Organic Esters of Bivalent Sulfur. I. Dialkoxy Disulfides

Q. E. THOMPSON,[1a] M. M. CRUTCHFIELD,[1b] M. W. DIETRICH, AND E. PIERRON

Research Department, Organic Chemicals Division, Monsanto Company, St. Louis 77, Missouri

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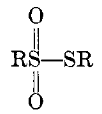
Organic esters of the hypothetical inorganic acid HOSSOH can be obtained in good yields by the action of sulfur monochloride on primary and secondary alcohols in the presence of tertiary amines. The simple acyclic esters have been shown to possess the unbranched dialkoxy disulfide (ROSSOR) structure. The activation energy for restricted rotation around the –S–S– bond of diethoxy disulfide was determined from the temperature dependence of the p.m.r. spectra to be 8.6 ± 1.7 kcal./mole.

Organic esters of two structural types, both formally derived from thiosulfurous acid, $H_2S_2O_2$, are recorded in the literature. One class, prepared recently by Zinner,[2] possesses the true thiosulfite structure, ROS(=O)SR, being derived from alkoxysulfinyl chlorides and mercaptans. Four members of a second class of so-called "thiosulfurous" esters[3] thought to possess the dialkoxy disulfide structure (I) have been known for many years.[4] The present paper is concerned with the preparation, reactions, and structures of these materials.

Whereas the Zinner thiosulfurous esters are derived from thionyl chloride, the parent acid chloride of the dialkoxy disulfides is sulfur monochloride. Indeed, dimethoxy and diethoxy disulfides were originally prepared[4] from the respective sodium alcoholates and sulfur monochloride in neutral medium. Despite having been discovered nearly 70 years ago, only the di-*n*-propyl and di-*n*-butyl esters have since been described.[5] Various alternatives (II, III, IV) to the linear disulfide structure I were considered by early workers.[5,6] Structures II[7] and III were readily eliminated, but a choice between I and IV was less clear. Raman spectra[6d,f] and dipole moment data[6d] favored the presently accepted[8] structure I, but IV, though unlikely on the basis of current thinking,[9a,b] could not be rigorously excluded. During the course of the present investigation, the question concerning unbranched *vs.* branched structures of products derived from alcohols and sulfur monochloride, represented by I and IV, respectively, again arose.

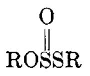
ROSSOR

I



$\mathrm{R\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}SR}$

II



$\mathrm{RO\overset{\overset{O}{\|}}{S}SR}$

III

$\mathrm{RO\overset{\overset{S}{\|}}{S}OR}$

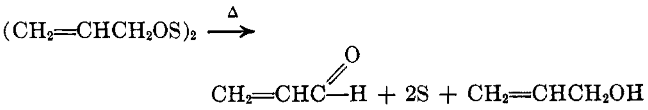
IV

The esters synthesized by earlier workers, and in fact all other recorded preparations,[10] involved the original Lengfeld[4] dry alkoxide method. In our hands this procedure was found to be reasonably satisfactory for making esters from the lower alcohols, but preparation of dry alcohol-free[10a,b] sodium alcoholates became increasingly troublesome with higher homologs. This difficulty was circumvented with surprising ease by allowing the alcohol to react with sulfur monochloride in chloroform or methylene chloride using tertiary amines as acid acceptors. Reaction proceeded

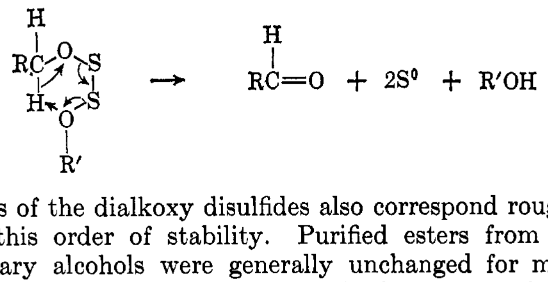
$$2ROH + S_2Cl_2 \xrightarrow{2Et_3N} ROSSOR + 2Et_3N{\cdot}HCl$$

smoothly at room temperature or below giving the corresponding ROSSOR compounds in high yield. The latter were sufficiently hydrolytically stable to permit aqueous extraction of the amine hydrochloride, thus greatly simplifying experimental procedures. Esters derived from common primary and secondary alcohols are listed in Table I.

