Residual polymer was then treated with a catalytic amount of diol sodium alcoholate as described in procedure B. Another 23.6 g. of distillate was obtained on heating under oil pump vacuum. The two samples of distillate were taken up in ether and washed several times with cold water. After drying and removing solvent, 39.4 g. of mobile oil remained. G.l.c. showed the presence of considerable amounts of a relatively volatile compound which suggested that the bulk of the material was suffering decomposition. Repeated fractionations revealed the presence of a relatively stable volatile component, ultimately identified as 6-methyl-1,3,2-dioxathiane (XXI), b.p. 36° (4.0 mm.), $n^{25}\mathrm{D}$ 1.4636, which was easily purified and which was stable to g.l.c. conditions.

Anal. Calcd. for $C_4H_8O_2S$: C, 39.98; H, 6.71; S, 26.68. Found: C, 40.00; H, 6.60; S, 26.45.

A second major component, considerably less stable than the first, was obtained from the higher boiling cuts. The infrared spectra of most cuts of this material indicated contamination with sulfite ester. Continued fractionation, however, gave the desired pure cyclic 1,3-butylene thionosulfite (XIX), b.p. 40° (0.1 mm.), $n^{25}\mathrm{D}$ 1.5291, $\lambda_{\max}^{\text{isooctane}}$ 244 mμ (ϵ 1230).

Anal. Calcd. for $C_4H_8O_2S_2$: C, 31.56; H, 5.30; S, 43.13. Found: C, 31.26; H, 5.36; S, 43.01.

In connection with the purification of XIX, it was observed that as the sample approached complete purity its stability[33] decreased. Toward the end of the distillation, material in the fractionating column became milky as elemental sulfur began separating. Head temperature dropped and essentially pure XXI began distilling out. In a separate experiment it was determined that XIX, on continued reflux, decomposed by loss of one atom of sulfur to yield the more stable sulfoxylate XXI. Determination of over-all yields of XIX or XXI from the starting diol were difficult to estimate because of this facile decomposition reaction. It appeared that the major product initially obtained (in the order of 10–15% over-all yield) was XIX.

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[33] There were indications of a sensitivity to light as well as to heat.

Organic Esters of Bivalent Sulfur. III. Sulfoxylates

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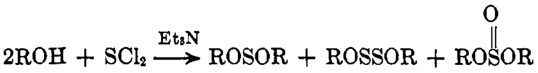
Received January 11, 1965

Saturated monohydric primary and secondary alcohols react with sulfur dichloride to give sulfoxylate esters, ROSOR, in 50–70% yield. Optimum temperatures are in the −75 to −95° range with methylene chloride or chloroform as solvent and triethylamine as acid acceptor. Benzyl and allyl alcohols behave abnormally and yield sulfinate esters. Glycols give polymeric materials as the major products, but cyclic sulfoxylates, *i.e.*, 1,3,2-dioxathianes (XI), are obtained from 1,3-diols. In addition, 1,3-propanediol gives a macrocyclic sulfoxylate XII and 2,2,4-trimethyl-1,3-pentanediol yields small amounts of 2,2,4,4-tetramethyl-3-thionotetrahydrofuran (XV).

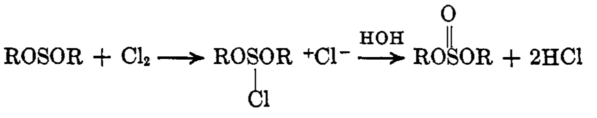
The dimethyl and diethyl esters (ROSOR) of sulfoxylic acid [$S(OH)_2$] are known. Their preparation, first described by Meuwsen and Gebhardt,[1] and subsequently utilized by others,[2] involved the alkoxide-catalyzed decomposition of the corresponding dialkoxy disulfides. As the latter were readily available[3a] the preparation of additional dialkyl sulfoxylates was undertaken. Despite the success achieved by Meuwsen and Gebhardt with diethyl sulfoxylate,[1] their method was found to give low yields, and in our hands, it was not generally useful. Appreciable decomposition of the dialkoxy disulfides according to reaction 2 was observed with concomitant complications arising from the presence of aldehydes. These facts and the easy availability of stabilized sulfur dichloride[4] prompted an investigation of the direct "acylation" of alcohols by sulfur dichloride similar to that previously found successful for sulfur monochloride.[3a] This reaction too proved feasible but under somewhat more specialized conditions than in the case of sulfur monochloride. Three sulfur esters, indicated in reaction 3, were always obtained in the direct reaction of alcohols with sulfur dichloride using triethylamine as an acid acceptor. Equilibration of sulfur dichloride as shown in reaction 4 apparently is responsible for the formation of the dialkoxy disulfide and the sulfite by-products. Sulfites appear to arise from attack of chlorine on the sulfoxylate. Some ancillary experiments suggested that this attack followed two pathways—reactions 5 and 6. When dibutyl sulfoxylate was treated with 1 mole of chlorine, a 50% yield of dibutyl sulfite was obtained as the only ester product. A noticeable reaction took place upon addition of water, presumably due to hydrolysis of a ROSOR–Cl_2 intermediate. Had the reaction gone entirely *via* eq. 5, all of the chlorine should have appeared as chloride ion. Approximately 30%, however, was converted to nonionic form, presumably to butyl chloride. The latter had previously been identified as a by-product in the preparation of dibutyl sulfoxylate. These facts suggest that conversion of sulfoxylate to sulfite may also be proceeding by

