acetone) which was identical to *meso*-**3** separated from the diastereomeric mixture of **3**.

***meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen D(−)-dibenzoyltartrate] (*meso*-8).** Utilizing the procedure previously described for resolution of (±)-**5**, 0.5 g (0.8 mmol) of *meso*-**5** and 0.8 g (1.7 mmol) of silver hydrogen D(−)-dibenzoyltartrate reacted to give 0.75 g (75%) of *meso*-**8** [D(−)-HDBT]: mp 149–151 °C dec; $[\alpha]^{24}{}_D = -91.3°$ (*c* 1.00, H_3COH); IR (KBr) ν 1724 (C═O), 1440 ($P\text{-}C_6H_5$), 1112 ($P\text{-}C_6H_5$), 998 ($P\text{-}C_6H_5$) cm^{-1}; ^1H-decoupled ^{31}P NMR ($DCCl_3$) +15.51; +15.54 ppm (relative to 85% phosphoric acid).

Anal. Calcd for $C_{72}H_{68}O_{16}P_2$: C, 69.11; H, 5.48; P, 4.95. Found: C, 68.96; H, 5.44; P, 4.96.

Metathesis of *meso*-1,1′-(1,2-Ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) Bis[hydrogen D(−)-dibenzoyltartrate] (*meso*-8) to the Corresponding Diperchlorate (*meso*-3). The phosphonium salt, *meso*-**8** [D(−)-HDBT] (200 mg, 0.16 mmol) and an aqueous solution (10 mL) of $NaClO_4$ (2.0 g, 0.016 mol) were allowed to react in the same manner utilized for metathesis of (−)-**7** [L(+)-HDBT] to give 0.085 g (75%) of *meso*-**3**, mp 291–293 °C, $[\alpha]^{24}{}_D = 0°$ (*c* 1.00, acetone) which was identical to *meso*-**3** separated from the diastereomeric mixture of **3**.

Acknowledgment. We gratefully acknowledge support of this work by the USPHS National Cancer Institute, Grant CA 22770 (K.D.B.). Spectral thanks are due to Dr. Kurt Loening of Chemical Abstracts Service for providing proper names for all compounds.

Registry No. (±)-**3**, 80799-71-9; *meso*-**3**, 80799-73-1; (+)-**3**, 80799-75-3; (−)-**3**, 81207-46-7; (±)-**4**, 81207-47-8; (±)-**5**, 81207-48-9; *meso*-**5**, 80799-76-4; *meso*-**6**, 81207-49-0; (±)-**7**, 81207-50-3; *meso*-**7**, 81207-51-4; (−)-**7**, 81207-52-5; (±)-**8**, 81207-53-6; *meso*-**8**, 81207-54-7; (+)-**8**, 81219-01-4; **11**, 81194-90-3.

Synthesis and Thermal Decomposition of 1,3-Dithietane and Its *S*-Oxides[1-3]

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Contribution from the Departments of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121, State University of New York at Albany, Albany, New York 12222, and Chemische Institut der Universität, Niederurseler Hang, 6000 Frankfurt, Germany.

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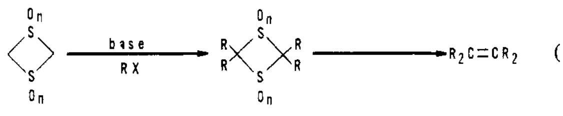
Abstract: Syntheses of 1,3-dithietane (**1**), 1,3-dithietane 1-oxide (**2**), 1,3-dithietane 1,1-dioxide (**3**), *cis*-1,3-dithietane 1,3-dioxide (**4**), *trans*-1,3-dithietane 1,3-dioxide (**5**), and 1,3-dithietane 1,1,3-trioxide (**6**) are reported for the first time. These compounds are converted in high yield to the previously described sulfene dimer 1,3-dithietane 1,1,3,3-tetraoxide (**7**). The structures of **2** and **7** are found to be respectively puckered (by microwave spectroscopy) and planar (by X-ray crystallography). Spectroscopic and physical data are discussed (photoelectron (PE) and NMR spectroscopy, pK_a values, oxidation potentials) along with some data on base-catalyzed H/D exchange. The PE spectra are assigned using MO models on different levels, including PNO/CEPA for thioformaldehyde (CH_2S). Thermal decomposition is investigated using three independent methods: mass, microwave, and PE spectroscopy. Two types of decomposition channels are observed: retro 2 + 2 and retro 3 + 1. Among others, species like thioformaldehyde and sulfine (CH_2SO, thioformaldehyde *S*-oxide) are produced. They are characterized by their microwave structure as well as by their PE ionization patterns and IR spectra.

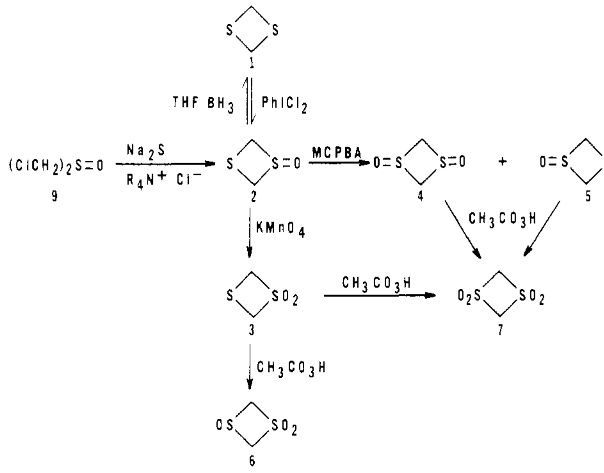
I. Introduction

The search for a new olefin synthesis based on the tetraalkylation–two-fold extrusion sequence depicted in eq 1[6] led us to the



(1)

development of a simple synthesis of the hitherto unknown 1,3-dithietane (**1**) and its several *S*-oxides **2**–**7**, utilizing the phase-transfer-catalyzed ring-closure reaction of bis(chloromethyl) sulfoxide with sodium sulfide followed either by reduction or oxidation (eq 2).[7] The synthesis of the novel diheterocyclobutanes



(2)

prompted physical measurements to determine their molecular properties. Thus structures of several of them have determined:

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(1) Part 9 of Flash Vacuum Pyrolysis Studies;[2] Part 101 of Photoelectron Spectra and Molecular Properties.[3]

(2) Part 8: Powers, D. E.; Arrington, C. A.; Harris, W. C.; Block, E.; Kalasinsky, V. F. *J. Phys. Chem.* **1979**, *83*, 1890–1892.

(3) Part 100: Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427–444.

(4) (a) University of Missouri—St. Louis. (b) State University of New York at Albany; address correspondence to author at this address. (c) Chemische Institut der Universität.

(5) National Science Foundation Undergraduate Research Participant, 1975.

(6) For a related "twofold extrusion" approach to the synthesis of olefins, see: (a) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305–310. (b) Also see: Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; pp 99–100. (c) Note also: Seelinger, R.; Sundermeyer, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 203–204.

(7) Preliminary communication: Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 5715–5717.

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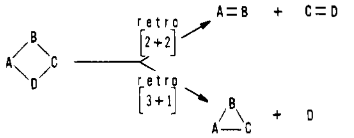
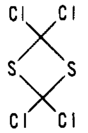
1,3-dithietane (**1**) is puckered in the gas phase but planar as a solid (Raman, IR spectroscopy),[8] 1,3-dithietane 1-oxide (**2**) is puckered (microwave spectroscopy),[7] and 1,3-dithietane 1,1,3,3-tetraoxide (**7**) is planar (X-ray crystallography).[7] The photoelectron spectra of **1**–**7** have been determined and analyzed. In connection with our search for methods of extrusion of sulfur or its oxides from compounds **1**–**7** (cf. eq 1), we have discovered that on flash vacuum pyrolysis (FVP) these molecules decompose by either of two formal reaction channels, e.g., retro 2 + 2 or 3 + 1 processes (eq 3). In our investigation of the thermal decomposition of **1**–**7**, we have coupled the following complementary spectroscopic techniques directly to the pyrolyses: mass spectroscopy ("quick and dirty" analysis), microwave spectroscopy (structures and half-lives of pyrolysis products), and photoelectron (PE) spectroscopy (visible "molecular fingerprints" allowing optimization of reaction conditions and product identification if PE bands of smaller molecules do not overlap). In the course of studying the pyrolysis of **1**–**7** we have serendipitously discovered and characterized a new small molecule, sulfine (thioformaldehyde *S*-oxide, CH_2SO),[9,10] and found a new route to pure samples of thioformaldehyde.



(3)

II. Synthesis

Although derivatives of 1,3-dithietane (**1**) have been known for over 100 years,[11] the parent compound has until now remained unknown. Two synthetic approaches to **1** were investigated. One approach involved the dechlorination of the readily available thiophosgene photodimer, 2,2,4,4-tetrachloro-1,3-dithietane (**8**).[11c]



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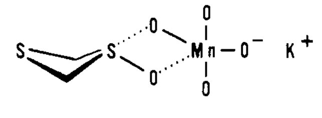
While tributyltin hydride, lithium aluminum hydride, and lithium aluminum hydride–aluminum chloride all reacted with **8** under mild conditions, the products were complex and could not be easily resolved. A more successful procedure involved the reaction of bis(chloromethyl) sulfoxide (**9**) with sodium sulfide. Initial experiments with aqueous solutions of sodium sulfide and **9** indicated the formation of 1,3-dithietane 1-oxide (**2**) in low yield after heating at 100 °C. It was discovered that addition of a phase-transfer catalyst (General Mills "Aliquat 336", "tricaprylylmethylammonium chloride") permitted the synthesis of **2** under gentler conditions and in improved yield. Thus on adding sodium sulfide to a vigorously stirred suspension of **9** and the phase-transfer catalyst in water, an exothermic reaction ensued. Compound **2**, a colorless crystalline solid, mp 71–73.5 °C, with a garlic-like odor could be isolated in 36% yield by chloroform extraction of the reaction filtrate (considerable polymer was also formed). It should be noted that reaction of bis(chloromethyl) sulfide with sodium sulfide leads only to polymer.[12] Presumably bis(chloromethyl) sulfide alkylates any 1,3-dithietane formed giving polymer; similar reaction between 1,3-dithietane 1-oxide and bis(chloromethyl) sulfoxide should be somewhat less favorable because of the diminished nucleophilicity at sulfide sulfur of the former and diminished reactivity in S_N2 processes of the latter.[13] Finally, bis(chloromethyl) sulfone was recovered unchanged after prolonged heating with a mixture of the phase-transfer catalyst and sodium sulfide in water, an observation consistent with the very low S_N2 reactivity of α-chloro sulfones.[13]

The reduction of **2** to 1,3-dithietane (**1**) was anticipated to require a particularly gentle reagent in view of the known sensitivity of thioacetal *S*-oxides to acids.[14] Of the various reagents tested, the best yield (ca. 70%) of **1** was obtained with excess 1 M borane–tetrahydrofuran complex at room temperature for 1 day. Compound **1** is a colorless, vile-smelling solid with a remarkably high melting point for a compound of such low molecular weight (105–106 °C).

In connection with microwave studies of **2**, it was necessary to incorporate ^{18}O into this compound. This was accomplished by reoxidizing **1** with iodobenzene dichloride in acetonitrile containing $H_2{}^{18}O$ and triethylamine to afford **2**-^{18}O.[15a] The remaining, previously unknown *S*-oxides of 1,3-dithietane were prepared through oxidation as summarized in eq 2. Compound **2** could be converted into 1,3-dithietane 1,1-dioxide (**3**, mp 141–142 °C) in 96% yield by treatment with $KMnO_4/MgSO_4$ in acetone at −20 °C.[15a] The remarkable selectivity of this oxidation (sulfide is more easily oxidized than sulfoxide with most oxidants) may reflect coordination of sulfoxide oxygen by permanganate as shown in (**10**).[15a] Oxidation of **2** with iodobenzene dichloride in aqueous pyridine at −30 °C or with *m*-chloroperbenzoic acid in methylene chloride at 0 °C produces respectively a 3:1 or 2:3 mixture of *cis*-1,3-dithietane 1,3-dioxide (**4**, mp 260 °C dec) and *trans*-1,3-dithietane 1,3-dioxide (**5**, mp 203–205 °C dec), readily separable by fractional recrystallization from dimethylformamide. Treatment of **3** in chloroform at 0 °C with peracetic acid gives 1,3-dithietane 1,1,3-trioxide (**6**, mp 231–234 °C) in 90% yield.