Owing to sluggish and incomplete reaction, no pure esters of tertiary alcohols could be obtained. Appreciable thermal breakdown was often observed with certain crude esters. This tendency was less apparent with products derived from secondary than from saturated primary alcohols. The product from propargyl alcohol decomposed below room temperature and diallyloxy disulfide disproportionated smoothly to acrolein, allyl alcohol, and elemental sulfur during attempted distillations. Decomposition to alcohol and aldehyde was fairly common to all of the primary esters. The observed order of stabilities (secondary > primary > allyl) suggested that a cyclic transition state was involved in this elimination reaction. Shelf lives of the dialkoxy disulfides also correspond roughly to this order of stability. Purified esters from secondary alcohols were generally unchanged for many months at room temperature while those from primary



$$(CH_2{=}CHCH_2OS)_2 \xrightarrow{\Delta} CH_2{=}CH\overset{\overset{O}{/\!/}}{C}{-}H + 2S + CH_2{=}CHCH_2OH$$



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[1] (a) To whom inquiries should be addressed. (b) Research Department, Inorganic Chemicals Division.

[2] G. Zinner, *Angew. Chem.*, **69**, 508 (1957).

[3] As both sulfur atoms are in the bivalent state their classification in earlier literature as thiosulfurous esters is misleading. Dialkoxy disulfide terminology, *i.e.*, dimethoxy disulfide, diethoxy disulfide, etc., will be used in the present paper.

[4] F. Lengfeld, *Ber.*, **28**, 449 (1895).

[5] H. Stamm and H. Wintzer, *ibid.*, **70**, 2058 (1937).

[6] (a) A. Meuwsen, *ibid.*, **B68**, 121 (1935); (b) H. Stamm, *ibid.*, **68**, 673 (1935); (c) A. Meuwsen, *ibid.*, **B69**, 935 (1936); (d) G. Scheibe and O. Stoll, *ibid.*, **71**, 1573 (1938); (e) A. Clow, H. M. Kirton, and J. M. C. Thompson, *Trans. Faraday Soc.*, **36**, 1029 (1940); (f) M. Goehring, *Ber.*, **80**, 219 (1947).

[7] The conclusions of Clow, *et al.*,[6e] in favor of II cannot now be given credence in light of subsequent evidence.

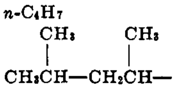
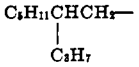
[8] M. Goehring and H. Stamm, *Angew. Chem.*, **A60**, 147 (1948).

[9] (a) *Cf.* O. Foss in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp. 75–77; (b) C. G. Krespan and W. R. Brasen, *J. Org. Chem.*, **27**, 3995 (1962).

[10] (a) A. Meuwsen and H. Gebhardt, *Ber.*, **B68**, 1011 (1935); (b) *ibid.*, **B69**, 937 (1936); (c) T. Whittelsey and C. E. Bradley, U. S. Patent 1,559,393 (1926); (d) A. R. V. Murthy, *Proc. Indian Acad. Sci.*, **A37**, 11 (1953); *Chem. Abstr.*, **47**, 12084 (1953).

