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°.

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

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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).

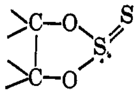
(2) (a) To whom inquiries should be addressed. (b) Research Department, Inorganic Chemicals Division.

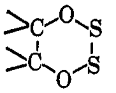
(3) O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950).

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

tions of sulfur monofluoride,[5] however, suggest that this molecule exists predominantly as $F{-}S({=}S){-}F$.

While studying the reaction between sulfur monochloride and 1,2-diols, cyclic sulfur esters were obtained to which only the branch-bonded five-membered ring system I can be ascribed.[6] Acyclic methyl and ethyl


I


II

ROSSOR

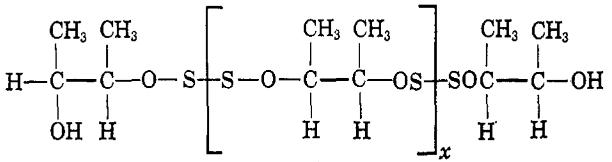
III


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

IV

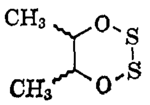
esters of structure III[7,8] have been known for many years.[9] In general, dialkoxy disulfides (*i.e.*, III) are most conveniently prepared by "acylation" of primary and secondary alcohols with sulfur monochloride in the presence of tertiary amines.

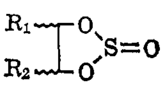
The present paper is concerned with the results obtained when this reaction was extended to 1,2-diols. In an effort to prepare the unknown 1,4,2,3-dioxadithiane ring system II, several common diols were allowed to react with sulfur monochloride under conditions previously employed with monohydric alcohols. Initial experiments, using *meso*-2,3-butanediol as the model glycol, showed that sulfur monochloride, when added to a diol–triethylamine mixture in methylene chloride, reacted smoothly. The products were low polymeric oils or glasses with gross composition corresponding roughly to V. Molecular weights varied between 600 and 1100 depending on the concentrations

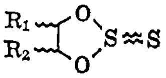

$$\mathrm{H{-}\underset{OH}{\overset{CH_3}{C}}{-}\underset{H}{\overset{CH_3}{C}}{-}O{-}S{-}\left[S{-}O{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{CH_3}{C}}{-}OS\right]_x{-}SO\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{CH_3}{C}}{-}OH}$$

V

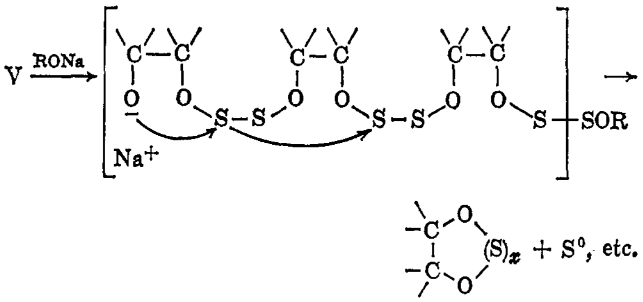
of the reactants. All crude polymers showed the presence of significant hydroxyl bands in the infrared and bands attributable to sulfite in the 1180–1240-cm.$^{-1}$ region. No significant monomeric products, *i.e.*, VIa or the corresponding cyclic sulfite VIIa, were


VIa, *cis*
b, *trans*


VIIa, $R_1 = R_2 = CH_3$ (*cis*)
b, $R_1 = R_2 = CH_3$ (*trans*)
c, $R_1 = R_2 = H$
d, $R_1 = H_1$; $R_2 = CH_3$


VIIIa, $R_1 = R_2 = CH_3$ (*cis*)
b, $R_1 = R_2 = CH_3$ (*trans*)
c, $R_1 = R_2 = H$
d, $R_1 = H$; $R_2 = CH_3$

obtained. Other common diols (*dl*-2,3-butanediol, propylene, and ethylene glycols, 1,3-butanediol and 1,4-butanediol) behaved similarly. The known susceptibility of ROS–SOR bonds[7] to nucleophilic attack suggested that an alkoxide-catalyzed intramolecular unzipping of the polymer molecule might be possible which would yield cyclic monomeric products. This proved



to be the case. Samples of the *meso*-2,3-butanediol polymer (V), when treated with catalytic amounts of the diol sodium alkoxide, degraded smoothly under reduced pressure at 80–120°. A mixture of cyclic sulfite VIIa, *meso*-2,3-butanediol, and a new compound, $C_4H_8O_2S_2$, distilled from the reaction mixture along with minor amounts of volatile products consisting primarily of acetoin and traces of biacetyl. A dark residue of tarry products and elemental sulfur remained. The new sulfur compound was at first thought to be VI, but subsequently it was found to be the branch-bonded thionosulfite VIIIa. The basis upon which the structure of the $C_4H_8O_2S_2$ material (and comparable products derived from related glycols) was assigned will be considered in detail shortly. For purposes of discussion, structure VIII, where the stereochemistry of the branch-bonded sulfur is unspecified, will be utilized. Aside from the product mentioned, no other sulfur-containing compounds were isolated from the polymer degradation. Both VIIa and VIIIa were stable to water, and both could be purified by conventional distillation and gas chromatographic techniques. Over-all yields of VIIIa were about 21%.

Since the molecular weights of the polymeric intermediate V decreased when prepared in more dilute solution, reaction of *meso*-2,3-butanediol and sulfur monochloride under high dilution conditions was carried out. This permitted the one-step preparation of VIIIa in 22% yield. Polymer was still the major product, however. Molecular weight determinations confirmed the monomeric nature of VIIIa. The latter was easily desulfurized with Raney nickel under very mild conditions to give pure *meso*-2,3-butanediol.[10] No carbonyl or hydroxyl bands were present in the infrared spectrum of VIIIa nor was there absorption in the 1180–1240-cm.$^{-1}$ region where sulfites absorb very strongly. Major bands around 1088, 893, 840, and 787 cm.$^{-1}$ were observed.[11] In contrast to acyclic

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[5] R. L. Kuczkowski and E. B. Wilson, *J. Am. Chem. Soc.*, **85**, 2028 (1963); R. L. Kuczkowski, *ibid.*, **85**, 3047 (1963); **86**, 3617 (1964); F. Seel, R. Budenz, and D. Werner, *Ber.*, **97**, 1369 (1964).

