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LETTERS

The Sila-Pummerer Rearrangement of 3,3-Dimethyl-3-Silathiane S-Oxide

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Abstract: The thermal conversion of sulfoxide 1 into the O-silylated cyclic O,S-acetal (2) is the first example of the sila-Pummerer rearrangement of cyclic organosilicon sulfoxides leading to ring expansion. The kinetics of the rearrangement are studied and thermodynamic parameters are determined. The results are in compliance with mechanism involving a pentacoordinated silicon atom.

The sila-Pummerer rearrangement is one of numerous intramolecular rearrangements characteristic of the α- and β-carbofunctional organosilicon compounds.[1] It consists in transformation of thermally unstable α-trimethylsilylmethyl(organyl)sulfoxides into the corresponding O-silylated O,S-acetals due to 1,3-migration of the silicon atom to the sulfoxide oxygen atom.[1,2]

Factors determining the ease of the rearrangement are most completely studied for acyclic saturated sulfoxides of the type $Me_3SiCR'R''S(O)R$. They are: (i) steric effects of the substituent(s) at the α-carbon atom; (ii) electronic effects of the substituent at the sulfur atom, and (iii) stereochemistry of the sulfoxide. The steric shielding of the sulfoxide group with one (R' = H, R'' = Alk, Ar, alkenyl, etc.) or two (R' = Ar, R'' = Alk, alkenyl) substituents at the α-carbon atom tends to slow down[3,4] or completely suppress the process[5] as compared to the unsubstituted analogues.[2] More negative charge on the oxygen atom facilitates migration of the silyl group so that alkyl sulfoxides (R = Alk) undergo the rearrangement much more readily (below room temperature)[6, 7] than the aryl derivatives (R = Ar).[2,4a] However, when a *t*-Bu group is attached to the sulfur atom the rearrangement of the alkyl sulfoxide proceeds only on heating.[6] The steric effect of a bulky $Si(OCH_2CH_2)_3N$ group is, apparently, responsible for the thermal stability (to 130-170°C) of alkylsulfoxides $RSOCH_2Si(OCH_2CH_2)_3N$ (R = Me, Et).[8]

One of the main factors affecting the ease of transformation of α-silylsulfoxides into the O-silyl-O,S-thioacetals is the stereochemistry of the Si–C–S=O fragment.[1c,6,7,9] A necessary condition for the rearrangement of α-silylsulfoxides is the *syn*-coplanarity of the Si–C and S=O bonds which facilitates the intramolecular interaction between the silicon and oxygen atoms.[7] The effect is most pronounced for cyclic sulfoxides having an exocyclic silicon atom: these sulfoxides are thermally stable only when the silyl and sulfoxide groups are *anti*-periplanar (*E*-configuration).[9-10]

The above trends are only qualitative since no kinetic studies of the rearrangement has been reported in the literature.

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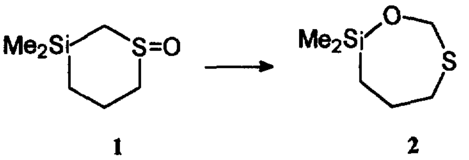
Here we report on the sila-Pummerer rearrangement of the recently obtained cyclic organosilicon sulfoxide,[11] 3,3-dimethyl-3-silathiane S-oxide **1** in which the sulfoxide group is predominatly equatorial. Heating **1** in THF for 2 h leads to its complete transformation into the seven-membered cyclic O,S-acetal **2**.[12] This reaction is the first example of a 1,3-migration of a silicon atom to a sulfoxide oxygen resulting in ring expansion.



Scheme 1

Ring expansion by intramolecular nucleophilic attack of an oxy-anion on a silicon atom has been described for cyclic α-silylcarbinols.[13]

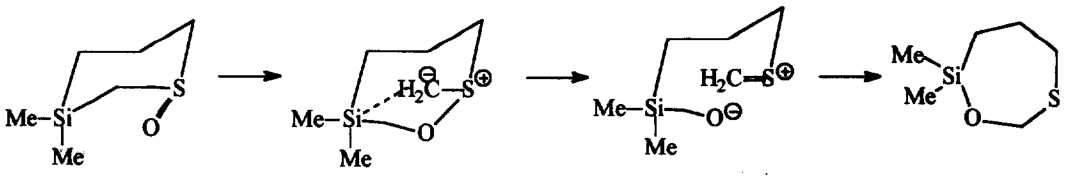
Acidic hydrolysis of the cyclic O-silyl O,S-acetal **2** affords, as judged from NMR spectroscopy and mass-spectrometry, a linear product, 1,1,3,3-tetramethyl-1,3-bis(3'-mercaptopropyl)disiloxane **3**.[14]

$$\mathbf{2} \longrightarrow \mathrm{HCHO} + (\mathrm{HSCH_2CH_2CH_2})\mathrm{Me_2SiOH} \longrightarrow \underset{\mathbf{3}}{[(\mathrm{HSCH_2CH_2CH_2})\mathrm{Me_2Si}]_2\mathrm{O}}$$

Scheme 2

The kinetics of the rearrangement were measured in CCl_4 at 65, 70, and 80°C by integration of the singlet assigned to the OCH_2S protons of **2** at 4.88 ppm (twice at each temperature, Fig. 1). The first-order rate constants *k* are 2.015×10^{-4}, 4.45×10^{-4}, and 7.12×10^{-4} s^{-1}, respectively. Activation parameters were found to be $\Delta E^{\neq}$ 50.8 kJ/mol, $\Delta H^{\neq}$ 47.7 kJ/mol, $\Delta S^{\neq}$ −171 J/mol·K. The value of $\Delta E^{\neq}$ is substantially lower than that found for a similar rearrangement of both linear and cyclic silylated ketones[15] which proceed with the silyl group migrating to the carbonyl oxygen through the transition state with a pentacoordinated silicon atom, and is consistent with the substantially higher thermal stability of β-silyl ketones as compared to α-silylsulfoxides of similar structure.

