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# THE SULFOXIDE-SILANE REACTION: A DICHOTOMY OF BEHAVIOR TOWARDS TRICHLOROSILANE

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As part of our continuing program on the studies of the chemistry of sulfur[2] and phosphorus[3] compounds, we are interested in the deoxygenation of sulfoxides and phosphine oxides. Both types of compounds can be reduced by lithium aluminum hydride, but sluggishly. Recently, Fritzche et al[4,5] reported on the facile reduction of phosphine oxides with silanes. This prompted our investigation into the reaction between sulfoxides and silanes.

We have found that aromatic sulfoxides (I) are reduced by trichlorosilane (II) in high yield to the corresponding sulfides (Table I). A mixture of one mole of sulfoxide and 2.5 moles of silane was stirred in ether. After the mixture was worked up by hydrolysis, the product was

$$\underset{\text{(I)}}{Ar_2S = O} \xrightarrow{HSiCl_3} Ar_2S$$

purified by column chromatography on alumina and identified by comparison with authentic samples.

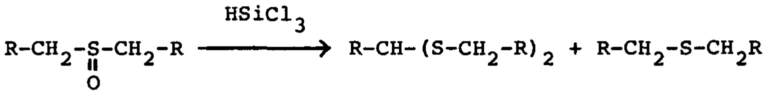
When benzyl sulfoxide (IIIa) was reacted with trichlorosilane under identical conditions and the product isolated as described, a solid crystalline material (IVa) was obtained in good yield, the physical and spectroscopic properties of which were distinctly different from that of

TABLE I

| SULFOXIDE | molar ratio sulfoxide/silane[a] | PRODUCT (YIELD) |
|---|---|---|
| Phenyl (Ia) | 1:2.5 | Phenyl sulfide (98%) |
| p-Tolyl (Ib) | " | p-Tolyl sulfide (100%) |
| p-Chlorophenyl (Ic) | " | p-Chlorophenyl sulfide (85%) |

a. Reaction conditions: ether solution, one hour stirring at room temperature.

the expected sulfide. While the mass spectrum of IVa has a strong peak at m/e = 213 (molecular weight of benzyl sulfide with the loss of hydrogen), there was a molecular ion at m/e = 336. The identity of this compound was revealed by its n.m.r. spectrum which included an AB quartet at τ = 6.40 and was assigned as magnetically non-equivalent benzylic methylene protons. This feature can only be accommodated by structure IVa, the benzyl mercaptal of benzaldehyde. The structure was subsequently proved by comparison with authentic sample[6].



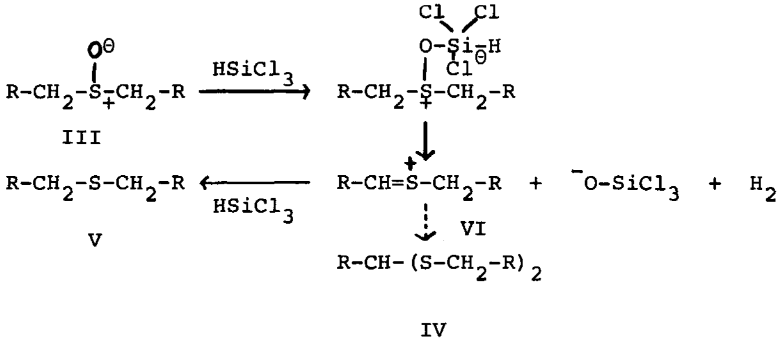
$$\mathrm{R\text{-}CH_2\text{-}\underset{\substack{\| \\ O}}{S}\text{-}CH_2\text{-}R} \xrightarrow{\mathrm{HSiCl_3}} \mathrm{R\text{-}CH\text{-}(S\text{-}CH_2\text{-}R)_2 + R\text{-}CH_2\text{-}S\text{-}CH_2R}$$

IIIa, R=$C_6H_5$    IVa, R=$C_6H_5$    Va, R=$C_6H_5$

b, $C_2H_5$    b, $C_2H_5$    b, $C_2H_5$

c, $C_3H_7$    c, $C_3H_7$    c, $C_3H_7$

Similarly, mercaptals were obtained from the corresponding n-propyl sulfoxide (IIIb) and n-butyl sulfoxide (IIIc) (Table II). There appears therefore to be a dichotomy of behavior toward trichlorosilane between aromatic and aliphatic sulfoxides which must have its origin in the presence of α-hydrogen in the aliphatic sulfoxides. We have adopted the following mechanism as a working hypothesis for the conversion of III to IV.



The intermediate VI has its analogy in the well-known Pummerer rearrangement[7,8]. As partial support of this mechanism, it was found that the use of excess trichlorosilane diverted VI to sulfide via reduction and thereby suppressed the formation of IV (Table I).

It is possible to postulate the cleavage of V by trichlorosilane to give $R-CH_3$ and mercaptide and the latter would react with VI to give mercaptal IV. However, in the case of IIIa, no toluene was detected by VPC; in addition, when the reaction of IIIb was carried out in an excess of benzyl sulfide, no mixed mercaptal was observed.

We are actively investigating the mechanism and synthetic utility of this reaction.

TABLE II

| SULFOXIDES | molar ratio sulfoxide/silane | REACTION TIME[a] | PRODUCT (Isolated yield) |
|---|---|---|---|
| Benzyl IIIa | 1:2 | 3 hrs. | Mercaptal IVa (85%)<br>Sulfide Va (13%) |
| Benzyl IIIa | 1:4 | 3 hrs. | Mercaptal IVa (52%)<br>Sulfide Va (46%) |
| n-Propyl IIIb | 1:2 | 1 hr. | Mercaptal IVb (53%)<br>Sulfide Vb (16%) |
| n-Propyl IIIb | 1:4 | 1 hr. | Mercaptal IVb (50%)<br>Sulfide Vb (35%) |
| n-Butyl IIIc | 1:2 | 1 hr. | Mercaptal IVc (59%)<br>Sulfide Vc (39%) |
| n-Butyl IIIc | 1:4 | 1 hr. | Mercaptal IVc (14%)<br>Sulfide Vc (75%) |

a. Reaction conditions: ether solution stirred at $0^{o}$.

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