DEOXYGENATION OF DIALKYL SULFOXIDES BY DIMETHYLSILYLENE: STERIC REQUIREMENTS

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Summary

Competition reactions of dialkyl sulfoxides with photochemically generated dimethylsilylene have been carried out. Sterically hindered sulfoxides are deoxygenated less efficiently than less encumbered sulfoxides. These results are discussed.

We have previously shown that photochemically generated dimethylsilylene [1] reacts with dimethyl sulfoxide to yield dimethyl sulfide and dimethylsilanone [2]. This latter reactive intermediate subsequently undergoes cyclooligomerization to yield hexamethylcyclotrisiloxane (I) and octamethylcyclotetrasiloxane (II).

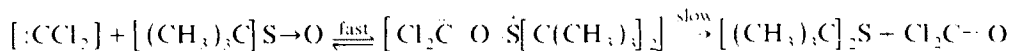$$\left[(CH_3)_2Si:\right] + (CH_3)_2S \to O \to (CH_3)_2S + \left[(CH_3)_2Si=O\right] \to I + II$$
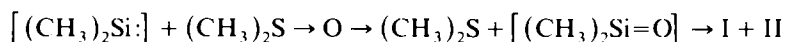
As part of our program to explore the reactivity of dimethylsilylene, we have attempted to determine the mechanism of the initial deoxygenation reaction of sulfoxides by dimethylsilylene. Competition between two different sulfoxides for reaction with dimethylsilylene has been utilized to explore the steric requirements of this reaction. We find that sterically hindered sulfoxides compete less effectively for dimethylsilylene than do sterically less encumbered sulfoxides. For example, di-t-butyl sulfoxide is about three times less reactive than dimethyl sulfoxide or diethyl sulfoxide both of which are approximately equal in reactivity. As might be expected, diisopropyl sulfoxide is about twice as reactive as di-t-butyl sulfoxide. In our experience tetramethylene sulfoxide is most reactive. Specifically, it is about three times more reactive than either dimethyl or diethyl sulfoxide toward dimethylsilylene. The high reactivity of tetramethylene sulfoxide is probably due to its conformational rigidity and to the steric accessibility of its sulfoxide functionality. (See Table 1 for supporting data).

These results are in contrast to those observed in the deoxygenation of sulfoxides by dichlorocarbene [3,4]. In these reactions, sterically hindered sulfoxides have been found to react more rapidly than less encumbered sulfoxides. Relief of steric strain
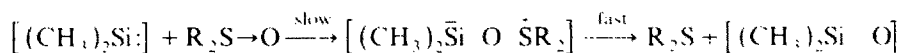
TABLE 1

COMPETITION REACTIONS OF SULFOXIDES FOR DIMETHYLSILYLENE

Competing sulfoxides	Molar ratio	Relative yields of corresponding sulfides
$(CH_3)_2S \rightarrow O / (CH_3CH_2)_2S \rightarrow O$	1.0 / 1.0	48.4 ± 0.7 51.6 ± 0.7
$(CH_3)_2S \rightarrow O$ / [cyclopentyl]$S \rightarrow O$	1.0 / 1.0	21.0 ± 0.2 79.0 ± 0.2
$(CH_3CH_2)_2S \rightarrow O$ / [cyclopentyl]$S \rightarrow O$	1.0 / 1.0	26.4 ± 0.4 73.6 ± 0.4
$[(CH_3)_2CH]_2S \rightarrow O$ / [cyclopentyl]$S \rightarrow O$	1.0 1.0	17.0 ± 0.3 83.0 ± 0.3
$[(CH_3)_3C]_2S \rightarrow O$ / [cyclopentyl]$S \rightarrow O$	1.0 / 1.0	7.0 ± 0.9 93.0 ± 0.9

in the complex apparently accelerates formation of products. These results have been interpreted as consistent with a rate-limiting decomposition of the initial dichloro-carbene-sulfoxide adduct to product.

$$[:CCl_2] + [(CH_3)_3C]_2S \rightarrow O \overset{fast}{\rightleftharpoons} [Cl_2C-O-\overset{+}{S}[C(CH_3)_3]_2] \overset{slow}{\rightarrow} [(CH_3)_3C]_2S - Cl_2C - O$$

We conclude that the mechanism of deoxygenation of sulfoxides by dimethylsilylene must be different. At least two mechanisms are consistent with our data. In the first, the rate-limiting step is attack of dimethylsilylene on the sulfoxide oxygen.

