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Oxa-Cope Rearrangement of Silenes Thermally Generated from 1,2-Bis[tris(trimethylsilyl)silylcarbonyl]alkanes

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Silenes are important organosilicon species as the analogues of alkenes. Although many papers concerning the synthesis and chemical behavior of silenes have been published to date, the chemical properties of silenes are not yet well understood when compared with those of alkenes and still need further studies.[1] Acylpolysilanes have been extensively studied as the efficient precursors of silenes. The 1,3-silyl shift from the polysilane unit to the carbonyl oxygen, giving silenes, under photochemical[1,2] and thermal conditions,[3] refers to Brook-type rearrangement and gives high yields of silenes including stable ones.[2b] To explore further the scope of the chemistry of acylpolysilanes, we prepared 1,2-bis[tris(trimethylsilyl)silylcarbonyl]ethane and cyclohexane (**1a** and **1b**) in which two acylpolysilane units are linked by an ethylene chain and investigated their thermally induced rearrangement. Interestingly, the silenes generated from the acylpolysilanes readily underwent skeletal rearrangement under the reaction conditions, as the first example of Cope-type rearrangement[4] of silenes.

When **1a** was heated in benzene at 150 °C for 20 h, rearranged product **2a** was obtained in 26% isolated yield (Scheme 1, Table 1). In this reaction, the starting **1a** was recovered in 38% yield. Similar treatment of **1a** at 200 °C gave **2a** in 94% yield. The formation of **2a** can be best explained by assuming the formation of silene **3a**, followed by oxa-Cope rearrangement, as shown in Scheme 1. Previously, Brook et al. have reported the reactions of the silenes produced by photochemical isomerization of acylpolysilanes with the precursor acylpolysilane[5a] and acylsilanes[5b] which afford cycloadducts or ene-type adducts. However, no intermolecular adducts were found to be formed in the thermolysis of **1a**.

Scheme 1

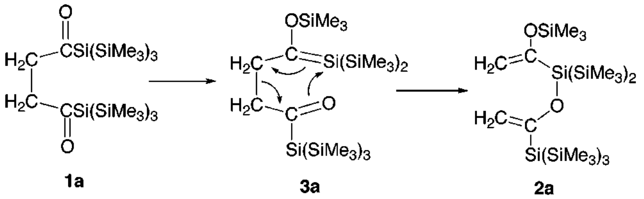
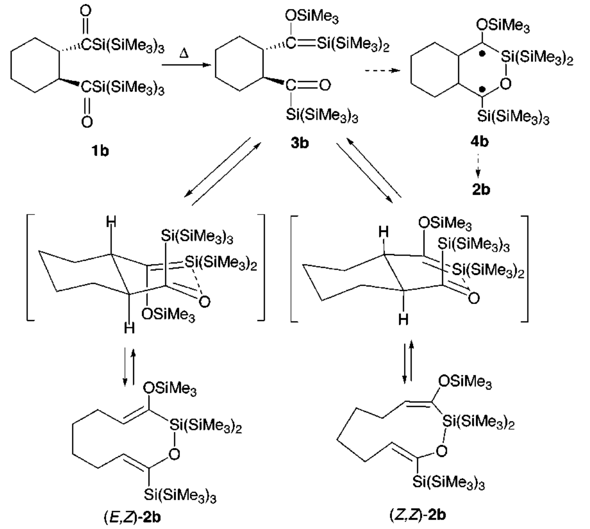


Table 1. Reactions of **1a** and **1b**

compound	temp/°C	time/h	yield/%[a]	
			2	**1**[b]
1a	150	20	26	38
	200	20	94	0
1b	150	20	12(87/13)[c]	76
	150	60	40(82/18)[c]	42
	200	20	94(22/78)[c]	3

[a] Isolated yield. [b] Yield of the starting **1** recovered. [c] Yield as a mixture with the ratio of (*E*,*Z*)-**2b**/(*Z*,*Z*)-**2b** in the parenthesis.

Scheme 2



Heating a benzene solution of **1b** at 150 °C for 20 h gave a mixture of (*E*,*Z*)- and (*Z*,*Z*)-2-trimethylsiloxy-3,3-bis(trimethylsilyl)-5-tris(trimethylsilyl)silyl-3-sila-4-oxacyclodeca-1,5-diene ((*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b**) in a ratio of (*E*,*Z*)-**2b**/(*Z*,*Z*)-**2b** = 87/13 in 12% combined yield, together with a 76% yield of the starting **1b** recovered (Scheme 2, Table 1). A longer reaction period led to a higher combined yield of the products with a slight decrease of the ratio of (*E*,*Z*)-**2b**/(*Z*,*Z*)-**2b**. At 200 °C, in contrast, (*Z*,*Z*)-**2b** was obtained as the major product.

