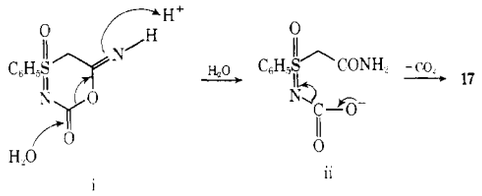
G. Robertson and his staff for microanalyses, to Drs. Jerrold Karliner and Ronald Rodebaugh for very helpful discussions of spectral data, to Professors Peter Yates and Paul Gassman for general suggestions, and to Drs. Neville Finch and Frank Clarke for interest and encouragement during this investigation.

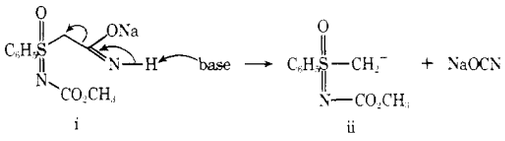
Registry No.—**7,** 4381-25-3; **10,** 61177-70-6; **11,** 61177-71-7; 11 isopropylcyclohexylammonia salt, 61218-49-3; **12,** 61177-72-8; **14,** 61177-73-9; **15a,** 61177-74-0; **15b,** 61177-75-1; **16,** 61177-76-2; **17,** 61202-86-6; **18,** 61177-77-3; **19,** 61177-78-4; **20,** 61177-79-5; **21,** 61177-80-8; **24b,** 61177-81-9; **27,** 61177-82-0; **27** Ag salt, 61177-83-1; **28,** 61177-84-2; **30,** 61177-85-3; **37a,** 61177-86-4; **37b,** 61177-87-5; 38 2HBr, 61177-88-6; methyl chloroformate, 79-22-1; *N*-isopropylcyclohexylamine, 1195-42-2; DMF diethyl acetal, 1188-33-6; phenyl isocyanate, 103-71-9; acetyl nitrate, 591-09-3; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; bromine, 7726-95-6.

References and Notes

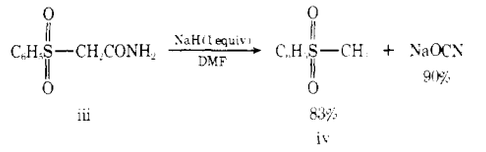
(1) A portion of this work was presented at the Fifth International Congress of Heterocyclic Chemistry, Ljubljana, Yugoslavia, July 8–13, 1975, Abstracts, p 305.
(2) Exchange Scientist, 1973, from the Research Department, Pharmaceutical Division, CIBA-GEIGY A.G., 4002 Basel, Switzerland.
(3) S. L. Huang and D. Swern, *Int. J. Sulfur Chem.*, **9,** 210 (1974); P. D. Kennewell and J. B. Taylor, *Chem. Soc. Rev.*, **4,** 189 (1975).
(4) See P. Stoss and G. Satzinger, *Chem. Ber.*, **108,** 3855 (1975), and references cited therein.
(5) T. R. Williams and D. J. Cram, *J. Org. Chem.*, **38,** 20 (1973).
(6) A. C. Barnes, P. D. Kennewell, and J. B. Taylor, *J. Chem. Soc., Chem. Commun.*, 776 (1973).
(7) Prepared by conversion of the commercially available acid via the acid chloride to the amide followed by oxidation with $NaIO_4$, mp 136–137 °C.
(8) (a) F. Misani, T. W. Fair, and J. Reiner, *J. Am. Chem. Soc.*, **73,** 459 (1951); (b) G. Satzinger and P. Stoss, *Arzneim.-Forsch.*, **20,** 1214 (1970).
(9) (a) Y. Tamura, K. Sumato, J. Minamikawa, and M. Ikeda, *Tetrahedron Lett.*, 4137 (1972); (b) C. R. Johnson, R. A. Kirchhoff, and H. G. Corkins, *J. Org. Chem.*, **39,** 2458 (1974).
(10) C. R. Johnson, M. Haake, and C. W. Schroeck, *J. Am. Chem. Soc.*, **92,** 6594 (1970).
(11) (a) A. T. Fuller, I. M. Tonkin, and J. Walker, *J. Chem. Soc.*, 636 (1945); (b) R. L. Heath and A. Lambert, *ibid.*, 1477 (1947).
(12) H. Bredereck, F. Effenberger, and H. Botsch, *Chem. Ber.*, **97,** 3397 (1964).
(13) The amide **17** might arise from simple attack of methoxide on the *N*-methoxycarbonyl of **15a** or by internal attack of the amide oxygen of **15a** giving rise to i which on hydrolysis and decarboxylation would give **17.**



