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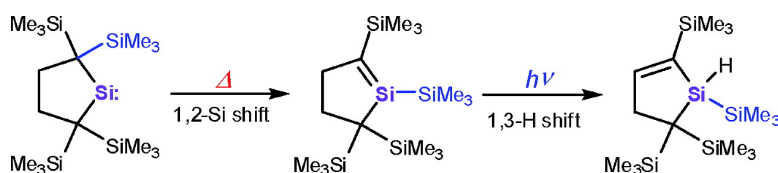
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Organometallics, **2009**, 28 (3), 919-921 • DOI: 10.1021/om800692b • Publication Date (Web): 12 January 2009

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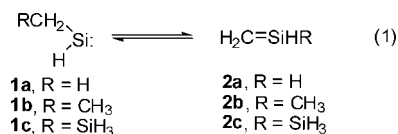
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Received July 21, 2008

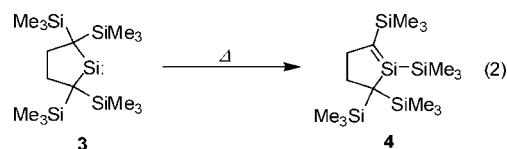
Summary: A kinetic study of the thermal irreversible isomerization of an isolable dialkylsilylene into the corresponding cyclic silene revealed that the activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) are $18.49 \pm 0.43 \text{ kcal mol}^{-1}$ and $-20.32 \pm 1.35 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively. The relatively low ΔH^\ddagger and negative ΔS^\ddagger values are in accord with the concerted 1,2-silyl migration via a cyclic transition state as previously proposed. The cyclic silene in benzene- d_6 isomerized photochemically into the corresponding alkenylsilane via 1,3-hydrogen shift.

A number of theoretical and experimental studies have been devoted to the relative stability between silylenes and the corresponding silenes and the barrier separating the two species.¹ On the basis of ample theoretical studies of the relationship between parent silene (**1a**) and methylsilylene (**2a**) (eq 1), we may now approve the conclusion that the energy difference between **1a** and **2a** is very small but the barrier height is very high (ca. 40 kcal mol⁻¹).^{1,2} Though the energy difference depends strongly on the computational methods and basis sets, the long controversial arguments seem to have converged to the conclusion that silylene **1a** is 3–4 kcal mol⁻¹ more stable than silene **2a**.² Substituent effects on both the energy difference and the barrier are known to be significant.^{1b} For instance, Nagase and Kudo³ have found that silylene **1b** is 10.3 kcal mol⁻¹ less stable than silene **2b** at the MP3/6-31G* level, while the isomerization between **1a** and **2a** and between **1c** and **2c** is almost thermoneutral. The barrier heights for the isomerization of **1a**, **1b**, and **1c** into **2a**, **2b**, and **2c** are calculated to be 43.0, 44.4, and 24.8 kcal mol⁻¹, indicating that the barrier for 1,2-silyl migration is remarkably lower than those for 1,2-hydrogen and 1,2-methyl migration.



In contrast to the detailed and systematic theoretical studies of silylene-silene isomerization,¹ experimental evidence for the

isomerization is very poor; a few studies have proposed that silene-to-silylene isomerization occurs during the high-temperature thermolysis of silacyclobutanes and polysilanes.^{4,5} In our previous paper reporting the synthesis of the first isolable dialkylsilylene **3**,⁶ we have mentioned that silylene **3** isomerizes into the corresponding silene **4** slowly at room temperature in solution (eq 2). In this note, we discuss kinetics and mechanisms of the silylene-to-silene isomerization of **3** and unprecedented photochemical isomerization of silene **4** into the corresponding alkenylsilane via 1,3-hydrogen shift.



When a hexane solution of silylene **3** in a sealed NMR tube was kept at room temperature in the dark, the characteristic orange color of **3** turned to pale yellow. Time course of the UV–vis spectrum of the solution is shown in Figure 1. With increasing time, the absorption bands I (440 nm) and III (260 nm) due to silylene **3**⁶ decreased and the new band II (338 nm) increased with the isosbestic points at 380 and 290 nm, indicating that silylene **3** isomerizes irreversibly into a single product quantitatively.⁷ The product was isolated as an air and moisture sensitive pale yellow oil and identified as silene **4** by ¹H, ¹³C, and ²⁹Si NMR spectroscopies.

The rates and activation parameters for the thermal isomerization were determined by monitoring the time-course of the absorbance at 440 nm of silylene **3** by UV–vis spectroscopy

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(7) Irreversible isomerization of silylene **3** to **4** was monitored also by ¹H NMR spectroscopy. See Supporting Information for the details.