[6] Subsequent to our preliminary communication[1] Professor R. Creegee has indicated (private communication) that a number of glycol disulfur esters were prepared in his laboratory. The structure of these materials could not be assigned at that time.

[7] Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich, and E. Pierron, *J. Org. Chem.*, **30**, 2692 (1965).

[8] The question of structures III *vs.* IV has been considered in detail in the first paper of this series[7] and in references cited therein.

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

[10] Depending on desulfurization conditions, one could obtain the pure *meso*-diol or, on longer exposure times and larger excesses of nickel, mixtures of *meso*- and *dl*-2,3-butanediol. Steric isomerization of each of the pure diol forms was found to occur under the latter conditions.

[11] The four cyclic esters of structure VIII had strong infrared absorption bands in the 1000–1090-cm.$^{-1}$ region, at about 900 and ~825 cm.$^{-1}$ with very strong absorption below ~780 cm.$^{-1}$. As the corresponding cyclic sulfites have similar patterns in these regions, no satisfactory assignment of the fundamental symmetric and asymmetric stretching vibrations of the $>S{=}S$ group seems possible at this time. The $>S{=}S$ chromophore may absorb in the far-infrared somewhere below ~780 wave numbers. No spectra in this region have been determined.

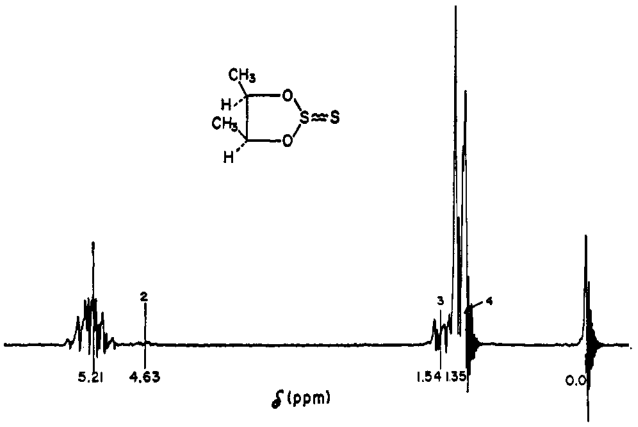


Figure 1.—P.m.r. spectrum of thionosulfite esters VIIIa from *meso*-2,3-butanediol; peaks 1 and 4, major isomer; peaks 2 and 3, minor isomer.

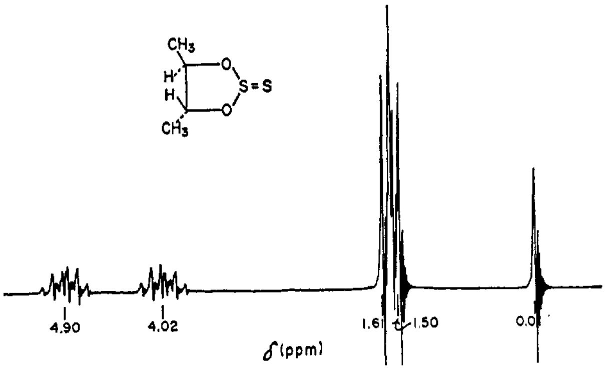


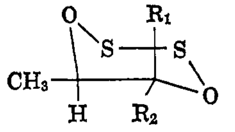
Figure 2.—P.m.r. spectrum of thionosulfite ester VIIIb from *dl*-2,3-butanediol.

compounds of structure III,[7] the cyclic sulfur ester exhibited appreciable absorption in the ultraviolet, $\lambda_{\max}^{\text{isooctane}}$ 255 m$\mu$ ($\epsilon$ 2549). While these observations were compatible with structure VI, p.m.r. spectroscopy eventually provided evidence to the contrary.

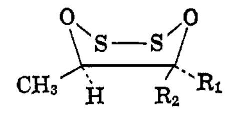
In the spectrum of VIIIa (Figure 1) both methyl groups of the molecule are seen to be equivalent. The relatively complex multiplet centered at 5.21 p.p.m.[12] representing the two ring protons is strikingly similar in appearance to that obtained from the sulfite ester isomers of VIIa.[13] Finally, despite the most careful attempts at purification, the p.m.r. spectrum of VIIIa indicated the presence of perhaps 5–10% of a structurally similar contaminant which appeared to be of the same empirical composition since elemental analyses were correct.

From *dl*-2,3-butanediol, the *trans*-dimethyl isomer VIIIb was readily prepared (43%). Although the latter resembled its *cis* counterpart closely, no difficulty was encountered in distinguishing the two from each other. In fact, ~2% of the *cis* isomer (resulting from a small but known amount of *meso* impurity in the *dl*-2,3-butanediol) was detected in crude VIIIb by g.l.c. Desulfurization of VIIIb yielded sterically pure *dl*-2,3-butanediol as the sole product thus indicating no alteration of the original diol structure. Molecular weight determinations and infrared and ultraviolet spectra, $\lambda_{\max}^{\text{isooctane}}$ 257 m$\mu$ ($\epsilon$ 2446), supported the conclusion that VIIIb differed from VIIIa only in the *trans* relationship of the methyl groups.

The p.m.r. spectra of VIIIb (Figure 2) and VIIIa were strikingly different. The *trans*-methyl groups as well as the two methenyl protons at 4.0 and 4.90 p.p.m. were notably nonequivalent. In addition, the spectrum of VIIIb closely resembled that of the corresponding sulfite VIIb. The p.m.r. spectra of the *cis* and *trans* isomers were essentially constant throughout the temperature range −40 to 158°. This evidence militates against a 1,4,2,3-dioxadithiane structure (VIb) for VIIIb since the former would be expected to exist as the chair conformer IXa in which both of the ring protons and the two methyl groups would be equivalent. In the case of the *cis* isomer IXb, the methyl groups and ring protons would likewise appear equivalent provided conformational inversion occurred sufficiently rapidly at −40° to prevent detection of the individual conformers. Although the boat conformation X would account for the nonequivalence of methyl groups and ring protons observed in the *trans* isomer, this structure would not be expected to retain its rigidity at elevated temperatures as is indicated by the p.m.r. spectra. Furthermore, a boat conformation X would require that the dihedral angle between the two sulfur–oxygen bonds be essentially zero. Aside from all other considerations, this is unfavorable by at least 8 kcal./mole[10,14,15] compared to the preferred angle of approximately 90°.[5] Further evidence that the products from 1,2-diols and sulfur monochloride were representatives of a new class of cyclic thionosulfites (I) was obtained on examination of the p.m.r. spectrum of the parent compound VIIIc from ethylene glycol. The latter was a mobile lachrymatory liquid which, like ethylene sulfite,[16] exhibited a clean $A_2B_2$ p.m.r. pattern centered at about 4.6 p.p.m. Propylene glycol was readily converted to a comparable disulfur ester VIIId, the p.m.r. spectrum of which suggested strongly that it was a mixture of two isomeric com-



IXa, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$



Xa, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$

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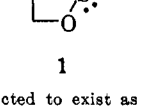
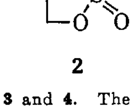
(12) P.m.r. data are reported in parts per million downfield from tetramethylsilane as zero.