(14) One possible explanation of this cleavage reaction which occurs with **15a** but *not* with **15b** would be the generation, even with 1 equiv of NaH, of the dianion of i which cleaves, as shown, to give ii and NaOCN. Proton abstraction by ii, now fulfilling the role of base would form **10.** Such a cleavage



would be unavailable to the *sec*-amide. Deprotonation of i could be accomplished by NaH but not by $NaOCH_3$. Treatment of the model sulfone iii with 1 equiv of NaH under these same conditions gave complete cleavage in 3 h at 100 °C with products isolated and identified as shown. No sulfone iv is formed in refluxing methanol–$NaOCH_3$. We intend to examine this



cleavage process more closely. The formation of LiOCN via a cleavage process has been reported by U. Schöllkopf and F. Gerhart, *Angew. Chem.*, **80,** 842 (1968).
(15) S. Oae, K. Harada, K. Isiyikara, and N. Furukawa, *Int. J. Sulfur Chem., Part A,* 49 (1972).
(16) The β carbon of vinyl ethers is somewhat shielded and appears in the 85–90-ppm (relative to Me_4Si) range, far below the 59.3-ppm value for **27.** See J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Table 5.47, p 184.
(17) (a) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77,** 6269 (1955); (b) H. vonPechmann and O. Baltzer, *Chem. Ber.*, **24,** 3148 (1891).
(18) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Am. Chem. Soc.*, **96,** 5648, 5650, 5651 (1974).
(19) A. Hortmann and R. L. Harris, *J. Am. Chem. Soc.*, **93,** 2471 (1971); A. Hortmann, R. L. Harris, and J. A. Miles, *ibid.*, **96,** 6119 (1974).
(20) For comparison, the comparable carbon in **2** resonates at 78.9 ppm, in 1,3,5-trimethylthiabenzene 1-oxide at 83.7 ppm, and in **35** (R = CH_3) at 92.1 ppm relative to Me_4Si.
(21) Y. Tamura, H. Taniguchi, T. Miyamoto, M. Isumekawa, and M. Ikeda, *J. Org. Chem.*, **39,** 3519 (1974).
(22) Unfortunately an excess of bromine was mistakenly employed in this final experiment which exhausted our supply of **30.**
(23) The ethoxycarbonyl derivative of **7** is reported as an oil in ref 5.
(24) Compound **24b,** mp 148–151 °C, was obtained in a similar manner in 4% yield.
(25) H. Meerwein, *Org. Synth.*, **46,** 113 (1966).

Reactions of Alkyl or Aryl Chlorosulfites with Thiocarboxylic Acids

Hiroaki Kagami, Hikaru Satsumabayashi, and Shinichi Motoki*

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, Japan

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Alkyl or aryl chlorosulfites (**7**) reacted with *p*-nitrothiobenzoic acid to give *S*-acylalkyl or *S*-acylaryl thiosulfites (**6**). However, treatment of alkyl chlorosulfites with aliphatic thiocarboxylic acids afforded acylalkyl sulfites (**5**) and acylalkoxy trisulfides (**8**) as a result of disproportionation of **6.** These trisulfides were also obtained by the reaction of dialkoxy disulfides with thiocarboxylic acids. Thermal decomposition of **6** gave **8** and carboxylic esters.

