Preparation and reactions of sulfoxides and phosphine oxides containing silicon and germanium

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The preparation of several sulfoxides containing silicon or germanium is reported. The thermal rearrangement of the silicon-containing sulfoxides has been observed but neither germanium-containing sulfoxides nor silicon-containing phosphine oxides were found to rearrange thermally at a detectable rate.

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Recently the first example of a thermal rearrangement of a β -functional organosilane, the isomerization of a β -ketosilane to its isomeric siloxyalkene, was reported (1).

Related rearrangements with other similarly substituted compounds appeared to be a possibility. In order to test this hypothesis members of several previously unreported classes of compounds were prepared: silylmethyl sulfoxides,

 R_3SiCH_2SR' ; germylmethyl sulfoxides, R_3Ge-O

 CH_2SR' ; and silylmethylphosphine oxides, R_3Si-

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 $CH_2PR'_2$. Of these, only the silylmethyl sulfoxides were found to rearrange, yielding siloxymethyl sulfides.

The silylmethyl sulfoxides were prepared in high yield by the reaction of methyl arylsulfinate esters with the Grignard reagents prepared from halomethyltrialkylsilanes.

 $\begin{array}{c} \mathsf{O} \\ \uparrow \\ \mathsf{R}_3\mathsf{SiCH}_2\mathsf{M}\mathsf{g}\mathsf{X} + \mathsf{Ar}\mathsf{SO}_2\mathsf{M}\mathsf{e} \to \mathsf{R}_3\mathsf{SiCH}_2\mathsf{SAr} \end{array}$

+ MeOMgX

$$1, R = Me, Ar = Ph$$

2, R = Et, $Ar = p - MeC_6H_4$ —

As outlined below, there was difficulty in obtaining pure sulfoxides and their structures were assigned primarily on the basis of spectroscopic data. The methylene group adjacent to the asymmetric sulfoxide group appeared as an AB system in the n.m.r. spectrum, and strong absorption characteristic of sulfoxides occurred at 9.67 μ in the infrared spectrum. A minor peak in the n.m.r. spectra of silylmethyl sulfoxides at $\delta = 5$ p.p.m. was assigned to the methylene group of the rearrangement product, the sil oxymethyl sulfide.

The polar character of the silylmethyl sulfoxides together with their tendency to rearrange thermally (vide infra) prevented preparation of pure samples. The sulfoxides could not be isolated in good yield from the magnesium halides present in a nonaqueous workup, and it was exceedingly difficult to free the sulfoxides from traces of water introduced by aqueous workup. This water led to hydrolysis of the sulfoxide, yielding hexaalkyldisiloxanes and methyl aryl sulfoxides.

$$\begin{array}{c} O & O \\ \uparrow \\ 2R_3SiCH_2SR' + H_2O \rightarrow R_3SiOSiR_3 + 2MeSR' \end{array}$$

Very careful drying of the crude silylmethyl sulfoxide prior to distillation, using desiccant grade silica gel, gave much lower yields of hydrolysis products and much higher yields of rearrangement products. The fact that the silylmethyl sulfoxides are readily cleaved by water is consistent with the generally observed tendency of β -functional silanes to undergo siliconcarbon bond cleavage: the closely related silylmethyl sulfones also readily undergo cleavage (2).

In the hope of being able to avoid aqueous workups with the attendant problems, attempts were made to prepare trimethylsilylmethyl phenyl sulfoxides from trimethylsilylmethyllithium and benzene sulfinyl chloride, but only uncharacterized gum, and chloromethyltrimethylsilane, the product of halogen-metal exchange, were isolated.

Two additional routes for the preparation of silylmethyl sulfoxides were investigated. The oxidation of silylmethyl sulfides with a variety of standard oxidizing agents showed some evidence of the formation of sulfoxides based on the infrared spectra, but upon workup only starting materials and silanols or disiloxanes were isolated. The second route investigated was the reaction between a halosilane and sodium methylsulfinyl carbanion in dimethyl sulfoxide (3).

 $\begin{array}{c} 0 & O \\ \uparrow & \uparrow \\ R_{3}SiCl + Na^{+}CH_{2}^{-} - S - R' \rightarrow R_{3}SiCH_{2}SR' + NaCl \end{array}$

The only characterizable products isolated from this very complex reaction were disiloxanes or silanols. These products probably arose from the reaction of the chlorosilane with dimethyl sulfoxide, since it has been shown that hexaphenyldisiloxane is the major product found when triphenylchlorosilane is dissolved in dimethyl sulfoxide (4).