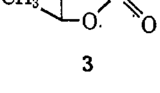
(13) Since the isolation of stable propylene glycol isomers by J. G. Pritchard and P. C. Lauterbur [*J. Am. Chem. Soc.*, **83**, 2105 (1961)] it has become clear that isomerism due to the >S=O oxygen atom may occur when cyclic sulfites contain groups attached to the ring carbon atoms. [See also P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 5307 (1963).] Thus, from propylene glycol, Pritchard and Lauterbur were able to isolate the two sulfites **1** and **2**. The sulfite ester of *meso*-2,3-butanediol would be



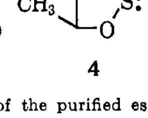
**1**



**2**



**3**



**4**

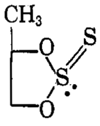
expected to exist as **3** and **4**. The p.m.r. spectrum of the purified ester clearly indicated a mixture of isomers. We were unable to effect their complete separation by g.l.c., but one isomer in approximately 90% steric purity was obtained. In any case, except for differences in chemical shift, the appearance of the multiplets representing the methenyl protons in **3**, **4**, and our compound VIIIa were essentially identical.

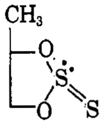
(14) G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961).

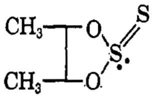
(15) See ref. 4, pp. 77–79.

(16) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "N.m.r. Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, No. 371.

pounds in approximately a 4:1 ratio. Again the p.m.r. spectrum was unchanged when determined at 158°. The lack of any detectable equilibrium between the two components of the mixture suggested strongly that two ($\beta$ and $\alpha$) thionosulfite isomers[17] (XI and XII), analogous to the sulfite isomers isolated by Pritchard and Lauterbur,[13] were present. Similarly, the minor

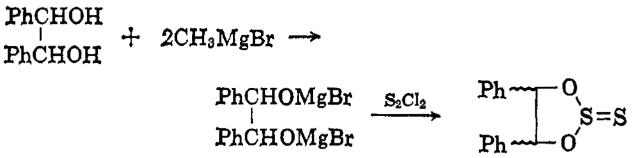

XI


XII


XIII

"impurity" observed in VIIIa seemed most likely to be one of the two thiono isomers (presumably the all-$\beta$ structure XIII) expected of VIIIa. Powerful evidence in support of this thesis was obtained when attention was directed to the hydrobenzoin system.

Reaction of *meso*-hydrobenzoin and sulfur monochloride under a variety of conditions failed to give satisfactory results. At high dilution, sulfur monochloride failed to react completely. Using ordinary conditions, the polymeric ester could not be degraded in a manner permitting the isolation of the desired monomeric products. Success was eventually achieved by conversion of the diol to its dimagnesium alkoxide. Reaction of the latter with sulfur monochloride under high dilution conditions produced a crude monomeric



XIVa, *cis*-phenyls
b, *trans*-phenyls

product (XIVa) in approximately 44% yield. From crude XIVa *two crystalline compounds of* $C_{14}H_{12}O_2S_2$ *composition could be isolated.* These consisted of a major isomer, m.p. 80–81°, and a minor isomer, m.p. 89–90°. Analysis and molecular weight determinations confirmed their empirical composition and monomeric nature. Desulfurization of each isomer under mild conditions produced pure *meso*-hydrobenzoin. The p.m.r. spectra of the two isomers (Figure 3) were quite different both in the appearance of the aromatic protons and in the chemical shifts of methenyl proton singlets. Assuming the two crystalline $C_{14}H_{12}O_2S_2$ compounds to be structure XIVa, one isomer then would have the branched sulfur atom located on the same side of the five-membered ring as the phenyl groups while the sulfur atom in the second isomer would reside on the opposite side. The corresponding sulfite of *meso*-hydrobenzoin would also be expected to exist in two comparable isomeric forms.[13,18] This proved to be the case. The p.m.r. spectrum of crude XVa clearly showed the presence of two isomers in approximately

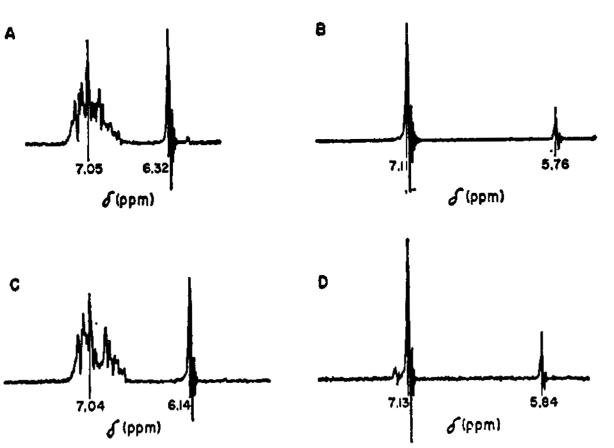
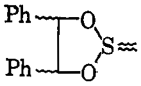


Figure 3.—P.m.r. spectra of ester from *meso*-hydrobenzoin: (A) major thionosulfite isomer, XVIb; (B) minor thionosulfite isomer, XVIIb; (C) major sulfite isomer, XVIa; (D) minor sulfite isomer, XVIIa.


