

Sila-Pummerer Rearrangement of Cyclic Sulfoxides: Computational Study of the Mechanism

Bagrat A. Shainyan,^{*,†} Svetlana V. Kirpichenko,[†] and Fillmore Freeman^{*,‡}

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of the Russian Academy, 664033 Irkutsk, Russia, and Department of Chemistry, University of California, Irvine, Irvine, California 92697-2025

Received May 18, 2004; E-mail: bagrat@iroch.irk.ru

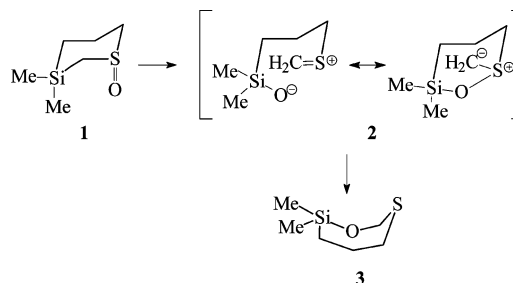
Migration of a silyl group from carbon to heteroatom (O, N, S) is a key step in numerous intramolecular rearrangements of carbofunctional organosilicon compounds which have been long investigated both experimentally and theoretically.^{1–12} The rearrangements proceed under anionotropic or cationotropic,⁸ as well as catalytic^{9,10} or thermal conditions.^{1,2} Among these, of special mechanistic and synthetic interest, is the sila-Pummerer rearrangement. It was discovered by Brook in 1968¹³ as thermal conversion of linear α -silyl sulfoxides into siloxymethyl sulfides and has been widely used in organic synthesis for the preparation of carbonyl compounds,¹⁴ vinyl sulfides,^{15–17} etc.^{14,18–23} However, its mechanism is not as yet fully understood although various assumptions have been made on the basis of the experiments.¹⁴ It is generally accepted that the driving force of the rearrangement is the formation of the O–Si bond and that the reaction proceeds via the ylide or carbocationic intermediates.^{14,24–27} In some works the intermediate ylides have been trapped by various dipolarophiles^{27,28} as well as fullerenes.^{29,30} Strange as it is, there is a lack of theoretical studies of the sila-Pummerer rearrangement; neither the transition states connecting the reagents, intermediate ylides, and products nor the involvement of pentacoordinated silicon species were investigated. At the same time, this could provide a better understanding of the mechanism of the reaction. For this reason as well as prompted by our earlier work on the kinetics of thermal ring expansion of 3,3-dimethyl-3-silathiane *S*-oxide (**1**)³¹ we report here on theoretical study of this reaction, namely, the sila-Pummerer rearrangement of 3,3-dimethyl-3-silathiane *S*-oxide (**1**) to the *O,S*-acetal (**3**) proceeding, as we suggested, by Scheme 1.

The stereochemistry of the Si–C $_{\alpha}$ –S=O fragment is an important factor affecting the ease of the rearrangement. The syn-configuration of the Si–C $_{\alpha}$ and S=O bonds provides the proximity of the silicon and oxygen atoms and thus favors the Si–O bond formation leading to the rearrangement.^{15,16}

From the two possible chair conformers of **1** we have taken the one with the S=O group axial since our previous DFT calculations gave it by 1.67 kcal/mol more stable than the equatorial.³²

The B3LYP/6-311+G(d,p) optimized geometry of the axial chair conformer of **1** gives the C $_{\alpha}$ –Si and S=O bonds to be synclinal with the dihedral angle Si–C $_{\alpha}$ –S=O of 53.7° and the O \cdots Si distance of 3.407 Å, i.e., the molecule is in a reasonable conformation for 1,3-migration of silicon to oxygen. Product **3** has a slightly distorted boat conformation with the sulfur atom at the bow and the Si–C(4) bond at the stern. Its energy is 41.22 (B3LYP) or 43.96 (MP2) kcal/mol lower than that for **1**, so, the reaction is very exothermic. The ylide **2** suggested as an intermediate was found to be a real minimum on the potential energy surface lying 3.46 (B3LYP) or 3.77 (MP2) kcal/mol higher than **1**. The optimized conformation of ylide **2** can be regarded as a slightly distorted boat

Scheme 1. Sila-Pummerer Rearrangement of 3,3-dimethyl-3-silathiane *S*-oxide (**1**) to the *O,S*-acetal (**3**)



with the oxygen and the C5 atom at the bow and the stern (Figure 1). It is noteworthy that, while boat conformations are generally unstable and are usually transition states, the 2,5-boat conformer of ylide **2** is a minimum on the potential energy surface. B3LYP and MP2 calculations show that there are other minima corresponding to the chair, twist, and boat conformers of ylide **2**, but the structure in Figure 1 is the one which lies between the two transition states on the reaction coordinate. Frequency calculations give the following relative thermodynamic parameters for the **1** \rightarrow **2** conversion: $\Delta H^{\circ} = 3.11$, $\Delta G^{\circ} = 1.72$ kcal/mol; and $\Delta H^{\circ} = -46.02$, $\Delta G^{\circ} = -45.06$ kcal/mol for the **2** \rightarrow **3** conversion. For the whole process **1** \rightarrow **3**: $\Delta H^{\circ} = -42.92$, $\Delta G^{\circ} = -43.34$ kcal/mol.