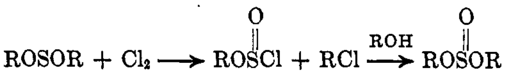
$$\mathrm{EtOSSOEt \xrightarrow{EtONa} EtOSOEt + S^0} \qquad (1)$$

$$\mathrm{RCH_2OSSOCH_2R \xrightarrow{RONa} RCHO + RCH_2OH + 2S^0} \qquad (2)$$


$$\mathrm{2ROH + SCl_2 \xrightarrow{Et_3N} ROSOR + ROSSOR + RO\overset{\overset{O}{\|}}{S}OR} \qquad (3)$$

$$\mathrm{2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2} \qquad (4)$$


$$\mathrm{ROSOR + Cl_2 \longrightarrow RO\underset{\underset{Cl}{|}}{S}OR\ {}^{+}Cl^{-} \xrightarrow{HOH} RO\overset{\overset{O}{\|}}{S}OR + 2HCl} \qquad (5)$$


$$\mathrm{ROSOR + Cl_2 \longrightarrow RO\overset{\overset{O}{\|}}{S}Cl + RCl \xrightarrow{ROH} RO\overset{\overset{O}{\|}}{S}OR} \qquad (6)$$

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[1] A. Meuwsen and H. Gebhardt, *Ber.*, **B68**, 1011 (1935); **B69**, 937 (1936).

[2] G. Scheibe and O. Stoll, *ibid.*, **71**, 1573 (1938); M. Goehring, *Z. Anorg. Chem.*, **253**, 304 (1947); *Chem. Abstr.*, **43**, 2886 (1949); *Ber.*, **80**, 219 (1947); A. Arbuzov and T. G. Shovasha, *Dokl. Akad. Nauk SSSR*, **69**, 41 (1949); see also M. Goehring and A. Stamm, *Angew. Chem.*, **60**, 147 (1948).

[3] (a) Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich, and E. Pierron, *J. Org. Chem.*, **30**, 2692 (1965); (b) Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich, *ibid.*, **30**, 2696 (1965).

[4] R. J. Rosser and F. R. Whitt, *J. Appl. Chem.*, 229 (1960).

TABLE I

YIELDS OF ESTERS FROM REACTION OF ISOPROPYL ALCOHOL AND SULFUR DICHLORIDE AT VARIOUS TEMPERATURES

	% yield of ester		
Temp., °C.	—OSO—	—OSSO—	$-\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{O}-$
25	30	20	24
0	40	16	20
−75	67	6	14
−95	60	5	17

pathway 6 during the course of the alcohol–sulfur dichloride reaction.

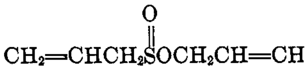
The yields of the desired sulfoxylate esters were enhanced greatly by very low reaction temperatures and fairly dilute conditions. This temperature effect is illustrated in Table I for the reaction of isopropyl alcohol and sulfur dichloride. Products of this reaction were sufficiently stable to permit analysis by g.l.c. The slightly lower yield of sulfoxylate observed at −95° reflected stirring and homogeneity problems rather than a true chemical effect. Thus, it was clear that best results were to be expected at minimal temperatures. Data on several esters derived from common monohydric alcohols are summarized in Table II. Cholesterol was also converted to a sulfoxylate ester in very low yields.

Unexpected results were obtained with allyl and benzyl alcohols. In the first case, reaction with sulfur monochloride appeared to occur normally. A moderate yield of a garlic-odored ester was obtained which had the correct analysis for the expected sulfoxylate I. Its p.m.r. spectrum, however, showed that the allylic methylene groups in the two allyl moieties were not equivalent. Instead of the expected doublet equal to four hydrogens, two doublets at 3.40 and 4.43 p.p.m.,[5] each amounting to two hydrogens, were obtained. The p.m.r. spectrum of the corresponding

$(CH_2{=}CHCH_2O)_2S$
I

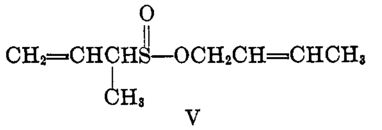
$(CH_2{=}CHCH_2OS)_2$
II

$(CH_2{=}CHCH_2O)_2S{=}O$
III



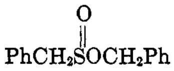
$CH_2{=}CHCH_2\overset{\overset{O}{\|}}{S}OCH_2CH{=}CH_2$