Similar to **2a**, the formation of isomerization products **2b** can be understood by assuming silene **3b** as the initial intermediate as shown in Scheme 2. However, attempted trapping of the silene was unsuccessful. Thus, in the presence of a large excess of methanol, which is known as an efficient trapping agent of silenes, the reaction of **1b** at 200 °C gave a complex mixture, and no major products were separated from the mixture.

The selective formation of (*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b**, depending on the reaction temperature, may be understood by a concerted mechanism (Scheme 2). At lower temperature, silene **3b** would undergo concerted oxa-Cope rearrangement via a chairlike six-membered cyclic transition state to afford (*E*,*Z*)-**2b**, while, for the concerted formation of (*Z*,*Z*)-**2b**, it would be necessary to assume an unfavorable boatlike transition state. Heating a 87/13 mixture of (*E*,*Z*)-**2b**/(*Z*,*Z*)-**2b** at 200 °C for 20 h resulted in a decrease of the ratio to 65/35, indicating that thermal isomerization of (*E*,*Z*)-**2b** to (*Z*,*Z*)-**2b** had occurred. This is probably due to retro-Cope rearrangement of (*E*,*Z*)-**2b** leading to **3b** and clearly

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[1] (a) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Willey: New York, 1997; Volume 2, Chapter 16. (b) Kira, M.; Miyazawa, T. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Willey: New York, 1997; Volume 2, Chapter 22. (c) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

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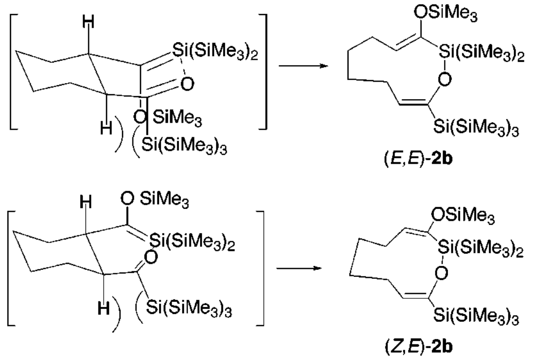
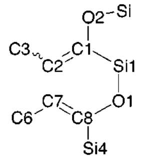
Scheme 3



indicates that compounds (*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b** are the kinetically and thermodynamically favored products, respectively. This is in accordance with the results of ab initio molecular orbital (MO) calculations on the model system described bellow.

It might be considered that a diradical intermediate (**4b** in Scheme 2) would be involved in this system. However, the fact that the reactions proceeded stereoselectively to form (*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b** and that there was no formation of (*E*,*E*)- and (*Z*,*E*)-isomers strongly excludes the existence of the diradical intermediate. As can be seen in Scheme 3, the concerted transition states leading to (*E*,*E*)- and (*Z*,*E*)-isomers seem to be disfavored due to the steric repulsion between the $(Me_3Si)_3Si$ group and an adjacent hydrogen atom, as compared with those of (*E*,*Z*)- and (*Z*,*Z*)-isomers.

Crystal structures of (*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b** were determined by X-ray diffraction studies.[6] Twisting of enol unit of Si1−C1($OSiMe_3$)═C2H−C3 in (*E*,*Z*)-**2b** is much more significant relative to that of (*Z*,*Z*)-**2b**, as indicated by the torsion angles of Si1−C1−C2−C3 and O2−C1−C2−C3, as shown in Figure 1. The longer bond length of C1−C2 in (*E*,*Z*)-**2b** than that in (*Z*,*Z*)-**2b**, as well as the smaller sum of bond angles around C1 (358.0° for (*E*,*Z*)-**2b** and 359.9° for (*Z*,*Z*)-**2b**) would also reflect the higher steric requirement in (*E*,*Z*)-**2b**. For the other enol fragment, there appear no significant differences in the torsion angles in (*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b** within 3.3°. However, the bond length of C7−C8 is certainly longer in (*E*,*Z*)-**2b** than in (*Z*,*Z*)-**2b**. Since there can be seen no significant contacts between the substituents in both (*E*,*Z*)-**2b**, and (*Z*,*Z*)-**2b**, the larger steric deformation in (*E*,*Z*)-**2b** than in (*Z*,*Z*)-**2b** would be due to the higher configurational ring strain.



