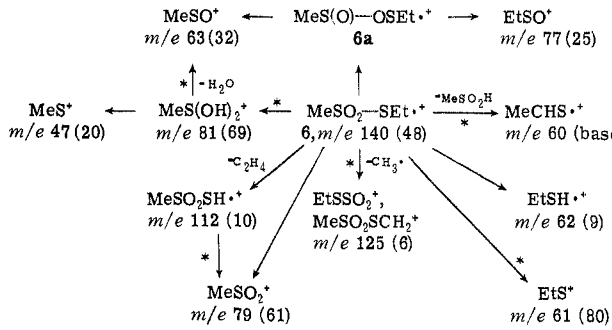
1 2 3

same paper[2] we indicated notable similarities as well as differences between electron impact and thermally (and photochemically) induced processes for the thiolsulfinate esters. The present paper extends our examination of electron impact induced processes of thermally and photochemically labile organic sulfur compounds to include dialkyl thiolsulfonates (2), disulfides (3), trisulfides, and α-disulfones (RSO_2SO_2R). Of these compounds, mass spectral studies have been previously reported only for dialkyl disulfides[3] and dimethyl trisulfide,[4] and these without substantiation for proposed fragmentation processes through deuterium labeling.

It is of interest that, as with dialkyl thiolsulfinates,[2] dialkyl thiolsulfonates, disulfides, and trisulfides are found naturally as components of the essential oils from plants of the *Allium* species (onion, garlic, chives, caucas);[5a] dialkyl trisulfides have also been detected in algae of the *Dictyopteris* species[5b] and in ponerine ants.[5c] The fact that mass spectrometry (generally in the form of GC–MS) is widely used as the primary analytical tool in these studies of naturally occurring organic polysulfide derivatives provided further impetus for the study described herein.

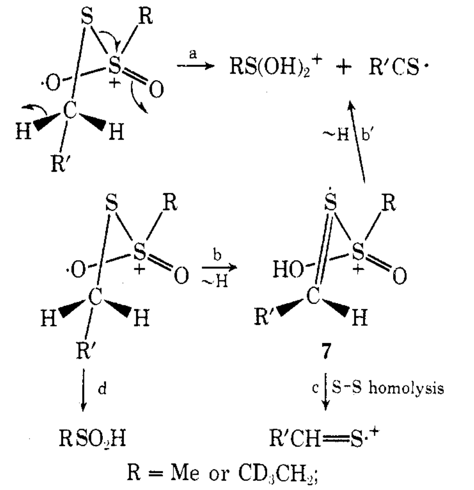
Alkyl Alkanethiolsulfonate Esters. Thiolsulfonate esters **2** are generally stable substances[6] while the isomeric α-disulfoxide [RS(O)S(O)R (**4**)] and sulfenic–sulfinic mixed anhydride [RS(O)OSR (**5**)], both variously postulated as intermediates in thermal and photochemical reactions involving thiolsulfonate as a final product,[7] have thus far eluded isolation and are thought to be unstable.[7] Under electron impact conditions we find evidence for the conversion of certain thiolsulfonates **2** to isomeric species **4** or **5**. Thus, the unsymmetrical ethyl methanethiolsulfonate [$MeSO_2SEt$ (**6**)] gives substantial fragments corresponding to *both* $MeSO^+$ and $EtSO^+$ with similar intensities (see Scheme I); the identity of the fragments was established by exact mass measurements as summarized in Table I. Similar results were obtained with $MeSO_2SCD_3$ ($MeSO^+$, rel intensity 56; CD_3SO^+, rel intensity 44). Other unsymmetrical alkyl alkanethiolsulfonates studied fail to give significant fragments corresponding to RSO^+ and therefore provide no information on oxygen migration. The formation of a fragment $R'SO^+$ from thiolsulfonate RSO_2SR' requires oxygen transfer which may be accomplished through isomerization of **2** to **5** as suggested in Scheme I (**6** → **6a**; this would be analogous to the known ionic or electron impact induced sulfone–sulfinate interconversion[8]) or, less likely, by oxygen migration with *retention* of the S–S bond giving **4**.[9] The electron impact induced oxygen migration observed with thiolsulfonates parallels that seen with α-disulfones (see below) but is to be contrasted with the absence of similar rearrangements in thiolsulfinates.[2]

Scheme I
Mass Spectral Fragmentation Pathways for Ethyl Methanethiolsulfonate (6)[a]



[a] An asterisk indicates that a metastable peak was observed. Figures in parentheses are relative intensities.