XVa, *cis*-phenyls
b, *trans*-phenyls

a 9:1 ratio. The major isomer, m.p. 130–131°, was easily obtained by recrystallization from ether in which the minor isomer appeared to be slightly more soluble. Chromatography on alumina provided a pure sample of the latter, m.p. 129–130°. The p.m.r. spectra of the major and minor sulfite isomers correspond almost exactly to the respective isomers of XIVa as shown in Figure 3. The isolation of two stable thionosulfite isomers of XIVa and their similarity to the corresponding cyclic sulfites XVa constitute the most compelling evidence in favor of branched sulfur bonding heretofore obtained. Finally, in order to exclude any possibility that the so-called minor isomers were merely *trans*-phenyl analogs, *i.e.*, XIVb and XVb, respectively,[19] the latter were prepared from *dl*-hydrobenzoin. In each case only the required single isomer was obtained. Their p.m.r. spectra were essentially identical and each showed the expected nonequivalence of the methenyl protons.

The striking similarities between the thionosulfite isomers XIVa and the sulfites XVa suggest that, with respect to the *cis*-phenyl groups, the stereochemistry of the >S=S and >S=O functions are identical for the major and the minor isomers, respectively, of each series. There exist at least two bases upon which a tentative assignment of S=O stereochemistry may be arrived at in XVa isomers. Pritchard and Lauterbur[13] have calculated directional effects on the p.m.r. shifts caused by the electric field and the diamagnetic anisotropy of the S=O bond. These suggest that, in ethylene sulfite derivatives, protons *cis* to the >S=O oxygen are shifted to lower field compared to *trans*-protons. The major isomers of both XVa and XIVa are seen to have methenyl protons at considerably lower field than their respective minor isomers. On this basis, the major isomers can be assigned structures

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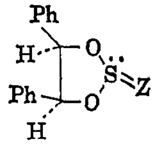
[17] A more rigorously correct name for the new class of compounds represented by XI might be 4$\beta$-methyl-1,3,2-dioxathiolane 2-$\beta$-sulfide. Because of their close structure and stereochemical analogy to sulfite esters, we prefer the thionosulfite terminology used herein. The $\alpha$ (down) and $\beta$ (up) notations commonly employed in steroid chemistry are used to denote steric relationships of ring substituents.

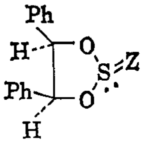
[18] Melting point variations reported for the *meso*-sulfite suggest this possibility: (a) C. C. Price and G. Berti report m.p. 126–128° [*J. Am. Chem. Soc.*, **76**, 1211 (1954)]; (b) Z. Kitasoto and C. Sone report m.p. 127–129° [*Ber.*, **64**, 1142 (1931)]; D. Reulos and S. LeTellier report m.p. 131° [*Compt. rend.*, **217**, 698 (1943)].

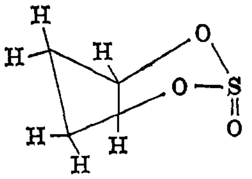
[19] An unlikely possibility in the case of the *trans* sulfite, since XVb has been reported to melt at 84–86°.[18a,c]

XVIa and XVIb while minor isomers would be XVIIa and XVIIb.

Assignments based on the infrared >S═O stretching frequency of the sulfites are in accord with this interpretation. The preference of the S═O oxygen in trimethylene sulfite derivatives for the axial position has been shown by Hellier, *et al.*[20] In fact, in the parent compound, only one conformation (XVIII) can be detected. Restriction of the S═O group to the axial position may be attributed to interaction of the sulfinyl oxygen with axial hydrogens in the 1,3-positions.[21] As a consequence of these effects, the axial >S═O stretching frequencies (∽1190 cm.$^{-1}$) are lower than the frequencies (∽1230 cm.$^{-1}$) of equatorial S═O groups which are devoid of such interaction. Assuming these factors to be operative in ethylene sulfite, that sulfite isomer of XVa possessing the lowest S═O stretching frequency would be assigned structure XVIa whereas the isomer with the higher stretching frequency would be XVIIa. In agreement with conclusions drawn previously, the major sulfite isomer (presumably XVIa) showed S═O absorption at 1220 cm.$^{-1}$ while that of the minor sulfite appeared at 1230 cm.$^{-1}$.

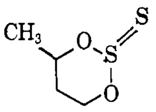

XVIa, Z=O
b, Z=S

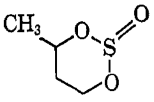

XVIIa, Z=O
b, Z=S

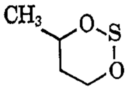

XVIII

The shapes of aromatic p.m.r. peaks represent the most striking difference between the major (XVI) and minor (XVII) isomers of each class. The complex multiplets of XVIa and XVIb appear to be characteristic for the *cis*-phenyl groups in other cyclic esters (carbonate, trithiocarbonate) derived from *meso*-hydrobenzoin.[22] Aromatic protons of the corresponding *trans*-phenyl analogs appear as sharp singlets. *cis* and *trans* isomers of 1,2-diphenylcyclopentane and 3,4-diphenylcyclopentanone appear also as multiplets and singlets, respectively.[23] Apparently, increased crowding in the all-*cis* minor isomers (XVII) is sufficient to spread the phenyl groups so their protons appear equivalent as in the *trans*-phenyl analogs.

Reaction of sulfur monochloride with 1,3- and 1,4-diols was investigated briefly. 1,3-Butanediol gave primarily a low polymeric condensation product. Alkoxide-catalyzed degradation of this material afforded low yields of the desired $C_4H_8O_2S_2$ cyclic ester XIX along with the corresponding cyclic sulfite XX and a third neutral sulfur ester identified as the cyclic sulfoxylate XXI.[24] Assignment of the branched sulfur structure XIX was made primarily on the basis of its absorption in the ultraviolet, $\lambda_{\max}^{\text{isooctane}}$ 244 m$\mu$ ($\epsilon$ 1230).[25] Compound XIX proved to be extremely unstable. One atom of sulfur was lost with ease, affording the more stable sulfoxylate XXI. The tendency to lose sulfur increased with increasing purity of XIX. Light catalysis appeared also to play a part in the transformation. Attempts to prepare a higher homolog of XIX from 1,4-butanediol resulted only in polymers from which no cyclic monomeric products could be obtained.