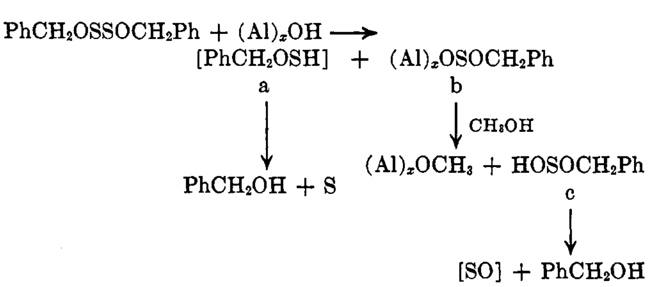
TABLE I

$$2ROH + S_2Cl_2 + 2R'_3N \longrightarrow ROSSOR + 2R'_3N{\cdot}HCl$$

R	B.p., °C. (mm.)	M.p., °C.	$n^{25}D$	Work-up procedure[a]	Yield, %	Formula	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S
i-C_3H_7	48 (1.2)	...	1.4658	A	71[b]	$C_6H_{14}O_2S_2$	39.53	7.74	35.18	39.31	7.70	35.10
n-C_3H_7	40 (0.45)	...	1.4750	A	74[b]	$C_6H_{14}O_2S_2$	39.53	7.74	35.18	39.27	8.00	35.39
n-C_4H_7	71 (0.65)	...	1.4740	A	70[b]	$C_8H_{18}O_2S_2$	45.68	8.62	30.48	45.93	8.84	30.58
 $CH_3\overset{CH_3}{\overset{\vert}{C}}H—CH_2\overset{CH_3}{\overset{\vert}{C}}H—$	87 (0.75)	...	1.4639	A	83[c]	$C_{12}H_{26}O_2S_2$	54.09	9.84	24.06	54.01	9.94	24.28
Cyclohexyl	...	...	1.5216	B	80[d]	$C_{12}H_{22}O_2S_2$	54.92	8.45	24.43	54.72	8.37	24.54
n-$C_{18}H_{37}$	...	50–51	...	B	85[d]	$C_{36}H_{74}O_2S_2$	71.69	12.37	10.63	71.63	12.42	10.53
n-$C_{12}H_{25}$	...	15–16	1.4692	D	85[d]	$C_{24}H_{50}O_2S_2$	66.29	11.59	14.75	66.41	11.79	14.72
n-C_8H_{17}	...	−22	1.4668	B	90[d]	$C_{16}H_{34}O_2S_2$	59.57	10.63	19.88	59.74	10.70	19.81
2-Ethyl-1-hexyl	147 (0.8) dec.	...	1.4721	B	85[d]	$C_{16}H_{34}O_2S_2$	59.57	10.63	19.88	59.64	10.66	20.00
 $C_5H_{11}\underset{C_3H_7}{\underset{\vert}{C}}HCH_2—$	...	...	1.4714	B	90[d]	$C_{20}H_{42}O_2S_2$	64.94	11.18	16.93	63.40	11.23	17.16
$C_2H_5SCH_2CH_2—$	135 (0.5) dec.	...	1.5473	C	70[d]	$C_8H_{18}O_2S_4$	35.00	6.61	46.72	34.94	6.79	46.54
$C_2H_5OCH_2CH_2—$	117 (1.1) dec.	...	1.4779	C	85[d]	$C_8H_{18}O_4S_2$	39.64	7.48	26.45	39.53	7.61	26.77
Cholesteryl	...	179–180 dec.	...	D	48[e]	$C_{54}H_{70}O_2S_2$	77.63	10.86	7.67	77.50	10.86	7.45
Benzyl	...	58–59	1.5974[f]	D	85[e]	$C_{14}H_{14}O_2S_2$	60.39	5.07	23.04	60.10	5.10	22.94
Allyl	...	...	1.5135	C	85[d]	$C_6H_{10}O_2S_2$	40.42	5.65	35.97	40.31	5.58	36.10

[a] See Experimental. [b] Determined from once-distilled material after correcting for impurities observed by g.l.c. [c] Determined as in *b* but estimated impurities by infrared spectra. [d] Estimated content of ROSSOR by comparison of infrared spectra of crude and pure materials. [e] Once-recrystallized material. [f] Determined on the supercooled liquid.

alcohols varied more in stability but could usually be stored indefinitely at 0°. The corresponding allyl and benzyl compounds decomposed in 1–2 months even at −5°. Because of their tendency to disproportionate internally on heating, distillation of esters containing more than 10–12 carbon atoms was seldom practical. In addition to small amounts of excess alcohol, the crude dialkoxy disulfides contained, as a primary impurity, 5–10% of the corresponding sulfite ester. Crude products not amenable to distillation or recrystallization could be purified by extraction with methanol. Sulfite ester and other more polar impurities migrated preferentially to the methanol phase. In general, acyclic dialkoxy disulfides were not stable to alumina. In the case of dibenzyloxy disulfide, two modes of decomposition were observed, depending on whether the alumina was basic or acidic. In the former case, a simple hydrolysis took place very probably according to the following sequence. After



placing the dibenzyloxy disulfide on an alumina column, one-half of the sulfur in the molecule was eluted rapidly. No other materials were obtained until methanol was added to the solvent system whereupon benzyl alcohol and approximately half of the remaining sulfur were then immediately obtained. Decomposition of the hydrolysis fragment a would account for the first sulfur observed. Collapse of fragment c, after it had been displaced from the alumina by methanol, would account for the rest of the sulfur arising presumably from a disproportionation of sulfur monoxide. On acidic alumina, the decomposition was less clean-cut but the major products were those of disproportionation, *i.e.*, benzyl alcohol, benzaldehyde, and sulfur.