Another interesting rearrangement seen with alkyl thiolsulfonates is the formation of substantial fragments corresponding to protonated alkanesulfinic acid, $RS(OH)_2^+$. This species constitutes a significant fragment in the mass spectra of $MeSO_2SMe$, $MeSO_2SEt$ [seen as $MeS(OH)_2^+$ at *m/e* 81[11a]], $MeSO_2SCD_3$ [$CH_3S(OD)_2^+$, *m/e* 83], $EtSO_2SMe$, and $EtSO_2SEt$ [$EtS(OH)_2^+$, *m/e* 95[11a]]; this species is *not* seen to any significant extent in the mass spectra of $MeSO_2S$-*i*-Pr or $MeSO_2S$-*t*-Bu. In the case of esters of the type RSO_2SMe, $RS(OH)_2^+$ must arise either via an unprecedented 2,2,1-bicyclic transition (eq 1, path a with R′ = H) or by sequential hydrogen transfer processes (eq 1, paths b and b′).[11b] To compare the preference for the novel fragmentation pathways of eq 1 with the preference for pathways involving the more common 3,2,1-bicyclic



(1)

$R = Me$ or CD_3CH_2;
$R' = H$, CD_3 or Me

transition state[12] (or its two-step counterpart), we have studied the fragmentation of specifically deuterated derivatives (8 and 9) of ethyl ethanethiolsulfonate with the results shown in Scheme II. From the data in Scheme II (processes a for 8 and c for 9) it is seen that the pathways of eq 1 are favored over the alternative 3,2,1 transition state,[14] presumably reflecting the lability of C–H bonds adjacent to the sulfur. The data available do not allow a choice between the concerted or stepwise routes to $RS(OH)_2^+$ in eq 1. Transfer of a single hydrogen to a sulfonyl oxygen via intermediate 7 (eq 1, paths b, c) or by a direct route d (eq 1), processes analogous to those seen in diethyl sulfone[14] and certain sulfonate esters,[12] accounts for the base peaks in the mass spectra of $MeSO_2SEt$ (*m/e* 60, C_2H_4S[11a]) and $MeSO_2S$-*i*-Pr (*m/e* 74, C_3H_6S[11a]). Consistent with the mechanism of eq 1, paths b–c or d, is the formation of $C_2D_3HS\cdot^+$ rather than $C_2D_2H_2S\cdot^+$ from $CD_3CH_2SO_2SCH_2CD_3$ (**8**).

Scheme II
Deuterium Distribution in Fragments from Deuterated $EtSO_2SEt$[13]

$CD_3CH_2SO_2SCH_2CD_3 \xrightarrow{a} CD_3CH_2S(OH)_2^+$ (67.5%),
8, 88% d_8, 12% d_5 $\quad CD_3CH_2S(OH)(OD)^+$ (30.8%),
$CD_3CH_2S(OD)_2^+$ (1.7%)

8. $\xrightarrow{b}$ CD_3CH_2SD (70%), CD_3CH_2SH (30%)

$CH_3CD_2SO_2SCD_2CH_3 \xrightarrow{c} CH_3CD_2S(OD)_2^+$ (58%),
9, 93% d_4, 3% d_3, $\quad CH_3CD_2S(OD)(OH)^+$ (40%),
4% d_2 $\quad CH_3CD_2S(OH)_2^+$ (2%)

9 $\xrightarrow{d}$ CH_3CD_2SH (85%), CH_3CD_2SD (15%)

Two other fragmentation processes of dialkyl thiolsulfonates have analogies in pyrolytic processes.[6] Of the several thiolsulfonates studied by us, extrusion of SO_2 was significant only in the mass spectrum of $PhCH_2SO_2SCH_2Ph$ (eq 2), a result consistent with previously described substituent