The silylmethyl sulfoxides 1 and 2 could be converted essentially quantitatively into the isomeric siloxymethyl sulfides 3 and 4.

$$O$$

$$\uparrow$$

$$R_{3}SiCH_{2}SR' \rightarrow R_{3}SiOCH_{2}SR'$$

$$I, R = Me, R' = Ph$$

$$3, R = Me, R' = Ph$$

2, R = Et, R' = p-MeC₆H₄ 4, R = Et, R' = p-MeC₆H₄

That the rearrangement products were siloxymethyl sulfides was verified by the alternative synthesis shown below:



The product, trimethylsiloxymethyl phenyl sulfide, **3**, had the same spectral and physical properties as the product obtained from the rearrangement of **1**. Trimethylsilyl phenyl sulfide was a major by-product.

Triethylsilyl *p*-tolyl sulfoxide was also shown to undergo an analogous rearrangement yielding **4.** Hexaethyldisiloxane and methyl *p*-tolyl sulfoxide were also isolated from the rearrangement.

The thermal rearrangement of trialkylsilylmethyl aryl sulfoxides may be represented mechanistically as follows:

$$\begin{array}{c} O^{-} & \Delta \\ R_{3}Si - CH_{2} - S - R' \xrightarrow{\Delta} \begin{bmatrix} & O \\ R_{3}Si & SR' \\ \hline CH_{2} \end{bmatrix} \\ R_{3}SiOCH_{2}SR' \leftarrow \begin{bmatrix} & & & \\ & \\ & & \\$$

The first step, attack on silicon by oxygen, is common to several previously studied rearrangements of oxygen-containing organosilicon compounds, such as the silulcarbinol to silul ether rearrangement (5, 6) and the β -ketosilane to siloxyalkene rearrangement (1). The formation of the strong silicon-oxygen bond would appear to provide a powerful driving force for these rearrangements. The intermediate formed in this process, 5, a sulfur ylid, is related to that proposed by Parham et al. (7, 8) or Oae et al. (9) for the Pummerer reaction and it may reasonably be expected to similarly dissociate into an ion pair, 6, which recombines giving the observed product, 7, the siloxymethyl sulfide. An attempt to study the rearrangement kinetically failed since the impure silvlmethyl sulfoxide gave unreproducible and uncharacterized results so that the order of the reaction could not be established.

Trimethylgermylmethyl phenyl sulfoxide, 8, which was synthesized in a similar way to its silicon analog, 1, was prepared in order to compare the rates of rearrangement of related silylmethyl and germylmethyl sulfoxides. Many reactions which involve nucleophilic attack on metalloid atoms proceed much more slowly, if at all, when germanium is substituted for silicon in the molecule (1,10–14). The germyl sulfoxide, 8, was unchanged after heating for 6 days at 60 °C, whereas 1 was totally decomposed after 1 h at 60 °C. However, the germylmethyl sulfoxide underwent hydrolysis to hexamethyldigermoxane and methyl phenyl sulfoxide at 60 °C over 50 days, in the presence of about 1 mole equivalent of water.

In view of the ready rearrangement of silylmethyl sulfoxides to siloxymethyl sulfides, a reaction which essentially results in the reduction of a sulfoxide to a sulfide, it appeared of interest to investigate whether silylmethylphosphine oxides would undergo a similar rearrangement.

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It was hoped that such a rearrangement would provide a simple, clean, and stereospecific pathway for the reduction of phosphine oxides to carbon-functional phosphines. The stereospecific reduction of phosphine oxides to phosphines using trichlorosilane has been reported by Horner and Balzer (15).

Trimethylsilylmethyldiphenylphosphine oxide, 9, prepared by metalation of diphenylmethylphosphine oxide, followed by coupling with trimethylchlorosilane, did not rearrange when heated at 180° for 21 h, but because of traces of water in the samples used, some cleavage of the silicon-carbon bond occurred, presumably by a reaction analogous to those observed with other β -functional silanes, e.g. the sulfones (2), sulfoxides, and ketones (16). Diphenylmethylphosphine oxide, 10, hexamethyldisiloxane, and recovered starting material were identified by their n.m.r. spectra as components of the reaction product. That 9 was, however, essentially unchanged was shown by its recovery in 57% yield along with 10 in 37% yield when a sample to which water had been added purposely was heated to 180° for 21 h.

General Methods

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Experimental

The infrared spectra reported were recorded using a Perkin-Elmer model 257 or model 237B instrument. The n.m.r. spectra of the compounds were recorded on a Varian model A60 or A100 instrument. The data reported for the AB systems observed in the sulfoxides are the calculated chemical shifts of the two protons, which were obtained from the relationship $\Delta \mathbf{v} = (Q^2 - J^2)^{\frac{1}{2}}$, where J is the coupling constant, Q is the distance in Hz between the first and third peaks of the AB system, and $\Delta \mathbf{v}$ is the difference in chemical shift between the two protons. A Varian Aerograph 202-1B dual column instrument was used for the purification of some of the compounds by gas-liquid chromatography. All melting points are uncorrected.

