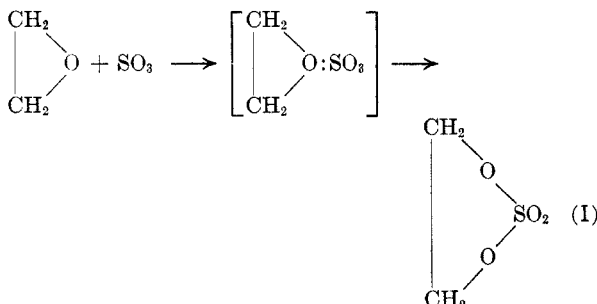


## Reaction of Ethylene Oxide with Sulfur Trioxide

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Received November 30, 1959

The reaction of certain aliphatic ethers with sulfur trioxide has been found to result in formation of the corresponding dialkyl sulfate. For example, Suter and Evans<sup>1</sup> report a yield of 85 to 90% of bis-(2-chloroethyl) sulfate from bis(2-chloroethyl) ether and sulfur trioxide. They describe the reaction as proceeding through the formation of the ether coordination compound which undergoes rearrangement to the sulfate on heating. Should it be possible to form the sulfur trioxide-ethylene oxide coordination compound, one might expect this to rearrange easily to the five-membered ring compound, ethylene sulfate.



Ethylene oxide was treated with sulfur trioxide under a variety of conditions in an attempt to prepare ethylene sulfate. The only reaction system which did not result in excessive charring involved the use of 1,4-dioxane-sulfur trioxide addition compound in 1,4-dioxane. When one mole of ethylene oxide was treated with one mole of sulfur trioxide in 1,4-dioxane, a homogeneous solution was obtained which when mixed with cold water gave no acid. Removal of the solvent *in vacuo* gave a slightly colored, very viscous liquid. All attempts to crystallize this material failed. However, a 9.5% yield of the expected white crystalline ethylene sulfate could be sublimed *in vacuo* from the viscous liquid. On continued heating the heavy viscous liquid decomposed.

### EXPERIMENTAL

To 200 ml. of dry redistilled 1,4-dioxane was added dropwise with cooling and stirring 19.3 g. (0.242 mole) of sulfur trioxide. By careful control of the temperature (*ca.* 10°) and rate of addition the sulfur trioxide could be added without charring. During addition the dioxane-sulfur trioxide addition compound precipitated from solution. After addition of sulfur trioxide was complete, ethylene oxide was passed slowly through the mixture which was stirred and cooled. When 0.25 mole of ethylene oxide had been added, the dioxane-sulfur trioxide addition compound had com-

pletely dissolved. The final volume of the reaction mixture was 210 ml.

A 5-ml. aliquot of this solution was added to about 50 ml. of water at room temperature and shaken vigorously. An oily layer separated from solution. This mixture was neutralized with less than 1 ml. of 0.100*N* sodium hydroxide solution.

The dioxane solution (50 ml.) was distilled under vacuum (2 mm.) until a pot temperature of 50° was reached. The residue (10.5 g.) was a dark viscous liquid. This material (1.69 g.) was heated to 70–80° in a micro sublimation apparatus at 2 mm. There was obtained 110 mg. (9.5%) of white crystalline ethylene sulfate, m.p. 96–97° (lit.,<sup>2</sup> m.p. 99°).

*Anal.* Calcd. for C<sub>2</sub>H<sub>4</sub>O<sub>4</sub>S: C, 19.35; H, 3.25. Found: C, 19.86; H, 3.36.

*Acknowledgment.* The author wishes to thank Dr. O. C. Dermer for helpful discussions and S. A. Sims for able assistance.

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(2) Wilson Baker and F. B. Field, *J. Chem. Soc.*, 86 (1932).

## Relative Basicities in the Series Dialkyl Sulfide, Sulfoxide, and Sulfone Toward Boron Trifluoride

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Received November 2, 1959

Strong evidence has been obtained that in the series R-S-R', R-SO-R', R-SO<sub>2</sub>R' (R = *n*-C<sub>12</sub>H<sub>25</sub>, R' = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>) the sulfoxide is considerably more basic toward the Lewis acid boron trifluoride than either the sulfide or sulfone. Each formed a 1:1 complex on passing boron trifluoride into a cold benzene solution, as indicated by abrupt saturation of the solution when close to one molar equivalent had been added. The benzene was then evaporated at aspirator pressure at or below room temperature. Only the sulfoxide formed a vacuum-stable complex. The starting sulfide and sulfone were recovered in the other two cases. Thus the dissociation of the sulfoxide complex must be much lower than that of the sulfide and sulfone complexes, *i.e.*, the sulfoxide is the strongest base towards boron trifluoride.