In contrast to ordinary sulfites and monothiosulfites,[1] RSS(O)OR′ (**1**), dithiosulfites,[2] RSS(O)SR (**2**) (R = Ar or *tert*-alkyl), prepared from thionyl chloride and mercaptans are relatively unstable compound and readily decompose to give di- and trisulfides. Previously, we have reported the preparation of diacyl dithiosulfites,[3] RCOSS(O)SCOR′ (**3**), and acylaryl dithiosulfites,[4] RCOSS(O)SR′ (**4**), by the reaction of acyl thiochlorosulfites with thiocarboxylic acids or thiophenols. These acyl derivatives of dithiosulfites were found to be reasonably stable on standing but decomposed to afford carboxylic anhydrides (from **3**) or disulfides and carboxylic anhydrides (from **4**) on heating. Acyl derivative of ordinary sulfites,[5] RCOOS(O)OR′ (**5**), are stable at room temperature but decompose on heating into carboxylic esters or carboxylic

Table I
p-$O_2NC_6H_4CSSOR'$
‖ ↓
O O
6

Registry no.	Compd	R′	Mp, °C	Yield, %	IR (KBr), cm^{-1} $\nu_{C=O}$	IR (KBr), cm^{-1} $\nu_{S\rightarrow O}$	Anal. Calcd (found), % C	H	S
61268-11-9	6a	CH_3	76–78	73	1670	1165	36.78 (37.09)	2.70 (2.77)	24.54 (24.32)
61268-12-0	6b	C_2H_5	84–85	52	1670	1170	39.27 (39.44)	3.30 (3.28)	23.29 (23.04)
61268-13-1	6c	n-C_3H_7	72–73	62	1665	1165	41.51 (41.82)	3.84 (3.63)	22.15 (21.98)
61268-14-2	6d	i-C_3H_7	96–98	58	1640	1135	41.51 (41.28)	3.84 (3.53)	22.15 (21.82)
61268-15-3	6e	C_6H_5	78–79	46	1630	1140	48.29 (48.30)	2.81 (2.66)	19.83 (19.80)
61268-16-4	6f	p-$CH_3C_6H_4$	74–76	64	1670	1140	49.86 (50.22)	3.29 (3.28)	19.01 (18.83)
61268-17-5	6g	p-$C_2H_5C_6H_4$	72–73	79	1650	1140	51.29 (51.60)	3.73 (3.73)	18.26 (18.31)
61268-18-6	6h	2,4-$(CH_3)_2C_6H_3$	87–88	74	1660	1150	51.29 (51.50)	3.73 (3.67)	18.26 (18.21)

Table II. NMR Spectral Data for *S*-Acyl Thiosulfites (6)

Compd	δ ($CDCl_3$)[a]
6a	8.14 (q, 4 H) 4.00 (s, 3 H)
6b	8.15 (q, 4 H) 4.42 (m, 2 H)[b] 1.49 (t, 3 H)
6c	8.17 (q, 4 H) 4.35 (m, 2 H)[b] 1.86 (m, 2 H) 1.02 (t, 3 H)
6d	8.17 (q, 4 H) 5.18 (m, 1 H) 1.47 (d, 6 H)
6f	8.09 (q, 4 H) 7.13 (s, 4 H) 2.33 (s, 3 H)
6g	8.11 (q, 4 H) 7.17 (s, 4 H) 2.67 (q, 2 H) 1.24 (t, 3 H)
6h	8.14 (q, 4 H) 7.11 (m, 3 H) 2.33 (s, 3 H) 2.29 (s, 3 H)

[a] Chemical shifts are in parts per million from internal Me_4Si. [b] $-OCH_2-$ protons showed ABX_3 or ABX_2 type coupling. Coupling constant and chemical shift: **6b**, J_{AB} = 9.35, $\nu_A - \nu_B$ = 19.6 Hz; **6c**, J_{AB} = 9.75, $\nu_A - \nu_B$ = 21.5 Hz, 20% $CDCl_3$, 60 MHz. Measurement of spectrum of **6e** was omitted, as it has no aliphatic protons.

anhydrides depending on the condition. Accordingly, we are interested in studying acyl derivative of monothiosulfites, RCOSS(O)OR′ (**6**), in the present investigation.