$$[(CH_3)_2Si:] + R_2S \rightarrow O \overset{slow}{\rightarrow} [(CH_3)_2\overset{-}{Si}-O-\overset{+}{S}R_2] \overset{fast}{\rightarrow} R_2S + [(CH_3)_2Si-O]$$
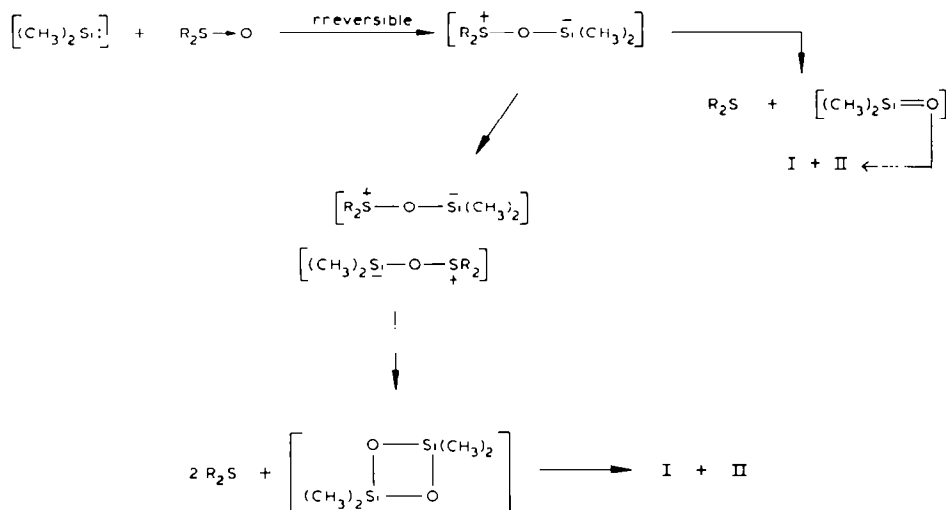
An alternative possibility is that the initial attack of dimethylsilylene on the sulfoxide oxygen is irreversible. If this latter possibility is correct, the formation of I, II and sulfide products may not involve a free dimethylsilanone intermediate. Rather, a bimolecular reaction between two zwitterionic intermediates might be possible (Fig. 1). At present, we cannot distinguish between these possibilities.

While a large number of reactions of silylenes have been found to be analogous to those of carbenes [5], our results join a growing number of examples in which carbenes and silylenes differ in their reactions and reactivities [6,7].

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. IR spectra were obtained as CCl_4 solution on a Perkin Elmer 281 spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT

$$\left[(CH_3)_2\overset{..}{Si}:\right] \;+\; R_2S \rightarrow O \;\xrightarrow{\text{irreversible}}\; \left[R_2\overset{+}{S}-O-\overset{-}{Si}(CH_3)_2\right] \longrightarrow$$

$$R_2S \;+\; \left[(CH_3)_2Si = O\right]$$

$$I + II \longleftarrow$$

$$\left[R_2\overset{+}{S}-O-\overset{-}{Si}(CH_3)_2\right]$$

$$\left[(CH_3)_2\underset{\cdot}{Si}-O-\underset{+}{S}R_2\right]$$

$$2\,R_2S \;+\; \left[\begin{array}{c} O-Si(CH_3)_2 \\ | \qquad\quad | \\ (CH_3)_2Si-O \end{array}\right] \longrightarrow I + II$$

mode using 5% solution in deuterochloroform with an internal standard of chloroform. GLPC analyses were performed on a Hewlett–Packard F&M 700 using 12' × 1/4", 10% Silar 7CP on 60/80 mesh Chromosorb W column. These were carried out in a temperature programming mode starting at 30°C with a rate of temperature increase of 3°C/min. Product yields were determined by GLPC using n-decane as an internal standard. All the starting materials and products are known compounds. In those cases where spectral data have not been previously reported we have included this information.

Dimethyl sulfoxide was obtained from Aldrich. It was distilled from calcium hydride under vacuum (b.p. 70°C/10 mmHg [8]) and finally stored over activated 4 Å molecular sieves.

Tetramethylene sulfoxide was obtained from Aldrich. It was purified by column chromatography on alumina. Small amounts of the corresponding sulfide were removed by elution with hexane. The desired tetramethylene sulfoxide was eluted with ether. It had spectral properties in complete agreement with literature values [9].

Diethyl, diisopropyl, and di-t-butyl sulfide were obtained from Aldrich.

Diethyl and diisopropyl sulfoxides were prepared by oxidation of the corresponding sulfides with hydrogen peroxide and titanium(III) chloride [10].

A solution of 30% aqueous hydrogen peroxide (7.0 mmol) in methanol (15 ml) was added dropwise at room temperature over a period of 1 h to a solution of dialkyl sulfide (70 mmol) and titanium trichloride (20% aqueous solution, 10 ml) in aqueous methanol. After completion of the addition, the reaction was stirred for 5 minutes and quenched by addition of ice–water (50 ml). The reaction mixture was extracted with chloroform (4 × 100 ml). The combined organic extracts were dried over anhydrous magnesium sulfate and filtered. Chloroform was removed by evaporation under reduced pressure. In this way the corresponding sulfoxide was obtained (71-75%) contaminated with starting sulfide (15%). The product was purified by column chromatography through alumina. The sulfide is eluted with hexanes while the desired sulfoxide eluted with ether. The ether solution was dried over anhydrous magnesium sulfate and filtered. Removal of the solvent under