Still another and more complex decomposition sequence was observed when homogeneous solutions (in chloroform) of dialkoxy disulfides and pyridine hydrochloride were allowed to stand for several days at room temperature. The major products from diisopropoxy disulfide were isopropyl sulfite (~30%), isopropyl alcohol, and elemental sulfur along with minor amounts of the ROSOR (sulfoxylate) ester.[11] The additional oxygen of the sulfite apparently came from an alkoxyl moiety. Independent experiments with the dibutyl ester indicated consumption of part of the chloride ion of pyridine hydrochloride and the formation of n-butyl chloride as an oxygen-free fragment.[12] Thus, the decomposition appears best described by the following sequence of reactions in which

$$2ROSSOR \overset{HCl}{\rightleftharpoons} 2ROSCl + 2(ROSH) \longrightarrow 2ROH + 2S^0$$

$$2ROSCl + 2ROH \longrightarrow 2ROSOR + 2HCl$$

$$ROSOR + HCl \rightleftharpoons ROCl + (ROSH) \longrightarrow ROH + S^0$$

$$ROCl + ROSOR \longrightarrow RCl + RO\overset{O}{\overset{\|}{S}}OR$$

75% of the sulfur is converted to the elemental state and the remainder is to be found as sulfite ester. Small amounts (~2–5%) of sulfoxylate ester, ROSOR, were almost always detectable among the products of the decomposition.

The simple dialkoxy disulfide esters underwent other reactions consistent with a labile -S–S- bond. Thus, treatment of dibenzyloxy disulfide with excess butyllithium gave n-butyl sulfide and benzyl alcohol as major products. Dimethoxy disulfide, when treated with 5,5-dimethyl-1,3-cyclohexanedione and catalytic amounts of potassium t-butoxide, gave the cyclohexyl sulfide V in 75% yield.

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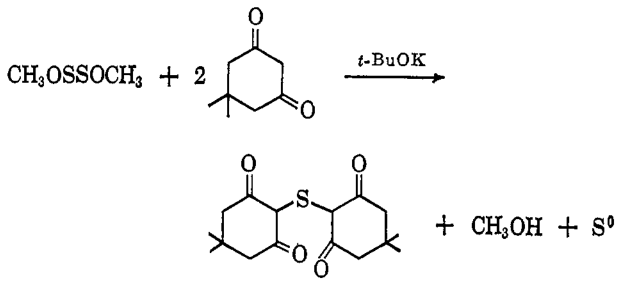
(11) Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965).

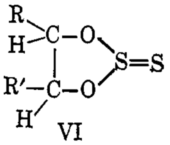
(12) Additionally, work-up of a reaction with O^{18}-labeled water indicated that the sulfite oxygen did not arise from this source.

$(PhCH_2OS)_2 + 4BuLi \longrightarrow 2PhCH_2OLi + 2Bu\text{-}S\text{-}Bu$



V

Aside from their inexplicably sluggish reactivity with ozone, first noted by Meuwsen[6c] and confirmed by us, there appeared to be no reason to question the correctness of the unbranched structure for the esters (*i.e.*, structure I *vs.* IV) at the onset of our work. Subsequent investigations of the esters obtained from sulfur monochloride and 1,2-diols revealed that the properties of these cyclic esters could only be explained on the basis of a five-membered structure (VI) with branch-bonded sulfur.[13] Consequently, the question of structure I *vs.* IV required additional consideration.

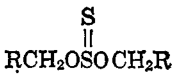


VI

$(C_3H_7O)_2S_2$
VIIa, isopropyl
b, *n*-propyl

$(i\text{-}C_3H_7O)_2S$
VIII

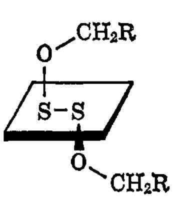
As pointed out by Foss,[9a] chemical methods cannot be relied upon to distinguish between the two possibilities. While work of earlier investigators[6d,f,8] had generally supported I, the evidence was inconclusive. A comparison of the ultraviolet absorption spectra of the isomeric dipropyloxy disulfides (VIIa, b) with the corresponding sulfoxylate ester VIII showed that VIII was transparent down to 190 mμ whereas both VIIa and b had $\lambda_{max}^{isooctane}$ 205 mμ (ϵ 2900). Other simple dialkoxy disulfides had comparable ultraviolet absorption but neither this fact nor the appearance of their infrared spectra were sufficient to resolve the structural question. On the other hand, p.m.r. spectroscopy of the simple esters afforded a means of distinguishing I from IV. Spectra of the ethyl, *n*-propyl, and butyl esters all revealed a nonequivalency of the methylene $R\text{-}CH_2\text{-}O\text{-}$ protons in the alkoxy moiety characteristic of methylene groups adjacent to an asymmetric center.[14] The much-studied case of diethyl sulfite[15] was of particular relevance to the present problem. Essentially, the p.m.r. spectrum of our diethoxy disulfide differed from that of diethyl sulfite only in a more pronounced nonequivalency of the methylene protons (shift differences of 0.19 p.p.m. for the neat diethoxy disulfide *vs.* 0.10 p.p.m. for diethyl sulfite in benzene solution). Superficially, this would seem to favor IXa over Xa since the tetrahedral sulfur of the -O-S(=S)-O- group would be directly comparable to that present in a sulfite. Disulfide linkages, however, are also asymmetric centers by reason of the nonplanarity of bond valences emanating from the two sulfur atoms and restricted rotation about the -S-S- bond.[16,17] This is illustrated by XI, in which mirror images are seen to be nonsuperimposable. Methylene protons adjacent to such an asymmetric system would thus be magnetically nonequivalent for reasons similar to the diethyl sulfite case. Because asymmetry in the disulfides is dependent upon a barrier of only about 8–14 kcal./mole[16,17] hindering free rotation, racemization, *i.e.*, free rotation, would be expected to be easily induced. Once the system has absorbed sufficient energy to overcome the rotational barrier and eliminate the asymmetric center, p.m.r. splittings arising therefrom would disappear.[18] One might, therefore, expect to distinguish between alternative structures IXa and Xa by observing the behavior of the methylene protons at elevated temperatures. The configurational stability of tetrahedral sulfur in sulfite esters[19] and that observed for cyclic thionosulfites[13] suggests that similar stability might also be expected of IXa. Thus, if the diethyl ester in fact had the branched structure, a persistent nonequivalency of methylene protons would be expected.