IV



$CH_2{=}CH\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{S}{-}OCH_2CH{=}CHCH_3$

V



$PhCH_2\overset{\overset{O}{\|}}{S}OCH_2Ph$

VI

$(PhCH_2OS)_2$
VII

diallyloxy disulfide[3a] II was normal (methylene doublet at 4.27 p.p.m.) as was that of diallyl sulfite (III, doublet at δ 4.43). Thus it appeared that the product actually obtained was allyl 2-propene-1-sulfinate (IV) with the higher field doublet representing the methylene group attached to sulfur. Inspection of the infrared spectrum showed a strong absorption band at 8.8 μ which appears to be characteristic of the >S=O moiety of sulfinate esters.[6] The possibility that an allylic shift had occurred during the reaction similar to that reported by Garmaise and co-workers[7] with thionocarbonyl chlorides was investigated. Using 2-buten-1-ol as the substrate alcohol, carbon–sulfur bond formation appeared to occur judging from the infrared spectrum. However, the mixture of esters was too complex to separate by distillation and too unstable to resolve by g.l.c.; thus, a rearranged sulfinate (V) could not be identified.

TABLE II

$$2ROH + SCl_2 + 2Et_3N \xrightarrow[-75 \text{ to } 95^\circ]{} ROSOR + 2Et_3N{\cdot}HCl$$

R	% yield	B.p., °C. (mm.)	$n^{25}D$	Formula	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S
n-C_3H_7	62	43 (7)	1.4270	$C_6H_{14}O_2S$	47.96	9.37	21.34	47.74	9.54	21.15
i-C_3H_7	67	55 (30)	1.4170	$C_6H_{14}O_2S$	47.96	9.37	21.34	47.79	9.38	21.23
n-C_4H_9	70	57 (2.0)	1.4355	$C_8H_{18}O_2S$	53.88	10.17	17.98	53.81	10.10	17.77
n-C_5H_{11}	56	67 (0.3)	1.4379	$C_{10}H_{22}O_2S$	58.20	11.23	15.54	58.12	11.28	15.63

Similarly, benzyl alcohol gave as the only isolable product low yields of a crystalline ester which was isomeric with the desired sulfoxylate and which exhibited nonequivalent methylene groups in its p.m.r. spectrum. Additional evidence indicating that the product was benzyl α-toluenesulfinate (VI) was obtained by desulfurization to a mixture of toluene and benzyl alcohol. Under identical conditions the analogous oxydisulfide ester VII gave only benzyl alcohol.

Attempts to prepare cyclic sulfoxylate esters from glycols in the manner found successful for sulfur monochloride[3b] proved only partially fruitful. 1,2-Diols reacted readily with sulfur dichloride, but even under high dilution conditions low polymers were the only products of reaction. Thus, in the case of propylene glycol, a polymer (mol. wt., *ca.* 800) was obtained whose infrared spectrum indicated the presence of hydroxyl and sulfite groups. These bands were relatively weak, however, and the crude product appeared to be essentially VIII (see Chart I). All attempts to degrade the polymer to the cyclic sulfoxylate IX were unsuccessful. Instead, low yields of the cyclic thionosulfite isomers[3b] Xa, identical with the mixture obtained previously from propylene glycol and sulfur monochloride, were obtained along with substantial amounts of the glycol cyclic sulfites. Similarly, Xb was obtained from *meso*-2,3-butanediol and sulfur dichloride. Limited success was achieved, however, in obtaining six-membered ring sulfoxylates, *i.e.*, 1,3,2-dioxathianes, by direct reaction of sulfur dichloride and 1,3-diols. Thus, 1,3-butanediol yielded XIa (20%) directly. Some additional XIa (13%) was produced by degradation of polymer which ac-

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[5] P.m.r. spectra were obtained on a Varian A-60 spectrometer. Samples were dissolved in carbon tetrachloride using tetramethylsilane as an internal standard. Results are reported in δ (parts per million) units downfield from tetramethylsilane as zero.

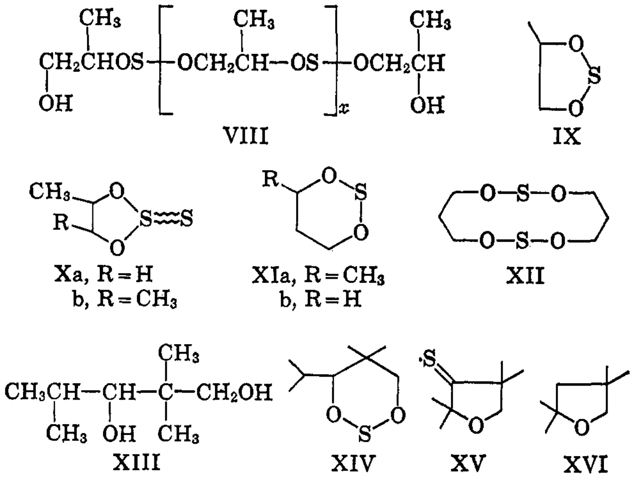
[6] *Cf.* "Sadtler Standard Spectra Catalog," Sadtler Research Laboratories, Philadelphia, Pa., 1962, Curve No. 19814 for *n*-propyl methanesulfinate.