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Finally, exposure of **3**–**6** to excess peracetic acid at 100 °C for several hours gives in 71–86% yield 1,3-dithietane 1,1,3,3-tetraoxide (**7**) with spectral and physical properties in complete agreement with those previously reported for the sulfene dimer.[15d]

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(8) Kalasinsky, V. F.; Block, E.; Powers, D. E.; Harris, W. C. *Appl. Spectrosc.* **1979**, *33*, 361–364.

(9) Preliminary communications: (a) Block, E.; Penn, R. E.; Olsen, R. J.; Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 1264–1265. (b) Block, E.; Bock, H.; Mohmand, S.; Rosmus, P.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 383–384.

(10) Penn, R. E.; Olsen, R. J. *J. Mol. Spectrosc.* **1976**, *61*, 21–28.

(11) (a) Behr, A. *Chem. Ber.* **1872**, *5*, 970–972 (repeated by Ried, W.; Klug, H. *Ibid.* **1961**, *94*, 368–372. (b) Rathke, B. *Justus Liebigs Ann. Chem.* **1873**, *167*, 195–211. (c) Schönberg, A.; Stephenson, A. *Chem. Ber.* **1933**, *66B*, 567–571. (d) Durig, J. R.; Lord, R. C. *Spectrochim. Acta* **1963**, *19*, 769–774. (e) Middleton, W. J. U. S. Patent 3 136 781, 1964; *Chem. Abstr.* **1964**, *61* 5612. (f) Middleton, W. J.; Howard, E. G.; Sharkey, W. H. *J. Org. Chem.* **1965**, *30*, 1375–1384. (g) Katritzky, A. R.; Mayer, R.; Morgenstern, J.; Sewell, M. J. *J. Chem. Soc.* **1965**, 5953–5957. (h) Krebs, B.; Beyer, H. *Z. Anorg. Allg. Chem.* **1969**, *365*, 199–210. (i) Wortmann, F. J.; Kiel, G.; Gattow, G. *Ibid.* **1970**, *376*, 73–78. (j) Greidanus, J. W. *Can. J. Chem.* **1970**, *45*, 3530–3536. (k) Yates, P.; Moore, D. R.; Lynch, R. T. *Ibid.* **1971**, *49*, 1456–1466. (l) Oae, S.; Nakaniski, A.; Tsujimoto, N. *Chem. Ind.* (*London*) **1972**, 575–576. (m) Nishio, T.; Yoshioka, M.; Aoyama, H.; Sugiyama, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2253–2254. (n) Ueno, Y.; Masuyama, Y.; Okawara, M. *Tetrahedron Lett.* **1974**, 2577–2580. (o) Gupta, S. K. *J. Org. Chem.* **1974**, *39*, 1944–1946. (p) Thimm, K.; Voss, *J. Tetrahedron Lett.* **1975**, 537–540. (q) Smith, Z.; Seip, R. *Acta Chem. Scand., Ser. A* **1976**, *30*, 759–766. (r) Diderrich, G.; Haas, A.; Yazdanbakhsch, M. *Chem. Ber.* **1977**, *110*, 916–920. (s) Mikolajczyk, M.; Kiebasinski, P.; Barlow, J. H.; Russell, D. R. *J. Org. Chem.* **1977**, *42*, 2345–2347. (t) Kato, S.; Hori, A.; Takagi, T.; Mizuta, M. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 787–788. (u) Thimm, K.; Schmuser, W.; Voss, J. *J. Chem. Res., Synop.* **1977**, 244. (v) Desjardins, C. D.; Passmore, J. *Can. J. Chem.* **1977** *55*, 3136–3146.

(12) Lal, J. *J. Org. Chem.* **1961**, *26*, 971–972.

(13) See ref 6b, pp 166–167; also note ref 6c.

(14) For example, see: Veenstra, G. E.; Zwanenburg, B. *Tetrahedron*, **1978**, *34*, 1585–1592, and references therein.

(15) (a) For additional examples of these oxidations, see: Block, E. In "The Chemistry of Functional Groups. Supplement El: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogs"; Patai, S., Eds.; Wiley: London, 1980; Chapter 13. (b) Optiz, G.; Mohl, H. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 73.

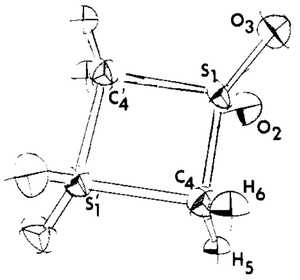


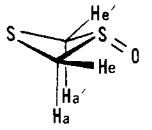
Figure 1. A perspective view of the 1,3-dithietane 1,1,3,3-tetraoxide (**7**) molecule with atom labels.

III. Structure and Properties

A. Structure. The structures of four-membered rings are of considerable interest owing in part to the low-frequency ring-puckering vibration and the accompanying conformational problems.[16] Structural data on 1,3-dithietane, 1,3-dithietane 1-oxide, and 1,3-dithietane 1,1,3,3-tetraoxide are summarized below.

1. 1,3-Dithietane (1). An analysis of infrared and Raman spectra of **1** in the solid state and trapped in an argon matrix at 18 K indicates that the "free" molecule is slightly puckered, while in the annealed solid the ring is planar, presumably because of crystal-packing forces.[8,17] An attempt was made to determine the gas-phase structure of 1,3-dithietane by microwave spectroscopy. No absorption lines were observed so we conclude that the dipole moment is very small, or possibly zero, suggesting a planar or nearly planar ring. Structural studies of various substituted 1,3-dithietanes have shown these compounds to be essentially planar,[11] while thietane shows a small (0.783 kcal/mol) preference for a puckered rather than planar conformation.[16]

2. 1,3-Dithietane 1-Oxide (2). The gas-phase structure of **2** has been determined by the isotopic substitution method from its microwave spectrum and the spectrum of eight isotopic modifications (^{18}O, $^{34}S_O$, ^{34}S, ^{13}C, d_1-a, d_1-e, d_3-aae, and d_4; details on deuterium incorporation will be presented below). The ring is puckered, the angle between the two CSC planes being 39.3 (2)°, with the oxygen equatorial (see **2a**). Other structural parameters



2a

are $r(S_O - O) = 1.473$ (3) Å, $r(C{-}S_O) = 1.81$ (2) Å, $r(C{-}S) = 1.82$ (2) Å, $\angle CS_OC = 81.7$ (8)°, $\angle CSC = 81.1$ (5)°, $\angle SCS_O = 91.2$ (5)°, $\angle CS_OO = 112.4$ (7)°, $\angle(H_aCSO_O) - (CS_O) = 25.5$ (14)°, and $\angle(H_eCS_O) - (CS_OO) = -99.3$ (24).° Compound **2** displays short nonbonded S···S and C···C distances (2.600 (7) and 2.37 (2) Å, respectively). The S–O distance and angle of pucker of **2** appear to be normal compared to data on thietane 1-oxides.[18]

3. 1,3-Dithietane 1,1,3,3-Tetraoxide (7). The structure of **7** has been determined by X-ray diffraction methods (see Experimental Section for crystal data and methodology). The four-atom ring of **7** is planar and almost square (Figure 1); the molecule is located on a crystallographically required center of symmetry at the center of the four-atom ring. The SCS′ and CSC′ angles are 91.5 (1) and 88.5 (1)°, respectively; other bond lengths and angles are in Table I.[19] The planes of the SO_2 and CH_2 groups are essentially perpendicular to the plane of the four atom ring (89.9 and 85°, respectively). Intramolecular nonbonded S···S and C···C distances are 2.590 (1) and 2.524 (3) Å, respectively. The former nonbonded distance is quite short and may be compared with the value for S···S in **2** of 2.600 (7) Å (see above) and published values of 2.684 (3) Å in 2,2,4,4-tetrachloro-1,3-dithietane[11h] and 2.672 Å in *trans*-2,4-dimethyl-2,4-bis(thioacetylthio)-1,3-dithietane.[11s]

Table I. Interatomic Bond Lengths and Angles for 1,3-Dithietane 1,1,3,3-Tetraoxide (7)

	distances, Å		
S1-O2	1.436 (2)	S1-C′4	1.804 (2)
S1-O3	1.433 (2)	C4-H5	0.96 (2)
S1-C4	1.813 (2)	C4-H6	0.87 (2)
	angles, deg		
O2-S1-O3	119.4 (1)	S1-C4-S1′	91.5 (1)
O2-S1-C4	110.9 (1)	H5-C4-H6	112 (2)
O2-S1-C4′	111.4 (1)	H5-C4-S1	115 (2)
O3-S1-C4	110.8 (1)	H5-C4-S1′	112 (1)
O3-C1-C4′	111.7 (1)	H6-C4-S1	107 (2)
C4-S1-C4′	88.5 (1)	H6-C4-S1′	117 (2)

Table II. Vertical Ionization Energies IE_n (eV) of 1,3-Dithietane and 1,3-Dithietane *S*-Oxides

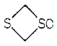
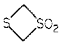
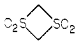
compd	1	2	3	4	5	6	7	8
	8.95	9.43	10.60	12.53	13.87	14.30	15.65	17.62
	9.19	9.87	10.65	12.49	13.21	14.83	15.29	16.57
	9.06	10.59	11.14	13.0	13.86	14.51	16.0	
	9.71	11.18	11.57	11.72	11.94	13.55	15.13	16.65
	11.00	12.55	13.51	15.35	16.17	17.64		

Figure 1a (supplementary material) illustrates the packing of the molecules in the solid state. The most important intermolecular contact distance is between S1 and the O2 atom in molecules related by the twofold screw axes. This S1···O2 intermolecular distance of 3.079 (2) Å is much shorter than the expected van der Waals distance of approximately 3.25 Å. Because of the strong intermolecular interactions between S1 and O_2, the structure may be considered as sheets of molecules whose centers are in the (001) plane. There are no very strong intermolecular interactions between sheets of molecules; the next shortest S···O distance is 3.470 (2) Å between S1 and O3 related by the center of symmetry at $^1/_2$, $^1/_2$, $^1/_2$. The shortest intermolecular contact involving carbon is a C4···O2 distance of 2.956 (2) Å which involves atoms related by the *c*-glide plane which relates molecules within the (001) sheets.

B. Photoelectron Spectra and Their Assignment. A variety of three- and four-membered heterocyclic systems with one ring heteroatom[20] have been investigated PE spectroscopically; replacing one of the methylene groups by a heterocenter removes the degeneracy of the highest occupied energy levels due to lower symmetry. The PE spectra of the novel 1,3-diheterocyclobutanes are also highly resolved (Figure 2) showing up to seven separated bands (Table II).

1. 1,3-Dithietane. The first two ionization energies of 1,3-dithietane (Table II) can be attributed to radical-cation states with predominant sulfur "lone pair" character. The fine structure

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(16) For example, see: Malloy, T. B., Jr.; Baumann, L. E.; Carreira, L. A. In "Topics in Stereochemistry"; Eliel, E. L., Allinger, N. L., Eds.; Wiley-Interscience: New York, 1979, Vol. XIV. Moriarty, R. M. *Ibid.* in 1974; Vol. VIII.

(17) An analogous effect has been observed for 1,3-disilacyclobutane: Irwin, R. W.; Laane, J. *J. Phys. Chem.* **1978**, *82*, 2845–2850.

(18) (a) Wing, R. M.; Uebel, J. J.; Andersen, K. K. *J. Am. Chem. Soc.* **1973**, *95*, 6046–6056. (b) Bevan, J. W.; Legon, A. C.; Millen, D. J. *Proc. R. Soc., London, Ser. A* **1977**, *354*, 491–509. (c) Hardgrove, G. L., Jr.; Bratholdt. J. S.; Lein, M. M. *J. Org. Chem.* **19748**, *39*, 246–248. (d) Barlow, J. H.; Hall, C. R.; Russell, D. R.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1975**, 133–134.