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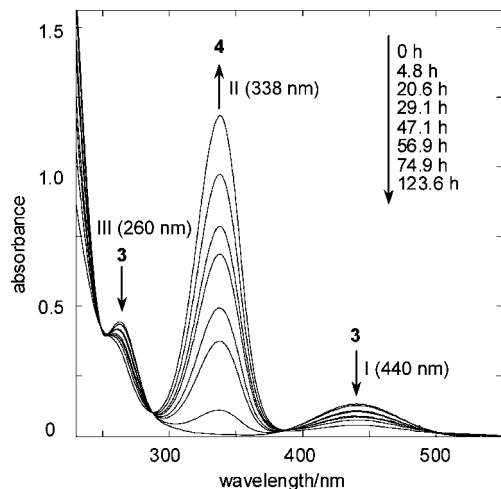


Figure 1. Time-course of UV-vis spectra of a solution of silylene **3** in hexane at 293 K.

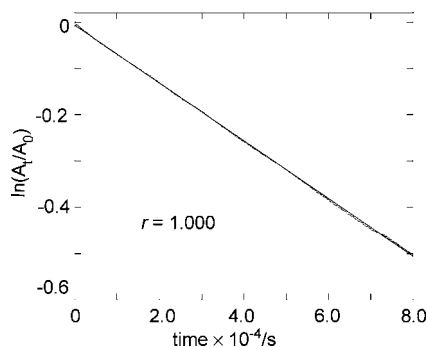


Figure 2. A plot for $\ln(A_t/A_0)$ vs time at 298 K; A_t and A_0 are the absorbance at 440 nm at $t = t$ and 0, respectively.

Table 1. First-Order Rate Constants (k) and Half-Lives ($t_{1/2}$) of the Isomerization of **3** to **4** at Various Temperatures

temperature/K	$k \times 10^6/\text{s}^{-1}$	$t_{1/2}/\text{min}$
298	6.24	1853
303	9.80	1179
308	18.1	639
313	28.3	408
318	47.7	242
323	64.2	180
328	121	95
333	188	61

at various temperatures. A plot of $\ln[A_t/A_0]$ (A_t and A_0 are the absorbance at 440 nm at $t = t$ and 0, respectively) at each temperature displayed good linear relationship, supporting the unimolecularity of the isomerization. A typical kinetic plot for the isomerization is shown in Figure 2. The rate constants and half-lives of **3** determined at various temperatures are summarized in Table 1. The activation parameters for the thermal isomerization of **3** to **4** were determined from the slope and intercept of the Eyring plot (Figure 3) to be $\Delta H^\ddagger = 18.49 \pm 0.43 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -20.32 \pm 1.35 \text{ cal mol}^{-1} \text{ K}^{-1}$.

The relatively large negative ΔS^\ddagger value suggests that the transition state of this isomerization would have a significantly restricted structure, and therefore, any multistep mechanism involving bond-cleavage at the rate controlling step may be eliminated from possible mechanisms.⁸ The ΔH^\ddagger value is

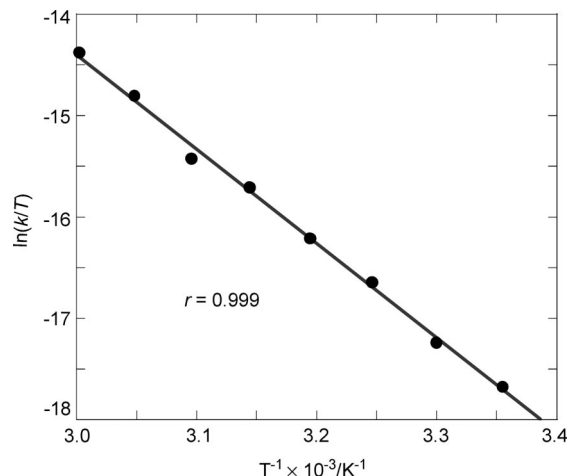
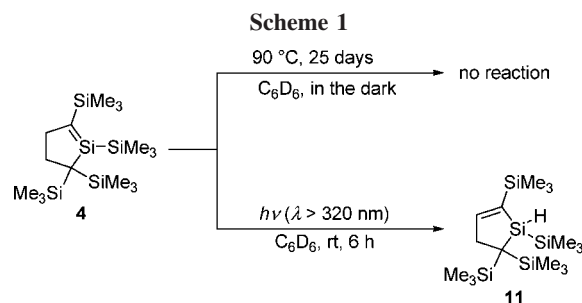


Figure 3. Eyring plot for the isomerization of **3** to **4**.



consistent with the theoretical barrier for the isomerization from **1c** to **2c** calculated by Nagase et al. ($E_a = 24.8 \text{ kcal mol}^{-1}$ at MP3/6-31G* level),³ suggesting that the present isomerization is a concerted *intramolecular* 1,2-silyl migration via the cyclic transition state similar to that located theoretically for the isomerization of **1c** to **2c**.³

Germanium and tin analogues of silylene **3**⁹ are thermally stable, showing no isomerization into the corresponding germene and stannene occurs even at 100 °C.⁶ The results are in good accord with the general trend that group-14 divalent species become more stable relative to the corresponding doubly bonded compounds with increasing the atomic number among the heavier group-14 metal elements.¹⁰

Silene **4** is thermally very stable; no reaction occurred when **4** was heated in benzene at 90 °C for 25 days (Scheme 1). The irreversible thermal silylene-to-silene isomerization suggests that silylene **3** is more than 3 kcal mol⁻¹ less stable than silene **4** in this particular case.