[7] D. L. Garmaise, A. Ucheyama, and A. F. McKay, *J. Org. Chem.*, **27**, 4509 (1962).

companied the formation of the cyclic monomer. Two sulfoxylates, the parent monomer 1,3,2-dioxathiane (XIb, 8%) and the macrocyclic dimer XII (~2%), were obtained from 1,3-propanediol. A small amount of higher melting crystalline material, apparently a mixture of larger macrocyclic sulfoxylates, was also obtained but isolation of a single entity could not be achieved.

Reaction of 2,2,4-trimethyl-1,3-pentanediol (XIII) with sulfur dichloride gave the expected cyclic sulfoxylate XIV and the corresponding cyclic sulfite ester along with hydroxyl- and carbonyl-containing decomposition products. In addition, a volatile pink compound was observed. The latter was present in crude samples of XIV, but it appeared also to be formed during fractionation of crude XIV. A small quantity of air-sensitive crystals, m.p. 31–32°, $\lambda_{\max}^{\text{alc}}$ 233 mμ (ε 4325), was obtained by g.l.c. Analysis and mass spectral data indicated an empirical formula of $C_8H_{14}OS$, differing from XIV by the elements of water. The infrared spectrum showed the absence of hydroxyl or carbonyl functions and the p.m.r. spectrum was extraordinarily simple. The latter consisted of two unsplit pairs of methyl groups at 1.21 and 1.33 p.p.m. and a single unsplit methylene group at 3.87 p.p.m. These data indicated that the pink by-product was probably the thio ketone XV. Desulfurization to 2,2,4,4-tetramethyltetrahydrofuran (XVI), a known compound,[8] supported this assignment. The formation of XV from XIV or an acyclic precursor may be rationalized on the basis of the following transformation. Attempts to prepare a seven-membered cyclic sulfoxylate from 1,4-butanediol were not successful.

Chart I



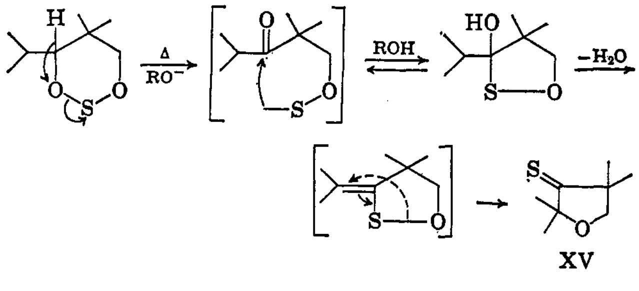
VIII IX

Xa, R = H
b, R = CH3

XIa, R = CH3
b, R = H

XII

XIII XIV XV XVI



XV

Experimental[9]

General Procedure for Preparation of Lower Alkyl ROSOR Esters.—One mole of the alcohol, 102 g. of triethylamine, and 370 ml. of dry methylene chloride were charged into an elongated 1-l., three-necked flask cooled in a large dewar flask with an acetone–liquid nitrogen mixture. With rapid stirring and protection from moisture, 51.5 g. of sulfur dichloride in 100 ml. of dry methylene chloride was added dropwise over 2–3 hr. Initially the temperature was held at *ca.* −95° but, in order to achieve better stirring, the mixture was allowed to warm to −80 ± 5° toward the end of the addition. Cooling was then terminated and the reaction mixture was allowed to warm to 0°. Water (400 ml.) was added and the organic layer was separated. After two additional water washes the methylene chloride solution was dried with Drierite and the solvent was removed in a rotating evaporator with only minimal heat applied. The crude esters so obtained were subjected to vacuum fractionation. In each case, the sulfoxylate was slightly more volatile than the corresponding sulfites which were the principal impurities present.

Effects of Reaction Temperature on the Yield of Diisopropyl Sulfoxylate.—Variable-temperature experiments with isopropyl alcohol, summarized in Table I, were carried out using the general procedure. The crude product was analyzed by g.l.c. using the LAC-3R-728 column[9] at 105°. Retention times (minutes) of the materials present were: ROH, 1.0; ROSOR, 1.4; ROSSOR, 3.8; and ROS(O)OR, 4.6.

Dicholesteryl Sulfoxylate.—Cholesterol (38.6 g.) and 10.2 g. of triethylamine in 300 ml. of dry methylene chloride were cooled to −90°. The resulting slurry was treated with 5.1 g. of sulfur dichloride in 30 ml. of methylene chloride as described for the simple aliphatic alcohols. During work-up, the product crystallized from the methylene chloride solution and additional chloroform was added as solvent. The solution was concentrated giving 6.7 g. of product (*ca.* 16%), m.p. 171–177°. After three recrystallizations from methylene chloride, the pure compound melted at 180–182° dec. Additional material of very low purity was obtained in subsequent crops.