(19) For comparative data on thietane 1,1-dioxides, see: (a) Ziegler, M. L.; Weiss, J.; Schildknecht, H.; Grund, N.; Sasse, H.-E. *Justus Liebigs Ann. Chem.* **1973**, 1702–1709. (b) Cistaro, C.; Fronza, G.; Mondelli, R.; Bradamante, S.; Pagani, G. A. *J. Magn. Reson.* **1975**, *17*, 219–228. (c) Also see ref 6c.

(20) (a) Mollere, P. D.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 3226–3233. (b) Schweig, A.; Thiel, W. *Chem. Phys. Lett.* **1973**, *21*, 541–543. (c) Gleiter, R.; Spanget-Larsen, J. *Top. Curr. Chem.* **1979**, *86*, 139–196. (d) For an ab initio calculation on **1**, see: Kao, J. *J. Mol. Struct.* **1977**, *41*, 321–324.

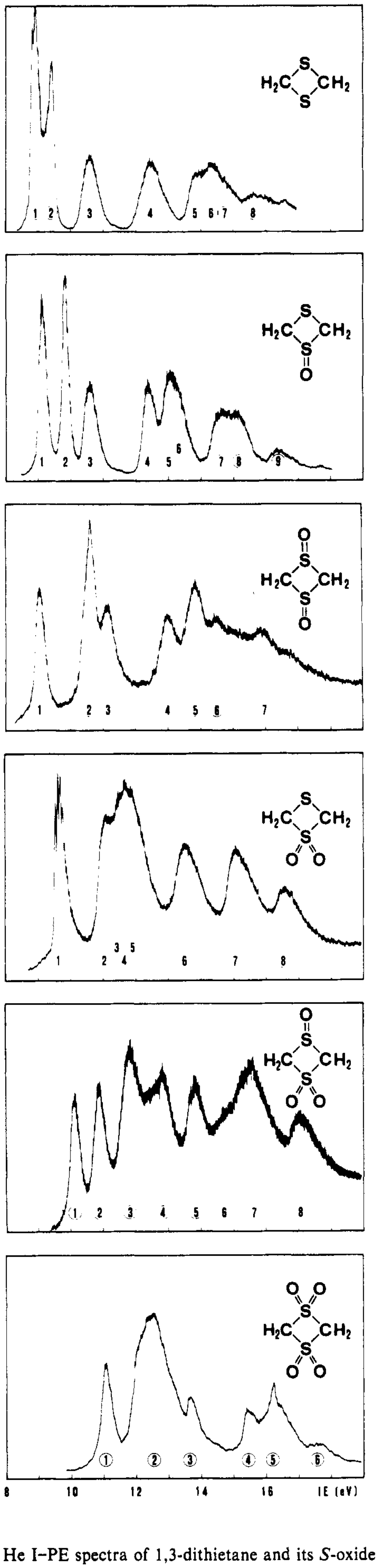

Figure 2. He I-PE spectra of 1,3-dithietane and its *S*-oxides.

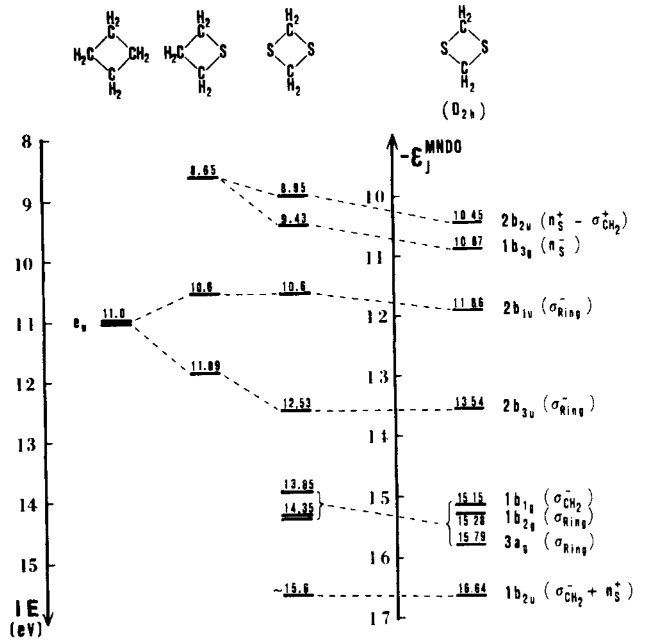

Figure 3. Comparison of some radical-cation states of cyclobutane and its sulfur derivatives and correlation with MINDO eigenvalues of 1,3-dithietane (**1**).

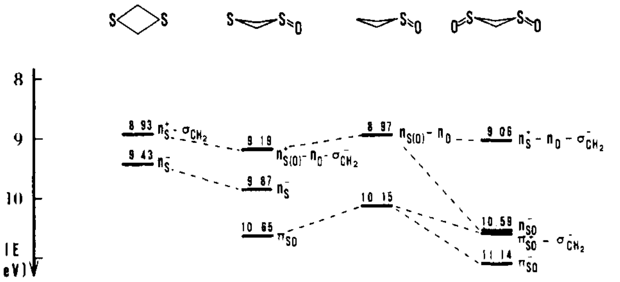

Figure 4. Sulfur lone pair and π_{SO} ionization patterns in four-membered ring sulfides and sulfoxides.

of the first band ($\nu^+ = 680 + 60$ cm^{-1} corresponds to the symmetric C–S stretching vibration of the neutral ground state ($\nu = 684$ cm^{-1}).

A comparison with the PE spectra of thietane[20a] and cyclobutane[20a] (Figure 3) demonstrates that the successive replacement of two CH_2 groups of cyclobutane in the 1 and 3 positions by sulfur each adds one band in the low-energy region and simultaneously removes the degeneracy of the e_u ring orbitals. A geometry-optimized MINDO calculation fully supports via Koopmans' theorem, $IE_n = -\epsilon_J^{MINDO}$, the results from the above radical-cation-state comparison (Figure 3). The MINDO geometry optimization yields an almost planar structure of the ring with a dihedral angle of only 2°, in agreement with the fact that no microwave absorptions could be observed for this molecule.[7,20d] Other structural parameters calculated are $r_{CS} = 1.75$ Å, $\angle SCS = 94°$, and $\angle CSC = 86°$.

2. 1,3-Dithietane 1-Oxide and 1,3-Dithietane 1,3-Dioxide. The PE spectrum of 1,3-dithietane 1-oxide (Figure 2) shows an increase in ionization energies relative to 1,3-dithietane (Table II) due to the effective nuclear charge of oxygen. The split of the two low-energy bands assigned to the sulfur "lone pairs" also exceeds the one in 1,3-dithietane. The PE spectrum of 1,3-dithietane 1-oxide (Figure 2) is best discussed by comparison with that of thietane *S*-oxide (Figure 4) because the obviously large perturbation S → SO can be replaced by the iso(valence)electronic one $CH_2 \rightarrow S$. In general, the three highest occupied orbitals of sulfoxides are the "long pairs" n_S and n_O as well as the π_{SO} bond.[21]

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[21] (a) Bock, H.; Solouki, B. *Chem. Ber.* **1974**, *107*, 2299–2318. (b) Wagner, G.; Bock, H. *Ibid.* **1974**, *107*, 68–77.

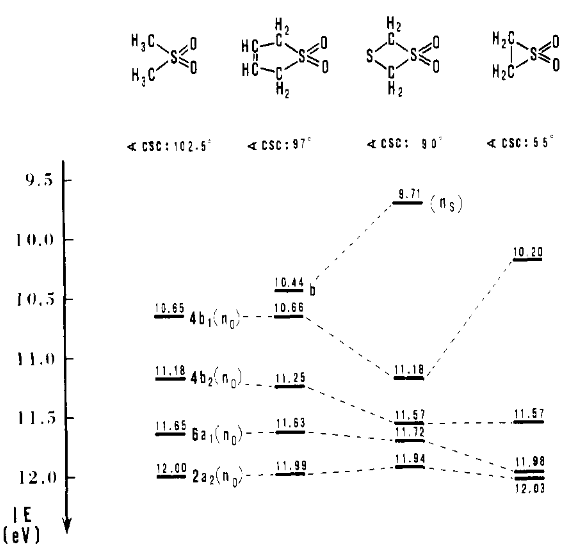


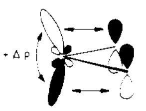
Figure 5. Correlation of the ionization energies between 9 and 12 eV of dimethyl sulfone, 2,5-dihydrothiophene 1,1-dioxide, 1,3-dithietane 1,1-dioxide (**3**), and thiirane 1,1-dioxide.

Starting from thietane *S*-oxide (Figure 4) and replacing the CH_2 group in the 3 position by a sulfur atom adds a sulfur "lone-pair" ionization and destablizes the n_O and π_{SO} radical-cation states.

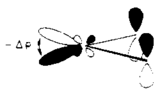
The ionization patterns (Figure 4) are correlated as follows: The first two ionization energies of 1,3-dithietane, $n_S^+ - \sigma_{CH_2}$ and n_S^-, are split by $\Delta IE_{1,2} = 0.4$ eV.[21b] According to a hyperconjugative MO model, the n_S^+ combination is destablized by about 1 eV relative to the basis orbital energy $\alpha(n_S) \sim -9.6$ eV[21b] due to the combination with the σ_{CH_2} (b_{2u}) orbital. In 1,3-dithietane 1-oxide, both sulfur "lone-pair" ionizations are further increased by the oxygen substitution. In thietane *S*-oxide both n_O and π_{SO} ionizations are lowered by the S → CH_2 substitution, whereas a $CH_2 \rightarrow SO$ replacement splits the n_O and π_{SO} ionizations and increases their centers of gravity. This radical-cation-state correlation (Figure 4) is supported both by EHMO and modified CNDO calculations based on the known structural parameters.[7] For 1,3-dithietane 1,3-dioxide (Figure 4), a considerable hyperconjugation of the σ_{CH_2} (b_{2u}) orbital is calculated both with the n_S^+ and π_{SO}^+ combinations. Therefore, the first ionization is best represented by $n_S^+ - n_O - \sigma_{CH_2}$, the second band of doubled intensity by n_S^- and $\pi_{SO}^+ - \sigma_{CH_2}^-$, and the third one by π_{SO}^- (Figure 2).

3. 1,3-Dithietane 1,1-Dioxide. Structural data are not known; the analogous 1,3-dithietane 1,1,3,3-tetraoxide displays a planar ring while thietane 1,1-dioxides are known to be almost planar.[19] The assumption of a C_{2v} structure also for the 1,1-dioxide is supported by the increase in CNDO/2 total energy upon bending of the molecular plane. The first band of the PE spectrum (Figure 2 and Table II) is assigned to the ionization of the sulfur "lone-pair" $n_S(-\pi_{SO_2}^+)$. Judging from its intensity, the multiple band between 11 and 12 eV should comprise four ionizations, which according to EHMO and modified CNDO calculations are represented by the characteristic orbitals of the sulfone group[22] $\pi_{SO}^+ - \sigma_{SO}^-$ ($4b_1$), n_O^- ($4b_2$), $\sigma_{SO_2}^+ - \pi_{SC}^+$ ($6a_1$), and $\pi_{SO_2}^-$ ($2a_2$) (Figure 5).

Comparison of the low-energy ionizations of dimethyl sulfone ($\angle CSC = 102.5°$ [23a]), 2,5-dihydrothiophene 1,1-dioxide ($\angle CSC = 97°$ [23b]), 1,3-dithietane 1,1-dioxide (estimated $\angle CSC = 90°$), and thiirane 1,1-dioxide ($\angle CSC = 55°$ [23c]) (figure 5) shows that the ionization energies assigned to the $^2B_1$ ($\pi_{SO_2}^+ - \sigma_{SC}^-$) states of these sulfones reach a maximum at a CSC angle of approximately 90°. This angular dependance can be rationalized qualitatively by the antibonding interactions in the corresponding b_1 orbital (see **11a** and **11b**).



