Thermolysis of Methoxymethylsilanes. I. The Formation of Methoxycarbene

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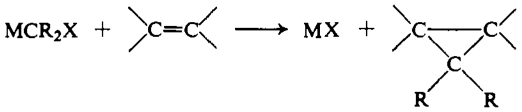
Abstract: A unique synthesis of (dimethoxymethyl)trimethoxysilane (I) is described. Compound I undergoes a low-temperature thermolysis to give tetramethoxysilane and methoxycarbene. Kinetic evidence is presented which demonstrates the formation of free methoxycarbene. Methoxycarbene generated *via* this method was shown to react with methanol, vinylsilanes, silicon hydrides, and stereospecifically with olefins.

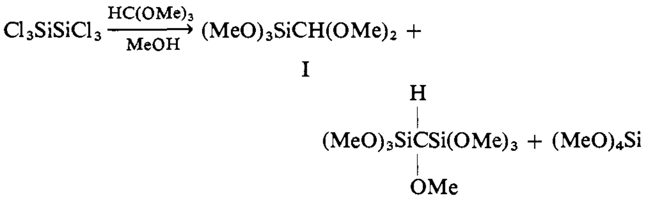
In recent years an increased interest in the reactions of organometallic compounds of the type MC(X)< (where X = halogen) has developed.[1–6] Compounds of this type are capable of *methylene* transfer reactions, or *methylenation*, in which transfer of a formally divalent carbon species is accomplished. The most commonly studied reaction of this type is the methylation of olefins. Reactions of this type have been reported for α-haloalkyl derivatives of numerous elements and a recent summary of this area is available.[7] Present evidence suggests that there is a continuum of mechanisms operative in these reactions, ranging from processes involving a free carbene to those involving a direct bimolecular transfer of methylene.[7]



The majority of *methylenation* reactions studied to date have involved elimination in α-haloalkyl derivatives. We have found that certain α-alkoxyalkylsilanes also undergo *methylenation* reactions and further, we have demonstrated that these reactions proceed *via* a free carbene mechanism.

Results and Discussion

We discovered a rather unique synthesis of (dimethoxymethyl)trimethoxysilane (I) during an attempted methoxylation of hexachlorodisilane with either methyl orthoformate[8] or a mixture of methyl orthoformate and methanol.[9] Also produced in this reaction was bis(trimethoxysilyl)methoxymethane (II) and tetramethoxysilane (III).[10]

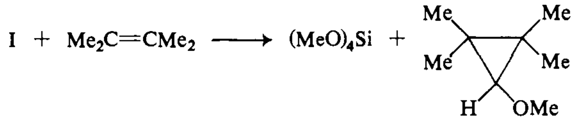


$$Cl_3SiSiCl_3 \xrightarrow[MeOH]{HC(OMe)_3} (MeO)_3SiCH(OMe)_2 + (MeO)_3Si\underset{OMe}{\overset{H}{C}}Si(OMe)_3 + (MeO)_4Si$$

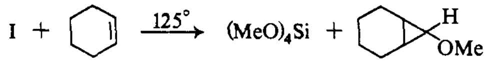
I

II III

Attempts to purify I by gas–liquid partition chromatography (glpc) indicated that this material was quite susceptible to thermal decomposition. Consideration of the known thermal *methylenation* reactions of α-halomethylsilanes[11–15] and the recently reported[16] *silylenation* reactions of methoxypolysilanes suggested that the thermolysis of I might yield methoxycarbene. Indeed, when the thermolysis of I was carried out in the presence of tetramethylethylene, an essentially quantitative yield of 1-methoxy-2,2,3,3-tetramethylcyclopropane (IV) was obtained. Compound IV was also obtained from the thermolysis of I and tetramethylethylene in the gas phase at 225–250°. Similarly, decomposition of I in the presence of cyclohexene gave high yields of 7-methoxynorcarane (V).