Results and Discussion

Alkyl or aryl chlorosulfites (**7**) prepared from thionyl chloride and alcohols or phenols were allowed to react with p-nitrothiobenzoic acid. Crystalline S-acyl thiosulfites (**6a–h**)

$$\text{R'OH} \xrightarrow{\text{SOCl}_2} \underset{\underset{\text{O}}{\downarrow}}{\text{R'OSCl}} \xrightarrow[\text{O}]{\text{RCSH}} \underset{\underset{\text{O O}}{\| \downarrow}}{\text{RCSSOR'}} \qquad (1)$$

7 6

were obtained in fairly good yields. The IR spectra of **6** showed the carbonyl and sulfinyl absorptions in the region of 1630–1670 and 1135–1170 cm^{-1}. The results are shown in Table I. The NMR spectrum of **6b** or **6c** showed ABX_3 or ABX_2 type coupling in its protons of methylene adjacent to the oxygen atom. This magnetic nonequivalence may arise by the asymmetric center of sulfinyl group as in the case of ordinary sulfites.[6] The pertinent NMR data are given in Table II.

On the other hand, the reaction of thioacetic acid with ethyl chlorosulfite gave an unexpected result. Two products, A and B, were obtained in nearly equal amount. The former low-boiling product A was found to be the already known acetylethyl sulfite (**5b**)[5] and the latter high-boiling product B was

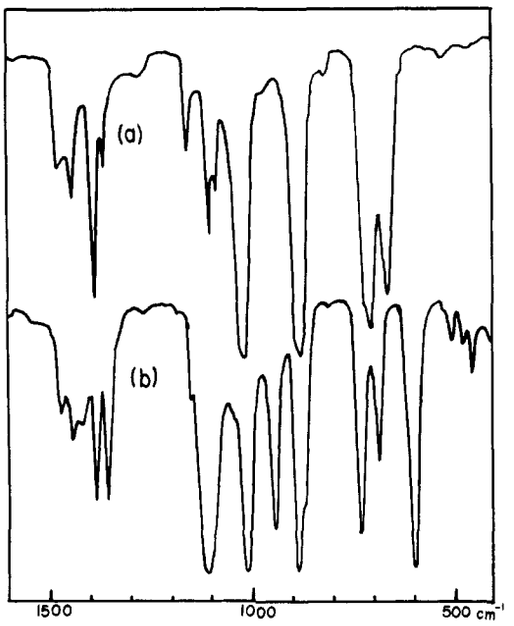

Figure 1. IR spectra of diethoxy disulfide (a) and acetylethoxy trisulfide (b) (neat).

proved to have a formula $C_4H_8O_2S_3$ by elemental analysis. The IR spectrum of B showed a carbonyl band at 1735 cm^{-1} but no sulfinyl band in the region of 1100–1200 cm^{-1}. In order to determine the structure of B we have carried out the following experiment. When diethoxy disulfide (**9**) was treated with equimolar thioacetic acid, one ethoxy group was readily displaced with CH_3COS group and acetylethoxy trisulfide and ethanol were obtained in good yield (eq 2). The IR spectrum

$$\underset{\mathbf{9}}{\text{R'OSSOR'}} + \text{RCSH} \longrightarrow \underset{\underset{\text{O}}{\|}}{\underset{\mathbf{8}}{\text{RCSSSOR'}}} + \text{R'OH} \qquad (2)$$

of this sulfide was completely identical with that of B. The sulfur linkage of dialkoxy disulfides is unbranched[7] and the IR spectra of B and diethoxy disulfide showed similar absorptions in –S–O– (660–730 cm^{-1}) and >C–O– (1010 and 880 cm^{-1}) stretching bands as shown in Figure 1. Accordingly, it has been elucidated that B is unbranched trisulfide

Table III. Reaction Products of Alkyl Chlorosulfites with Aliphatic Thiocarboxylic Acids

		RCOSOR′ (5)				RCSSSOR′ (8)					
R	R′		Yield, %[a]	Bp, °C (mm)	Registry no.		Yield, %[a]	Bp, °C (mm)	Anal. Calcd (found), % C	H	S	Registry no.
CH_3	CH_3	5a	36	43–44 (3)	5308-06-5	8a	29	51 (0.4)	21.16 (21.44)	3.55 (3.43)	56.49 (56.33)	61268-22-2
CH_3	C_2H_5	5b	49	51 (2)	5308-11-2	8b	41	62 (0.4)	26.07 (26.31)	4.37 (4.20)	52.20 (52.06)	61268-23-3
CH_3	n-C_3H_7	5c	78	66–66.5 (2.5)	1666-21-3	8c	35	72 (0.5)	30.27 (30.64)	5.10 (5.30)	48.50 (48.26)	61268-24-4
CH_3	i-C_3H_7	5d	75	56–57 (1.5)	61268-19-7	8d	58	73.5 (0.6)	30.27 (30.54)	5.10 (5.11)	48.50 (48.37)	61268-25-5
C_2H_5	C_2H_5	5e	56	64–65 (2)	61268-20-0	8e	30	71 (0.35)	30.27 (30.31)	5.10 (5.20)	48.50 (48.47)	61268-26-6
n-C_3H_7	C_2H_5	5f	48	67–68 (1)	61268-21-1	8f	39	82–83 (0.5)	33.94 (34.02)	5.70 (5.78)	45.30 (45.18)	61268-27-7