$RCH_2O\overset{\overset{\displaystyle S}{\|}}{S}OCH_2R$

IXa, R = CH_3
b, R = C_6H_5

$RCH_2OSSOCH_2R$
Xa, R = CH_3
b, R = C_6H_5



XI

Determination of the p.m.r. spectrum of diethoxy disulfide at various elevated temperatures did, indeed, show the disappearance of methylene proton nonequivalency. The complex ABX_3 pattern observed at 30° simplified to a typical A_2X_3 spectrum by 100°. The change in the methylene multiplet is shown in Figure 1. Moreover, the average lifetimes, *t*, in seconds, for the kinetic process which eliminates the nonequivalency was estimated according to described procedures[20] from the actual line shapes observed during initial peak coalescence and subsequent peak narrowing for seven temperatures in the range 30 to 100°. The activation energy for the rotational process was then determined from an Arrhenius plot of log $(1/t)$ *vs.* the reciprocal absolute temperature (see Figure 2). The slope of the best least-squares line through the data yielded an activation energy of 8.6 ± 1.7 kcal./mole with the uncertainty limits indicating statistical 90% confidence limits. Since this value falls within the range expected for restricted

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[13] Evidence in support of this is presented in the second paper of this series: Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich, *J. Org. Chem.*, **30**, 2696 (1965).

[14] H. S. Gutowsky, *J. Chem. Phys.*, **37**, 3751 (1962); G. M. Whitesides, F. Kaplan, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **48**, 112 (1962); E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).

[15] H. Finegold, *Proc. Chem. Soc.*, **283** (1960); J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4666 (1961).

[16] See ref. 9a, pp. 77, 78.

[17] G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961).

[18] *Cf.* the similar case of restricted rotation in biphenyls: W. L. Meyer and R. B. Meyer, *ibid.*, **85**, 2170 (1963).

[19] (a) J. G. Pritchard and P. C. Lauterbur, *ibid.*, **83**, 2105 (1961); P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 5307 (1963). (b) We have confirmed the persistent nonequivalence of methylene protons in diethyl sulfite[11] by p.m.r. measurements at 145°.

[20] (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 220–225; (b) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

rotation around unbranched disulfide linkages,[16,17] structure Xa is strongly indicated as the correct structure. As an independent check on our conclusions that acyclic esters in general possess unbranched sulfur linkages (I), the crystalline benzyl ester Xb was examined by X-ray powder and single crystal techniques. Results are summarized in Table II. The molecule possesses a center of symmetry and appears to contain the unbranched -S-S- linkage. Examination of various types of molecular models showed the fit into the unit cell volume to be good for Xb but poor for the alternative branch-bonded structure IXb. Thus, we conclude that early workers were correct in assigning the unbranched ROSSOR structure to the acyclic esters obtained by Lengfeld.[4]

Table II

Crystallographic Data on Dibenzyloxy Disulfide (Xb)

Crystal lattice	Orthorhombic
Space group	Pmmm-D_2^1
Unit cell dimensions	a_0 = 15.580 Å.
	b_0 = 14.292 Å.
	c_0 = 11.414 Å.
Unit cell volume	2541.5 Å.^{3}
Unit cell content	8[$C_{14}H_{14}O_2S_2$]
Density	
Calcd.	1.435
Found	1.455