IV



V

(*exo*/*endo* ratio = 7.0)

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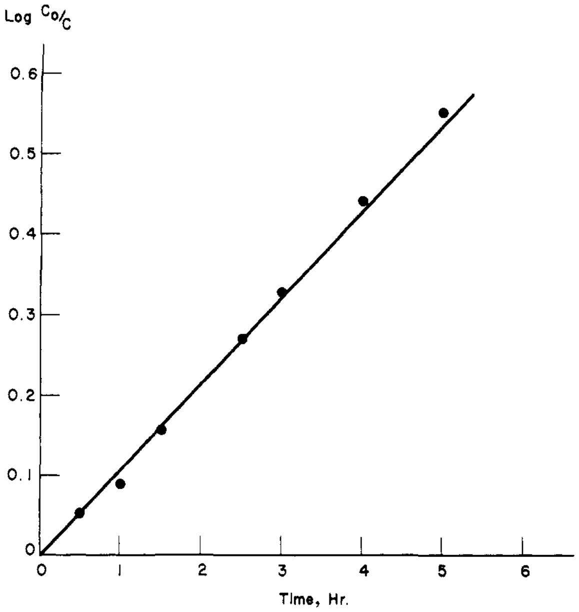


Figure 1. Kinetic plot for the thermolysis of I in the presence of methanol (mole ratio MeOH/I = 3.0) at 125 ± 2°; $k = 7.0 \times 10^{-5}$ sec^{-1}.

Table I. Kinetic Data Obtained from the Thermolysis of $(MeO)_3SiCH(OMe)_2$ (I) at 125 ± 2°

System		10^5k, sec^{-1}
MeOH/I (2:1 ratio)		6.6
MeOH/I (3:1 ratio)		6.9
$Me_2C{=}CMe_2$/I (2:1 ratio)		6.4
	Av	6.7

Recent reports[1,17-20] describing the "trapping" of carbenes with methanol suggested the thermolysis of I in the presence of this reagent. Heating I and methanol gave tetramethoxysilane and dimethoxymethane as the only observable products. While the formation of dimethoxymethane is consistent with the "trapping" of

$$I + MeOH \xrightarrow{125°} (MeO)_4Si + MeOCH_2OMe$$

methoxycarbene with methanol, methanolysis of the Si–C bond would lead to the formation of identical reaction products.

The assignment of a reaction path involving a rate-determining formation of free carbene to both the tetramethylethylene and methanol reactions follows from an examination of the kinetics of these reactions. The results of this kinetic study of I, in which the rates were followed by monitoring the disappearance of I by glpc, are shown in Table I. An example of a typical first-order plot of the rate data is shown in Figure 1. These reactions are first order in silane I and zero order in the trapping agents, methanol and tetramethylethylene. Furthermore, the

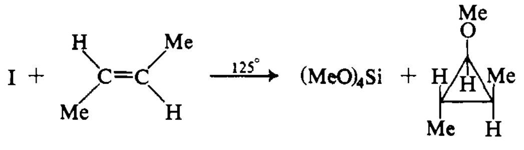
$$I \rightarrow (MeO)_4Si + :CH(OMe)$$

$$:CH(OMe) + MeOH \rightarrow MeOCH_2OMe$$

$$:CH(OMe) + Me_2C{=}CMe_2 \rightarrow IV$$

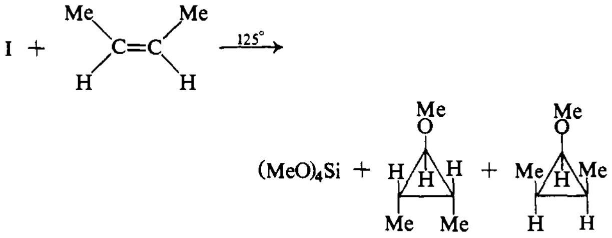
rate of disappearance of I is nearly identical in the presence of these drastically different trapping agents. The gas-phase reactions of I provide further support for the formation of free methoxycarbene.

Previously, the reactions of lithium chloromethylalkyl ethers in the presence of olefins have been shown to proceed stereospecifically.[21] The thermolysis of I in the presence of *trans*-butene-2 gave only tetramethoxysilane and 1-methoxy-*trans*-2,3-dimethylcyclopropane (VI). In



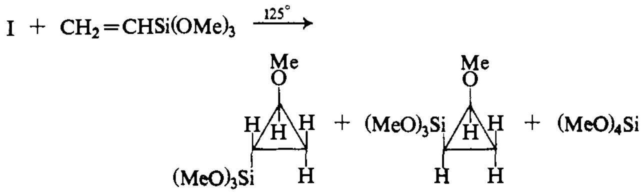
VI

the presence of *cis*-butene-2 only tetramethoxysilane and a mixture of *exo*-/*endo*-1-methoxy-*cis*-2,3-dimethylcyclopropane (VII) was obtained. Thus, these reactions also proceed stereospecifically.