[a] Yields of 5 and 8 are calculated on the basis of eq 3.

Table IV. Spectral Data for Acylalkoxy Trisulfides (8)

Compd	NMR, δ (CCl_4)[a]			IR (neat), $\nu_{C=O}$, cm^{-1}
8a	3.73 (s, 3 H)	2.46 (s, 3 H)		1735
8b	3.93 (q, 2 H)	2.45 (s, 3 H)	1.23 (t, 3 H)	1735
8c	3.83 (t, 2 H)	2.45 (s, 3 H)	1.67 (m, 2 H)	1735
	0.93 (t, 3 H)			
8d	4.14 (m, 1 H)	2.47 (s, 3 H)	1.28 (d, 6 H)	1735
8e	3.94 (q, 2 H)	2.71 (q, 2 H)	1.29 (t, 3 H)	1725
	1.23 (t, 3 H)			
8f	3.94 (q, 2 H)	2.70 (t, 2 H)	1.71 (m, 2 H)	1730
	1.25 (t, 3 H)	0.95 (t, 3 H)		

[a] Chemical shifts are in parts per million from internal Me_4Si.

$CH_3C(O)SSSOC_2H_5$ (**8b**). Similarly, the other acylalkoxy trisulfides (**8**) were obtained by the reaction of alkyl chlorosulfites (**7**) with aliphatic thiocarboxylic acids or by the reaction of dialkoxy disulfides (**9**) with thiocarboxylic acids. The results are shown in Tables III and IV.

Thermal decomposition of *S*-*p*-nitrobenzoylisopropyl thiosulfite (**6d**) gave bis(*p*-nitrobenzoyl) disulfides, isopropyl *p*-nitrobenzoate, and *p*-nitrobenzoylisopropoxy trisulfide. As it has been considered that isopropyl *p*-nitrobenzoate would formed from *p*-nitrobenzoylisopropyl sulfite with loss of sulfur dioxide, this result indicates that **5** and **8** would be formed by disproportionation of initially formed **6** (eq 3). This decomposition of **6** is characteristic as compared with those of the related compounds **2–5.**

$$6 \longrightarrow \tfrac{1}{2}\mathrm{RCOSOR'} + \tfrac{1}{2}\mathrm{RCSSSOR'} \quad (3)$$

(5 = $\tfrac{1}{2}$RCOSOR′; 8 = $\tfrac{1}{2}$RCSSSOR′)

$$5 \longrightarrow \mathrm{RCOR'} + SO_2$$

The alkoxy group of **8** could be further displaced by –SR′ or –SC(O)R′ group. Reaction of **8b** with ethyl mercaptan was carried out at room temperature to give acetylethyl tetrasulfide and ethanol (eq 4). Reaction of **8b** with thiobenzoic acid or *p*-chlorothiobenzoic acid proceeded in refluxing CCl_4 and symmetrical trisulfides, sulfur, and ethanol were obtained. These products are assumed to be formed by disproportionation of initially formed acetylbenzoyl tetrasulfide to dibenzoyl tetrasulfide and diacetyl tetrasulfide followed by desulfurization.

$$\mathbf{8b} + C_2H_5SH \longrightarrow CH_3CSSSSC_2H_5 + C_2H_5OH \quad (4)$$

$$\mathbf{8b} + \mathrm{RCSH} \xrightarrow[-C_2H_5OH]{} [CH_3CSSSSCR] \longrightarrow \tfrac{1}{2}\mathrm{RCSSSCR} + \tfrac{1}{2}CH_3CSSSSCCH_3 + S \quad (5)$$