Vibrational frequency calculations verified that there are two transition states on the way from **1** to **3** (Figure 2). The first one ([**TS-1**][‡]) connects sulfoxide **1** and the intermediate ylide **2**. It lies 25.97 (B3LYP) or 23.06 (MP2) kcal/mol higher than **1** and has one imaginary frequency of -169 cm $^{-1}$. The second transition state ([**TS-2**][‡]) connects the ylide **2** and the product of rearrangement **3**. It lies 22.86 (B3LYP) or 26.36 (MP2) kcal/mol higher than **1** and has one imaginary frequency of -317 cm $^{-1}$.

Moving along the reaction path from **1** to [**TS-1**][‡] results in elongation of the S–O and Si–C $_{\alpha}$ bonds by 0.115 and 0.469 Å, respectively, shortening of the S–C $_{\alpha}$ bond by 0.100 Å, and formation of a partial O \cdots Si bond. The silicon atom adopts a distorted trigonal bipyramidal structure with the C4, O, and Me equatorial and the C2 and the other Me axial. Further progress along the reaction path leads the system to ylide **2** with the lengths of the Si–O (1.668 Å) and O–S (1.851 Å) bonds close to the values for those of ordinary covalent bonds, and possessing the double bond S=CH $_2$ (1.628 Å). Moving uphill from ylide **2** to [**TS-2**][‡] is accompanied by elongation and rupture of the O–S bond from 1.851 to 2.462 Å, and disrotation around the Si–C(4) and C(6)–S bonds so that the oxygen and C(2) atoms approach each other to 2.432 Å.

Frequency calculations give the following relative thermodynamic parameters for the **1** \rightarrow [**TS-1**][‡] conversion: $\Delta H^{\circ} = 21.68$, $\Delta G^{\circ} = 23.12$ kcal/mol; and $\Delta H^{\circ} = 21.61$, $\Delta G^{\circ} = 21.84$ kcal/mol

[†] Siberian Division of the Russian Academy.

[‡] University of California, Irvine.

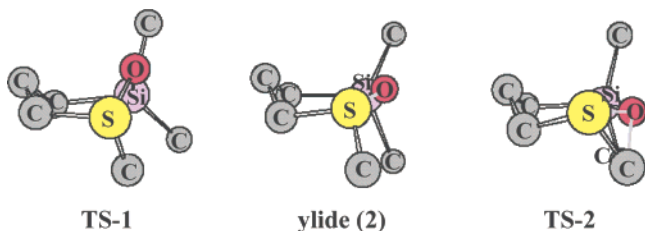


Figure 1. Structures of transition states TS-1 and TS-2 and ylide 2.

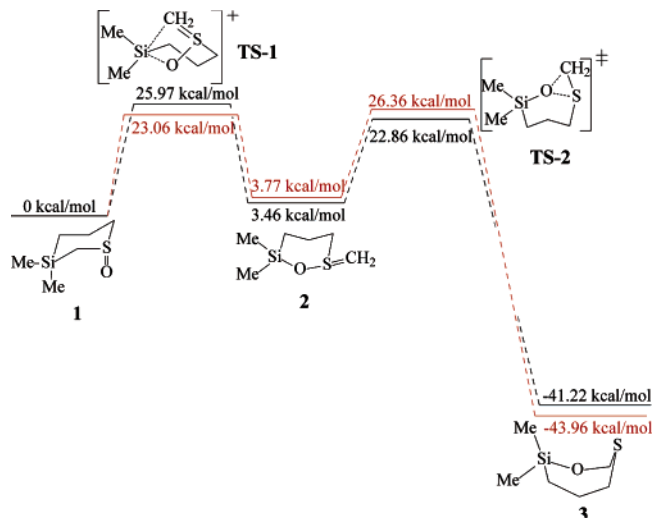


Figure 2. B3LYP/6-311+G(d,p) (black) and MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p) (red) potential energy diagram for the sila-Pummerer rearrangement $1 \rightarrow 3$.

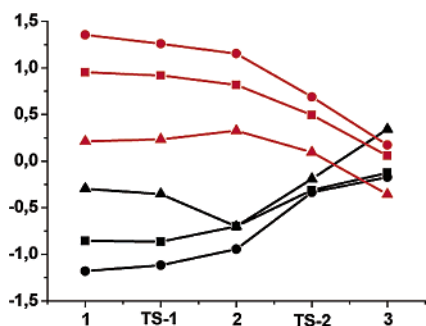


Figure 3. Variation of atomic charges on C2 (black) and S (red) atoms along the reaction path. (■) Mulliken; (●) NPA; (▲) electrostatic.

for the $2 \rightarrow [\text{TS-2}]^\ddagger$ conversion. The experimental energy of activation found by us earlier was 12.1 kcal/mol.³¹