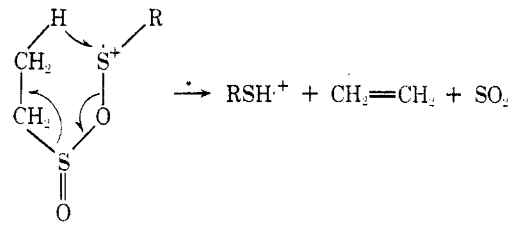
$$PhCH_2SO_2SCH_2Ph\cdot^+ \xrightarrow[-SO_2]{*} (PhCH_2)_2S\cdot^+ \text{ (11\% base)} \quad (2)$$

effects on thiolsulfonate pyrolyses.[6] The *m/e* 48 peak of $EtSO_2SMe$ (90% base intensity) identified as MeSH[11a] and the analogous *m/e* 62 (EtSH[11a]) fragment identified in the mass spectra of $MeSO_2SEt$ and $EtSO_2SEt$ are presumably

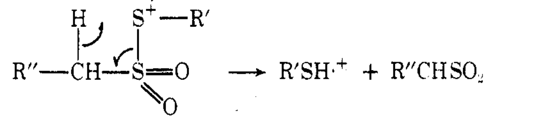
Table I
High-Resolution Mass Spectral Data

Compd	*m/e*	Formula	Assignment	% base
$MeSO_2SEt$	60.0028	C_2H_4S	$MeCH{=}S\cdot^+$	100
	62.0177	C_2H_6S	$EtSH\cdot^+$	9
	62.9884	CH_3SO	$MeSO^+$	32
	77.0059	C_2H_5SO	$EtSO^+$	25
	80.9991	CH_5SO_2	$MeS(OH)_2^+$	69
$(CD_3CH_2S)_2$	79.9739	CH_2DS_2	$CH_2DS_2^+$	7
EtSSSEt	97.9327	H_2S_3	$HSSSH\cdot^+$	6
	125.9629	$C_2H_6S_3$	$EtSSSH\cdot^+$	1.4
$EtSO_2SMe$	48.0028	CH_4S	$CH_3SH\cdot^+$	85
	95.0159	$C_2H_7SO_2$	$EtS(OH)_2^+$	10
$MeSO_2S$-*i*-Pr	74.0168	C_3H_6S	$Me_2C{=}S\cdot^+$	100

the consequence of competitive processes of the type depicted in eq 3 and 4. Studies with deuterated thiolsulfonates 8 and 9 indicate that the fragmentation in eq 3 is substantially favored over that in eq 4 (see Scheme II, paths b and d). Reaction 4 may also occur thermally.[6]



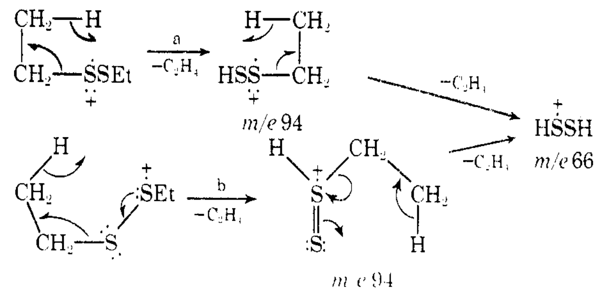
(3)



(4)

R and R' = Me or Et;
R'' = H or Me

Dialkyl Disulfides and Trisulfides. While the mass spectra of a variety of dialkyl disulfides have been previously examined,[3] mechanistic speculations on fragmentation processes have not been supported by deuterium labeling. In the relatively simple mass spectrum of diethyl disulfide there are major peaks at *m/e* 94 ($EtSSH^+$), 66 ($HSSH^+$), and 29 ($C_2H_5^+$) in addition to the molecular ion (*m/e* 122), which is the base peak, and minor, yet significant peaks at *m/e* 107 ($EtSSCH_2^+$) and 79 (MeS_2^+). The formation of the *m/e* 94 and 66 fragments may be rationalized in terms of the sequential elimination processes of eq 5a[3c] or 5b.[11b] That this sequence cannot be the only frag-



(5)

mentation path leading to *m/e* 94 and 66 is shown by the data on bis(ethyl-*1,1*-d_2) disulfide in Scheme III. Support for the occurrence of one-step hydrogen transfer processes 126 → 96 and 97, 96 → 66 and 67, and 97 → 67 and 68 is provided by metastable analysis (metastable ions are seen for *all* of these processes) and by direct analysis of daughter ions (DADI) studies[17] of the *m/e* 126 and 96 species.