Trimethylsilylmethyl Phenyl Sulfoxide, 1

A solution of 14.0 g (0.09 mole) of methyl benzenesulfinate (17) in 25 ml of tetrahydrofuran was added to 72 ml of a stirred solution of trimethylsilylmethylmagnesium bromide (18) (0.1 mole) in dry ether at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was hydrolyzed with dilute aqueous hydrochloric acid and the aqueous layer was extracted with ether. After very careful drying of the ethereal extracts with sodium sulfate (anhyd.), and removal of the ether by evaporation at room temperature *in vacuo*, 17.5 g (90%) of trimethylsilylmethyl phenyl sulfoxide was obtained. This product was shown by n.m.r. to be ca. 90% pure, the main impurity being a small amount of rearrangement product 2. The material was further dried by dissolving it in dry ether and passing it through a short column $(1'' \times 2'')$ containing desiccant grade silica gel. After removal of the ether, 12.5 g of reasonably dry 1 was isolated, but since it could not be freed of the rearrangement product an analytical sample could not be obtained. N.m.r. (CCl₄): δ 0.14 (s, 9H, Me₃Si), 2.28 and 2.36 (AB, 2H, J = 13.5 Hz, CH₂SO), and 7.2–7.8 p.p.m. (m, 5H, C₆H₅); infrared (neat): 9.67 (S \rightarrow 0), 8.0, and 11.75 μ (Si—Me).

Thermal Rearrangement of 1

A 10.5 g sample of the above material was placed in a small scale fractional distillation apparatus and heated in a nitrogen atmosphere at 60 °C for 1 h at atmospheric pressure. The reaction mixture was then distilled *in vacuo* to give 8.25 g (79%) of trimethylsiloxymethyl phenyl sulfide, **3**, 0.4 g (10%) of hexamethyldisiloxane, collected in a trap cooled with dry ice/acetone, and undistillable gum. The crude **3** was shown by n.m.r. to contain about 10% methyl phenyl sulfoxide. Redistillation of the crude sulfide at 67° (0.55 mm) gave pure material. $n_{\rm p}^{23}$ 1.5242; n.m.r. (CCl₄) δ 0.11 (s, 9H, Me_3 Si), 5.07 (s, 2H, SCH₂O), and 7.05–7.6 p.p.m. (m, 5H, C₆H₅); infrared (neat): 9.3 (C—O—Si), 8.0, and 11.7 μ (Si—Me).

Anal. Calcd. for $C_{10}H_{16}OSSi: C$, 56.56; H, 7.60; S, 15.1; mol. wt., 212.4. Found: C, 56.80; H, 7.63; S, 15.4; mol. wt. (osmometer), 211.5.

The Preparation of 3 from Thiophenol, Formaldehyde, and Trimethylchlorosilane

n-Butyllithium (0.1 mole) in 65 ml of hexane was added to a solution of 11.0 g (0.101 mole) of thiophenol in 100 ml of dry ether. Formaldehyde gas was bubbled through the solution until the reaction was complete $(1\frac{1}{2}$ h). Trimethylchlorosilane (11 g, 0.101 mole) was added to the above solution at 0°, and the mixture was stirred at room temperature for 1 h. After filtration of the precipitated lithium chloride, distillation of the filtrate gave 11 g (60%) of trimethylsilyl phenyl sulfide (b.p. 37° (0.75 mm), lit. (19) 72° (8 mm)) and 4.9 g (23%) of 3, which was identical with the material obtained from the rearrangement of 1.

Triethylsilylmethyl p-Tolyl Sulfoxide, 2

Using similar techniques to those used in the preparation of 1, the reaction of triethylsilylmethylmagnesium chloride with methyl *p*-toluenesulfinate gave an 80% yield of 2, again slightly contaminated with rearrangement product so that a pure sample for analysis could not be obtained. N.m.r. (CCl₄) δ 0.33–1.22 (m, 15H, Et_3 Si), 2.23 and 2.38 (AB, 2H, J = 13.5 Hz, CH_2 SO), 2.34 (s, 3H, *p*-MeC₆H₄), 7.22, and 7.46 (AA'BB' analyzed as AB, 4H, J = 8.5 Hz, *p*-MeC₆H₄); infrared (neat): 9.68 (S \rightarrow 0), 8.05, and 11.60 μ (Si—Et).