XIX


XX


XXI

Foss[3] has discussed in detail the distinction between $^{X}_{X}{>}S\rightarrow S$ and $^{X}_{X}{>}S{=}S$ branched bonding. According to this rationale, coordinated >S→S bond formation would require the X substituents to be strongly electron donating. Formation of the double bonded >S═S group, on the other hand, requires the expansion of the octet of the central sulfur atom. This would be favored only by strongly electron-withdrawing X substituents. Observations[5,6] concerning the structure of sulfur monofluoride and our results fulfill the dictum of Foss[3] that "the divalent sulphur compounds most susceptible to add sulphur to form double bonds >S═S should be monosulphur difluoride, dichloride, and monosulphur dialkoxides."

## Experimental[26]

**Preparation of Pure *meso*- and *dl*-2,3-Butanediols.**—Two liters of commercial[27] synthetic 2,3-butanediols consisting of an approximately equal mixture[28] of *meso* and *dl* isomers was subjected to careful fractionation at reduced pressure.

The slightly more volatile *dl* isomer was concentrated in the early cuts and the *meso*-diol in the residues. As the progress of separation was easily followed by g.l.c., no difficulty was experienced in obtaining *dl*-2,3-butanediol in ∼98% steric purity by systematic collection, recombination, and refractionation of appropriate cuts. Residues rich in the *meso* isomer were recrystallized repeatedly from isopropyl ether as recommended by Wilson and Lucas[29] until a constant-melting (33–34°) material was obtained. G.l.c. indicated the *meso*-diol to be of >98% steric purity.

**Cyclic 1β,2β-Dimethylethylene Thionosulfite (VIIIa). A. In Concentrated Solution.**—A mixture of *meso*-2,3-butanediol (90.1 g.), 204 g. of triethylamine, and 500 ml. of dry methylene chloride was cooled to 10° with good stirring. A solution of 135 g. of sulfur monochloride in 150 ml. of methylene chloride was

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(20) D. G. Hellier, J. G. Tillett, H. F. Von Woerden, and R. F. M. White, *Chem. Ind.* (London), 1956 (1963).

(21) *Cf.* S. E. Forman, A. J. Durbetaki, M. V. Cohen, and R. A. Olofson, *J. Org. Chem.*, **30**, 169 (1965).

(22) C. G. Overberger and A. Drucker, *ibid.*, **29**, 360 (1964).

(23) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961); **84**, 836 (1962).

(24) See Q. E. Thompson [*J. Org. Chem.*, **30**, 2703 (1965)] for the preparation of this and other ROSOR compounds *via* the reaction of alcohols and sulfur dichloride.

(25) That this does not necessarily exclude the unbranched –OSSO– structure is recognized. At best the assignment of XIX is tentative.

(26) Melting points are uncorrected. Gas chromatography was done using either an Aerograph Model A-90C or a Model A-90P instrument attached to a 1-mv. Brown recorder equipped with a disk chart integrator. Except as otherwise specified, the 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. N.m.r. spectra were obtained with Varian HR-60 or A-60 spectrometers. The latter was equipped for variable-temperature work. Molecular weights were determined using a Mecrolab vapor pressure osmometer, Model 301.

(27) Eastern Chemical Corp., Pequannock, N. J.

(28) Satisfactory resolution of the isomers was achieved using a 2 m. × 0.25 in. g.l.c. column packed with 20% Carbide and Carbon polypropylene glycol 1025 on 30–60-mesh Chromosorb P. Under optimum conditions, retention time of the *dl* isomer was approximately 9.4 min. and that of the *meso* isomer 10.5 min. with a column temperature of 137°. Packings described in footnote 24 failed to resolve the two isomers.

(29) C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, **58**, 2396 (1936).

added slowly over about 2 hr. while keeping the temperature at 10–15°. When addition was complete, the slurry was stirred for an additional 15 min. Cold water (500 ml.) was then added and the organic layer was separated. After several additional water washes, the methylene chloride solution was dried with Drierite and the solvent was removed under reduced pressure in a rotating vacuum evaporator. A red viscous oil (147 g.) remained. Its infrared spectrum showed the presence of some hydroxyl and sulfite ($>S{=}O$ at 1212 cm.$^{-1}$) groups. These observations and its average molecular weight (845) suggested that the crude material was a low polymer, primarily structure V, with some sulfite bridging between the monomer units.

*Anal.* Calcd. for $(C_4H_8O_2S_2)_x$: C, 31.56; H, 5.30; S, 42.13. Found: C, 31.38; H, 5.43; S, 40.80.

The crude polymer (145 g.), contained in a three-necked flask equipped with a heavy paddle stirrer and set up for short-path distillation at <1-mm. pressure, was treated with 10 ml. of *meso*-2,3-butanediol in which 500 mg. of metallic sodium had been dissolved. On application of heat and reduced pressure, a colorless product began to distill at ~54° (0.5 mm.). Distillation was continued for about 2 hr. with the pot temperature climbing slowly to 120°. The infrared spectrum of the crude distillate showed the presence of large amounts of alcohols. The latter were removed by dissolving the distillate in 200 ml. of hexane and washing several times with water. The hexane solution was dried with Drierite and the solvent was removed, leaving 41 g. of a thin, pale yellow liquid. G.l.c. analysis showed ~4% of low and high boiling materials, 21% of a compound subsequently identified as the diol cyclic sulfite VIIa, and 75% of a material eventually identified as VIIIa. On this basis, the overall yield of VIIIa from the starting diol was approximately 21%. About 5 g. of pure cyclic 1β,2β-dimethylethylene thionosulfite (VIIIa), b.p. 36° (0.13 mm.), $n^{25}D$ 1.532, $\lambda_{\max}^{\text{isooctane}}$ 255 mμ (ε 2549), was obtained after three fractionations through a 15-plate column. Samples of pure material could be stored in a refrigerator for several years without decomposition.

*Anal.* Calcd. for $C_4H_8O_2S_2$: C, 31.56; H, 5.30; S, 42.13; mol. wt., 152. Found: C, 31.50; H, 5.55; S, 41.88; mol. wt., 162.

The lower boiling cyclic sulfite was also obtained pure; it was readily identified by comparison of its g.l.c. retention times and infrared spectrum with those of authentic material obtained by reaction of thionyl chloride and *meso*-2,3-butanediol. Examination of volatile materials collected in various Dry Ice traps indicated that acetoin was the major volatile by-product (identification by g.l.c. retention times, infrared spectrum, and its semicarbazone).