The strongly negative value of $\Delta S^{\neq}$ imply a very constrained transition state and may be indicative of the Si-O bond formation preceding the Si-C bond breaking in the first stage of the Brook ylide mechanism, as illustrated below. The formation of an ylide as a kinetically independent species (proved in some cases by trapping experiments[16]) is in our case still dubious because of substantially lower (cf. ref.[15]) energy of activation. More definite conclusions on the mechanism require additional studies which are in progress now.



Scheme 3

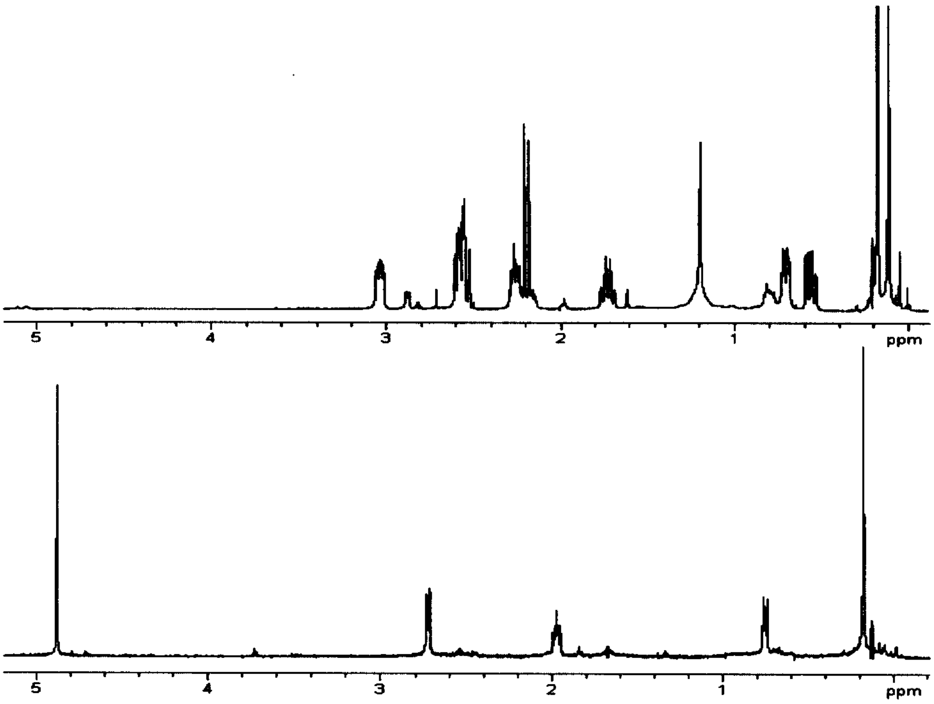


Fig. 1.^{1}H NMR spectra of the reaction mixture (Scheme 1) – initial (above), and final (below)

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References and Notes

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12. *Typical Experimental Procedure*: Sulfoxide **1** (0.24 g, 1.5 mmol) was heated in THF (10 mL) for 2 h, then the solvent removed under vacuum. Yield of the crude product 0.23 g (97%). Due to its hydrolytic instability, preventing purification by column chromatography, the analytically pure sample of **2** was obtained by preparative GC (10% Lukopren on Chromaton N-AW, column temperature 125°C). n_D^{20} 1.4880. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) d 0.17 (6H, s, Me_2Si), 0.75 (2H, *XX'*-part of the *XX'AA'MM'* spin system, J_{5ax6ax} 9.5 Hz, J_{5ax6eq} 6.4 Hz, J_{5eq6eq} 3.3 Hz, $SiCH_2C$), 1.96 (2H, *AA'*-part of the *XX'AA'MM'* spin system, CCH_2C), 2.72 (2H, *MM'*-part of the *XX'AA'MM'* spin system, J_{6ax7ax} 8.4 Hz, J_{6ax7eq} 5.6 Hz, J_{6eq7eq} 2.8 Hz, CCH_2S), 4.88 (2H, s, SCH_2O). Found, %: C 44.86, H 8.85, Si 17.39, S 19.85. $C_6H_{14}SiOS$. Calcd, %: C 44.40, H 8.69, Si 17.30, S 19.19.
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14. *Hydrolysis of* **2**: To a solution of **2** (0.62 g, 2 mmol) in THF (20 mL) was added conc. HCl (6 mL, 60 mmol) and the reaction mixture was stirred for 2 h at room temperature. The solution was washed with 5% NH_4HCO_3 and dried over $MgSO_4$. A viscous oil (0.58 g) obtained after removal of the solvent was filtered through a silica plug and identified as thiol **3**. n_D^{20} 1.4741 (lit.[17] n_D^{20} 1.4739). ^{1}H NMR ($CDCl_3$) d 0.05 (6H, s, Me_2Si); 0.62 (2H, m, $SiCH_2$), 1.31 (1H, br.s, SH), 1.69 (2H, m, CCH_2C), 2.68 (2H, m, CCH_2S). Mass spectrum: $[HSCH_2CH_2CH_2Si(CH_3)_2]_2O$, M^+ 282 (1%), 280 (12%), 265 (6%), 223 (24%), 191 (12%), 181 (37%,), 149 (100%), 133 (13%), 119 (10%), 103 (5%), 90 (7%), 75 (13%), 73 (34%), 59 (20%), 41 (18%).
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