	(*E*,*Z*)-**2b**	(*Z*,*Z*)-**2b**
C1-C2	1.325(6)	1.299(8)
C7-C8	1.340(5)	1.310(6)
Si1-C1-C2-C3	-154.3(5)	6(1)
O2-C1-C2-C3	9.1(8)	-175.4(8)
Si4-C8-C7-C6	21.5(6)	-22.4(9)
O1-C8-C7-C6	-161.2(5)	157.9(6)

Figure 1. Bond distances (Å) and dihedral angles of enol units in the crystal structures of (*E*,*Z*)-**2b** and (*Z*,*Z*)-**2b**.

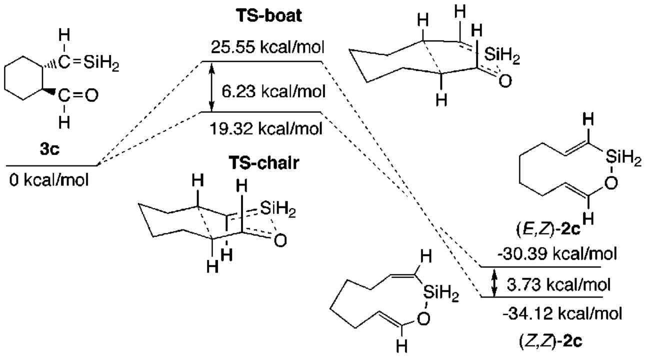


Figure 2. Energy diagram derived from MO calculations at RHF/6-31G level, for the concerted oxa-Cope rearrangement of silene **3c**.

To know more about the oxa-Cope rearrangement of the silenes, we carried out MO calculations at the level of RHF/6-31G on simplified model systems with silene **3c** as the reactant (Figure 2). The optimized geometries of (*E*,*Z*)- and (*Z*,*Z*)-**2c** closely resemble those of the crystal structures of (*E*,*Z*)- and (*Z*,*Z*)-**2b**, respectively. Figure 2 represents the energy diagram for the reactions. As can be seen in Figure 2, the transition state with chairlike configuration (**TS-chair**), which leads to the formation of (*E*,*Z*)-**2c**, was calculated to be more stable than the boatlike transition state (**TS-boat**), producing (*Z*,*Z*)-**2c** by 6.23 kcal/mol. However, (*Z*,*Z*)-**2c** was found to be slightly more stable than (*E*,*Z*)-**2c**. These results agree well with the experimental observation described above. Thus, at lower temperature silene **3b** produced from **1b** would undergo rearrangement via a chairlike transition state similar to **TS-chair** to give (*E*,*Z*)-**2b**. At elevated temperature, however, more stable and thermodynamically favored isomer (*Z*,*Z*)-**2b** would be formed.

In conclusion, we have demonstrated that the silenes, generated from **1a** and **1b**, underwent concerted Cope-type rearrangement, leading to isomerization products. The stereochemistry of the reactions of **1b** provided the mechanistic interpretation for the product formation, in which a transition state with a chairlike conformation gave the kinetically favored products as often observed for the Cope rearrangement of alkenes. It is also noteworthy that the Cope rearrangement of the silenes presumably proceeded in a reversible fashion. Although Cope rearrangement of alkenes comprises an important class of organic reactions, as being applicable to the synthesis of complex molecules,[4] no reports concerning the Cope-type rearrangement of silenes have been published so far, and the present observation is the first example of it, to the best of our knowledge.

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Supporting Information Available: Experimental details of the preparation of **1a** and **1b**, and their thermal reactions. ORTEP drawing, tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds (*E*,*Z*)-**2b**, and (*Z*,*Z*)-**2b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[6] Crystal Data for (*E*,*Z*)-**2b**: $C_{26}H_{64}O_2Si_8$, space group *P*-1 (No. 2) with $a = 10.4000(4)$ Å, $b = 13.6060(7)$ Å, $c = 16.4700(9)$ Å, $\alpha = 70.966(2)°$, $\beta = 86.573(3)°$, $\gamma = 75.269(3)°$, $V = 2130.0(2)$ Å^3, $Z = 2$, $T = 233$ K, refl($I > 3\sigma(I)$)/para = 21.5, $R = 8.4\%$, $R_w = 11.5\%$. Crystal data for (*Z*,*Z*)-**2b**: $C_{26}H_{64}O_2Si_8$, space group $P2_1/n$ (No. 14) with $a = 16.207(5)$ Å, $b = 10.103(9)$ Å, $c = 26.820(5)$ Å, $\beta = 103.94(2)°$, $V = 4262(4)$ Å^3, $Z = 2$, $T = 296$ K, refl($I > 3\sigma(I)$)/para = 13.1, $R = 5.8\%$, $R_w = 5.5\%$.