Experimental Section

Infrared spectra were measured with a Hitachi EPI-G2 spectrometer. The NMR spectra were determined on $CDCl_3$ or CCl_4 solution with a Varian A-60 spectrometer. *p*-Nitrothiobenzoic acid was prepared as previously described.[3] Alkyl chlorosulfites,[8] phenyl chlorosulfite,[9] and dialkoxy disulfides[7,10] were prepared by the method of the literature. *p*-Tolyl chlorosulfite, bp 81 °C (1.5 mm), *p*-ethylphenyl chlorosulfite, bp 83 °C (1.5 mm), and 2,4-dimethylphenyl chlorosulfite, bp 94 °C (1.5 mm), were prepared in a similar way to the preparation of alkyl chlorosulfites. All other reagents were obtained commercially.

***S*-Acylalkyl and *S*-Acylaryl Thiosulfites (6a–h).** To a solution of 3.4 g (0.03 mol) of methyl chlorosulfite in 10 ml of ether, a solution 5.5 g (0.03 mol) of *p*-nitrothiobenzoic acid in 40 ml of ether was added dropwise over 0.5 h at −30 °C. The stirring was continued for an additional 3 h and then the temperature of the mixture was allowed to rise to −10 °C. The reaction mixture was evaporated under reduced pressure and the residual solid was recrystallized from chloroform–petroleum ether to give 5.7 g (73%) of **6a** as light yellow needles, mp 76–78 °C. The other compounds (**6b–h**) were prepared in a similar way.

Reaction of Alkyl Chlorosulfites with Aliphatic Thiocarboxylic Acids. A solution of 22.8 g (0.3 mol) of thioacetic acid in 20 ml of ether was added to a stirred solution of 38.5 g (0.3 mol) of ethyl chlorosulfite in 80 ml of ether at −30 °C during 1 h. The stirring was continued for an additional 2 h and then the temperature of the mixture was allowed to rise to room temperature. The reaction mixture was evaporated under reduced pressure and fractional distillation of the residue gave two fractions. Rectification of these fractions gave 8.9 g of acetylethyl sulfite (**5b**), bp 51 °C (2 mm) [lit.[5] bp 44 °C (1 mm)], identified by elemental analysis and IR spectrum, $\nu_{C=O}$ 1750, $\nu_{S\rightarrow O}$ 1190 cm^{-1}, and 10.5 g of acetylethoxy trisulfide (**8b**), bp 62 °C (0.4 mm). The other compounds (**5** and **8**) were obtained in a similar way.

Decomposition of 6d. *S*-*p*-Nitrobenzoylisopropyl thiosulfite (**6d**, 1.3 g) was heated at 110–120 °C for 1 h under nitrogen atmosphere. After standing at room temperature, the mass turned to a reddish-yellow solid. Recrystallization of the solid from chloroform–petroleum ether gave 0.4 g of bis(*p*-nitrobenzoyl) disulfide, mp 183–184 °C (lit.[11] mp 183 °C). The filtrate was evaporated and the residue was chro-

matographed on silica gel using benzene as eluent to give 0.1 g of isopropyl *p*-nitrobenzoate, mp 107–110 °C (lit. mp 108–110 °C), and 0.1 g of *p*-nitrobenzoylisopropoxy trisulfide: mp 77–79 °C; IR $\nu_{C=O}$ 1685 cm^{-1}; NMR ($CDCl_3$) δ 8.22 (q, 4 H), 4.23 (m, 1 H), 1.33 (d, 6 H). Anal. Calcd for $C_{10}H_{11}NO_4S_3$: C, 39.33; H, 3.63; S, 31.50. Found: C, 39.41; H, 3.65; S, 31.52.

Reaction of Dialkoxy Disulfides with Thiocarboxylic Acids. A solution of 3.8 g (0.05 mol) of thioacetic acid in 20 ml of CCl_4 was added to a stirred solution of 7.7 g (0.05 mol) of diethoxy disulfide in 30 ml of CCl_4 at room temperature, and then the temperature of the mixture was gradually raised to 60 °C during 1 h. Finally, the reaction mixture was refluxed for 1 h and EtOH was removed as its CCl_4 azeotrope by evaporation. The residual liquid was distilled to give 5.8 g of acetylethoxy trisulfide (**8b**), bp 60–61 °C (0.35 mm), yield 63%. Similarly, **8a, 8d,** and **8e** were obtained: yield of **8a,** 65%; **8d,** 69%; **8e,** 77%. *p*-Nitrobenzoylisopropoxy trisulfide was purified by recrystallization from *n*-hexane, mp 79 °C, yield 74%.