Anal. Calcd. for $C_{54}H_{90}O_2S$: C, 80.73; H, 11.29; S, 3.99. Found: C, 80.71; H, 11.15; S, 3.86.

Oxidation of Dibutyl Sulfoxylate with Chlorine.—A mixture of 17.8 g. (100 mmoles) of sulfite-free dibutyl sulfoxylate and 20.4 g. of triethylamine in 100 ml. of dry methylene chloride was cooled to −30°. A standard solution (87 ml.) of chlorine (100 mmoles of Cl_2) in methylene chloride was added slowly over 30 min. The clear yellow solution was allowed to warm to 10° and 2 ml. of water was added. An exothermic reaction took place and triethylamine hydrochloride separated. After 20 min., additional water was added and the reaction mixture was worked up. The water washes were found to contain 140 mmoles of chloride ion. Removal of methylene chloride gave 10.4 g. of yellow oil which was found by g.l.c. and its infrared spectrum to be >95% sulfite for an over-all yield of ~50%.

Allyl 2-Propene-1-sulfinate (IV).—Allyl alcohol (58.1 g.), triethylamine (102 g.), and sulfur dichloride (51.5 g.) were caused to react as described in the general procedure. The crude tarry material isolated after removal of solvent was immediately subjected to rapid vacuum distillation giving 42.1 g. of pale yellow oil, b.p. 46–50° (0.4 mm.). This product was not stable to analysis by g.l.c. The crude distillate was subjected to careful fractionation, and four cuts were collected. The progress of separation was followed by observing the decrease in the absorption of a sulfite band at 8.2 μ in the infrared spectrum.[10] The fourth fraction (16 g.) was essentially free of sulfite. Refractionation of this cut gave pure material, b.p. 34° (0.2 mm.), $n^{25}\text{D}$ 1.4789, as a mobile, colorless liquid with a strong odor of salami. The p.m.r. spectrum had two doublets, equivalent to two hydrogens each, at δ = 3.40 and 4.43 p.p.m., thus indicating structure IV rather than I. The infrared spectrum exhibited very strong absorption at 8.9, 10.2, 10.8, and 12.95 μ with no appreciable absorption bands at 8.25 μ characteristic of diallyl sulfite.

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[8] A. Franke, *Monatsh.*, **17**, 85 (1896).

[9] Melting and boiling points are uncorrected. Gas chromatograms and infrared and ultraviolet spectra were obtained as described in the previous paper of this series.[3a] P.m.r. spectra were obtained and the data are reported as noted in footnote 5. Sulfur dichloride was freshly distilled and stabilized[4] no longer than 5 days before use. Methylene chloride was dried by distillation from phosphorus pentoxide.

[10] Pure sulfite, prepared by reaction of thionyl chloride and allyl alcohol using triethylamine as the acid acceptor, was used for comparison.

Anal. Calcd. for $C_6H_{10}O_2S$: C, 49.49; H, 6.89; S, 21.93. Found: C, 49.43; H, 6.88; S, 22.02.

Benzyl α-Toluenesulfinate (VI).—Benzyl alcohol (120 g.), 102 g. of triethylamine, and 51.5 g. of sulfur dichloride were allowed to react at −75° as described in the general procedure for the preparation of ROSOR esters. A pale yellow oil (130 g.) remained after work-up of the reaction mixture. On standing overnight in a refrigerator, part of the oil crystallized affording 40 g. of sticky white crystals. Several recrystallizations from hexane gave pure material as shining plates, m.p. 51–52°. The p.m.r. spectrum showed two slightly broadened bands at δ = 3.90 and 4.88 p.p.m. corresponding to nonequivalent benzylic methylene groups. The infrared spectrum again showed a strong band at ~8.8 μ. The sulfinate structure VI was thus strongly indicated.

Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73; S, 13.02. Found: C, 68.13; H, 5.70; S, 12.80.

Desulfurization of Benzyl α-Toluenesulfinate.—To a slurry of 20 g. of Raney nickel in 50 ml. of isopropyl alcohol was added 4 g. of benzyl α-toluenesulfinate with good stirring. The temperature rose from 25 to 38° over about 5 min. and then gradually dropped. After being stirred for 2 hr., the nickel sludge was removed by filtration and the filtrate was examined by g.l.c. Besides solvent and traces of water, two peaks corresponding to toluene and benzyl alcohol in equal quantities were clearly evident. Appropriate addition of authentic materials, *i.e.*, toluene or benzyl alcohol, to samples of the filtrate confirmed the identification. A control experiment using 2.0 g. of dibenzyloxy disulfide[3a] gave only benzyl alcohol as the desulfurization product.