The order of basicity in this series toward boron trifluoride and toward protons will not necessarily correspond, especially if steric factors are involved.<sup>1</sup> However, Wimer<sup>2</sup> has obtained results from non-aqueous titrations which indicate that the order is the same. His data, combined with the known *pK<sub>A</sub>* of protonated phosphine oxides (R<sub>3</sub>POH<sup>+</sup>),<sup>3</sup> would

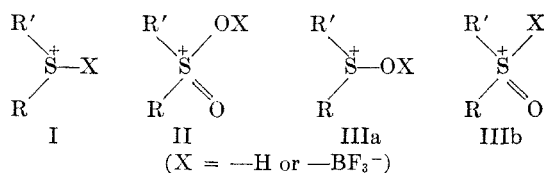
(1) E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, Inc., N. Y., (1955), pp. 634ff.

(2) D. C. Wimer, *Anal. Chem.* **30**, 2060 (1958).

(1) C. M. Suter and P. B. Evans, *J. Am. Chem. Soc.*, **60**, 536 (1938).

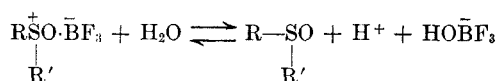
suggest that the  $pK_A$  of  $R_2SOH^+$  is probably slightly less than zero.<sup>4</sup>

The order of basicity in this series has a bearing on the structure of the sulfoxide complex. In the sulfide and sulfone complexes the acceptor atom (proton or boron trifluoride) is unambiguously on sulfur or on oxygen respectively (I and II), whereas it could be on either atom in the sulfoxide complex (IIIa or IIIb).



However, a consistent picture of the observed trend in basicity is obtained only if the acceptor atom is assumed to reside on oxygen in the sulfoxide (IIIa). If it were on sulfur, the sulfoxide should be less basic than either the sulfide or sulfone.<sup>5</sup> In agreement with the inference above concerning the structure of the sulfoxide-acid complexes it has recently been demonstrated that the oxygen in dialkyl sulfoxides is more nucleophilic than the sulfur.<sup>6</sup>

It was observed that the hydrolysis of ethyl-*n*-dodecyl sulfoxide-boron trifluoride in water is readily reversible. If the complex is placed in water, a turbid suspension with a very low  $pH$  (1.6) is obtained. If this is extracted with chloroform, sulfoxide is recovered.<sup>7</sup> If the solution is freeze-dried, it is principally the complex that is recovered, as indicated by the infrared spectrum. These observations may be accounted for by the following equilibrium:



(3) P. Nylen, *Z. Anorg. allgem. Chem.*, **246**, 227 (1941).

(4) F. G. Bordwell and P. J. Boutan [*J. Am. Chem. Soc.* **79**, 1717 (1957)] have obtained evidence that sulfoxides are largely protonated by *ca.* 1.5% trifluoroacetic acid in acetic acid.

(5) The sulfur atom in the sulfoxide is electron deficient compared to the sulfide sulfur because of the highly polar S—O bond, whose bond moment (*ca.* 2.8 D) is directed towards oxygen. Therefore the sulfoxide should be less basic than the sulfide if the acceptor were on sulfur in the sulfoxide. Similarly, in comparing a sulfoxide complex with the acceptor on the electron deficient sulfur and the sulfone complex with the acceptor on an electron rich oxygen, one would expect from electrical considerations that the latter would be the stronger complex, *i.e.*, the sulfone would be the stronger base. The second predicted relationship is probably not so well founded as the first, because in the first the donor atom is sulfur in both cases, while in the second it is sulfur in one case and oxygen in the other. This does not alter, however, the electrical status of the atoms in being electron deficient or abundant, and this is assumed to play the major role.

(6) S. G. Smith and S. Winstein, *Tetrahedron* **3**, 317 (1958); R. Kuhn and H. Trischmann, *Ann.* **611**, 117 (1958).

(7) This observation, incidentally, provides evidence that the complex formation is a simple Lewis acid-base interaction.

As this sulfoxide is insoluble in water, the equilibrium is probably driven far to the right (as indicated by the low  $pH$ ) and the sulfoxide may be readily extracted. However, the removal of water by freeze-drying apparently shifts the equilibrium to the left. Hydroxyfluoboric acid, the postulated acidic product, is known to be a strong acid.<sup>8</sup>

#### EXPERIMENTAL

*Preparation of compounds.* Methyl- and ethyl-*n*-dodecyl sulfide were prepared by the method of Kuhn and Dann<sup>9</sup> from the lower alkyl mercaptan and dodecyl bromide.