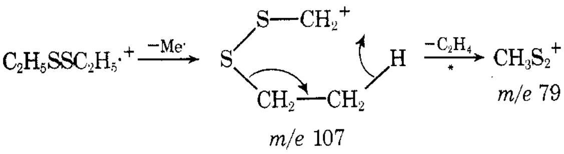
Scheme III
Deuterium Distribution in Fragments from Bis(ethyl-*1,1-d*$_2$) Disulfide

$(CH_3CD_2S)_2\cdot^+ \longrightarrow$
m/e 126,
96.5% d_4
3.5% d_3

$$\left\{\begin{matrix} CH_3CD_2SSH\cdot^+ \ (87\%,\ m/e\ 96) \\ CH_3CD_2SSD\cdot^+ \ (13\%,\ m/e\ 97) \end{matrix}\right\} \longrightarrow \left\{\begin{matrix} H_2S_2\ (64\%,\ m/e\ 66) \\ HDS_2\ (31\%,\ m/e\ 67) \\ D_2S_2\ (5\%,\ m/e\ 68) \end{matrix}\right.$$

Support for one-step nonspecific hydrogen transfer processes of the type indicated by the data in Scheme III is also obtained from DADI studies on $CD_3CH_2SSCH_2CD_3$.[18] All of these studies show that the hydrogen transfers shown in eq 5 are more favorable than the 1,2 or 1,3 shifts presumably responsible for the m/e 97, 68, and 67 species of Scheme III.

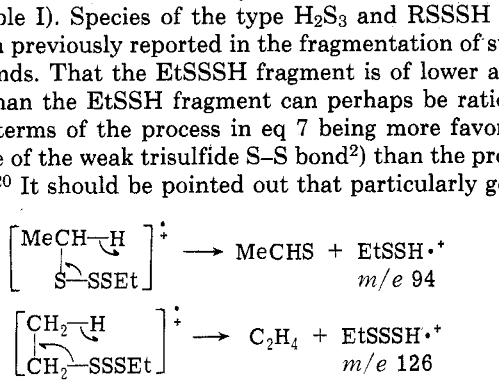
Analysis of the mass spectra of variously deuterated samples of diethyl disulfide also allows the origin of the m/e 79 rearrangement ion (CH_3SS^+) to be written with some confidence as in eq 6, since the m/e 79 fragment is



(6)

shifted to m/e 80 ($CH_2DS_2^+$[11a]) in $(CD_3CH_2S)_2$ and to m/e 81 ($CD_2HS_2^+$) in $(CH_3CD_2S)_2$.[19]

We have also examined the mass spectra of several dialkyl trisulfides with the results for diethyl trisulfide summarized in Scheme IV. The composition of the m/e 126 and 98 fragments were established by exact mass measurements (see Table I). Species of the type H_2S_3 and RSSSH have not been previously reported in the fragmentation of sulfur compounds. That the EtSSSH fragment is of lower abundance than the EtSSH fragment can perhaps be rationalized in terms of the process in eq 7 being more favorable (because of the weak trisulfide S–S bond[2]) than the process in eq 8.[20] It should be pointed out that particularly gentle



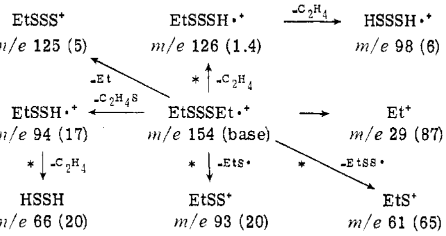
conditions must be used to obtain meaningful mass spectra of the thermally labile trisulfides. Even with a redistilled sample of EtSSSEt, for example, a substantial peak at m/e 122 corresponding to the parent ion of EtSSEt was observed along with its fragment ions and metastable peaks. That the m/e 122 peak corresponds primarily to EtSSEt produced according to eq 9 rather than to eq 10 could be

$$\mathrm{EtSSSEt} \rightleftharpoons \mathrm{EtSSEt} + \mathrm{EtSSSSEt} \qquad (9)$$

$$\mathrm{EtSSSEt}\cdot^+ \xrightarrow{-S} \mathrm{EtSSEt}\cdot^+ \qquad (10)$$

shown by (a) the simultaneous appearance in the mass spectrum of EtSSSEt under GC–MS conditions of small peaks corresponding to *both* EtSSEt and EtSSSSEt and (b) the variation in the m/e 122/154 peak height ratio with method of sample introduction and source temperature, with ratios as low as 0.05 being observed under some conditions. In none of the spectra of EtSSSEt examined was there observed a metastable peak corresponding to the process m/e 154 −S → m/e 122.