Reaction of Propylene Glycol and Sulfur Dichloride.—A mixture of 38.1 g. of propylene glycol and 102 g. of triethylamine in a graduated dropping funnel was diluted to a total volume of 250 ml. with dry methylene chloride. To a second funnel was added 51.5 g. of sulfur dichloride which was similarly diluted to 250 ml. with methylene chloride. The two solutions of reactants were added slowly and concurrently to 600 ml. of dry methylene chloride suitably protected from moisture and stirred rapidly at *ca.* −90°. This temperature was maintained during most of the 2–3 hr. addition period and allowed to increase only slightly near the end to permit efficient stirring.

When addition was complete, cooling was terminated and the mixture was allowed to warm to 0°. Water (400 ml.) was added and the methylene chloride layer was separated. After two additional washes with cold water, the solution was dried with Drierite and the solvent was removed under reduced pressure using a rotating evaporator. A light reddish, viscous oil was obtained which showed only small amounts of hydroxyl and fairly significant amounts of $>S{=}O$ (band at 8.25 μ) in the infrared spectrum. An average molecular weight[11] of 800 was indicated.

Anal. Calcd. for $(C_3H_6O_2S)_x$: C, 33.95; H, 5.70; S, 30.20. Found: C, 33.60; H, 5.61; S, 31.00.

As no monomeric IX appeared to be present in the crude oil, alkoxide-catalyzed degradation was attempted in an effort to obtain IX. Sodium metal (~300 mg.), dissolved in 6 ml. of propylene glycol, was added to the well-stirred oil and the mixture was then warmed under oil pump vacuum. At a pot temperature of about 85° a clear liquid began to distil, and a total of 29 g. of oil, b.p. 45–65° (1 mm.), was eventually collected. The infrared spectrum of this crude material showed the presence of large amounts of hydroxyl- and carbonyl-containing products along with sulfite ester. The crude mixture was taken up in 100 ml. of ether and washed with three 100-ml. portions of cold water. After drying and removing solvent, 16 g. of pale yellow oil remained. G.l.c. showed this to be 50% cyclic 1-methylethylene thionosulfite (Xa), about 30% isomeric propylene glycol cyclic sulfites,[12] and several components of greater volatility. None of the last was present in sufficient amount to be of significant interest. Distillation of the crude yellow oil yielded 2.0 g. of product, b.p. 44–46° (1.1 mm.), $n^{25}D$ 1.5272 (lit.[3] $n^{25}D$ 1.5325). The g.l.c. indicated that this refined material contained about 93% Xa and 6% sulfite esters. A comparison of infrared spectra showed the identity of the cyclic 1-methylethylene thionosulfite mixture Xa obtained in this experiment with that previously produced from propylene glycol and sulfur dichloride.[3b]

6-Methyl-1,3,2-dioxathiane (XIa).—A mixture of 45 g. of 1,3-butanediol and 102 g. of triethylamine was caused to react with 51.5 g. of sulfur dichloride exactly as described in the preceding experiment with propylene glycol. A light tan oil (60 g.) remained after the initial reaction mixture had been worked up. Monomeric sulfur esters, 13.5 g., b.p. 40–45° (1.6 mm.), were removed by vacuum distillation. G.l.c. indicated this crude cut to be 88% of the desired sulfoxylate XIa (20% over-all yield). A small amount of additional monomeric esters was obtained by treatment of the nonvolatile residue with 5 ml. of the diol containing 500 mg. of dissolved sodium. Subsequent heating gave 20.3 g., b.p. 43–65° (1.9 mm.), of crude distillate which g.l.c. indicated to be a mixture of XIa (40%), sulfite (40%), and two unidentified high boilers. On the basis of these analyses the over-all yield of XIa was ~33%. G.l.c. retention times and the infrared spectrum of pure 6-methyl-1,3,2-dioxathiane prepared by this method (pure sample isolated from g.l.c.) were identical with those of XIa obtained in previous work.[3b]

1,3,7,9-Tetraoxa-2,8-dithiacyclododecane (XII) and 1,3,2-Dioxathiane (XIb).—1,3-Propanediol (38.1 g.) and 102 g. of triethylamine in methylene chloride solution were allowed to react with 51.5 g. of sulfur dichloride as described in the preceding experiments with propylene glycol and 1,3-butanediol. A crude oil (47.7 g.) was obtained on work-up which partially crystallized on standing. Two grams of sticky white needles was collected by filtration and extracted with 80 ml. of hot hexane. Cooling gave 0.8 g. of small white needles, m.p. 120–122°, which after nine recrystallizations still appeared to be impure, m.p. 166–170°. Analysis of an intermediate fraction, m.p. 137–140°, indicated that the hexane-insoluble materials were probably macrocyclic homologs of XIb.

Anal. Calcd. for $(C_6H_6O_2S)_x$: S, 30.21. Found: S, 30.08.

Evaporation of the mother liquors from the first three recrystallizations gave 0.60 g. of a distinct compound, m.p. 123–124°, which crystallized from hexane in long white needles. Three additional recrystallizations failed to change the melting point.