The sulfoxides were prepared by nitric acid oxidation of the sulfide.<sup>10</sup> Methyl-*n*-dodecyl sulfoxide was found to melt at 59–61°.

*Anal.* Calcd. for  $C_{13}H_{28}SO$ : S, 13.8. Found: S, 13.7.

Ethyl-*n*-dodecyl sulfoxide was found to melt at 52–52.5°.

*Anal.* Calcd. for  $C_{14}H_{30}SO$ : S, 13.0. Found: S, 12.9.

The principal infrared band of these sulfoxides is at 9.9 $\mu$ . The very intense sulfone bands at 7.9 and 9.0 $\mu$  were absent. The infrared spectra were taken on mulls.

Methyl-*n*-dodecyl sulfone was prepared by heating the sulfide with a 50% excess of 10% hydrogen peroxide in aqueous acetic acid (prepared from 60% hydrogen peroxide and glacial acetic acid) on the steam bath for 1 hr., diluting with several volumes of water, filtering, and drying. The compound was found to melt at 80–82°.

*Anal.* Calcd. for  $C_{13}H_{28}SO_2$ : S, 12.9. Found: S, 12.7. The compound was transparent in the infrared at 9.9 $\mu$ , indicating the absence of sulfoxide.

*Reactions with boron trifluoride.* Methyl-*n*-dodecyl sulfone (0.036 mole) was dissolved in 250 ml. of benzene in a 500 ml. 3-neck flask fitted with gas addition tube, stirrer, thermometer, and a drying tube on the open neck. Boron trifluoride was passed into the solution at 10–15°; when 0.043 mole (1.2 moles/mole of sulfone) had passed in, boron trifluoride fumes abruptly commenced emerging from the drying tube. When the amount used was corrected for the amount necessary to displace the air in the flask, the amount absorbed was one mole/mole sulfone within weighing error. When this solution was evaporated to dryness at room temperature and slightly below in a rotating Rinco evaporator at aspirator pressure, a crystalline solid was obtained which was shown by infrared to be essentially pure recovered sulfone.

Methyl-*n*-dodecyl sulfide behaved exactly like the sulfone. One mole of boron trifluoride was absorbed and the sulfide was recovered on evaporation of solvent.

Ethyl-*n*-dodecyl sulfoxide<sup>11</sup> also absorbed one mole of boron trifluoride. The residue, after evaporation of benzene, was semisolid at room temperature. It had two very broad infrared bands at 8.6–9 $\mu$  and 11.3–11.6 $\mu$ . Similar bands are found in dimethyldodecylamine-boron trifluoride (prepared in the same way as the sulfoxide complex) at 8.7 and 10.8–11.0 $\mu$ .

*Anal.* of the sulfoxide complex: Calcd. for  $C_{14}H_{30}SOBF_3$ : S, 11.2; B, 3.45. Found: S, 10.3;<sup>12</sup> B, 3.5.

When the sulfoxide complex was mixed with water, the turbid solution extracted with chloroform, and the chloroform evaporated after drying over calcium sulfate, crystal-

(8) C. A. Wamser, *J. Am. Chem. Soc.* **70**, 1209 (1948).

(9) R. Kuhn and O. Dann, *Ber.* **73B**, 1092 (1940).

(10) I. D. Webb, U. S. Patent **2,787,595**, April 2, 1957.

(11) Methyl-*n*-dodecyl sulfoxide behaved similarly but was not so extensively investigated.

(12) The compound exploded when mixed with sodium peroxide in the standard Parr-bomb analysis for sulfur. A successful analysis, although somewhat low, was obtained by enclosing the sample in a gelatin capsule before carrying out the oxidation.

line sulfoxide was recovered. Freeze-drying the turbid suspension re-formed the complex largely, as indicated by infrared spectra. A suspension of 0.5 g. of complex in 50 ml. of distilled water had a pH of 1.6.

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## Derivatives of Sulfenic Acids. XL. Phenyl Migration during Sulfenylation of *trans*-Stilbene

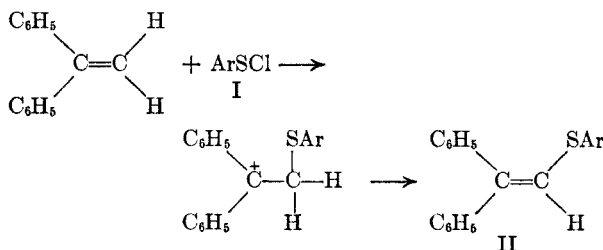
NORMAN R. SLOBODKIN AND NORMAN KHARASCH

Received August 31, 1959

In connection with a study of the kinetics of addition of 2,4-dinitrobenzenesulfonyl chloride, I, to *cis* and *trans*-stilbene, we encountered a migration of the phenyl group in the reaction of I with *trans*-stilbene at elevated temperatures. To our knowledge, this is the first example of a phenyl group rearrangement during the course of addition of a sulfonyl halide to an olefin.