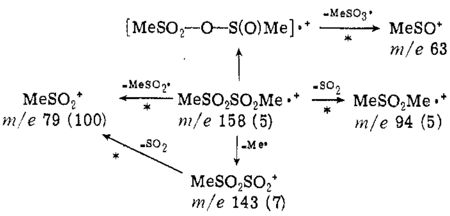
Scheme IV
Mass Spectral Fragmentation of Diethyl Trisulfide[a]



[a] See Scheme I, footnote *a*.

Dialkyl α-Disulfones. The mass spectra of α-disulfones have not been previously described.[21] Scheme V summarizes the fragments formed from dimethyl α-disulfone, $MeSO_2SO_2Me$. The fragmentation processes generally parallel the thermal and photochemical results reported for diaryl α-disulfones.[22] In contrast to the fragmentation of $MeSO_2SMe$, there is no indication of the formation of $MeS(OH)_2^+$ from $MeSO_2SO_2Me$.

Scheme V
Mass Spectral Fragmentation of Dimethyl α-Disulfone[a]



[a] See Scheme I, footnote *a*.

Experimental Section

Mass spectra were determined at the University of Missouri—St. Louis on an A. E. I. MS-12 mass spectrometer at an ionizing voltage of 70 eV using an all-glass inlet maintained at 100–150° and at Drexel University on a Hitachi Perkin-Elmer RMU-6 mass spectrometer operating under similar conditions. In the case of thermally sensitive samples the material was placed in a finely constricted melting point capillary or adsorbed on powdered graphite and introduced via a probe directly into the source of the mass spectrometer. Coupled gas chromatography–mass spectrometry was accomplished using a Hewlett-Packard Model 5750 gas chromatograph (flame ionization detector) coupled, via an all-glass Watson-Biemann separator, to the source of the A. E. I. MS-12 mass spectrometer. Exact mass measurements were made on an A. E. I. MS-9 double-focusing mass spectrometer at Harvard University while defocusing and DADI studies were performed on a Varian MAT CH5 double-focusing mass spectrometer at the University of Illinois—Urbana. The synthesis of all of the thiolsulfonates[2] (except $MeSO_2SCD_3$), the deuterated diethyl disulfide,[2] and dimethyl α-disulfone[23] have been described elsewhere.

Methyl-d_3 Methanethiolsulfonate. To 1.18 g (12 mmol) of bis(methyl-d_3) disulfide[24] in 80 ml of 50% aqueous acetone was added 2.04 g (12 mmol) of silver nitrate and 1.22 g (12 mmol) of sodium methanesulfinate.[25,26] After stirring at room temperature for 1 hr, the bright yellow suspension was filtered to remove $AgSCD_3$ and the filtrate was extracted with two 25-ml portions of ether. The combined ether extracts were dried over Na_2SO_4 and the ether was evaporated to yield 1.46 g (94%) of methyl-d_3 methanethiolsulfonate, bp 84° (1.7 mm), NMR ($CDCl_3$) δ 3.35 (singlet). Mass spectral analysis indicated 98.4% methyl-d_3 methanethiolsulfonate and 1.6% methyl-d_2 methanethiolsulfonate.

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Supplementary Material Available. Full mass spectral data for the compounds $MeSO_2SMe$, $MeSO_2SCD_3$, $MeSO_2SEt$, $EtSO_2SMe$, $EtSO_2SEt$, $MeSO_2S$-*i*-Pr, *i*-$PrSO_2SMe$, *i*-$PrSO_2S$-*i*-Pr, $MeSO_2$-*t*-Bu, $MeCD_2SO_2SCD_2Me$, $CD_3CH_2SO_2SCH_2CD_3$, $PhCH_2SO_2SCH_2Ph$, $(CD_3CH_2S)_2$, $(MeCD_2S)_2$, EtSSSEt, and $MeSO_2SO_2Me$ will appear 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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2770.