Experimental[21]

General Procedure for Preparation of Acyclic Dialkoxy Disulfides.—Slightly more than 1 mole (*ca.* 1.05 moles)[22] of the alcohol along with 102 g. (~1 mole) of triethylamine was dissolved in 300 ml. of dry methylene chloride.[23] To this well-stirred solution at 10–15° was added 67.5 g. (0.5 mole) of sulfur monochloride diluted with 150 ml. of methylene chloride at a rate regulated to keep the temperature in the 5–15° range. Addition usually required approximately 1 hr., after which the reaction was stirred another 15 min. with no external cooling. Ice–water (500 ml.) was then added to the reaction vessel and the layers were separated. The organic layer was washed with three 250-ml. portions of ice–water to remove amine hydrochloride. The methylene chloride solution was then dried with Drierite and the solvent was removed under reduced pressure using a rotating evaporator. The residual ester (usually a reddish oil) was then purified by one of the following methods depending on its physical properties.

Purification Procedures for Dialkoxy Disulfides. Procedure A.—Esters sufficiently stable to be distilled under reduced pressure were best purified by an initial rapid distillation followed by subsequent fractionations. In every case encountered, the corresponding sulfite ester, usually boiling a few degrees lower than the dialkoxy disulfide, was the principal impurity along with small amounts of elemental sulfur.

Procedure B.—Noncrystalline esters insufficiently volatile to distill without appreciable decomposition were purified by stirring several minutes at room temperature with 2–5 vol. of methanol. Hydroxylic material, sulfite ester, triethylamine, and other polar impurities were preferentially soluble in the methanol phase. Three methanol extractions were usually sufficient to effect essentially complete purification. The dialkoxy disulfide was then warmed under reduced pressure to remove traces of the solvent. Finally, the ester was dissolved in 10–20 vol. of hexane and chromatographed on an activated charcoal column to eliminate minor amounts of colored impurities. Removal of hexane gave a colorless ester of analytical purity.

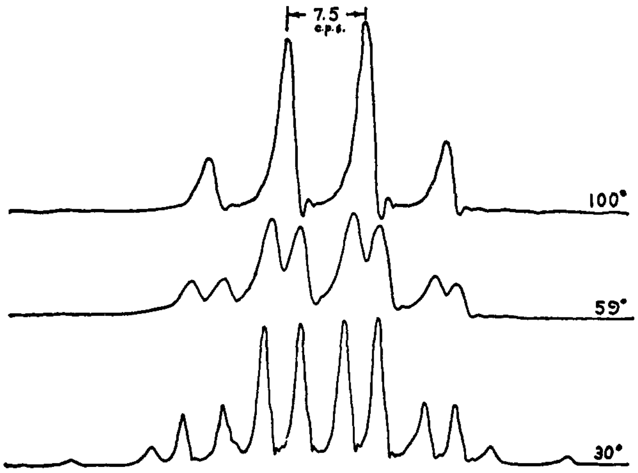

Figure 1.—Temperature dependence of the methylene proton resonance band for neat diethoxy disulfide.

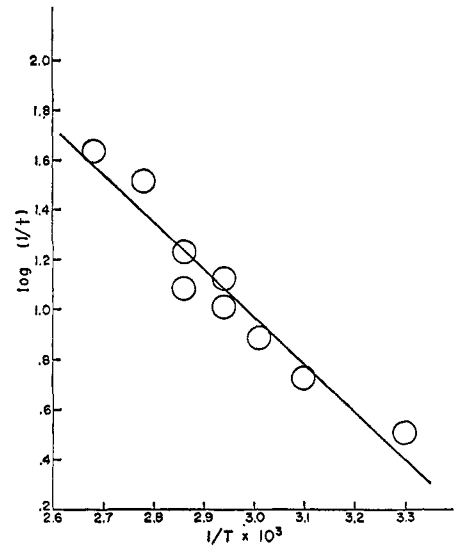

Figure 2.—Arrhenius plot for restricted rotation about the disulfide -S-S- bond in diethoxy disulfide.

Procedure C.—Dialkoxy disulfide esters derived from ethylene glycol monoethyl ether, its ethylthio analog, and allyl alcohol could not be distilled satisfactorily and were too methanol-soluble for procedure B. A few grams of each of these ROSSOR esters were purified by chromatography on an activated carbon column (12–40-mesh coconut charcoal) using hexane or pentane as the eluent.