B. **High Dilution Method.**—A mixture of 45 g. of *meso*-2,3-butanediol and 102 g. of triethylamine was diluted to 500 ml. with dry methylene chloride in a 500-ml. graduated dropping funnel. Sulfur monochloride (67.5 g.) was similarly diluted in a second funnel. One liter of alcohol-free chloroform was placed in a 3-l. reaction vessel and cooled to 5–10°. Slow concurrent addition of the two solutions was begun with addition of the glycol–amine mixture very slightly ahead of the addition of sulfur monochloride. Slow addition with rapid agitation was maintained over about 5 hr. When admixture had been completed the solution was stirred for an additional hour before quenching with 700 ml. of cold water. The organic layer was washed free of amine hydrochloride and dried, and the solvent was removed as in procedure A. The thin reddish oil remaining (75 g.) was subjected immediately to vacuum distillation. A pale yellow oil (27 g.), b.p. 57–62° (1.1 mm.), distilled from the pot, the temperature of which gradually increased to 128°. The thick residue remaining was treated with about 5 ml. of sodium alcoholate as described in method A. Only 5.5 g. of additional distillate was obtained in this attempt to degrade the polymers present. G.l.c. analysis indicated that this distillate contained about 1 g. of VIIIa. The remaining products of this cut were biacetyl (~1%), acetoin (11%), 2,3-butanediol (45%), and the cyclic sulfite VIIa (21%). The composition of the main cut of distillate (27 g.) as indicated by g.l.c. is summarized in Table I. On this basis, the over-all yield of VIIIa by the high dilution method was approximately 23%.

**Cyclic 1α,2β-Dimethylethylene Thionosulfite (VIIIb).**—This compound was prepared by the high dilution method starting with *dl*-2,3-butanediol exactly as described for the *cis* isomer VIIIa. The over-all yield of VIIIb determined by g.l.c. of the crude distillate was 31 g. (43%). A trace (~2%) of the *cis* isomer was detected in the crude sample reflecting approximately this amount of steric impurity known to be present in the starting diol. Two careful fractionations of the crude distillate through an efficient column gave 6.0 g. of VIIIb, b.p. 32° (0.45 mm.), $n^{25}D$ 1.5148, $\lambda_{\max}^{\text{isooctane}}$ 257 mμ (ε 2446), free of all impurities. An additional 15 g. of ~91–93% purity was obtained in the slightly higher boiling fractions. Authentic mixtures of VIIIa and VIIIb were easily separable by g.l.c.

TABLE I

COMPOSITION AND RETENTION[a] TIMES OF DISTILLABLE MATERIALS OBTAINED FROM THE HIGH DILUTION REACTION OF *meso*-2,3-BUTANEDIOL AND SULFUR MONOCHLORIDE

| Time, min. | % composition | Identity[b] |
|---|---|---|
| 0.6 | 5 | Diacetyl, $CHCl_3$ |
| 1.2 | 2 | Acetoin |
| 1.9 | 6 | *meso*-Diol |
| 2.4 | 23 | Cyclic sulfite |
| 3.7 | 64 | VIIIa |

[a] On the 2-m. LAC-3R-728 column at 138°. [b] Retention times and infrared spectra checked with authentic materials. The latter were also added to the mixtures to observe increase in peak area of the g.l.c. curve.

*Anal.* Calcd. for $C_4H_8O_2S_2$: C, 31.56; H, 5.30; S, 42.13. Found: C, 31.37; H, 5.29; S, 42.27.

**Desulfurization of Cyclic 1β,2β- and 1α,2β-Dimethylethylene Thionosulfites (VIIIa and VIIIb).**—As a check on the identity and steric purity of the two isomeric dimethyl thionosulfites, several desulfurizations were carried out under various conditions. Approximately 2 g. of Raney nickel in isopropyl alcohol was placed in each of two vials. To the first of the vials was added 0.25 ml. of the *cis* isomer VIIIa and to the second the same amount of the *trans* isomer VIIIb. Each reaction mixture was shaken (exothermic) for 10 min., the nickel was centrifuged down, and the supernatant liquids were analyzed by g.l.c. Aside from the solvent, no compound other than the respective glycols could be detected. The *cis*-dimethyl ester yielded *meso*-2,3-butanediol while the *trans* ester gave the *dl*-diol.

In another experiment, however, when 1 g. of VIIIa was stirred for 24 hr. with 20 g. of Raney nickel, a mixture of both *dl*- and *meso*-diols resulted. In a third experiment, it was demonstrated that under these conditions the pure *meso*-diol alone was equilibrated to a mixture of *meso* and *dl* isomers.

**Cyclic 1-Methylethylene Thionosulfite Isomers XI and XII.**—Propylene glycol (76.1 g.) and 204 g. of triethylamine were treated with 135 g. of sulfur monochloride exactly as described in procedure A for the preparation of VIIIa. A crude viscous polymer amounting to 140 g. was obtained. The infrared spectrum showed only small amounts of hydroxyl and sulfite groups to be present.

*Anal.* Calcd. for $[C_3H_6O_2S_2]_x$: C, 26.07; H, 4.38; S, 46.40. Found: C, 26.40; H, 4.61; S, 45.61; mol. wt., 1100.

Degradation of the polymer as described in procedure A for VIIIa gave 68 g. of crude distillate, b.p. 67–80° (3.0 mm.). Removal of glycol by washing gave 41 g. of thin yellow oil, the g.l.c. of which showed it to consist of 4% low boilers, 28% cyclic sulfite, 67% (over-all yield 21.6%) of the desired 1-methylethylene thionosulfite isomers (XI, XII), and 2% higher boiling materials. The pure isomeric mixture (11 g.), b.p. 34° (0.4 mm.), $n^{25}D$ 1.5323, $\lambda_{\max}^{\text{isooctane}}$ 258 mμ (ε 2236), was obtained by two fractionations. Propylene glycol cyclic sulfite[13] was readily identified by its g.l.c. retention time and infrared spectrum. Samples of purified XI–XII mixtures were best stored in a refrigerator. Under these conditions they were stable for more than 1 year. One sample survived 1 year at room temperature, but others decomposed after several months.

*Anal.* Calcd. for $C_3H_6O_2S_2$: C, 26.07; H, 4.38; S, 46.40; mol. wt., 138.2. Found: C, 25.78; H, 4.30; S, 46.60; mol. wt., 150.