11a

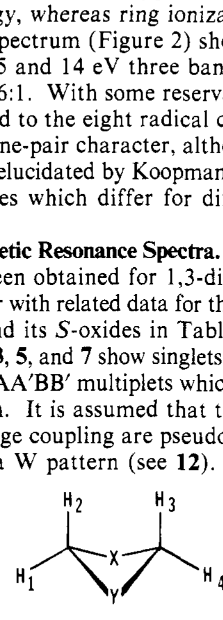


11b

The plausible assignment (Figure 5) can be further substantiated by a comparison of the PE spectra of 1,3-dithietane with its 1-oxide and 1,1-dioxide (Figure 2): the first band, assigned to n_S ionization, shifts with increasing oxygen substitution to higher energy (Table II), an argument similarly applicable to band 2 of the sulfide and the sulfoxide. Band 3 of the sulfoxide corresponds to the π_{SO} ionization, and bands 2 through 5 of the sulfone correspond to SO_2 group ionizations. Bands 3 and 4 in the sulfide, 4 and 5 in the sulfoxide, and 6 in the sulfone are assigned to ring ionizations.

4. 1,3-Dithietane 1,1,3,3-Tetraoxide. For this 12-atom compound a D_{2h} structure has been determined by X-ray crystallography. Nevertheless, the interpretation of its He I spectrum (Figure 2) is rather difficult because of the many overlapping ionizations, and because the results of EHMO and CNDO/2 calculations disagree. For the low-energy region, a tentative assignment can be based on the following argument. From the assigned PE spectra of other sulfones such as 1,3-dithietane 1,1-dioxide, it follows that the oxygen lone pairs are ionized at relatively low energy, whereas ring ionizations occur at higher energies. The PE spectrum (Figure 2) shows in the low-energy region between 10.5 and 14 eV three bands in an approximate intensity ratio of 1:6:1. With some reservation, these eight ionizations are assigned to the eight radical cation states with predominant oxygen lone-pair character, although the exact orbital sequence cannot be elucidated by Koopmans correlation using the eigenvalue sequences which differ for different semiempirical calculations.

C. Nuclear Magnetic Resonance Spectra. Proton and carbon-13 NMR data have been obtained for 1,3-dithietanes **1**-**7** and are summarized together with related data for thietane and its *S*-oxides and 1,3-dithiane and its *S*-oxides in Table III. While the ^1H NMR spectra of **1**, **3**, **5**, and **7** show singlets, the ^1H NMR spectra of **2**, **4**, and **6** show AA′BB′ multiplets which were analyzed using a LAOCN-3 program. It is assumed that those protons showing the largest long-range coupling are pseudo-equatorial protons 1 and 4 which form a W pattern (see **12**). There is reasonable agreement between the coupling constants presented here for 1,3-dithietanes **2**, **4**, and **6** and the values previously reported for thietane and its *S*-oxides.[24]



12

The carbon-13 NMR chemical shifts for 1,3-dithietanes **1**-**7** show several interesting features. (1) The carbon atoms of 1,3-dithietane (**1**) appearing at δ_c 18.6 are unusually shielded compared to the α carbons of thietane (δ_c 26.1) or C_2 of 1,3-dithiane (δ_c 32.0). (2) A much larger deshielding effect occurs on going from a sulfoxide to a sulfone (or a disulfoxide to a disulfone) in the dithietane series (e.g., **2** → **3**, $\Delta\delta_c = 15.3$ ppm; **3** or **4** → **7**, $\Delta\delta_c = 23$ ppm) than in the dithiane series (e.g., 1,3-dithiane 1-oxide → 1,3-dithiane 1,1-dioxide, $\Delta\delta_c = 1.7$ ppm; 1,3-dithiane 1,3-dioxide → 1,3-dithiane 1,1,3,3-tetraoxide, $\Delta\delta_c = 7.3$ ppm). We have termed this latter feature the "four-membered-ring sulfone effect" and discuss it more fully elsewhere.[25]

D. pK_a Values and Carbanion Formation. In connection with our planned study of the chemistry of carbanions derived from

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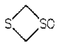
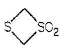
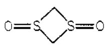
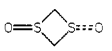
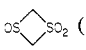
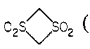
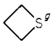
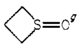
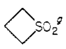
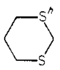
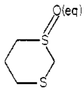
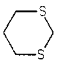
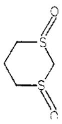
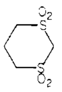
[22] Solouki, B.; Bock, H.; Appel, R. *Chem. Ber.* **1975**, *108*, 897–913.

[23] (a) Oberhammer, H.; Zeil, W. *J. Mol. Struct.* **1970**, *6*, 399–404. (b) Sands, D. E.; Day, V. W. *Z. Kristallogr.* **1967**, *124*, 220–227. (c) Natano, Y.; Saito, S.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 368–371.

[24] Cistaro, C.; Fronza, G.; Mondelli, R.; Bradamante, S.; Pagani, G. A. *J. Magn. Reson.* **1974**, *15*, 367–381.

[25] Block, E., Bazzi, A. A.; Lambert, J. B.; Wharry, S. M.; Andersen, K. K.; Dittmer, D. C.; Patwardhan, B. H.; Smith, D. J. H. *J. Org. Chem.* **1980**, *45*, 4807–4810.

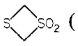
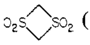
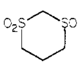
Table III. ^1H and ^{13}C NMR Chemical Shifts and Coupling Constants for 1,3-Dithietanes **1–7** and Related Compounds

compd	chemical shifts, δ ^1H	chemical shifts, δ ^{13}C	coupling constants gem H_1H_2	coupling constants trans H_1H_3	coupling constants cis H_1H_4	coupling constants cis H_2H_3
 (**1**)	4.05^a	18.6				
 (**2**)	4.23^b 3.37, 3.73^c	53.1	−7.53^e	0.73^f	5.56^f	0.005^f
 (**3**)	5.27^{b,d}	68.4				
 (**4**, cis)	4.78, 5.72^d	69.1	−13.40^e	1^f	3.76^f	1^f
 (**5**, trans)	4.97^d	69.0				
 (**6**)	5.47, 5.88^d	87.4	−14.1^e	1^f	6.6^f	2.2^f
 (**7**)	6.40^b	92.1				
 [g]	3.21	26.1^i	−8.71	−0.2	0.90 (av)	
 [g]	3.09, 3.46	52.7^i	−10.29	−0.95	6.10	−0.57
 [g]	4.09	65.6^i	−14.0	−1.24	2.24 (av)	
 [h]		32.0^j				
 [h]	3.78 (av)^j	50.3^j	12.6			
	4.1^j	52^j	14.4			
 *cis*	4.2^j	63.0^j	12.5			
		70.3^j				

[a] In $CDCl_3$. [b] In $(CD_3)_2SO$. [c] In C_6D_6. [d] In CF_3COOH. [e] Negative sign assumed. [f] Sign unknown. [g] ^1H NMR data from ref 24 for protons on carbons 2 and 4; solvent is $(CD_3)_2CO$. [h] Carey, F. A.; Dailey, O. D., Jr.; Hutton, W. C. *J. Org. Chem.* 1978, *43*, 96–101. [i] α-Carbon. [j] Carbon 2.

1,3-dithietanes **1–7** it was of interest to determine the equilibrium acidities of these compounds. Acidity data[26] on 1,3-dithietanes **3**, **6**, and **7** and two model compounds are given in Table IV. While **7** is considerably more acidic than 1,3-dithiane 1,1,3,3-tetraoxide or bis(methylsulfonyl)methane, it should be noted that cyclobutanone is also more acidic (by 2 pK_a units)[26] than 3-pentanone, observations which may indicate the enhancement of acidity by ring-strain effects.

Table IV. pK_a Values of Some 1,3-Dithietane *S*-Oxides and Related Compounds in Me_2SO^a

compd	pK_a^{b}
 (**3**)	20.7 ± 0.3
 (**6**)	13.8 ± 0.1
 (**7**)	12.5 ± 0.08
$(MeSO_2)_2CH_2$	15.0 ± 0.02
	15.5^c

[a] See ref 26. [b] Average of runs with several different indicators. [c] Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* 1980, *45*, 3305–3313.

It has been reported that **7** undergoes ready H/D exchange with $NaOD/D_2O$.[15b] We find that 1,3-dithietane 1-oxide (**2**) undergoes partial H/D exchange (ca. 30% D incorporation) when heated with 0.3 N $NaOD/D_2O$ at 60 °C. After 1 h at 60 °C, recovered **2** (94% recovery) showed by mass spectral analysis 72% **2**-d_0, 25% **2**-d_1, 2.4% **2**-d_2, and ca. 0.2% each of **2**-d_3 and **2**-d_4. Analysis of the relative intensities of the microwave lines associated with various deuterated species indicated the composition 70% **2**-d_0, 26% **2**-d_{1a}, 4% **2**-d_{1e} (30% **2**-d_1 total), and negligible polydeuterio-**2**. After 4 h at 60 °C, mass spectral analysis of recovered, recrystallized **2** indicated 23% **2**-d_0, 44% **2**-d_1, 27% **2**-d_2, 5% **2**-d_3, and <1% **2**-d_4. Microwave analysis of this same sample indicated the composition 23.6% **2**-d_0, 46.7% **2**-d_{1a}, 7.7% **2**-d_{1e} (54.5% **2**-d_1 total), 7.7% **2**-d_{2aa}, 5.8% **2**-d_{2ae}, 6.5% **2**-$d_{2ae'}$ (20.0% **2**-d_2 total; **2**-$d_{2ee'}$ not measured but assumed to be small), and 2.0% **2**-$d_{3aa'e}$ (2.0% **2**-d_3; **2**-$d_{3aee'}$ not measured); **2**-d_4 could not be detected (see **2a** for labeling).[27] From the above data for the "4-h sample" it may be calculated that the ratio of protons in the "equatorial" position to protons in the "axial" position should be ca. 1.46:1. In fact, careful integration of the NMR spectrum of the recovered, recrystallized **2** in benzene-d_6 showed the ratio of the high-field

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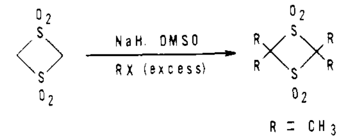
(26) Data kindly provided by F. G. Bordwell and W. A. Kirsch.

(27) For another example of the use of microwave techniques in the analysis of polydeuterated stereoisomers, see: Backvall, J.-E.; Karlsson, O.; Ljunggren, S. O. *Tetrahedron Lett.* **1980**, *21*, 4985–4988.

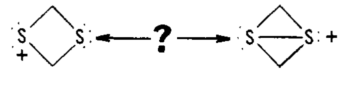
multiplet to the low-field multiplet to be 1.5 to 1. The assignment of the high-field multiplet to the "equatorial" protons (trans to the S–O bond) in **2** agrees with the aromatic solvent induced shift effect seen with sulfinyl compounds.[28] Our analysis of the pattern of deuterium incorporation in **2** indicates an approximately 6:1 preference of "axial" monodeuteration over "equatorial" monodeuteration (at odds with the predictions of the gauche effect theory which would predict greater reactivity for the quasi-equatorial protons gauche to both the S–O bonding pair and the lone pair[28,29]). Treatment of **2** with KO-*t*-Bu/DO-*t*-Bu at 25 °C for 1 h led to formation of **2**-d_3 and **2**-d_4 (28 and 66%, respectively), required for the microwave study of **2**.

While attempts to alkylate **2**, **3**, or **6** on carbon have not yet succeeded, it proved possible to effect a "fourfold alkylation" of 1,3-dithietane 1,1,3,3-tetraoxide (**7**) on treatment of **7** in dimethyl sulfoxide with sodium hydride and methyl iodide (eq 4).[51]



(4)

E. One-Electron Oxidation and Polymerization of 1,3-Dithietane. The oxidation potential of 1,3-dithietane, (**1**) (1.13 V) is very similar to that of 1,3-dithiane (1.14 V) and thiolane (1.13 V), indicating the absence of any unusual transannular interactions in the cation radical **13** as is seen with 1,5-dithiacyclooctane (oxidation potential of 0.343 V).[30a] On exposure to X-radiation



13

or on prolonged standing at room temperature, **1** polymerizes to a material identified by its X-ray powder pattern as the hexagonal form of polythioformaldehyde.[30b]

IV. Thermal Decomposition

A. Method I: Mass Spectroscopy. Mass spectrometers have been widely used for the direct detection of reactive molecules produced by flash vacuum pyrolysis (FVP).[31] The device employed by us is quite simple, consisting of a solid probe for an AEI MS-12 mass spectrometer hollowed to accept a length of electrically heated heavy-wall 2-mm quartz capillary fitted with a chromel–alumel thermocouple and a standard taper joint for the sample vessel. The sample, heated or cooled as necessary to provide a suitable pressure and signal intensity, is evaporated at low pressures through the capillary, and mass spectra are recorded at low ionizing voltage (to minimize electron-impact-induced peaks and emphasize parent molecular ions) as a function of temperature. Generally, the growth in intensity of the molecular ions of the pyrolysis products is coupled with the disappearances of the original parent ion and its fragment peaks, as illustrated by the data for the pyrolysis of 1,3-dithietane 1-oxide shown in Figure 6.