Procedure D.—Solid esters recrystallized in the usual way included dicholesteryloxy disulfide (methylene chloride) and dibenzyloxy disulfide (hexane–*t*-butyl alcohol). Di-*n*-dodecyloxy disulfide was recrystallized from hexane at low temperatures.

Reactions of Dibenzyloxy Disulfide. A. Decomposition on Alumina.—Two grams (7.2 mmoles) of dibenzyloxy disulfide in hexane was placed on 55 g. of basic alumina (Woelm) and elution was begun. The only material passing through the column was elemental sulfur, 227 mg. (7.1 mmoles). The column was then eluted with ether but no significant weight of material was obtained until a mixture of methanol and ether was used. Immediately, ~100 mg. of elemental sulfur was

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(21) Melting points are uncorrected. Gas chromatography was carried out using either an Aerograph Model A-90P instrument attached to a 1-mv. Brown recorder equipped with a disk chart integrator. Except as otherwise specified, column packing was 20% LAC-3R-728 polyester (Cambridge Industries Co., Inc., Cambridge, Mass.) or neopentyl glycol succinate polyester (Wilkins Instrument Co.) supported on siliconized Chromosorb W. Percentages of composition determined by g.l.c. were calculated on a simple area ratio basis without internal standards and thus are somewhat approximate. Infrared spectra were obtained with a Perkin-Elmer Infracord, or a Perkin-Elmer Model 221 instrument. P.m.r. spectra were obtained with Varian HR-60 or A-60 spectrometers. The latter was equipped for variable temperature work.

(22) In a single exception, 0.2 mole of cholesterol, 0.2 mole of triethylamine, and 0.1 mole of sulfur monochloride were caused to react in more dilute solution with volumes of solvent, etc., essentially the same as described herein for preparation on a molar scale.

(23) Alcohol-free chloroform was preferable in the rare cases where the dialkoxy disulfide crystallized out during the reaction.

obtained followed by 1.3 g. of essentially pure benzyl alcohol. The latter was identified by its g.l.c. retention time and infrared spectrum.

In a second experiment identical with the first except that acidic alumina was used, approximately 135 mg. (4.2 mequiv.) of sulfur was obtained immediately followed by 320 mg. of benzaldehyde. Finally, by eluting with ether–methanol, approximately 300–400 mg. of benzyl alcohol was obtained. The latter materials were again identified by their g.l.c. retention times.

B. **Reaction with Butyllithium.**—To 28 g. (100 mmoles) of dibenzyloxy disulfide in 200 ml. of ether was added dropwise, at 0°, 124 ml. of 1.62 *M* butyllithium in hexane. When addition was complete, the mixture was stirred for 1 hr. Water (300 ml.) was added and the layers were separated. After an additional wash, the organic layer was dried and the solvent was fractionated. A yellow oil (40 g.) remained which was distilled, giving 32.5 g. of pale yellow oil, b.p. 40–135° (11 mm.). Gas chromatography of this distillate revealed five components, all of which were readily identified by comparison of their retention times and infrared spectra with authentic materials. The identity and approximate quantity (in millimoles) of each component was as follows: di-*n*-butyl sulfide (61), di-*n*-butyl disulfide (13), di-*n*-butyl trisulfide (4), benzyl alcohol (184), and benzaldehyde (8). Thus, most of the benzyl groups, but only about half of the sulfur, appeared in the volatile products.

Bis(2,6-diketo-4,4-dimethylcyclohexyl) Sulfide (V).—Dimethoxy disulfide[10a] (3.15 g.) and 3.5 g. of 5,5-dimethyl-1,3-cyclohexanedione were mixed in 30 ml. of dry tetrahydrofuran under nitrogen. Potassium *t*-butoxide solution (0.5 ml., 1 *N*) in *t*-butyl alcohol was added and the mixture was refluxed on a steam bath for 6 hr. A white solid separated gradually over this period. The crystals (V), when collected by filtration, washed with tetrahydrofuran and water, and then dried, weighed 2.92 g. (75%), m.p. 224–230°. Another 400 mg. of impure V, along with some elemental sulfur, was obtained from the filtrate. Two recrystallizations of the main crop from dioxane gave pure V, m.p. 230–231°.[24]

Anal. Calcd. for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.15; S, 10.33. Found: C, 61.86; H, 7.17; S, 10.32.