VII (*exo*/*endo* ratio = 1.52)

The reaction of methoxycarbene with silicon-containing substrates has also been examined. Thermolysis of I in the presence of vinyltrimethoxysilane gave tetramethoxysilane and a mixture of *cis*-/*trans*-1-methoxy-2(trimethoxysilyl)cyclopropane (VIII).



VIII (*trans*/*cis* ratio = 2.8)

Decomposition of I in the presence of trimethoxysilane gave, in addition to tetramethoxysilane, good yields of the Si–H insertion product (methoxymethyl)trimethoxysilane (IX). Compound IX was also formed by the

$$I + (MeO)_3SiH \rightarrow (MeO)_4Si + \underset{IX}{(MeO)_3SiCH_2OMe}$$

thermolysis of I and trimethoxysilane in the gas phase at 250°. Thus, the recently reported additions of dichloro-

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carbene to vinylsilanes[1,22] and silicon hydrides[1,23,24] also occur with methoxycarbene.

Thus far, attempts to generate $:CH_2$ from IX have been unsuccessful because of the thermal stability of this latter compound. Heating IX and tetramethylethylene at 300° for 16 hr gave mainly unreacted starting materials and only a small amount of tetramethoxysilane.

The availability of methoxycarbene under mild reaction conditions suggests numerous applications in organic and organometallic chemistry. Investigations are currently in progress to further elucidate the chemistry and the relative nucleophilic character of methoxycarbene.

Experimental Section

All nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard and carbon tetrachloride as solvent. The molecular weights were determined with a 90° sector single-focusing mass spectrometer of 12 in. radius (A.E.I. Model MS-12). Vapor phase chromatography was done with an F & M Model 810 unit and helium was the carrier gas. The column used consisted of either a 4 ft × 0.25 in. stainless steel tubing packed with a mixture of Dow Corning Silphenylene (25%) and Dow Corning KP-5365 fluid (75%) on 80–100 mesh Chromosorb W (10% by wt Silphenylene) (column A) or 6 ft × 0.25 in. stainless steel packed with 20% Dow Corning FS-1265 on 80–100 mesh Chromosorb W (column B). Because of the ease of thermal decomposition of I, injection port temperatures of $\leqslant$225° were used for all glpc work. The heating source used for all reactions and kinetic studies was a Blue M Ultra-Temp Mechanical Convection Oven, Model No CW-66126-1. The gas phase thermolysis reactions were carried out in a 2.5 × 62 cm quartz tube packed with quartz chips. The tube reaction zone was heated by a Lindberg Hevi-Duty "Mini-Mite" Tube Furnace, Model 55031A (length of heated zone was 35 cm). Additions were made with a Sage Syringe Pump, Model 249.

Preparation of (Dimethoxymethyl)trimethoxysilane (I). A mixture of 742 g (7.0 mol) of methyl orthoformate and 22.4 g (0.7 mol) of anhydrous methanol was added to 295 g (1.10 mol) of hexachlorodisilane over a 2-hr period. The reaction was exothermic and a mixture of methyl chloride and methyl formate was removed continuously by means of a Dean-Stark trap. Subsequent to the initial exotherm the reaction mixture was heated at 60–70° for an additional 10–12 hr with continuous removal of low-boiling materials. The neutral reaction mixture was strip-distilled on a 36-in. spinning-band column (90 mm) to remove excess methyl orthoformate and the by-product, tetramethoxysilane.[25] Fractional distillation gave 43 g (20% based on Si_2Cl_6) of I, bp 82–84° (20 mm), $n^{25}D$ 1.3990.

Anal. Calcd for $C_6H_{16}O_5Si$: C, 36.7; H, 8.15; Si, 14.3; mol wt, 196. Found: C, 36.4, 36.5; H, 8.00, 8.00; Si, 14.5, 14.6; mol wt, 196.

The nmr spectrum of I showed three singlets at τ 5.78, 6.47, and 6.67 (1:9:6 ratio) due to the CH, COMe, and SiOMe protons, respectively.

Continued distillation gave 46.7 g (30% based on $2Si_2Cl_6$) of bis(trimethoxysilyl)methoxymethane (II), bp 90–91° (2 mm), $n^{25}D$ 1.4120.