The FVP–mass spectroscopic (FVP–MS) technique is very useful in defining the temperature profile for pyrolysis and suggesting the molecular formulas for major pyrolysis products. As sufficient data can often be collected in 30 min per run, the technique permits the screening of a variety of potential pyrolytic sources of a particular transient and facilitates comparative pyrolysis studies on a series of related compounds. These techniques have been utilized in our previously reported pyrolytic approaches to silacyclobutenes,[32] methanesulfenic acid,[33] allene episulfide,[34] and alkanethial *S*-oxides/alkenesulfenic acids.[35]

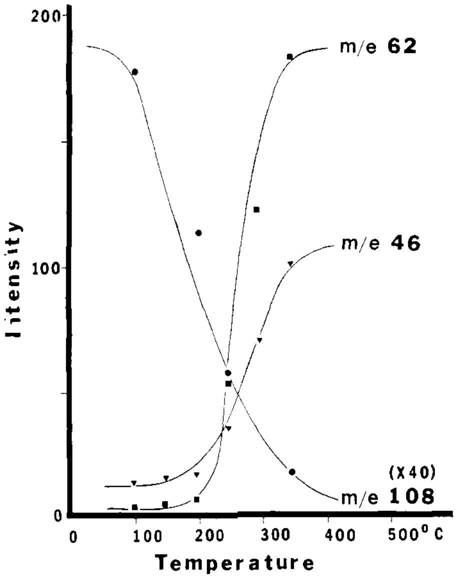


Figure 6. Relative intensities of selected ions in a FVP–mass spectral study of 1,3-dithietane 1-oxide (**2**).

Difficulties with the FVP–MS technique are the following: (1) occasionally a pyrolytic process will be so facile that it will occur in the source of the mass spectrometer (e.g., with *tert*-butyl sulfoxides and thiosulfinates) necessitating cooling of the source; (2) only the elemental composition (and not the structure) of the pyrolysis products is indicated, although ionization and appearance potentials can sometimes provide structural information; (3) very limited data can be obtained by this technique on the quantitative composition of the pyrolysate; (4) some pyrolysis products give very low intensity ions, making detection in the presence of other products virtually impossible.

B. Method II: Microwave Spectroscopy. The combination of FVP and microwave spectroscopy for the direct examination of pyrolysis products at low pressures is also an extensively employed technique for the study of short-lived molecules and molecular fragments.[36] Microwave spectroscopy can be used in this manner to provide detailed structural information on the transient such as bond distances, bond angles, molecular dipole moments, rotational barriers, conformation preferences, location of isotopic labels, gas-phase lifetime, and identification of decomposition products from the transient.

Experimentally, the FVP–microwave procedure in its initial stages is somewhat similar to the FVP–MS technique. The sample, heated or cooled as necessary to provide ca. 25 μ pressure, is vaporized into the wave guide, and the microwave spectrum of the starting material is recorded. The sample is then passed through a hot zone and note is taken of the changing spectra near the optimum decomposition temperature (generally previously

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(28) Barbarella, G.; Garbesi, A.; Fava, A. *J. Am. Chem. Soc.* **1975**, *97*, 5883–5889.

(29) Rauk, A.; Wolfe, S.; Czismadia, I. G. *Can. J. Chem.* **1969**, *47*, 113–135.

(30) (a) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryand, M. D.; Musker, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 1040–1042. (b) R. Baughman, unpublished results.

(31) (a) Schissel, P.; McAdoo, D. J.; Hedaya, E.; McNeil, D. W. *J. Chem. Phys.* **1968**, *49*, 5061–5066. (b) Hedaya, E.; Krull, I. S.; Miller, R. D.; Kent, M. E.; D'Angelo, P. F.; Schissel, P. *J. Am. Chem. Soc.* **1969**, *91*, 6880–6881. (c) Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *Ibid.* **1976**, *98*, 7421–7422. (d) Volkova, V. V.; Gusel'nikov, L. E.; Perchenko, V. N.; Zaikin, V. G.; Eremina, E. I.; Nametkin, N. S.; *Tetrahedron Lett.* **1978**, 577–580, and references therein.

(32) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630–1632.

(33) Penn, R. E.; Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 3622–3623.

(34) Block, E., Penn, R. E.; Ennis, M. D.; Owens, T. A.; Yu, S.-L. *J. Am. Chem. Soc.* **1978**, *100*, 7436–7437.

(35) Block, E.; Penn, R. E.; Revelle, L. K. *J. Am. Chem. Soc.* **1979**, *101*, 2200–2201.

(36) (a) Johnson, D. R.; Powell, F. X.; Kirchhoff, W. U. *J. Mol. Spectrosc.* **1971**, *39*, 136–145. (b) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *Chem. Phys. Lett.* **1976**, *42*, 460–461. (c) Hopkins, M. M.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Chem. Soc., Chem. Commun.* **1976**, 513–515. (d) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399–402. (e) Tanimoto, M.; Saito, S. *Chem. Lett.* **1977**, 637–640. (f) Ford, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2389–2390. (g) Blackman, G. L.; Brown, R. D.; Brown, R. F. C.; Eastwood, R. W.; McMullen, G. L. *J. Mol. Spectrosc.* **1977**, *68*, 488–491, and references therein.

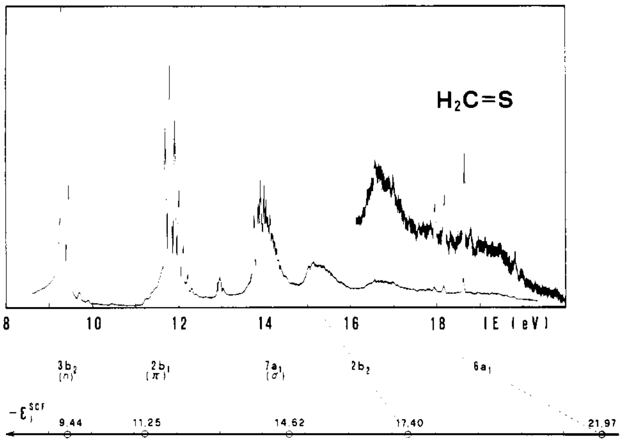


Figure 7. PE spectrum of thioformaldehyde from the thermal decomposition of 1,3-dithietane (1) and assignment.

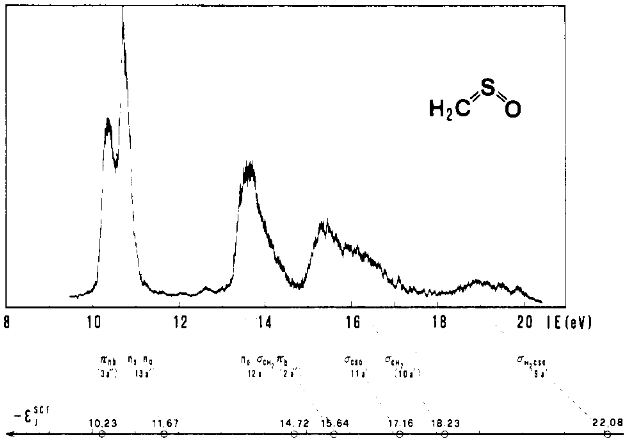


Figure 8. PE spectrum of sulfine from the thermal decomposition of 1,3-dithietane 1,3-dioxide (4, 5) and assignment.

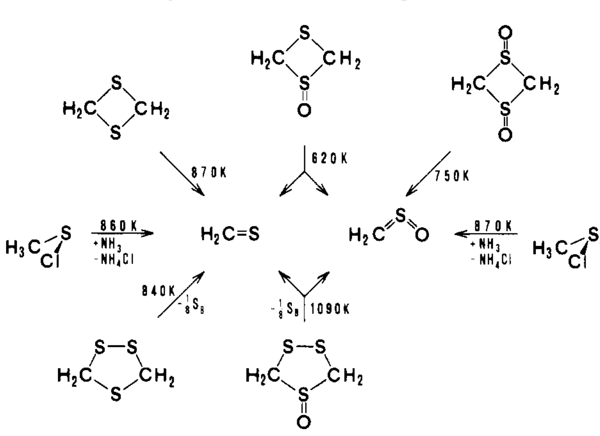
determined by FVP–MS). At this temperature a search is made for the presence of a short-lived molecule by isolating the wave guide from the flow of pyrolysate ("static mode" of operation) and observing which of the lines decrease in intensity with time and the approximate half-life of disappearance. Further optimization of the pyrolysis temperature can then be achieved by maximizing the signals associated with the transient product (lines having the same half-life). The "substitution structure" of the transient pyrolysis product can be determined by continuous pyrolysis of the normal and isotopically labeled starting material or by isotopic exchange with the pyrolysate[33] followed by spectral analysis. The characterization of volatile decomposition products of the transient can be made by assignment of the spectral lines which, in the "static mode" of operation described above, increase with time at approximately the same rate as the spectral lines of the transient decrease in intensity.

As in the case of FVP–MS method, the FVP–microwave technique is of limited value in providing quantitative data on the composition of the pyrolysate. Furthermore, molecules lacking, or having very small dipole moments, cannot be detected by microwave spectroscopy.

C. Method III: Photoelectron Spectroscopy. Photoelectron spectroscopy is well suited to analyze and to optimize gas-phase reactions in flow systems. The characteristic ionization patterns of small to medium-sized molecules are "fingerprints", and their appearance or disappearance allows one to optimize reaction conditions and to identify reaction products[37] of low-temperature decompositions. Ring ovens of 30- and 60-cm length were used for the pyrolysis of the resublimed substances. The quartz reaction tubes had a diameter of 1.5 cm and were loosely filled with quartz wool. About 100–200-mg samples were needed for the pyrolysis. This amount is enough to conduct a study of the reaction conditions up to 1300 K in 50° intervals. Examples of the FVP–PE method are given below.

D. Results. In the following section the pyrolysis of 1,3-dithietane derivatives **1–5** and **7** will be discussed, emphasizing the use of PE spectroscopic methods (see Table II for data on the starting materials). In several of these cases analogous results were obtained by FVP–microwave techniques. In one instance (pyrolysis of 1,3-dithietane 1-oxide (**2**)) the pyrolysate was trapped in an argon matrix at 18 K and the products were characterized by infrared spectroscopy as detailed elsewhere.[2]

1. 1,3-Dithietane (1). The thermal decomposition of 1,3-dithietane begins at 720 K and is complete at 870 K, yielding thioformaldehyde as the only PE spectroscopically detectable reaction product (Figure 7). The thioformaldehyde molecule has been detected in interstellar space[38a] and is also formed by HCl elimination from methylsulfenyl chloride[38b] or by pyrolysis of 1,2,4-trithiolane,[39] 1,2,4-trithiolane 1-oxide, or 1,3-dithietane 1-oxide,[9,39] among other sources[36a] (see eq 5). Thioformaldehyde can be identified by its ionization pattern, which has been independently calculated by the PNO–CEPA (pseudo-natural orbital coupled electron pair) approach.