Decomposition of Dialkoxy Disulfides by Pyridine Hydrochloride. A. Diisopropoxy Disulfide.—A sample of very pure diisopropoxy disulfide (36.4 g. or 200 mmoles) in 300 ml. of dry methylene chloride was treated with 200 mmoles of dry pyridine hydrochloride. The latter was prepared by addition of a standard hydrogen chloride–ether solution to the calculated amount of pyridine followed by removal of ether. The mixture was stirred for 64 hr. at room temperature. A sticky yellow precipitate, primarily elemental sulfur, separated. Water (100 ml.) was added to wash out pyridine hydrochloride. The gummy precipitate (about 10 g.) was removed by filtration. After two additional washes, the organic layer was dried with Drierite and the solvent was removed by fractional distillation. An orange liquid, 18 g., remained from which a few crystals of sulfur separated on standing. G.l.c. showed the presence of five components, all of which were readily identified by suitable comparisons of their g.l.c. retention times and infrared spectra with authentic materials. The per cent composition of the residue was as follows: isopropyl alcohol, 21%; diisopropyl sulfoxylate,[11] 6.2%; pyridine, 16.1%; isopropyl sulfite, 61.5%; and unchanged diisopropoxy disulfide, 7%.

The presence of free pyridine and the relatively large amount of sulfite ester suggested the consumption of hydrogen chloride during the reaction. A second decomposition using di-*n*-butoxy disulfide, described in B, was carried out to demonstrate this point.

B. **Di-*n*-butoxy Disulfide.**—Decomposition of 10 mmoles of di-*n*-butoxy disulfide by 9.5 mmoles of pyridine hydrochloride in 10 ml. of dry chloroform was carried out essentially as described in A. Using an identical solution except with *n*-butyl alcohol instead of the dialkoxy disulfide as a control, it was ascertained that 3.0 mmoles of chloride ion had been converted to nonionic chloride. G.l.c. examination of the volatile materials indicated the presence of *n*-butyl chloride but the amount could not be determined with accuracy in the presence of the relatively large quantity of chloroform solvent.

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[24] N. Kojola [*Suomen Kemistilehti*, **B13**, 20 (1940); *Chem. Abstr.*, **35**, 2477 (1941)] gives m.p. 234–235°.

Organic Esters of Bivalent Sulfur. II. Branch-Bonded Sulfur Esters from 1,2-Diols and Sulfur Monochloride[1]

Q. E. THOMPSON,[2a] M. M. CRUTCHFIELD,[2b] AND M. W. DIETRICH

Research Department, Organic Chemicals Division, Monsanto Company, St. Louis 77, Missouri

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A new class of cyclic sulfur esters has been obtained from the reaction of sulfur monochloride and simple 1,2-diols (ethylene and propylene glycols; *meso*- and *dl*-2,3-butanediol). These have been shown to possess the five-membered ring system I in which sulfur atoms are branch-bonded, *i.e.*, $>S{=}S$. The esters are thus thiono analogs of cyclic sulfites and like sulfites possess a tetrahedral sulfur at the branching position $>\ddot{S}{=}S$, $>\ddot{S}{=}O$. As a consequence, cyclic members of both classes are capable of isomerism depending on whether the double-bonded oxygen or sulfur atom is *cis* or *trans* to other ring substituents. Two such isomeric thionosulfites (XVIb and XVIIb) have been obtained in pure form from *meso*-hydrobenzoin. Proton magnetic resonance spectra of the major (XVIb) and minor (XVIIb) isomers are significantly different from each other but closely resemble the major (XVIa) and minor (XVIIa) cyclic sulfite isomers, respectively. *dl*-Hydrobenzoin yielded a single sulfite (XVb) and thionosulfite (XIVb) as expected. In all cases, yields of monomeric cyclic products were quite low, 5–44%. From 1,3-butanediol low yields of a very unstable cyclic ester XIX were obtained. The latter readily lost an atom of sulfur to give 6-methyl-1,3,2-dioxathiane (XXI).

The possibility that two or more sulfur atoms may be linked in a branched fashion, $>S{=}S$, as opposed to the usual linear –S–S– linkage has been a matter of debate for many years. The facile conversion of polysulfides to disulfides by alkalis or cyanides has often been adduced to indicate that the removable sulfur atoms were branched-bonded. Foss[3] has pointed out that the chemical behavior of polysulfides is, in fact, consistent with unbranched chain structures. The last 20 years has witnessed a mounting body of spectrochemical, X-ray, and other physical evidence contraindicating the possibility of branched sulfur bonding in any system heretofore examined. These results have been summarized by Foss.[4] Recent investiga-

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[1] Preliminary communication: Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich, *J. Am. Chem. Soc.*, **86**, 3891 (1964).

[2] (a) To whom inquiries should be addressed. (b) Research Department, Inorganic Chemicals Division.

[3] O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950).

[4] O. Foss, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, pp. 75–77.