Anal. Calcd. for $(C_3H_6O_2S_2)_2$: C, 33.95; H, 5.71; S, 30.21; mol. wt., 212. Found: C, 33.69; H, 5.81; S, 30.07; mol. wt., 219.[11]

The infrared and particularly the p.m.r. spectra supported the macrocyclic structure XII. Two sets of protons in the ratio 2:1 were observed; the former was a clean triplet centered at δ = 4.15 p.p.m., and the latter was a five-peak system centered at δ = 1.94 p.p.m. representing the center methylene protons of the trimethylene system. The oil from which the crystals had been obtained was treated with 6 ml. of 1,3-propanediol in which had been dissolved 200 mg. of sodium metal. Vacuum distillation gave 14.6 g. of clear distillate, b.p. 60–95° (14 mm.), which according to g.l.c. contained at least eight components; only three were present in major amounts. These were: 1,3,2-dioxathiane (XIb, 28%, over-all yield ~8%), trimethylene sulfite (29%), and an unidentified alcoholic material (27%). Trimethylene glycol (~5%) and 3-chloro-1-propanol (~5%) were identified among the minor products by their g.l.c. retention times and by comparison of the infrared spectra of authentic materials with those collected from the g.l.c. column. G.l.c. served to isolate the XIb in about 90% purity but difficulty was encountered in freeing this from 3-chloro-1-propanol. This was accomplished, however, by dissolving the mixture in pure pentane and passing the solution through a small column of powdered cellulose. Subsequent collection by g.l.c. gave 1 g. of pure XIb, $n^{23}D$ 1.4948, b.p. ~60° (20 mm.), as a clear lachrymatory liquid.

Anal. Calcd. for $C_3H_6O_2S$: C, 33.95; H, 5.70; S, 30.21. Found: C, 33.76; H, 5.45; S, 30.30.

4-Isopropyl-5,5-dimethyl-1,3,2-dioxathiane (XIV).—A mixture of 71.3 g. of 2,2,4-trimethyl-1,3-pentanediol and 102 g. of triethylamine in methylene chloride was caused to react with 51.5 g. of sulfur dichloride as described in preceding experiments. Work-up gave a fairly thin oil (85.2 g.) which contained hydroxyl and sulfite moieties according to the infrared spectrum. The crude oil was subjected to vacuum distillation. Two fractions, 40.8 g., b.p. 54–75° (1.2 mm.), and 24 g., b.p. 75–87° (1.2 mm.), were collected. G.l.c. of the larger cut showed two major and four minor components to be present. The desired sulfoxylate XIV (58%) and the diol cyclic sulfite (~25%) were found to be the major constituents. Two relatively nonvolatile minor products, one identified as the starting diol, were each present to the extent of about 2–3%. Two volatile minor products A

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(11) Mechrolab vapor pressure osmometer, Model 301.

(12) J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

(~7%) and B (~4.5%) were the remaining components of the distillate.

The second fraction was found to contain only 13% of the desired sulfoxylate ester XIV along with some sulfite and several unidentified nonvolatile components. Surprisingly, both volatile A (12%) and B (15%) were present in greater concentration than in the first distillation cut.

Isolation of pure sulfoxylate XIV involved fractional distillation of the 40.8 g. of the first-cut distillate to give 15 g., b.p. 30–35° (0.2 mm.), of about 90% purity. This material, on subsequent refractionation, gave 3.0 g. of essentially pure XIV, b.p. 31.5–32° (0.25 mm.), n^{25}_{D} 1.4692.

Anal. Calcd. for $C_8H_{16}O_2S$: C, 54.50; H, 9.15; S, 18.19. Found: C, 54.14; H, 9.10; S, 17.80.

The pure material appeared to be quite unstable; viscosity and index of refraction changed appreciably after only 1 week at −5°. On the basis of g.l.c. analysis the total yield of XIV was roughly 29%.

Isolation of 2,2,4,4-Tetramethyl-3-thionotetrahydrofuran (V).—During the various distillations required to isolate the sulfoxylate XIV from higher boiling by-products, it was observed by g.l.c. that two volatile materials A and B appeared to arise as a result of decomposition attending distillation of the more crude fractions. These materials were concentrated to some extent in the Dry Ice traps of the vacuum system. No attempt was made to isolate and identify[13] the volatile A component, but volatile B was readily obtained as a pink solid in the cold-trap system. Approximately 1.5 g. of this material (~70% purity) was fractionated by preparative g.l.c. affording 0.5 g. of pink crystals, m.p. 31–32°, $\lambda_{\max}^{\text{alc}}$ 233 mμ (ϵ 4325). The infrared spectrum showed no carbonyl or hydroxyl bands. Bands in the 6–13-μ region were 6.85 (m), 7.30 (w), 7.36 (m), 7.84 (m), 8.21 (m), 8.5 (w), 8.67 (2), 8.85 (s), 9.64 (vs), 10.39 (w), 10.71 (vw), 11.11 (s), and 12.45 (m) μ. The very simple p.m.r. spectrum contained three unsplit resonances at δ = 1.21, 1.33, and 3.87 p.p.m. in a 3:3:1 ratio corresponding to two pairs of methyl groups and a methylene group. Structure XV was assigned on this basis.