Anal. Calcd for $C_8H_{22}O_7Si_2$: C, 33.6; H, 7.69; Si, 19.6; mol wt, 286. Found: C, 33.7, 33.2; H, 7.79, 7.56; Si, 19.7, 19.7; mol wt, 286.

The nmr spectrum of II showed three singlets at τ 6.47, 6.68, and 7.27 (18:3:1 ratio) characteristic of the SiOMe, COMe, and CH protons, respectively.

Reaction of I and Tetramethylethylene. a. In an Ampoule at 125°. A mixture of 5.0 g (0.026 mol) of I and 4.3 g (0.032 mol) of tetramethylethylene was heated in an ampoule at 125° for 16 hr. Nmr analysis showed a mole ratio of $Me_2C{=}CMe_2/(MeO)_4Si$/1-methoxy-2,2,3,3-tetramethylcyclopropane (IV) of 1:1:0.95 indicating an almost quantitative yield of IV.

The two products codistilled at bp 120–122°. The distillate was hydrolyzed in an ether–dilute hydrochloric acid mixture to remove tetramethoxysilane. The ether-extracted residue was dried and the product, IV, isolated by preparative glpc (2.7 g, 88%).

Anal. Calcd for $C_8H_{16}O$: C, 75.2; H, 12.5; mol wt, 128. Found: C, 75.1, 75.3; H, 12.3, 12.6; mol wt, 128.

The nmr spectrum of IV showed singlets at τ 6.76, 7.66, 9.01, and 9.04 (3:1:6:6 ratio) characteristic of the COMe, CH, and CMe protons, respectively.

b. In the Gas Phase at 250°. A mixture of 4.0 g (0.02 mol) of I and 2.57 g (0.03 mol) of tetramethylethylene was added to the heated quartz tube at a rate of 3.25 ml/hr. The formation of tetramethoxysilane and IV was confirmed by glpc analysis using known standards. Only a trace of unreacted I was observed. The glpc area ratio of $(MeO)_4Si$/IV was 1.5.

Reaction of I and Cyclohexene. A mixture of 10.0 g (0.05 mol) of I and 12.5 g (0.15 mol) of cyclohexene was heated at 125° in a sealed ampoule for 16 hr. The glpc (column B) area ratio of $(MeO)_4Si$/7-methoxynorcarane (V) was 1.25. The reaction mixture was hydrolyzed in ether–dilute hydrochloric acid to remove tetramethoxysilane. The ether extracted residue was dried and the product, V, isolated by distillation on an 18-in. spinning-band column, bp 36–38° (75 mm), 3.0 g (47.6%).

The nmr spectrum of V (A_2X type) gave an *exo*/*endo* ratio of 7.0. For the *endo* isomer COMe was at τ 6.69 and HCO at 7.00 (triplet, $J_{AX} = 6.5$ cps). For the *exo* isomer COMe was at τ 6.80 and HCO at 7.25 (triplet, $J_{AX} = 3.0$ cps) in agreement with the previously reported[21] values.

Thermolysis of I in the Presence of Methanol. A mixture of 2.0 g (0.01 mol) of I and 0.65 g (0.02 mol) of anhydrous methanol was heated in an ampoule at 125° for 16 hr. Nmr analysis showed the formation of only tetramethoxysilane and dimethoxymethane [ratio $(MeO)_4Si/(MeO)_2CH_2$ was 1.1].

General Procedure for Kinetic Studies. Compound I and either methanol or tetramethylethylene were mixed in the specified mole ratio. A known amount of benzene was added as an internal standard. Small samples of these standard solutions were sealed in ampoules and heated at 125 ± 2°. The tubes were analyzed at the indicated times using glpc (column A with methanol reactions, column B with tetramethylethylene reactions) and the area ratio C_0/C determined relative to the benzene internal standard. Each point represents the average value of 3 or more chromatograms. The results are given in Table I.

Reaction of I and *trans*-Butene-2. A mixture of 15.7 g (0.08 mol) of I and 6.84 g (0.12 mol) of *trans*-butene-2 was heated in an ampoule at 125° for 16 hr. Glpc (column A) gave an area ratio of $(MeO)_4Si$/1-methoxy-*trans*-2,3-dimethylcyclopropane (VI) of 1.34. Distillation using an 18-in. spinning-band column gave 5.3 g (66%) of VI, bp 79–80°.