Reaction of 8b with Ethyl Mercaptan. A solution of 2.4 g (0.038 mol) of ethyl mercaptan in 20 ml of CCl_4 was added to a stirred solution of 7.0 g (0.038 mol) of **8b** in 30 ml of CCl_4 at room temperature for 1 h and then stirring was continued for an additional 3 h. The CCl_4 solution was then concentrated under reduced pressure and the residual liquid was distilled to give 3.0 g (47%) of acetylethyl tetrasulfide: bp 67–71 °C (0.3 mm); NMR δ 2.50 (s, 3 H), 2.93 (q, 2 H), 1.42 (t, 3 H). Anal. Calcd for $C_4H_8OS_4$: C, 23.98; H, 4.03; S, 64.01. Found: C, 24.06; H, 4.08; S, 63.98. IR $\nu_{C=O}$ 1730 cm^{-1}.

Reaction of 8b with Thiobenzoic Acid. A solution of 2.7 g (0.015 mol) of **8b** and 2.0 g (0.015 mol) of thiobenzoic acid in 50 ml of CCl_4 was stirred at 70 °C for 10 h and the solution became light yellow. The reaction mixture was cooled and the precipitate was collected and recrystallized from benzene to give 0.79 g (34%) of dibenzoyl trisulfide, mp 114–115 °C, IR $\nu_{C=O}$ 1690 cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_2S_3$: C, 54.86; H, 3.29; S, 31.39. Found: C, 54.92; H, 3.30; S, 31.24. The filtrate was chromatographed on silica gel using CCl_4–chloroform (1:1) as eluent to give 0.45 g (11%) of dibenzoyl disulfide, mp 127–129 °C (lit.[12] mp 130 °C), and a small amount of diacetyl disulfide and trisulfide. Similarly, *p*-chlorothiobenzoic acid reacted with **8b** to give bis(*p*-chlorobenzoyl) trisulfide, mp 124–125 °C (lit.[4] 125–126 °C), and a small amount of diacetyl disulfide and trisulfide. Disulfide was formed during the operation of chromatography.

Registry No.—**7** (R′ = CH_3), 13165-72-5; **7** (R′ = Et), 6378-11-6; **7** (R′ = Pr), 22598-38-5; **7** (R′ = Pr-*i*), 22598-56-7; **7** (R′ = Ph), 13165-73-6; **7** (R′ = *p*-$CH_3C_6H_4$), 61268-28-8; **7** (R′ = *p*-$C_2H_5C_6H_4$), 61268-29-9; **7** (R′ = 2,4-$(CH_3)_2C_6H_3$), 61268-30-2; **9** (R′ = CH_3), 28752-21-8; **9** (R′ = Pr), 3359-05-5; **9** (R′ = Pr-*i*), 3359-04-4; **9** (R′ = Et), 28752-22-9; RCOSH (R = O_2N-*p*-C_6H_4), 39923-99-4; RCOSH (R = CH_3), 507-09-5; RCOSH (R = C_2H_5), 1892-31-5; RCOSH (R = C_3H_7), 3931-64-4; RCOSH (R = Ph), 98-91-9; *p*-nitrobenzoylisopropoxy trisulfide, 61268-31-3; ethyl mercaptan, 75-08-1; acetylethyl tetrasulfide, 61268-32-4; dibenzoyl trisulfide, 61268-33-5.