Anal. Calcd. for $C_8H_{14}OS$: C, 60.71; H, 8.92; S, 20.23; mol. wt., 158. Found: C, 60.40; H, 8.90; S, 20.13; mol. wt., 158 (mass spectroscopy).

Desulfurization of 2,2,4,4-Tetramethyl-3-thionotetrahydrofuran (XV).—To a slurry of 3.0 g. of Raney nickel in 6 ml. of pentane was added 180 mg. of XV. An immediate discharge of the pink color was observed on mixing. After 20 min., the nickel was removed by centrifugation. Solvent was removed by careful fractionation leaving 120 mg. of a colorless oil. G.l.c. indicated that this mixture contained ~60% of one component. Approximately 50 mg. of the pure compound was collected by g.l.c. Infrared and p.m.r. spectra were identical with those of authentic 2,2,4,4-tetramethyltetrahydrofuran prepared as described below.

2,2,4,4-Tetramethyltetrahydrofuran (XVI).—The method used was essentially that described by Franke[8]; the yield of XVI was, however, relatively low. A solution of 2,2,4-trimethyl-1,3-pentanediol (XIII) in 250 ml. of 10% (by volume) sulfuric acid solution was steam distilled very slowly for 3 hr. A clear oil (6 g.) with a camphor-like odor steam distilled from the reaction. This was taken up in ether and washed with water and the solution was dried. Removal of ether and distillation of the residue gave 1.5 g. of colorless oil, b.p. 118–126°.[14] G.l.c. showed this material to be ~70% XVI. Both infrared and p.m.r. spectra of the pure ether, collected from the g.l.c. column, were compatible with XVI. The p.m.r. spectrum showed two pairs of uncoupled methyl resonances at δ = 1.08 and 1.20 p.p.m. and two unsplit methylene resonances at δ = 1.53 and 3.42 p.p.m.

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[13] Subsequent findings suggested that volatile A was probably 2,2,4,4-tetramethyltetahydrofuran (XVI), but this was not established.

[14] Franke[8] gives b.p. 120–122°.

Aralkyl Hydrodisulfides.[1] III. The Reaction with Tertiary Phosphines

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Received September 15, 1964

Triphenylmethyl hydrodisulfide, $(C_6H_5)_3CSSH$, is attacked on the sulfhydryl sulfur atom by tertiary phosphines (triphenyl- or triethylphosphine) and gives the phosphine sulfide and thiol in a manner similar to that reported for hydroperoxides. Benzhydryl or benzyl hydrodisulfide is attacked by the phosphine both on the sulfhydryl and sulfenyl sulfur atoms, in contrast to the results for hydroperoxides. Nucleophilic attack on the sulfenyl sulfur atom yields diaralkyl disulfide, hydrogen sulfide, and hydrocarbon, besides phosphine sulfide. Steric effects in the hydrodisulfide and thiophilicity of the nucleophile are the factors which govern whether the sulfhydryl or sulfenyl sulfur atom is attacked.

In previous papers of this series the free-radical, thermal decomposition of benzhydryl hydrodisulfide[1] and the reaction[3] of benzyl and benzhydryl hydrodisulfides with the free-radical scavengers were reported. Hydrodisulfides, RSSH, which can be considered the thio analogs of hydroperoxides, have not been studied in reference to nucleophilic attack, although hydroperoxides as well as organic polysulfides and some disulfides were reported to be cleaved by nucleophiles, for example, by tertiary phosphines and phosphites. Hydroperoxide is reduced to alcohol by tertiary phosphine, which in turn is oxidized to phosphine oxide.[4,5] In this work, aralkyl hydrodisulfides (RSSH: benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) were allowed to react with tertiary phosphines (R'_3P: triphenyl- or triethylphosphine) in order to examine whether the hydrodisulfide function behaves like hydroperoxide. Since empty d-orbitals of the sulfur atom may be utilized in bond formation by accepting electrons from phosphorus, sulfur is known to be more susceptible to attack by phosphine than is the oxygen atom.[6] In this respect, the nucleophilic reactions of tertiary phosphines with hydrodisulfide seem interesting.

Results and Discussion

In a stream of nitrogen a tertiary phosphine (triphenyl- or triethylphosphine) in ether was added dropwise, at room temperature, to an aralkyl hydrodisulfide (benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) in ether. The reverse addition of the reactants, that is, addition of benzyl hydrodisulfide to triphenyl-

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[1] Part II: T. Nakabayashi and J. Tsurugi, *J. Org. Chem.*, **28**, 813 (1963).

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