reduced pressure gave the pure sulfoxides. Diethyl sulfoxide b.p. 56–58°C (0.5 torr) was obtained in 75% yield (Lit. b.p. 45–47°C/0.15 torr) [11]. NMR δ 2.77 (q, 2H, J 7 Hz), 1.45 (t, 3H, J 7 Hz). IR: ν(S=O) 1070 cm^{-1}. Diisopropyl sulfoxide b.p. 60–62°C (0.5 torr) was obtained in 71% yield (Lit. b.p. 50°C/0.1 torr [3]). NMR δ 2.78 (sept, 2H, J 7 Hz), 1.31 (d of d, J 7 and 3.6 Hz ppm). IR: ν(S–O) 1050, 1020 cm^{-1}.

Di-t-butyl sulfoxide was prepared according to the following procedure [12]. A solution of m-chloroperbenzoic acid (40 mmol) in 100 ml of anhydrous methylene chloride was added dropwise over a period of 1 h to a solution of di-t-butyl sulfide (41.0 mmol) in methylene chloride (100 ml) at 0–5°C (ice bath). The solution was stirred for 5 h, then allowed to come to ambient temperature overnight. The solution was cooled (ice–water), filtered to remove the m-chlorobenzoic acid, washed with a saturated solution of sodium bicarbonate (3 × 100 ml), and finally dried over magnesium sulfate. After filtration, the solvent was removed under reduced pressure. In this way colorless crystals of di-t-butyl sulfoxides, yield 3.9 g (60%) were obtained. These were purified by column chromatography. Di-t-butyl sulfoxide had the following properties, m.p. 62–63°C (lit. m.p. 63.5–65°C [13]). NMR: δ 1.37 (s, 9 H) ppm. IR: ν(S=O) 1040, 1020 cm^{-1}.

General procedure for photochemical competition reactions of sulfoxides

The procedure below should be considered typical for the photochemical reduction of sulfoxides by dimethylsilylene.

Competition reaction [14] of dimethyl sulfoxide and diethyl sulfoxide for photochemically generated dimethylsilylene. Dodecamethylcyclohexasilane [15,16] (34.8 mg, 0.10 mmol); dimethyl sulfoxide (78 mg, 1.0 mmol) and diethyl sulfoxide (106 mg, 1.0 mmol) were dissolved in dry spectroquality dioxane. n-Decane (14.2 mg, 0.1 mmol) was added to the mixture as internal standard. The solution, total volume (1 ml) was placed in a 5 mm quartz NMR tube. The solution was photolyzed with a 450 W medium pressure Hanovia Hg lamp housed in a water cooled quartz well for 90 min at 5°C in an ice–water bath. Dimethyl sulfide and diethyl sulfide were obtained in 48 and 52% relative yield, by GLPC.

Acknowledgement

References

1 M. Ishikawa and M. Kumada, J. Organometal. Chem., 42 (1972) 325.

2 H.S.D. Soysa, H. Okinoshima and W.P. Weber, J. Organometal. Chem., 133 (1977) C17.

3 J.C. Dyer and S.A. Evans, Jr., J. Org. Chem., 45 (1980) 5350.

4 H.S.D. Soysa and W.P. Weber, Tetrahedron Lett., (1978) 1969.

5 For a recent review of silylene chemistry see: P.P. Gaspar in M. Jones, Jr. and R.A. Moss (Eds.), Reactive Intermediates, Wiley Interscience, New York, 1978, Vol. 1, p. 229–277.

6 K.P. Steele and W.P. Weber, J. Am. Chem. Soc., 102 (1980) 6095.

7 K.P. Steele, D.J. Tzeng, and W.P. Weber, J. Organometal. Chem., 231 (1982) 291.

8 R.G. LeBel and D.A.I. Goring, J. Chem. Eng. Dat., 7 (1962) 100.

9 T. Cairns, G. Eglinton and D.T. Gibson, Spectrochimica Acta, 20 (1964) 31.

10 Y. Watanabe. T. Numata and S. Oae, Synthesis, (1981) 204.

11 H.J. Leonard and C.R. Johnson, J. Org. Chem., 27 (1962) 282.

12 D.M. Frieze, P.F. Hughes, R.L. Merrill and S.A. Evans, Jr., J. Org. Chem., 42 (1977) 2206.

13 D. Barnard, L. Bateman, M.E. Cain, T. Colclough, and J.I. Cunneen, J. Chem. Soc., (1961) 5359.

14 W. von E. Doering and W.A. Henderson, Jr., J. Am. Chem. Soc., 80 (1958) 5274.

15 R. West, Ann. N.Y. Acad. Sci., 239 (1974) 262.

16 M. Laguerre, J. Dunogues, and R. Calas, J. Chem. Soc. Chem. Commun., (1978) 272.