Registry No.—$MeSO_2SEt$, 2043-76-7; $(CD_3CH_2S)_2$, 52754-14-0; EtSSSEt, 3600-24-6; $EtSO_2SMe$, 2144-05-0; $MeSO_2S$-*i*-Pr, 32846-80-3; $CH_3SO_2SCH_3$, 31761-75-8; $C_2H_5SO_2SC_2H_5$, 682-91-7; $CD_3CH_2SO_2SCH_2CD_3$, 55800-38-9; $CH_3CD_2SO_2SCD_2CH_3$, 55800-39-0; *i*-$C_3H_7SO_2SCH_3$, 55800-40-3; *i*-$C_3H_7SO_2S$-*i*-C_3H_7, 10027-69-7; CH_3SO_2S-*t*-C_4H_9, 55800-41-4; $C_6H_5CH_2SO_2SCH_2C_6H_5$, 16601-40-4; $CH_3CD_2SSCD_2CH_3$, 52754-13-9; $CH_3SO_2SO_2CH_3$, 10383-49-0; methyl-d_3 methanethiolsulfonate, 55800-37-8; bis(methyl-d_3) disulfide, 7282-94-2.

References and Notes

(1) (a) University of Missouri—St. Louis; (b) University of Maine; (c) Drexel University.

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(3) (a) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **67**, 648 (1963). (b) B. G. Gowenlock, J. Kay, and J. R. Majer, *Trans. Faraday Soc.*, **59**, 2463 (1963). (c) J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc. B*, 946 (1966). (d) R. C. Gillis and J. L. Occolowitz, *Tetrahedron Lett.*, 1997 (1966). (e) W. R. Cullen, D. C. Frost, and M. T. Pun, *Inorg. Chem.*, **9**, 1976 (1970), and references cited therein. (f) Also see D. N. Harpp and J. G. Gleason, *J. Org. Chem.*, **36**, 73 (1971), for a recent discussion of some novel mass spectral fragmentation processes in cystine derivatives. (g) For a recent study of the mass spectra of fluorine-containing polysulfides, see N. R. Zack and J. M. Shreeve, *J. Fluorine Chem.*, **5**, 153 (1975).

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(6) (a) For studies on the pyrolysis of various thiolsulfonates, see J. L. Kice, R. H. Engebrecht, and N. E. Pawlowski, *J. Am. Chem. Soc.*, **87**, 4131 (1965), and earlier papers in the series. (b) A cyclic thiolsulfonate has recently been reported to lose SO_2 on photolysis: J. Meinwald and S. Knapp, *J. Am. Chem. Soc.*, **96**, 6532 (1974). (c) Photolysis of $MeSO_2SMe$ in dioxane or tetrahydrofuran affords $MeSO_2H$, MeSSMe, and $MeSO_3H$ as major products with lesser amounts of SO_2, MeSH, CH_4, and Me_2S (trace): M. D. Bentley, unpublished results.

(7) (a) P. Koch, E. Ciuffarin, and A. Fava, *J. Am. Chem. Soc.*, **92**, 5971 (1970); (b) E. Block and J. O'Connor, *ibid.*, **96**, 3929 (1974); (c) J. L. Kice in "Sulfur in Organic and Inorganic Chemistry", Vol. I, A. Senning, Ed., Marcel Dekker, New York, N.Y., 1971, Chapter 5; (d) J. A. Howard and E. Furimsky, *Can. J. Chem.*, **52**, 555 (1974).

(8) D. Darwish and R. McLaren, *Tetrahedron Lett.*, 1231 (1962); R. M. Dodson, P. D. Hammen, and R. A. Davis, *J. Org. Chem.*, **36**, 2693 (1971), and references cited therein.

(9) An example of oxygen migration in the mass spectrum of an unsymmetrical diaryl thiolsulfonate is described by Oae,[10] who postulates "an intermediate with [a] three-membered ring containing oxygen" which we would view as the transition state in the rearrangement of **2** to **4**. While we cannot exclude the intervention of **4**, structure **5** should be of somewhat lower energy, since it avoids the destabilizing interaction anticipated for the adjacent sulfoxide dipoles of **4**. Furthermore, recent experiments[7d] suggest that the initial product of coupling of alkanesulfinyl radicals has structure **5** rather than **4**.