Anal. Calcd for $C_6H_{12}O$: C, 72.0; H, 12.0; mol wt, 100. Found: C, 72.0, 72.2; H, 12.5, 12.4; mol wt, 100.

The nmr spectrum of VI (ABX type) showed COMe at τ 6.71 and HCO at 7.25 (quartet, $J_{AX} = 3$ cps, $J_{BX} = 6$ cps) in agreement with the previously reported[21] values.

Reaction of I and *cis*-Butene-2. A mixture of 15.7 g (0.08 mol) of I and 6.84 g (0.12 mol) of *cis*-butene-2 was heated in an ampoule at 125° for 16 hr. Glpc analysis (column A) gave an area ratio of $(MeO)_4Si$/*exo*-/*endo*-1-methoxy-*cis*-2,3-dimethylcyclopropane (VII) of 1.08. The *exo*-VII/*endo*-VII ratio was 1.52. Distillation using an 18-in. spinning-band column gave 6.0 g (75%) of VII, bp 82–83°.

The nmr spectrum (A_2X type) of VII showed COMe at τ 6.78 and HCO at 7.61 (triplet, $J_{AX} = 3$ cps) for the *exo* isomer and COMe at τ 6.71 and HCO at 7.10 (triplet, $J_{AX} = 7$ cps) for the *endo* isomer. These values agree well with those previously reported[21] for VII.

Reaction of I and Vinyltrimethoxysilane. A sealed ampoule containing a mixture of 8.2 g (0.042 mol) of I and 6.2 g (0.042 mol) of vinyltrimethoxysilane was heated at 125° for 16 hr. Glpc analysis (column A or B) gave an area ratio of $(MeO)_4Si$/*cis*-/*trans*-1-methoxy-2-(trimethoxysilyl)cyclopropane (VIII) of 1.05. Distillation on an 18-in. spinning-band column gave 3.3 g (50%) of VIII, bp 105–106° (58 mm).

Anal. Calcd for $C_7H_{16}O_4Si$: C, 43.8; H, 8.33; mol wt, 192. Found: C, 43.7, 43.6; H, 8.30, 8.25; mol wt, 192.

In the nmr spectrum of VIII the bands at τ 6.52 and 6.74 charac-

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[23] D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *ibid.*, **7**, 405 (1967).

[24] D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Am. Chem. Soc.*, **90**, 2944 (1968).

[25] For a discussion of the toxicity of silicate esters see, "Industrial Hygiene and Toxicology," Vol. II, 2nd ed, F. A. Patty, Ed., Interscience Publishers, New York, N. Y., 1963, p 1933.

teristic of SiOMe and COMe protons, respectively, were assigned to the *trans* isomer. The τ 6.54 (SiOMe) and 6.71 (COMe) bands were assigned to the *cis* isomer. The *trans*/*cis* ratio based on this tentative assignment was 2.8. Additional bands at τ 6.70 (multiplet overlapping COMe bands), 9.32 (multiplet), and 10.25 (multiplet) were present in the spectrum characteristic of the HCO–, $-CH_2-$, and $SiCH_2-$ protons, respectively, of these isomers.

Reaction of I with Trimethoxysilane. a. In an Ampoule at 125°. A mixture of 8.0 g (0.048 mol) of I and 11.75 g (0.096 mol) of trimethoxysilane was heated in an ampoule at 125° for 16 hr. Glpc analysis (column A) gave an area ratio of $(MeO)_4Si$/(methoxymethyl)trimethoxysilane (IX) of 1.10. Distillation on an 18-in. spinning-band column gave 4.35 g (54.3%) of IX, bp 36–37° (8 mm).

Anal. Calcd for $C_5H_{14}O_4Si$: C, 36.1; H, 8.43; mol wt, 166. Found: C, 36.2, 36.3; H, 8.40, 8.35; mol wt, 166.

The nmr spectrum of IX showed bands at τ 6.48, 6.72, and 6.93 (9:3:2 ratio) due to the –SiOMe, –COMe, and $-CH_2-$ protons, respectively.

b. In the Gas Phase at 250°. A mixture of 16.1 g (0.082 mol) of I and 23.5 g (0.19 mol) of trimethoxysilane was added to the heated quartz tube at a rate of 5.05 ml/hr. Glpc analysis (column A) gave an area ratio of $(MeO)_4Si$/IX of 1.55. Distillation using an 18-in. spinning-band column gave 4.5 g (32%) of IX, bp 36–37° (8 mm).