**Cyclic Ethylene Thionosulfite (VIIIc).**—Ethylene glycol (62 g.) and 204 g. of triethylamine were used to react with sulfur monochloride as described in procedure A for XIIIa. Approximately 130 g. of light orange polymer was obtained. The latter was treated with catalytic amounts of sodium alcoholate followed by *very careful*[30] *distillation* during which the pot temperature was

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(30) On several occasions the decomposition got out of control blowing the apparatus apart and spewing heavy sulfurous polymers about the laboratory.

allowed to rise gradually to 130°. At 40°, elemental sulfur appeared to precipitate from the polymeric oil. A crude lachrymatory liquid, b.p. 60–75° (1.6 mm.) (56 g.), distilled from the pot. This distillate was taken up in ether and washed with water to remove ethylene glycol. Only 18 g. of material was recovered after drying and removal of ether. G.l.c. showed the presence of 50% ethylene sulfite (appropriate comparisons with authentic material), about 5% high and low boiling materials, and 45% of the desired cyclic ethylene thionosulfite VIIIc. The best cuts of VIIIc, on repeated fractionation, b.p. *ca.* 51–52° (2.4 mm.), still contained some sulfite impurity. Preparative gas chromatography, however, permitted the isolation of several grams of material (about 98% pure, $n^{25}\text{D}$ 1.5638) which was found to be a lachrymatory, unstable, colorless fluid. Small samples sealed in n.m.r. tubes varied in stability at −5° from a few days to several months. Copious amounts of sulfur were deposited upon decomposition.

*Anal.* Calcd. for $C_2H_4O_2S_2$: C, 19.34; H, 3.25; S, 51.64. Found: C, 19.42; H, 3.26; S, 51.29.

**Cyclic 1β,2β-Diphenylethylene Thionosulfite Isomers XIVa.**—A solution of 10.7 g. (50 mmoles) of *meso*-hydrobenzoin[31] in 100 ml. of dry tetrahydrofuran was added dropwise to 120 mmoles of methylmagnesium bromide in 150 ml. of dry tetrahydrofuran at 30–40°. When all of the glycol had been added, the cloudy solution was transferred under nitrogen to a graduated dropping funnel. To a second graduated funnel was added 8.1 g. of sulfur monochloride which was diluted with ether to a volume equal to that occupied by the diol–alkoxide solution. The two solutions were added slowly and concurrently to 50 ml. of dry tetrahydrofuran. This concurrent addition required 1–1.5 hr. and was regulated so that the alkoxide was always very slightly in excess in the reaction zone. The temperature was held at 15–20° by slight cooling.

After both solutions were added, the reaction was stirred for 15 min. and quenched with 300 ml. of water. Water-insoluble products were taken up in ether. The ether phase was washed and dried with Drierite and the solvent was removed *in vacuo*. A yellow-orange oil was obtained which partially crystallized on scratching. The material in 100 ml. of ether was then poured through a column of neutral alumina. A blue phase passed rapidly down the column. This was collected in the first 200 ml. of eluent. Removal of ether gave 8.8 g. of greenish blue oil which rapidly decolorized in air. The residue was again dissolved in about 10 ml. of ether, leaving behind 1.0 g. of elemental sulfur.

A. **Isolation of Minor (β-Thiono) Isomer XVIIb.**—The ether solution from which the free sulfur had been removed by filtration was chilled *in vacuo*. Large white crystals separated rapidly. These were immediately collected; 2.0 g., m.p. 89–90°. Two recrystallizations from hexane did not change the melting point; $\lambda_{\max}^{\text{isooctane}}$ 242 mμ (ε 3500), shoulders at ~258 and 265 mμ.

*Anal.* Calcd. for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38; S, 23.30; mol. wt., 276. Found: C, 61.10; H, 4.65; S, 23.09; mol. wt., 280.

B. **Isolation of Major (α-Thiono) Isomer XVIb.**—The mother liquor from which XVIIb had been obtained was concentrated and the solvent was replaced with hexane. Approximately 6 g. of somewhat sticky crystals, m.p. 70–80°, was obtained. Recrystallization of this material five times from hexane afforded 1.0 g. of analytically pure XVIb, m.p. 80–81°, $\lambda_{\max}^{\text{isooctane}}$ 258 mμ (ε 4000), shoulders at 252 and 265 mμ. Mother liquors and miscellaneous fractions were recombined, the hexane was removed, and the crude material in ether was again poured through a column of neutral alumina. An additional 2.2 g. of XVIb, m.p. 79–80°, was obtained by this treatment.

*Anal.* Calcd. for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38; S, 23.20; mol. wt., 276. Found: C, 60.97; H, 4.48; S, 23.49, mol. wt., 280.

Both isomeric compounds were unstable at room temperature or when exposed to light for more than a few hours. The major isomer could be stored in the dark at −5° for many months without deterioration, but the minor isomer showed evidence of decomposition after 2 months. Both compounds were very soluble in all organic solvents except hexane. P.m.r. spectra and those of the corresponding sulfite esters are shown in Figure 3.

**Desulfurization of XVIb and XVIIb.**—A 100-mg. sample of each of the isomers was dissolved in 10 ml. of isopropyl alcohol to which was added about 5 g. of a Raney nickel–isopropyl alcohol sludge. The suspension was stirred at ambient temperature for 5 min. The nickel was removed by filtration and the filtrate was concentrated *in vacuo*. In each case, approximately 80 mg. of slightly sticky brownish crystals were obtained. These were dissolved in hot hexane and the solution was filtered for clarification. On cooling, 50 and 55 mg. (from the XVIb and XVIIb isomers, respectively) of shining plates, m.p. 133–135°, were obtained. Infrared spectra and mixture melting points showed the desulfurized products to be *meso*-hydrobenzoin.

A control experiment starting with 100 mg. of pure *meso*-dihydrobenzoin was carried out exactly in the same way. From this, 55 mg., m.p. 134–135°, of *meso*-hydrobenzoin was recovered.