(10) S. Kozuka, H. Takahashi, and S. Oae, *Bull. Chem. Soc. Jpn.*, **43**, 129 (1970).

(11) (a) See Table I for confirmation by exact mass. (b) This possibility was suggested by a referee.

(12) See, for example W. E. Truce and L. W. Christensen, *J. Org. Chem.*, **33**, 2261 (1968).

(13) In undeuterated $EtSO_2SEt$, the relative intensities of the *m/e* 95 $[EtS(OH)_2^+]$ and 62 $(EtSH\cdot^+)$ fragments are 33 and 61, respectively. The relative amounts of deuterated forms of key fragments are given for each fragment type. These approximate values have been corrected for contributions from heavy isotopes (C, S, O) and incomplete deuteration but not for isotope effects. The fragmentation process *m/e* 160 (**8**, $M\cdot^+$) → *m/e* 99 $[CD_3CH_2S(OH)(OD)^+]$ is supported by metastable analysis. Extensive hydrogen scrambling in **8** and **9** *prior* to fragmentation according to eq 1 is considered unlikely in view of the negligible transfer of *two* deuterium atoms or *two* hydrogen atoms in processes a and c, Scheme II, respectively.

(14) In the mass spectra of aliphatic sulfones the species $RS(OH)_2^+$ is formed.[15] However, the transition state for formation must differ from that proposed for fragmentation of thiolsulfonates (eq 1), since $EtSO_2H\cdot^+$ rather than $EtS(OH)_2^+$ is formed from diethyl sulfone, and no $RS(OD)_2^+$ is formed from α-, β-, or γ-d_4 or δ-d_6 dibutyl sulfone.[15] A similar situation exists in the fragmentation of alkyl alkanesulfonate esters.[12]

(15) R. Smakman and T. J. de Boer, *Org. Mass Spectrom.*, **3**, 1561 (1970).

(16) The relative amounts of the two fragment types has been corrected for contributions from heavy isotopes (C, S, O) and from incomplete deuteration but not for isotope effects. Extensive hydrogen scrambling prior to fragmentation can be excluded because of the low intensity of the $D_2S_2\cdot^+$ fragment. The relative extent of deuterium incorporation into fragments did not change substantially on reducing the ionizing voltage to 10 eV.

(17) Also referred to as mass-analyzed ion kinetic energy spectra (MIKES). For a recent review of the technique, see J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Y. Ridley, *Anal. Chem.*, **45**, 1023 (1973).

(18) The daughter ions $CD_3CH_2SSD\cdot^+$ and $CD_3CH_2SSH\cdot^+$ from $(CD_3CH_2S)_2$ were found by DADI analysis to have their intensities in the ratio of 7.5:1, respectively. Similarly, the ions D_2S_2 and DHS_2 from CD_3CH_2SSD had intensities in the ratio of 3.9:1 while the ions DHS_2 and H_2S_2 derived directly from CD_3CH_2SSH had intensities in the ratio of 5.3:1, respectively.

(19) Additional characteristics of α-disulfide carbonium ions, such as the *m/e* 107 fragment of eq 6, generated under electron impact as well as solvolytic conditions may be found in E. Block, *J. Org. Chem.*, **39**, 734 (1974).

(20) In the mass spectrum of MeSSSMe[4] there is a significant fragment corresponding to MeSSH (14% of base intensity) possibly produced according to eq 7.

(21) Following the completion of this work, a brief report of the mass spectral fragmentation of di-*p*-tolyl disulfone appeared: T. Graafland, J. B. F. N. Engberts, and W. D. Weringa, *Org. Mass Spectrom.*, **10**, 33 (1975).

(22) (a) Photolysis: M. Kobayashi, K. Tanaka, and H. Minato, *Bull. Chem. Soc. Jpn.*, **45**, 2906 (1972). (b) Pyrolysis: J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, **35**, 116 (1970).

(23) H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **69**, 1127 (1950).

(24) I. B. Douglass, *Int. J. Sulfur Chem.*, **8**, 441 (1973).

(25) I. B. Douglass, *J. Org. Chem.*, **30**, 633 (1965).

(26) This method of preparing thiolsulfonate esters has been previously described: M. D. Bentley, I. B. Douglass, and J. A. Lacadie, *J. Org. Chem.*, **37**, 333 (1972).