Atomic charges were calculated by different schemes of partitioning the electron density. Most adequately varied along the reaction path (Scheme 1) are the electrostatic charges. This relates first of all to the charges on atoms C2 and S (Figure 3). Only the electrostatic scheme gives a sharp increase of the negative charge on C2 up to -0.701 for ylide 2 and a high positive charge on it (0.343) for product 3 in which C2 is connected with two

electronegative atoms, O and S (Scheme 1). As to the sulfur atom, both the Mulliken and NPA charges on it monotonically decrease along the reaction path, being positive for all species involved. On the contrary, the electrostatic scheme gives the maximum of the positive charge (0.327) on the sulfur atom in ylide 2 and a negative charge on it (-0.356) in product 3, and this is in compliance with chemical reasoning (Scheme 1).

Thus, it may be concluded that the sila-Pummerer rearrangement of organosilicon cyclic sulfoxides includes the intermediate ylide. The reaction pathway also includes two transition states, the first one with pentacoordinated Si, connecting the reagent and the ylide, and the second one on the way from the ylide to the product of rearrangement.

Acknowledgment. B.A.S. and S.V.K. are grateful to the Russian Foundation for Basic Research for financial support (Grant No. 04-03-32131).

Supporting Information Available: Optimized geometries and atomic charges (Mulliken, NPA, and electrostatic) for all stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Brook, A. G.; *Acc. Chem. Res.* **1974**, *7*, 77.
- Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 149.
- Kwart, H. *Phosphorus Sulfur* **1983**, *15*, 293.
- Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 8597.
- Paderes, M. D.; Alonso, R. *J. Org. Chem.* **2000**, *65*, 2292.
- Moser, W. H. *Tetrahedron* **2001**, *57*, 2065.
- Takeda, K.; Sumi, K.; Hagiwara, S. *J. Organomet. Chem.* **2000**, *611*, 449.
- Honda, T.; Mori, M. *J. Org. Chem.* **1996**, *61*, 1196.
- Nakajima T.; Segi M.; Sugimoto F.; Hioki R.; Yokota S.; Miyashita, K. *Tetrahedron* **1993**, *49*, 8343.
- Le Bideau, F.; Malacria, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *107*, 275.
- Gevorgyan, V.; Borisova, L.; Lukevics, E. *J. Organomet. Chem.* **1992**, *436*, 277.
- Choi, J.; Imai, E.; Mihara, M.; Oderaotoshi, Y.; Minakata, S.; Komatsu, M. *J. Org. Chem.* **2003**, *68*, 6164.
- Brook, A. G.; Anderson, D. G. *Can. J. Chem.* **1968**, *46*, 2115.
- Block, E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281.
- Bonini, B. F.; Lenzi, A.; Maccagnani, G.; Barbaro, G.; Giogianni, P.; Macciantelli, D. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2643.
- Bonini, B. F.; Mazzanti, G.; Zani, P.; Maccagnani, G. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2083.
- Miller, R. D.; Hassig, R. *Tetrahedron Lett.* **1984**, *25*, 5351.
- Iwao, M. *Heterocycles*, **1994**, *38*, 45.
- Dardaine, M.; Langlois, N. *Tetrahedron Lett.* **1992**, *33*, 3641.
- Dardaine, M.; Chiaroni, A.; Riche, C.; Langlois, N. *Tetrahedron Lett.* **1992**, *33*, 6143.
- Still, I. W. J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *58*, 129.
- Still, I. W. J.; Strautmanis, J. R. *Can. J. Chem.* **1990**, *68*, 1408.
- Choi, J.; Imai, E.; Mihara, M.; Oderaotoshi, Y.; Minakata, S.; Komatsu, M. *J. Org. Chem.* **2003**, *68*, 6164.
- Hart, D. J.; Tsai, Y.-M. *Tetrahedron Lett.* **1983**, *24*, 4387.
- Bhupathy, M.; Cohen, T. *Tetrahedron Lett.* **1987**, *28*, 4793.
- Block, E.; Yencha, A.; Aslam, M.; Eswarakrishnan, V.; Luo, J.; Sano, A. *J. Am. Chem. Soc.* **1988**, *110*, 4748.
- Aono, M.; Hyodo, C.; Terao, Y.; Achiva, K. *Tetrahedron Lett.* **1986**, *27*, 4039.
- Aono, M.; Terao, Y.; Achiva, K. *Chem. Lett.* **1987**, 1851.
- Ishida, H.; Ohno, M. *Tetrahedron Lett.* **1999**, *40*, 1543.
- Ishida, H.; Itoh, K.; Ohno, M. *Tetrahedron* **2001**, *57*, 1737.
- Kirpichenko, S. V.; Suslova, E. N.; Albanov, A. I.; Shainyan, B. A. *Tetrahedron Lett.* **1999**, *40*, 185.
- Shainyan, B. A.; Kirpichenko, S. V. *Russ. J. Gen. Chem.* **2003**, *73*, 1709.

JA047083U