**Cyclic 1α,2β-Diphenylethylene α-Thionosulfite (XIVb).**—*dl*-Hydrobenzoin[32] (6.42 g.) was converted to its magnesium alkoxide by addition to 66 mmoles of methylmagnesium bromide essentially as described for the *meso* isomer in the preparation of XIVa. Similarly, the *dl*-alkoxide was caused to react with sulfur monochloride under high dilution conditions. From this reaction, 7.4 g. of pale yellow oil was obtained which crystallized on standing. The crude crystals were dissolved in 100 ml. of hot hexane. On cooling ~500 mg. of white crystals separated, m.p. 113–115°. This material was hydroxylic as judged from its infrared spectrum and it was discarded. The hexane solution was concentrated to about 40 ml. and cooled. A second crop of crystals, 3.4 g., m.p. 74–80°, was obtained. Three recrystallizations of this material from hexane gave 1.0 g. of pure XIVb, m.p. 78–80°. Mother liquors and miscellaneous fractions were combined. This crude material, in ether, was put through a column of neutral alumina. Another 1.0 g. of essentially pure XIVb, m.p. 77–79°, was eventually obtained *via* this treatment.

*Anal.* Calcd. for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38; S, 23.20. Found: C 61.15; H, 4.35; S, 22.90.

**Cyclic 1β,2β-Diphenylethylene Sulfite Isomers XVIa, XVIIa.**—To 10.7 g. of *meso*-hydrobenzoin[31] dissolved in 50 ml. of methylene chloride and 30 ml. of pyridine was slowly added 6.0 g. of thionyl chloride. The mixture became warm and within a few minutes pyridine hydrochloride separated. The mixture was stirred for 4 hr. and then quenched with water. Additional methylene chloride was added, and the aqueous layer was separated and discarded. Excess pyridine was removed from the organic layer by several washes with dilute hydrochloric acid. After a final water wash, the solution was dried and the solvent was removed *in vacuo*. The crude white sulfite remaining, 12.0 g., m.p. 122–126°, appeared from its p.m.r. spectrum to consist of two products in approximately a 9:1 ratio.

A. **Major Sulfite Isomer XVIa.**—The crude ester was taken up in hot ether (~500 ml.) and four crops of crystals were obtained: (1) 7.0 g., m.p. 126–131°; (2) 2.6 g., m.p. 110–116°; (3) 1.1 g., m.p. 103–112°; and (4) 0.8 g., m.p. 100–115°. Recrystallization of the first-crop material twice from ether gave pure material, m.p. 130–131°, as evidenced by its p.m.r. spectrum (Figure 3). A comparable melting point has been reported previously.[18c]

B. **Minor Sulfite Isomer XVIIa.**—P.m.r. spectra of the third and fourth crops from A indicated their composition to be 30–50% of the second sulfite isomer. Attempts to obtain the latter by fractional crystallization were unsuccessful. Subsequently, it was found that the minor isomer traveled slightly faster on alumina than did the major isomer. Thus, from 1.0 g. of a composite sample of the third and fourth crops from A, approximately 100 mg. of fine white needles, m.p. 129–130°, was obtained. The p.m.r. spectrum showed this material to be free of the other isomer (XVIa).

*Anal.* Calcd. for $C_{14}H_{12}O_3S$: C, 64.59; H, 4.65; S, 12.32. Found: C, 64.44; H, 4.71; S, 12.30.

**Cyclic 1α,2β-Diphenylethylene Sulfite (XVb).**—*dl*-Hydrobenzoin[32] (2.14 g.) and thionyl chloride (1.19 g.) were caused to react as described previously for the *meso* isomer. The crude cyclic sulfite (2.3 g.) was recrystallized thrice from ether–hexane giving 1.3 g. of white needles, m.p. 85–86°, lit.[18a,c] m.p. 84–86°.

**Cyclic 1,3-Butylene Thionosulfite (XIX) and 6-Methyl-1,2,3-dioxathiane (XXI).**—1,3-Butanediol (90 g.), 204 g. of triethylamine, and 135 g. of sulfur monochloride were caused to react under high dilution conditions as described in procedure B for VIIIa. After work-up, 150 g. of dark oil was obtained. This was subjected to vacuum distillation. Approximately 31 g., b.p. 60–65° (1 mm.), of yellow liquid distilled from the pot.

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[31] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Rev., D. C. Heath and Co., Boston, Mass., 1957, p. 175.

[32] Reference 31, p. 189.

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.), $n^{25}D$ 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.), $n^{25}D$ 1.5291, $\lambda_{max}^{isooctane}$ 244 m$\mu$ ($\epsilon$ 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.

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# Organic Esters of Bivalent Sulfur. III. Sulfoxylates

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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).

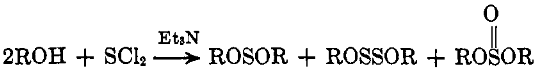
The dimethyl and diethyl esters (ROSOR) of sulfoxylic acid [$S(OH)_2$] are known. Their preparation, first described by Meuwsen and Gebhardt,[1] and subsequently utilized by others,[2] involved the alkoxide-catalyzed decomposition of the corresponding dialkoxy disulfides. As the latter were readily available[3a] the preparation of additional dialkyl sulfoxylates

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

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 di-

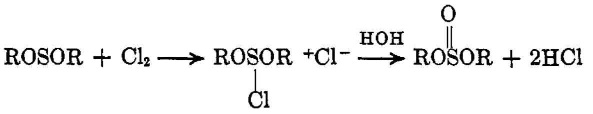
$$\text{RCH}_2\text{OSSOCH}_2\text{R} \xrightarrow{\text{RONa}} \text{RCHO} + \text{RCH}_2\text{OH} + 2S^0 \qquad (2)$$

chloride[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

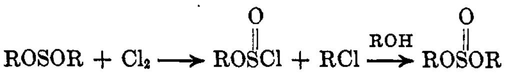


$$2\text{ROH} + \text{SCl}_2 \xrightarrow{\text{Et}_3\text{N}} \text{ROSOR} + \text{ROSSOR} + \text{RO}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{OR} \qquad (3)$$

$$2\text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2 \qquad (4)$$



$$\text{ROSOR} + \text{Cl}_2 \longrightarrow \text{RO}\underset{\text{Cl}}{\underset{|}{\text{S}}}\text{OR}\ {}^{+}\text{Cl}^{-} \xrightarrow{\text{HOH}} \text{RO}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{OR} + 2\text{HCl} \qquad (5)$$



$$\text{ROSOR} + \text{Cl}_2 \longrightarrow \text{RO}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{Cl} + \text{RCl} \xrightarrow{\text{ROH}} \text{RO}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{OR} \qquad (6)$$

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

[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).