The Rearrangement of 2

Using similar techniques as were applied to the thermolysis of trimethylsilylmethyl phenyl sulfoxide, the thermolysis of 2 gave triethylsiloxymethyl *p*-tolyl sulfide 4 (50%), hexaethyldisiloxane (12%), methyl *p*-tolyl sulfoxide (12%), and undistillable gums. The yields of hexaethyldisiloxane (δ 0.3–1.2 p.p.m., *Et*₃Si) and methyl Can. J. Chem. Downloaded from www.nrcresearchpress.com by CONCORDIA UNIV on 11/11/14 For personal use only.

p-tolyl sulfoxide (δ 2.28 p.p.m., p-MeC₆H₄) were estimated from the n.m.r. spectrum of the fraction containing both materials. Gas-liquid chromatography of a small amount of the impure 4 using a $20' \times 3/8''$ aluminium column packed with 20% SE 30 (silicone gum rubber) on Chromosorb W (60-80 mesh) at 265°, flow rate 150 ml/min with helium as carrier gas, gave a sample which after distillation gave 4: b.p. 120° (0.01 mm) (Kugelrohr); n_D^{23} 1.5280; n.m.r. (CCl₄) δ 0.3–1.3 (m, $15H, Et_3Si$; 2.28(s, 3H, p-MeC₆H₄), 5.01(s, 2H, SCH₂O), 7.02, and 7.30 p.p.m. (AA'BB' analyzed as AB, 4H, J = 8.5 Hz, p-MeC₆H₄); infrared (neat): 8.0 and 11.7 (Si-Et), and 9.3 µ (C-O-Si).

Anal. Calcd. for C14H24OSSi: C, 62.63; H, 9.01. Found: C, 62.72; H, 8.96.

Trimethylgermylmethyl Phenyl Sulfoxide, 8

Using techniques similar to those used in the preparation of 1, the reaction of trimethylgermylmethylmagnesium chloride (20, 21) with methyl benzenesulfinate gave a 78% yield of 8. Distillation of this material gave pure trimethylgermylmethyl phenyl sulfoxide: b.p. 120° (0.01 mm) (Kugelrohr); $n_{\rm D}^{22}$ 1.5528; n.m.r. (neat) δ 0.27 (s, 9H, Me_3 Ge), 2.48 and 2.56 (AB, 2H, J = 12.5 Hz, CH_2 SO), 7.34-7.84 p.p.m. (m, 5H, C₆H₅); infrared (neat): 9.67 $(S \rightarrow 0)$, 8.07, and 12.00 μ (Ge—Me).

Anal. Calcd. for C10H16GeOS: C, 46.76; H, 6.28. Found: C, 46.85; H, 6.33.

Trimethylsilylmethyldiphenylphosphine Oxide, 9

n-Butyllithium (0.06 mole) in hexane (35 ml) was added to a solution of 9.3 g (0.043 mole) of diphenylmethylphosphine oxide, 10, in 50 ml of tetrahydrofuran at 10° (22). The mixture was left at 10° for 10 min before 6.5 g (0.06 mole) of trimethylchlorosilane in hexane (10 ml) was added dropwise. The resulting solution was stirred at room temperature for $\frac{1}{2}$ h. Workup gave 10 g of crude product. Chromatography of this material on silica gel gave 6.5 g (53%) of trimethylsilylmethyldiphenylphosphine oxide, m.p. 118-119° after recrystallizations from 1:1 cyclohexane and *n*-hexane: n.m.r. (acetone- d_6) δ 0.02 (s, 9H, Me_3 Si), 2.01 (d, 2H, J = 15 Hz, CH_2 P), and 7.3-8.2 p.p.m. (m, 10H, (C₆H₅)₂P); infrared (Nujol mull): 6.98 (P-C₆H₅), 8.51 (P=O), 8.02, and 11.80 μ (Si-Me).

Anal. Calcd. for C₁₆H₂₁OPSi: C, 66.64; H, 7.34. Found: C, 66.53; H, 7.42.

Also recovered was 2.8 g (30%) of diphenylmethyl-phosphine oxide, m.p. 108–111°, identified by a mixed melting point.

The Attempted Thermolysis of Trimethylsilylmethyldiphenylphosphine Oxide, 9

A 0.2 g sample of 9 was heated at 180° for 21 h. The n.m.r. spectrum of the product showed only starting material (76%), diphenylmethylphosphine oxide (24%), and hexamethyldisiloxane (20%). A further experiment was carried out by heating 9 (1.25 g) (0.00435 mole) containing water (ca. 0.05 g) in a sealed tube at 180° for

21 h. The mixture was estimated to contain 60% of 9 and 40% of diphenylmethylphosphine oxide, 10. Chromatography of this sample gave 0.38 g (37%) of 10, m.p. 110-112° (mixed melting point undepressed), and 0.71 g (57%) of 9, m.p. 118-119° (mixed melting point undepressed). The n.m.r. and infrared spectra of both of these samples were identical with the respective spectra of authentic samples.

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