Previous studies<sup>1</sup> have shown deviations from 1:1 adduct formation with 2,4-dinitrobenzenesulfonyl chloride, I, and olefins. The product of the reaction of 4-methoxystyrene and I were governed by the reaction temperature, the vinyl sulfide being formed at the higher temperatures,<sup>2</sup> and olefins like 1,1-diphenylethylene were found also to lead to the vinyl sulfide.<sup>1</sup>

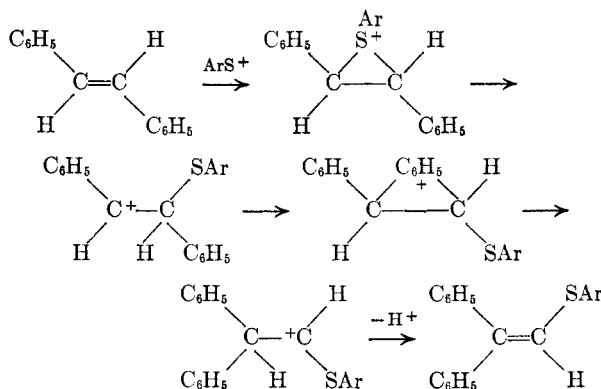
It has now been found that the product from the reaction of I with *trans*-stilbene in refluxing acetic acid was not the 1:1 adduct, but a vinyl sulfide. Oxidation of the vinyl sulfide to benzophenone and desulfuration of the vinyl sulfide with Raney nickel to 1,1-diphenylethane showed the vinyl sulfide to be 1,1-diphenyl-(2',4'-dinitrophenylthio)ethane, which is the expected product from 1,1-diphenylethylene assuming addition of ArS<sup>+</sup> and subsequent loss of a proton; Ar = 2,4-dinitrophenyl. The product from 1,1-diphenylethylene and the rearrangement product from *trans*-stilbene were found to be identical.



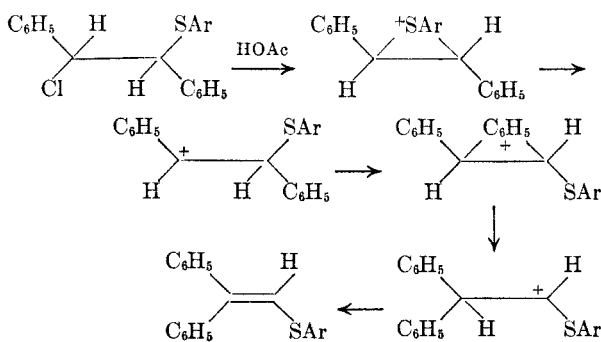
(1) N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956); Cf. also, R. B. Langford and D. D. Lawson, *J. Chem. Ed.*, **34**, 510 (1957) and N. Kharasch, *Organic Sulfur Compounds*, Vol. I, Pergamon Press, New York-London. (In press).

(2) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956).

The following sequence is suggested to explain the rearrangement with *trans*-stilbene, involving a cyclic episulfonium ion, subsequent participation by phenyl, followed by loss of a proton.



Since acetolysis of the 1:1 adducts of I and olefins have been postulated to proceed through a sulfonium ion with sulfur participation,<sup>3</sup> acetolysis of the 1:1 adduct in acetic acid would be expected to yield the vinyl sulfide. Acetolysis of the 1:1 adduct yielded the vinyl sulfide and some  $\beta$ -acetoxy compound while acetolysis with sodium acetate added yielded only the  $\beta$ -acetoxy compound. S<sub>N</sub>2 acetolysis conditions with sodium acetate in anhydrous acetone, failed to give detectable reaction. The sequence leading to the same product, as shown above from *trans*-stilbene, is given below.



Systems such as those used in this study can thus permit interesting comparisons of the relative participations by neighboring sulfur and aryl groups.

### EXPERIMENTAL

Reaction of 2,4-dinitrobenzenesulfonyl chloride, I, with *trans*-stilbene. To a refluxing solution of dry acetic acid was

(3) A. J. Havlik and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1207 (1956).