References and Notes

(1) G. Zinner, *Angew. Chem.*, **69,** 508 (1957).
(2) L. Field and W. B. Lacefield, *J. Org. Chem.*, **31,** 3555 (1966).
(3) S. Motoki and H. Satsumabayashi, *J. Org. Chem.*, **38,** 3654 (1973); **39,** 3617 (1974).
(4) S. Motoki and H. Kagami, *J. Org. Chem.*, **41,** 2759 (1976).
(5) M. Kobayashi and A. Yamamoto, *Chem. Ind. (London)*, 1930 (1965); M. Kobayashi and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **39,** 961 (1966); M. Kobayashi, *ibid.*, **43,** 905 (1970).
(6) F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83,** 4666 (1961).
(7) Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich, and E. Pierron, *J. Org. Chem.*, **30,** 2692 (1965).
(8) M. S. Newmann and W. S. Fones, *J. Am. Chem Soc.*, **69,** 1046 (1947).
(9) W. E. Bissinger and F. E. Kung, *J. Am. Chem. Soc.*, **70,** 2664 (1948).
(10) A. Meuwsen, *Ber.*, **B68,** 121 (1935).
(11) A. M. Khaletskii and A. M. Yanovitskaya, *J. Gen. Chem. USSR (Engl. Transl.)*, **19,** 1187, 1193 (1949).
(12) H. Adkins and Q. E. Thompson, *J. Am. Chem. Soc.*, **71,** 2242 (1949).

An X-Ray Crystallographic Structural Study of Sulfoxides Derived from 2-Phenyl-1,3-dithiane

Francis A. Carey,* Peter M. Smith, Robert J. Maher, and Robert F. Bryan*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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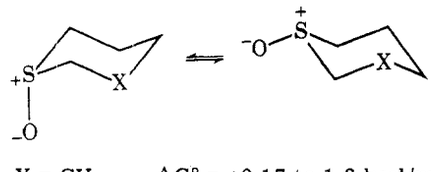
Single-crystal x-ray structure analyses have been carried out for *trans*-2-phenyl-1,3-dithiane 1-oxide (**5**), *cis*-2-phenyl-1,3-dithiane 1-oxide (**6**), and 2-phenyl-1,3-dithiane *trans*-1,*trans*-3-dioxide (**7**) to examine the effects of oxygen substitution on the geometry of the 1,3-dithiane ring. For **5**, a = 12.206 (2), b = 5.749 (1), c = 14.809 (2) Å, β = 97.11 (1)°; for **6**, a = 5.007 (1), b = 20.134 (4), c = 10.095 (3) Å, β = 98.76 (3)°; and for **7**, a = 12.315 (3), b = 5.851 (1), c = 14.829 (3) Å, β = 98.44 (2)°. The space group is $P2_1/c$ in each case with Z = 4. The dithiane rings have a chair conformation somewhat more puckered than that of cyclohexane with endocyclic torsion angles in the range 58–73°. The endocyclic C(2) valence angle shows a marked variation from compound to compound, being 109.6° in **5,** 112.9° in **6,** 114.2° in **7,** as compared to 114.9° in 2-phenyl-1,3-dithiane (**4**) itself. An argument accounting for the steric dependence of this angular variation is offered in terms of transannular dipolar interactions between the two sulfur atoms and oxygen and is discussed in relation to conformational equilibria in solution. Short C–H···O contacts indicative of significant dipolar interactions are found in all three crystal structures.

The conformational preferences exhibited by six-membered cyclic sulfoxides are strongly dependent upon the nature of the other ring atoms, especially those which bear a 1,3 relationship to the sulfoxide group (eq 1).[1] The more stable chair



(1)

1, X = CH_2	$\Delta G°$ = +0.17 to 1.3 kcal/mol
2, X = O	$\Delta G°$ = +0.6 kcal/mol
3, X = S	$\Delta G°$ = −0.6 kcal/mol

conformation of thiane 1-oxide (**1**) has the oxygen axial.[2] This conformation appears to be the more stable for 1,3-oxathiane 3-oxide (**2**) as well.[3] In 1,3-dithiane 1-oxide (**3**), however, it is the conformation with the sulfoxide oxygen equatorial which is the more stable.[3a,4] The reasons for these differences in conformational preference are not completely understood. It has been suggested that the axial conformation of **1** is stabilized by an attractive van der Waals interaction between the sulfoxide oxygen and the syn-axial C–H bonds.[2a,b] Electrostatic interactions between the polar sulfoxide group and the cross-ring heteroatom are expected to make important contributions to the conformational energies of **2** and **3.** Indeed, molecular mechanics calculations indicate that most of the