Acknowledgments. The authors are grateful to Mrs. Barbara Taub for preliminary technical assistance in this study. In addition the assistance and cooperation of our analytical department throughout this work is gratefully acknowledged.

Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). III. The Sulfide-Catalyzed Disproportionation of Aryl Thiolsulfinates[1a]

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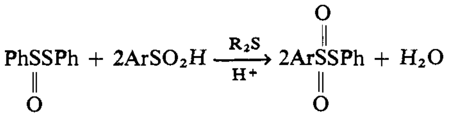
Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received September 26, 1968*

Abstract: In acetic acid–1% water containing some sulfuric acid the disproportionation of phenyl benzenethiolsulfinate (**1**) to phenyl disulfide and phenyl benzenethiolsulfonate is markedly catalyzed by added alkyl or aryl sulfides. Although the formal kinetics of this sulfide-catalyzed disproportionation are exactly the same as those of the previously studied sulfide-catalyzed **1**-sulfinic acid[2] and **1**-mercaptan[3] reactions, *i.e.*, the reaction is first-order in both **1** and sulfide and subject to specific-H^+ catalysis, the dependence of its rate on sulfide structure (Table IV) is entirely different from that observed for the other two sulfide-catalyzed reactions. Experiments using esr offer no indication that free radicals are intermediates in the reaction. For this reason the only mechanism for the sulfide-catalyzed disproportionation which appears to be compatible with both the kinetics and the dependence of rate on sulfide structure is the one shown in Chart III. This involves as its key step the sulfenylation of **1** by the ion R_2S^+SPh (**2**); and, while it might seem that this would normally lead to a greater than first power dependence of rate on thiolsulfinate concentration, it is shown that this is not the case, provided the sulfenylation step is faster than the hydrolysis of **2** to PhSOH and sulfide. Since arguments can be given why this should be the case, the mechanism in Chart III appears to be an acceptable one.

In acid solution phenyl benzenethiolsulfinate (**1**) undergoes a rapid sulfide-catalyzed reaction with sulfinic acids which has the stoichiometry shown in eq 1.[2] Kinetic studies[2] have shown that this reaction is first order in both catalyzing sulfide and thiolsulfinate, but that its rate is *independent* of sulfinic acid concentration. The dependence of its rate on the acidity of the medium and the solvent isotope effect both suggest that the acid catalysis of the reaction is of the specific lyonium ion variety. The mechanism shown in Chart I was accordingly suggested.[2] This mechanism, which involves rate-determining nucleophilic attack of the alkyl sulfide on the protonated thiolsulfinate (eq 3), predicts that alkyl sulfides should also catalyze the reaction of other reagents NuH with **1** *via* a mechanism analogous to that shown in Chart I (NuH = $ArSO_2H$). Furthermore, because of the nature of this mechanism, the rate of such a sulfide-catalyzed **1**-NuH reaction should be the same under a given set of conditions as the rate of the sulfide-catalyzed **1**-$ArSO_2H$ reaction. Study[3] of sulfide catalysis of the reaction of **1** with a mercaptan RSH has shown that these predictions are in fact



$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{PhSSPh}} + 2\mathrm{ArSO_2H} \xrightarrow[\mathrm{H^+}]{\mathrm{R_2S}} 2\mathrm{Ar}\overset{\substack{\mathrm{O} \\ \|}}{\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{S}}}\mathrm{SPh} + \mathrm{H_2O} \qquad (1)$$

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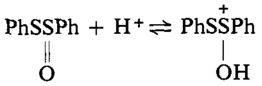
Chart I. Mechanism of the Sulfide-Catalyzed Thiolsulfinate–Sulfinic Acid Reaction



$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{PhSSPh}} + \mathrm{H^+} \rightleftharpoons \overset{+}{\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{PhSSPh}}} \qquad (2)$$

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[1] (a) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Grants AF-AFOSR-106-63 and 106-65 and by the National Science Foundation under Grant GP-6952. (b) National Science Foundation Cooperative Fellow, 1964–1966.

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