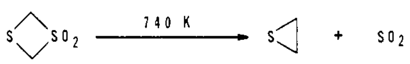


(5)

2. 1,3-Dithietane 1-Oxide (2). Thermolysis at 620 K yields a 1:1 mixture of thioformaldehyde and sulfine (eq 5). The PE spectrum of pure sulfine can be obtained in the pyrolysis of methanesulfinyl chloride after depositing the HCl eliminated after NH_3 injection as NH_4Cl[39] or by heating 1,3-dithietane 1,3-dioxide (Figure 8). Sulfine has been detected in the thermal decomposition of 1,2,4-trithiolane 1-oxide[9b,39] as well as in that of 1,3-dithietane 1-oxide[9b,39] (eq 5). It PE spectrum can be fully assigned based on ab initio SCF calculation[9b] and by radical-cation-states comparison with SO_2 and SSO.[9b]

3. *cis*- and *trans*-1,3-Dithietane 1,3-dioxide (4,5). Thermolysis at 750 K yields pure sulfine (Figure 8). As illustrated above (eq 5), sulfine is also formed in other pyrolysis reactions and its PE spectrum can be unequivocally assigned via Koopman's correlation $IE_n = -\epsilon_J^{SCF}$ with ab initio eigenvalues.

4. 1,3-Dithietane 1,1-Dioxide (3). The PE spectrum of **3** starts to change at 570 K and the decomposition at 10^{-2} torr is complete at 740 K as gathered from the disappearance of the characteristic bands (Figure 9). After graphical substraction of SO_2 bands, the PE spectrum of thiirane remains (Figure 9).[40] The decomposition in the lowest temperature reaction channel therefore proceeds exclusively according to eq 6. Thermolysis reactions



(6)

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[37] Bock, H.; Solouki, B.; Bert, G.; Hirabayashi, T.; Mohamand, S.; Rosmus, P. *Nachr. Chem. Tech.* **1978**, *26*, 634–639.

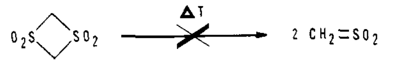
[38] (a) Sinclair, M. W.; Fouikis, N.; Ribes, J. C.; Robinson, B. J.; Brown, R. D.; Godfrey, P. D. *Aust. J. Phys.* **1973**, *26*, 85–91. (b) Solouki, B.; Rosmus, P.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 6054–6055.

[39] Bock, H.; Solouki, B.; Mohmand, S.; Block, E.; Revelle, L. K. *J. Chem. Soc., Chem. Commun.* **1977**, 288–290.

[40] Frost, D. C.; Herring, F. G.; Katrib, A.; McDowell, C. A. *Chem. Phys. Lett.* **1973**, *20*, 401–403.

involving SO_2 elimination have been widely investigated and are of considerable synthetic utility.[41]

5. 1,3-Dithietane 1,1,3,3-Tetraoxide (7). Noticeable thermal decomposition begins at 700 K and is complete at 870 K. Ethylene is identified in the product spectrum by the vibrational fine structure of its π band. In addition, characteristic bands due to SO_2 and formaldehyde are also observed. There is no evidence under the pyrolysis conditions chosen for a decomposition reaction similar to that observed for 1,3-dithietane or its 1,3-dioxide, i.e., yielding the monomer $CH_2{=}SO_2$ (sulfene; eq 7).

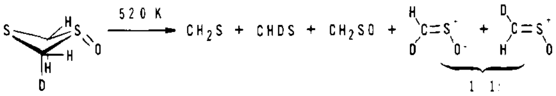


(7)

V. Summary and Concluding Remarks

Exposure of a molecule to high temperature results in excitation of the various vibrational degrees of freedom followed by rupture of one or more bonds as a particular reaction channel is taken.[42] Of interest in the present study is the basis for the selection between retro 2 + 2 and retro 3 + 1 decomposition channels, processes which have ample precedence in the thermal decomposition of various four-membered rings, e.g., as shown in Scheme I. Examples a[43] and b,[44] Scheme I, illustrate two mechanistic features of the retro 2 + 2 process (also illustrated by eq c, Scheme I[31d,45]) related to the two bond cleavages, namely, the regioselectivity and the timing (essentially simultaneous for a concerted $\sigma_a^2 + \sigma_s^2$ process, eq a, or stepwise for a process involving a 1,4-diradical, eq b).

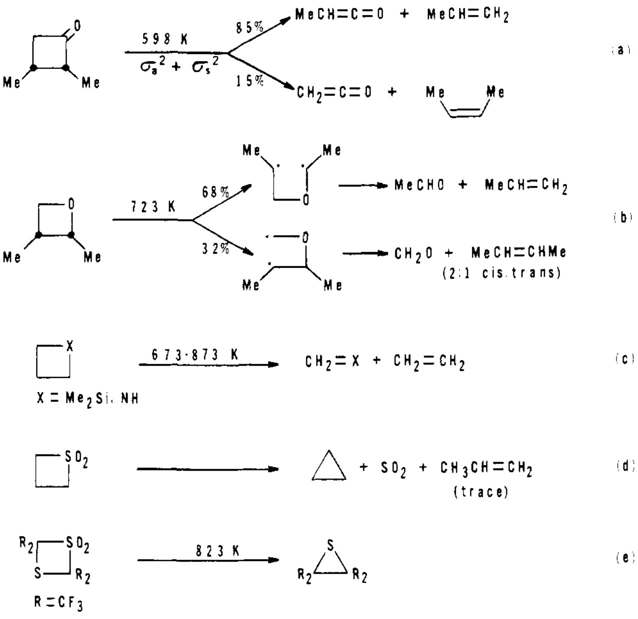
Scheme II depicts the range of decomposition channels possible for 1,3-diheterocyclobutanes such as **1**–**7**, to wit, stepwise bond cleavage (a, b) followed by generation of the π systems (f, g) or by expulsion of X or Y leading ultimately to heterocyclopropanes (h/j or i/k) or their decomposition products. Alternatively concerted $\sigma_a^2 + \sigma_s^2$ cleavage (c, c′) can occur, or as another possibility, concerted explusion of X or Y giving the delocalized species CH_2YCH_2 or CH_2XCH_2, respectively (e/e′ or d/d′). Not included in Scheme II are "wall" reactions (heterogeneous surface-catalyzed processes), which should be important under reaction conditions such as ours but whose consequences would be difficult to predict. The well-known concerted generation and electrocyclic ring closure of thiocarbonyl ylides (eq 8) provides precedence for sequences d/d′ or e/e′ if X or Y is S.[6b] Additional precedence for retro 3 + 1 decomposition processes in four-membered rings is provided by eq d[46] and e,[6c,11e] Scheme I.



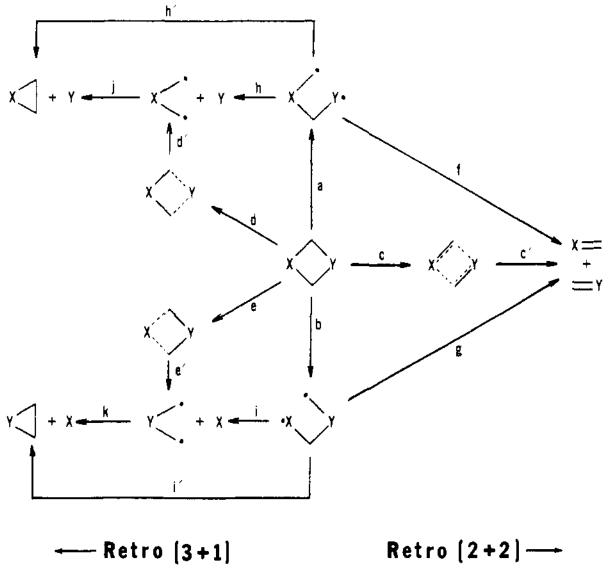
(8)

The direction favored in stepwise decomposition of 1,3-dithietanes **1**–**7** (e.g., a or b) should be influenced by the stabilization felt by the respective developing radical centers while the subsequent selection between retro 2 + 2 and 3 + 1 routes should be influenced by the stability of π systems CH_2X and CH_2Y (paths f and g) relative to the stability of X/CH_2YCH_2 and Y/CH_2XCH_2 (paths i and h, respectively). Relevant to these considerations are the facts that the order of spin delocalization in sulfur-substituted free radicals is $RSCH_2\cdot > RS(O)CH_2\cdot > RSO_2CH_2\cdot$ and that the order of leaving group abilities, e.g., for species Y in path h, should be $SO_2 > SO > S$.[41b]

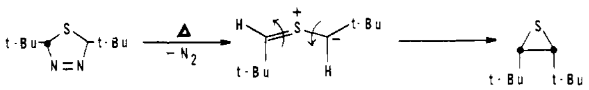
Scheme I



Scheme II



In a single experiment designed to examine the question of concerted vs. stepwise decomposition of compounds **1**–**7**, we have employed FVP–microwave techniques in a study of the decomposition of stereospecifically deuterated **2**-d_1 prepared as described earlier. Unfortunately, the experimental results, shown in eq 9,



(9)

can be rationalized by postulating either generation of a 1,4-diradical or concerted decomposition followed by isomerization of monodeuteriosulfine. Further work is clearly needed to identify the preferred decomposition pathways for diheterocyclobutanes such as **1**–**7**.

In conclusion, we note that 1,3-dithietane and its *S*-oxides are readily available, interesting new compounds whose chemistry warrents further exploration. We also note that the FVP spectroscopic methodology employed in this work represents a useful technique for mechanistic studies which may be profitably applied to diverse systems.

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[41] (a) Vögtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 515–529. (b) Also see ref 6b, Chapter 5.

[42] For a detailed treatment of pyrolysis, see: Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980.

[43] Metcalfe, J.; Carless, H. A. J.; Lee, E. K. C. *J. Am. Chem. Soc.* **1972**, *94*, 7235–7241.

[44] Braslavsky, S.; Heicklen, J. *Chem. Rev.* **1977**, *77*, 473–511.

[45] Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18–25.

[46] (a) Cornell, D.; Tsang, W. *Int. J. Chem. Kinet.* **1975**, *7*, 799–806. (b) Padwa, A.; Gruber, R. *J. Org. Chem.* **1970**, *35*, 1781–1788. (c) Trost, B. M.; Schinski, W. L.; Chen., F; Mantz, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 676–684.

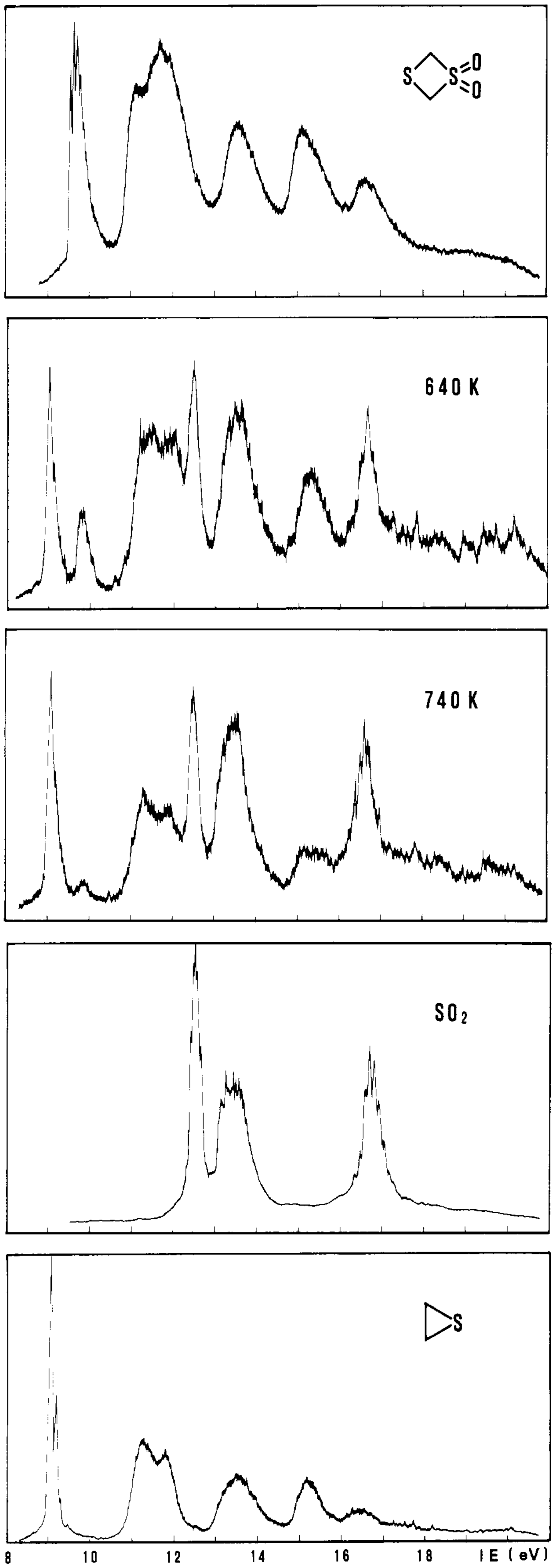

Figure 9. PE spectroscopic analysis of the gas-phase decomposition of 1,3-dithietane 1,1-dioxide (3).

VI. Experimental Section

The melting points are corrected. The IR spectra were determined on either a Perkin-Elmer 137 or 337 spectrophotometer while UV spectra were determined in 95% ethanol on a Perkin-Elmer 202 or 450 UV spectrophotometer. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. The helium I PE spectra were recorded using a Perkin-Elmer PS 16 spectrometer with 127° electrostatic deflection analyzer and calibrated by the Xe and Ar $^2P_{3/2}$ ionizations. A resoluton of 25–30 meV was routinely achieved. For the evaporation of low-vapor-pressure samples a heated inlet system was employed.

Microwave spectra were observed with a conventional 25-kHz Stark-molulated microwave spectrometer employing free-running klystrons and a 3-m, brass, X-band waveguide absorption cell. The FVP–microwave experiments involved evaporation of starting materials at pressures of ca. 25 mtorr through a pyrolysis tube consisting of an 20-cm section of 0.8-mm i.d. quartz capillary, wrapped with heating coils and fitted with a chromel–alumel thermocouple.

NMR spectra were obtained on either a Varian T-60 or JEOL FT 100-MHz NMR spectrometer using tetramethylsilane as an internal standard. Some NMR data and computer simulation studies were also performed on a Nicolet FT 150-MHz NMR spectrometer and a Bruker FT 200-MHz NMR spectrometer. Low-resolution mass spectroscopy and FVP–mass spectroscopic studies were performed on an AEI MS-1201 B mass spectrometer while high-resolution mass spectra were obtained on an AEI MS-9 mass spectrometer at Indiana University. Vapor-phase chromatography (VPC) was accomplished on a Hewlett-Packard Model 5750 gas chromatograph (flame ionization detector).

1,3-Dithietane 1-Oxide (2). A mixture of 100 g of bis(chloromethyl) sulfoxide[47] (0.68 mol), 100 g of tricaprylylmethylammonium chloride (ca. 0.2 mol; General Mills "Aliquat 336"), and 665 mL of water in a 3-L three-necked flask equipped with a mechanical stirrer and thermometer was heated rapidly to 65 °C with vigorous stirring to homogenize the mixture. To the cooled emulsion was added all at once with vigorous stirring 212 g (0.88 mol) of freshly and finely pulverized $Na_2S\cdot 9H_2O$. The temperature of the greenish-yellow solution fell to 11 °C and then began to rise rapidly, peaking out at 45 °C. The mixture at this point was red-orange and heterogeneous. Vigorous stirring was continued for 45 min; the solution was cooled to 10 °C, neutralized with concentrated HCl, and filtered through a coarse sintered-glass filter. The aqueous phase passed through the filter rapidly, leaving behind the red-brown organic phase. The filtrate was rinsed with a small quantity of ether to remove traces of red liquid that passed through the filter.

The aqueous filtrate was saturated with NH_4Br, extracted with $CHCl_3$ (5 × 700 mL; mixing was accomplished with a mechanical stirrer to ensure vigorous agitation), and the $CHCl_3$ layer was dried ($MgSO_4$) and concentrated in vacuo. The material in the funnel was repeatedly washed with $CHCl_3$ until the washings were colorless, the washings were concentrated in vacuo, and the deep red tricaprylylammonium salt was mixed with 350 mL of water and stirred vigorously at 65 °C for 1 h. The aqueous layer was separated, saturated with NH_4Br, and extracted with $CHCl_3$ (3 × 350 mL); the $CHCl_3$ layer was dried and concentrated in vacuo. The total concentrate from the extractions of the aqueous layers (31 g) was recrystallized from 150 mL of CCl_4 affording 25 g of **2** (34% yield) as colorless crystals, mp 71–73.5 °C, showing a single peak on VPC analysis (retention time 3.3 min at 100 °C on a 6 ft × $^1/_8$ in. UCW-98 column): IR (KBr) 1150, 1080, 1035 cm^{-1} (all s); UV (C_2H_5OH) λ_{max} 207 (ϵ 674), 222 (578), 266 nm (101); NMR (CD_3Cl) δ 4.15 (m), (C_2D_6SO) δ 4.23 (m), (C_6D_6) AA′BB′ system, δ_A 3.37, δ_B 3.73; mass spectrum *m/e* 107.9708 (65%; parent; calcd for $C_2H_4S_2O$, 107.9704), 63 (17%), 62 (30%), 60 (72%), 59 (19%), 46 (100%), and 45 (69%).

Anal. Calcd for $C_2H_4S_2O$: C, 22.21; H, 3.73. Found: C, 22.04; H, 3.79.

The $CHCl_3$-insoluble material left in the funnel was combined with additional material which precipitated from the chloroform washings on standing overnight. This material was washed with acetone and then ether giving 23 g (32% yield) of colorless polymer, mp (with decomposition) ca. 90 °C.

Anal. Calcd for $[C_2H_4S_2O]_n$: C, 22.21; H, 3.73. Found: C, 21.54; H, 3.56.

1,3-Dithietane-*1*-^{18}*O* (*2*-^{18}*O*). To a solution of 0.092 g (1 mmol) of 1,3-dithietane (**1**) in 3 mL of anhydrous acetonitrile were added 0.202 g (2 mmol) of triethylamine, 0.2 mL of $H_2{}^{18}O$ (28% ^{18}O), and then, over a period of 20 min, a solution of 0.275 g (1 mmol) of iodobenzene dichloride in 3 mL of anhydrous acetonitrile. Stirring was continued at 25 °C for an additional 30 min. Although VPC anlaysis indicated that only about 15% reaction had occurred, the reaction mixture was worked up by removing acetonitrile in vacuo, extraction of the residue with pentane to remove unreacted **1** and other materials, and recrystallization of the residue from CCl_4 after first drying the solution with $MgSO_4$.

There was obtained 0.014 g of 1,3-dithietane 1-oxide which on analysis by mass spectroscopy at 9.5 eV showed 28% ^{18}O.

Deuterium Exchange Studies with 1,3-Dithietane 1-Oxide (2). To 50 mL of D_2O, 0.3 M in NaOD, was added 0.545 g (5.1 mmol) of **2**. The homogeneous solution was stirred at 60 °C for 4 h. The solution, which had turned yellow, was cooled to 0 °C, neutralized with concentrated hydrochloric acid, and extracted with two 10-mL portions of ether. The yellow ether extract was discarded. The aqueous phase was saturated with NH_4Br and extracted with 75 mL of $CHCl_3$; the $CHCl_3$ layer was separated, dried ($MgSO_4$), and concentrated in vacuo giving 0.203 g of a slightly yellow solid. Recrystallization of this solid from 1 mL of hot CCl_4 gave 0.110 g of colorless, partially deuterated **2**: NMR (C_6D_6) δ 3.18 (m, area 1.5) and 3.55 (m, area 1); mass spectrum (low eV) *m/e* 108 ($C_2H_4S_2O^+$, 23%), 109 ($C_2H_3DS_2^+$, 44%), 110 ($C_2H_2D_2S_2O^+$, 27%), 111 ($C_2HD_3S_2O^+$, 5%), 112 ($C_2D_4S_2O^+$, 0.8%) (percentages have been corrected for other isotopic species as ^{34}S and ^{13}C).

1,3-Dithietane (1). To 10.8 g of 1,3-dithietane 1-oxide (**2**, 0.10 mol) was added all at once 300 mL of 1 M THF-borane (Aldrich; 0.3 mol), and the homogeneous solution was kept at 25 °C in an argon atmosphere for 26 h. The reaction mixture was added cautiously to 1.5 L of water and ice in a large separatory funnel. Considerable gas evolution was associated with the decomposition of unreacted borane. To the resulting suspension of a white solid in water was then added 600 mL of pentane and the mixture was shaken and then filtered to remove undissolved solid. The pentane layer in the filtrate was separated from the aqueous layer, and the latter was extracted with an additional 100 mL of pentane. The white solid was gently boiled with the combined pentane layers until all of the solid had dissolved; the solution was shaken with water (3 × 1000 mL) to remove THF, dried ($MgSO_4$), and concentrated by boiling until a solid began to crystallize out. On cooling 4.05 g (44%) of 1,3-dithietane was collected as large, colorless crystals with a powerful, obnoxious odor, mp 105–106 °C, showing a single peak on VPC analysis (retention time 1.3 min at 100 °C on a 6 ft × $^1/_8$ in. UCW-98 column; under these same conditions **2** has a retention time of 3.3 min while **3** has a retention time of 3.8 min): IR (KBr) 1195 (m), 880 (m), 735 (w), 705 (m), 684 (m) cm^{-1}; UV (C_2H_5OH) λ_{max} 216 (ϵ 860), 293 (38), 311 nm (sh, 20); mass spectrum 91.9760 (99%, parent; calcd for $C_2H_4S_2$, 91.9755), 76 (7%), 64 (11%), 46 (base peak), 45 (47%); NMR ($CDCl_3$) δ 4.05 (s).

Anal. Calcd for $C_2H_4S_2$: C, 26.06; H, 4.37. Found: C, 25.90; H, 4.36.

1,3-Dithietane 1,1-Dioxide (3). To a solution of 1.01 g (9.37 mmol) of 1,3-dithietane 1-oxide in 100 mL of acetone containing 7 g of suspended $MgSO_4$ was added with vigorous stirring at −20 to −25 °C during the course of 3 h a solution of 0.99 g of $KMnO_4$ (6.32 mmol) in 112 mL of acetone. The brown slurry was stirred for an additional 2 h at −15 to −25 °C and then warmed to room temperature, filtered through a pad of Celite, and concentrated in vacuo giving 1.14 g (98% yield) of colorless needles which on recrystallization from absolute ethanol had mp 140–142 °C and showed a single peak on VPC analysis (retention time 3.8 min at 100 °C on a 6 ft × $^1/_8$ in. UCW-98 column; under these same conditions **2** has a retention time of 3.3 min while **1** has a retention time of 1.3 min); IR (KBr) 1393 (m), 1315 (s), 1200 (s), 1130 (s), 555 (s), 440 (s) cm^{-1}; NMR (CF_3COOH or Me_2SO-d_6) δ 5.27 (s); UV (C_2H_5OH) λ_{max} 217 (ϵ 200), 245 nm (sh, 30); mass spectrum 123.9659 (47%; parent; calcd for $C_2H_4S_2O_2$, 123.9653), 76 (6%), 64 (14%), 60 (59%), 59 (21%), 48 (18%), 46 (31%), 45 (100%).

Anal. Calcd for $C_2H_4S_2O_2$: C, 19.34; H, 3.25. Found: C, 19.53; H, 3.30.

***cis*- and *trans*-1,3-Dithietane 1,3-Dioxide (4 and 5).** To a solution of 1.08 g (10 mmol) of 1,3-dithietane 1-oxide in 40 mL of $CHCl_3$ at 0 °C was added with stirring during 1.5 h 2 g (10.5 mmol) of 40% peracetic acid. A white precipitate separated during the reaction. The mixture was warmed to room temperature and filtered; the solid was washed in the funnel with ether giving 1.15 g (93% yield) of colorless solid which showed by NMR analysis (see below) 42% **4** and 58% **5**. Recrystallization of this solid from 115 mL of dimethylformamide deposited at room temperature 0.475 g (38% yield) of *cis*-1,3-dithietane 1,3-dioxide (**4**), mp 260 °C dec: IR (KBr) 1132 (s), 1100 (s), 1062 (s), 998 (s), 760 (m), 700 (m), 643 cm^{-1} (m); NMR (CF_3COOH) AA′BB′ system δ_A 4.78, δ_B 5.72; mass spectral molecular weight 123.9662 (calcd for $C_2H_4S_2O_2$, 123.9653).

Anal. Calcd for $C_2H_4S_2O_2$: C, 19.34; H, 3.24. Found: C, 19.16; H, 3.28.

The mother liquor was concentrated down to 15 mL and chilled, whereupon 0.404 g (32% yield) of *trans*-13-dithietane 1,3-dioxide (**5**) crystallized out. This was recrystallized again from 38 mL of boiling 95% ethanol to give fine needles with mp 203–205 °C dec: IR (KBr) 1159 (m), 1059 (vs), 870 (m), 760 (m), 700 (m), 650 cm^{-1} (m); NMR (CF_3COOH) 4.97 (s); mass spectral molecular weight 123.9662 (calcd for $C_2H_4S_2O_2$, 123.9653).

Anal. Calcd for $C_2H_4S_2O_2$: C, 19.34; H, 3.25. Found: C, 19.16; H, 3.28.

The oxidation of 1,3-dithietane 1-oxide was repeated with a variety of other oxidants, and the solid product was analyzed by NMR (in CF_3COOH). Trifluoroperacetic acid (prepared from trifluoroacetic anhydride and 50% H_2O_2 in CH_2Cl_2) at −78 °C gave **4** and **5** in a ratio of 39 to 61 (overall yield of **4** + **5**, 48%). With *m*-chloroperbenzoic acid a 84% yield of a 40:60 mixture of **4** and **5** was obtained; with iodobenzene dichloride in pyridine at −30 °C a 64% yield of a 71:29 mixture of **4** and **5** was obtained.

1,3-Dithietane 1,1,3-Trioxide (6). To a solution of 0.93 g of 1,3-dithietane 1,1-dioxide (7.5 mmol) in 40 mL of $CHCl_3$ at 0 °C was added slowly 1.24 mL of 40% CH_3CO_3H (7.5 mmol). A fluffy colorless precipitate appeared which was collected by filtration, affording 0.81 g (86% yield) of **6** which, on recrystallization from *N*,*N*-dimethylformamide, had mp 231–234 °C: IR (KBr) 1324, 1300, 1170, 1085 cm^{-1} (all s); NMR (CF_3COOH) AA′BB′ system δ_A 5.47, δ_B 5.88 (C_2D_6SO), AA′BB′ system δ_A 5.17, δ_B 5.72; mass spectrum 139.9609 (49%, parent; calcd for $C_2H_4S_2O_3$, 139.9602), 78 (12%), 76 (38%), 64 (20%), 62 (41%), 59 (13%), 50 (14%), 48 (59%), 46 (100%), 45 (34%).

Anal. Calcd for $C_2H_4S_2O_3$: C, 17.14; H, 2.88. Found: C, 17.59; H, 2.99.

1,3-Dithietane 1,1,3,3-Tetraoxide (7). (a) In four separate test tubes were placed 40-mg samples of 1,3-dithietane 1,1-dioxide (**3**), *cis*-1,3-dithietane 1,3-dioxide (**4**) 1,3-dithietane 1,1,3-trioxide (**6**), and a 20-mg sample of *trans*-1,3-dithietane 1,3-dioxide (**5**) with 2 mL of 40% peracetic acid being added to the first three and 1.2 mL of peracetic acid being added to **5**. The test tubes were heated at 100 °C for 4 h and cooled to 0 °C; the contents were filtered and the white solid from each reaction was washed on the funnel with ether and air-dried. The yields of 1,3-dithietane 1,1,3,3-tetraoxide were 82% from **3**, 77% from **4**, 71% from **5**, and 86% from **6**. In each case the IR spectra of the product was identical with that of authentic **7** prepared as described below by a reaction discovered by Opitz and Mohl.[15b] The NMR of **7** (Me_2SO-d_6) shows a singlet at δ 6.40 (lit.[15b] δ 6.42). (b) To a 12-L three-necked flask containing 5 L of THF was added 154 g (2.6 mol) of trimethylamine. At −20 °C with vigorous stirring was added 115 g (1 mol) of methanesulfonyl chloride. Stirring was continued at −15 °C for 24 h, the flask was stored at 0 °C for 90 h, and the reaction mixture was filtered; the solid filter cake was washed with 5% aqueous hydrochloric acid, water, and acetone and air-dried giving 16.1 g of colorless solid. Additional solid could be obtained through concentrations of the THF filtrate (followed by washing with 5% HCl, acetone, and air-drying) and by refiltering all HCl washes. The total crude solid was recrystallized from boiling dimethylformamide, affording 19.8 g (25% yield) of **7**.[51]

Solid-State Structure of 1,3-Dithietane 1,1,3,3-Tetraoxide (7). Crystals of the tetraoxide, $C_2H_4O_4S_2$, are monoclinic with $a = 5.582$ (2), $b = 5.759$ (2), $c = 8.954$ (4) Å, and $\beta = 116.84$ (4)°; cell parameters were determined by least-squares refinement of 15 reflections with $2\theta \geq 19.6°$. A calculated density of 2.017 g cm^{-3} and an experimental density of 2.01 g cm^{-3} indicate two formula units per cell. Systematic absences of $0k0$ reflections with k odd and $h0l$ reflections with l odd are consistent with space group $P2_1/c$. X-ray intensity data were collected from a 0.22 × 0.24 × 0.28 mm crystal on a Syntex $P2_1$ diffractometer with the θ–2θ scan mode and a scan speed of 2° min^{-1}.[48] Backgrounds were measured at each of the scans (2θ scan range: $2\theta K\alpha_1 - 1.0°$ to $2\theta K\alpha_2 + 1.0°$) for a total time equal to one-half the scan time. Data were collected with Mo Kα (λ 0.71069 Å) radiation (graphite monochromator) to a scattering angle of $2\theta = 75°$ for a total of 1138 intensities greater than $3\sigma(I)$ from 1540 reflections scanned. Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{counter}(I)^2 \times (0.04I)^2]^{1/2}$, where $\sigma_{counter} = (I \times KB)^{1/2}$; I = net intensity, B = total background counts, and K = ratio of scan time to background time. Lorentz and polarization corrections were applied.[49] No absorptions corrections were made ($\mu = 9.2$ cm^{-1}).

The structure of the tetraoxide was solved with program MULTAN. The locations of the four nonhydrogen atoms in the asymmetric unit were obtained from the initial E map. The two hydrogen atoms were located in a Fourier synthesis after refinement of the four heavier atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for C, O, and S and isotropic thermal parameters for H resulted in final discrepancy values of

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(47) (a) Mann, F. G.; Pope, W. J. *J. Chem. Soc.* **1923**, *123*, 1172–1178. (b) Venier, C. G.; Hsieh, H-H.; Barager, H. J., III *J. Org. Chem.* **1973**, *38*, 17–19. (c) Grossert, J. S.; Langler, R. F. *Can. J. Chem.* **1977**, *55*, 407–420. (d) In our work we prepared bis(chloromethyl) sulfoxide by peracetic acid oxidation (69% yield) of bis(chloromethyl) sulfide (Truce, W. E.; Birum, G. H.; McBee, E. T. *J. M. Chem. Soc.* **1952**, *74*, 3594–3599).

(48) An earlier report[7] of this structure used a data set obtained by the ω–2θ scan technique.

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.032$$

$$R = [\sum(w|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.043$$

Atomic scattering factors and anomalous dispersion components for sulfur were taken from the "International Tables for X-ray Crystallography".[50] The largest residual peak in the final electron density difference map was 0.4 eÅ^{-3}.

The labeling of atoms is shown in Figure 1 and the bond lengths and angles are in Table I. The coordinates of atoms with thermal parameters are listed in Table Ia (supplementary material) along with observed and calculated structure factors.

2,2,4,4-Tetramethyl-1,3-dithietane 1,1,3,3-Tetraoxide (14). To 1.908 g of 60% NaH dispersion (48 mmol) rinsed with pentane and placed under argon in a 25-mL three-necked flask equipped with a condenser with a three-way stopcock, thermometer, and septum was added a solution of 1g 1,3-dithietane 1,1,3,3-tetraoxide (7, 6.4 mmol) in 30 mL of anhydrous dimethyl sulfoxide. With cooling, 4.56 g (32 mmol) of methyl iodide was added slowly. An immediate exothermic reaction occurred with gas evolution; ice-water cooling was necessary to maintain a temperature of 35–50 °C. After the reaction had subsided, an additional 4.6 g of methyl iodide (32 mmol) was added and stirring was continued overnight. The mixture was poured onto water and the precipitate collected and dried at 130 °C affording 0.7641 g (56% yield) of the title compound. Fine white crystals decomposing at 270–274 °C were obtained by recrystallization from hot dimethylformamide. These showed IR (KBr) 1460 (s), 1340 (vs), 1165 (vs), 1090 (vs), 920 (s), 703 (s), 664 (s), and 490 (s) cm^{-1}; NMR (CF_3CO_2H) δ 2.0 (s); mass spectral mol wt 212; calcd for $C_6H_{12}S_2O_4$, 212.

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Registry No. 1, 287-53-6; **2**, 58816-63-0; **3**, 60743-07-9; **4**, 60743-08-0; **5**, 60743-09-1; **6**, 60743-10-4; **7**, 21511-46-6.

Supplementary Material Available: Figure of stereoscopic view of the unit cell of **7**, table of final positional and thermal parameters of **7**, and structure factor table (9 pages). Ordering information is given on any current masthead page.

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(49) Local versions of the following programs were used for crystallographic calculations: (1) SYNCOR, W. Schmonsees' program for data reduction; MULTAN, Germain, Main, and Woolfson's program for structure solutions; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP, C. K. Johnson's program for drawing crystal models.

(50) MacGillavry, C. H., Riech, G. D., Lonsdale, K., Eds. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1962; Vol. III.

(51) **Note Added in Proof.** Following submission of this work a report appeared (Rheude, U.; Sundermeyer, W. *Chem. Ber.* **1981**, *114*, 3378–3384) on the twofold and threefold silylation of **7** with trimethylsilyl nonafluorobutanesulfonate, using triethylamine as base. Metalation of the threefold silylated product with *n*-butyllithium followed by silylation led to O-silylation, giving a product which the authors claim is "the first enol ether of a sulfone". In our opinion their O-silylated product would be more appropriately described as a cyclic sulfoxonium ylide.

The Efficiency of Benzil-Sensitized Photoepoxidation: A Correction

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Abstract: Photosensitized epoxidation of norbornene by benzil leads to about two epoxide molecules or less per diketone molecule consumed, not the larger numbers previously reported.[3] It is not necessary to postulate a chain mechanism for this epoxidation, although side reactions still complicate the process in many cases.

In the original report[3] of photoepoxidation of olefins by α-diketones, a survey was made of a number of olefins in reaction chiefly with biacetyl and benzil, comparing the yields and sensitizer efficiencies. Whereas the biacetyl-sensitized epoxidation always required 1 mol of biacetyl to produce up to 2 mol of epoxide, much higher recoveries of benzil were reported, indicating epoxidation efficiencies up to 16 mol of epoxide per mol of benzil consumed.

In the course of following up the implications of these material balances for the reaction mechanism, we have found a serious error in the analytical procedure for the benzil photosensitizations, amounting to nonseparation of benzil from its photolysis products, phenyl benzoate and biphenyl. Careful repetition of the relevant analyses in our two laboratories has shown that with benzil, as with biacetyl, 2 mol of epoxide is an approximate upper limit to the product of photosensitization from 1 mol of diketone. The lowest yields of epoxide were in the reactions with low norbornene

Table I. Epoxide Yields in Benzil-Sensitized Epoxidation of Norbornene, 7–10 °C, in Benzene

vol of benzene, mL	initial mmol of olefin	initial mmol of benzil	t, h	mmol of epoxide	mmol of benzil recovered	epoxide/benzil consumed	ref
20	3.0	2.0	1.5	1.92	1.02	1.96	1
18	2.7	1.8	1.5	1.81	0.82	1.85	1
20	2.0	2.0	1.5	0.92	1.10	1.02	1
15	4.0	2.0	1.0	1.23	1.15	1.45	1[a]
15	4.0	2.0	0.58	1.78	1.18	2.17	2
15	3.0	2.0	0.58	1.78	1.12	2.02	2

[a] Average of four analyses.

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(3) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.

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