To further elucidate the 1,2-silyl migration between heavier group-14 metallylenes into the corresponding metallenes, geometries, and energies of model metallylenes **5**, **7**, and **9**, metallenes **6**, **8**, and **10**, and the transition states TS1, TS2, and TS3 for the 1,2-silyl migration were optimized at several theoretical levels of DFT calculations (Scheme 2).¹¹ The results are summarized in Table 2. As expected, the activation energy

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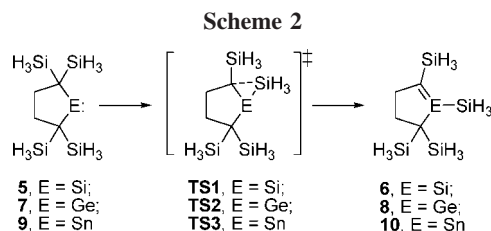
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Table 2. Relative Energies for Silylene-to-Silene and Related Rearrangements^a

reaction	method/basis	E_a^b /(kcal mol ⁻¹)	ΔE^c /(kcal mol ⁻¹)
5 → 6 (Si)	B3LYP/6-311G(d)	21.3	-0.7
	B3LYP/Lan12dz	21.7	-3.0
7 → 8 (Ge)	B3LYP/6-311G(d)	28.7	15.9
	B3LYP/Lan12dz	27.9	11.0
9 → 10 (Sn)	B3LYP/Lan12dz	36.0	25.8

^a Energy with zero point energy. ^b Activation energy for the forward reaction. ^c Relative energy between metallylene and metallene. Positive values mean metallylene is more stable than metallene.



and the relative stability of metallylene (ΔE) both increased in the order $E = \text{Si} < \text{Ge} < \text{Sn}$, while significant dependence on the theoretical levels was observed.¹¹ The ΔE value between silylene **5** and silene **6** is less negative than that expected from the irreversible isomerization from **3** to **4**. The reason would be ascribed to the larger energy of steric repulsion between two geminal trimethylsilyl groups in **3** than that between two geminal trihydrosilyl groups in **5**; i.e., the energy relieved during the reaction **3** → **4** is much larger than that during the reaction **5** → **6**.

Irradiation of silene **4** in benzene-*d*₆ using a filtered light ($\lambda > 320$ nm) at room temperature gave an isomeric cyclic alkene **11** via an interesting 1,3-hydrogen shift, instead of an inverse isomerization to silylene **3** (Scheme 1). Although there have been a number of photochemical 1,3-sigmatropic rearrangements known, the present finding constitutes the first silene-to-alkenylsilane rearrangement via 1,3-hydrogen sigmatropy.^{12,13}

Experimental Section

¹H (300 MHz), ¹³C (75 MHz), and ²⁹Si (59 MHz) NMR spectra were recorded on a Bruker AC-300P spectrometer. Mass spectra were obtained on a JEOL JMS-600W mass spectrometer. UV-vis spectra were recorded on a Milton Roy SP3000 or a Hewlett-Packard G1103A (8453E) spectrometer equipped with a temperature controller and a magnetic stirring cell holder for kinetics. IR spectra were recorded on a Shimadzu FTIR-8600PC Fourier transform

infrared spectrophotometer. Samples of silylene **3** for spectroscopic measurements were prepared in a VAC MO-40-M glovebox.

Synthesis of 4 via Thermolysis of 3. When a mixture of silylene **3** (50 mg, 0.13 mmol) and benzene-*d*₆ (0.5 mL) in a sealed NMR tube was kept at 60 °C for 24 h in the dark, the initial orange solution turned gradually pale yellow. The quantitative formation of silene **4** was confirmed by ¹H, ¹³C, and ²⁹Si NMR spectroscopies. Pure silene **4** was obtained as an air and moisture sensitive pale yellow oil by simple distillation of volatiles. Spectroscopic data of **4** are shown in the previous paper.^{6a} ¹³C NMR signals in C₆D₆ were assigned as follows using the DEPT experiments: δ 0.9 (SiMe₃), 1.7 (SiMe₃), 1.9 (2 × SiMe₃), 19.2 (C), 35.3 (CH₂), 38.8 (CH₂), 145.4 (C=Si). Repeated measurements of the UV-vis spectra of **4** in 3-methylpentane confirmed that the absorptivity (ϵ) at $\lambda_{\text{max}} = 388$ nm is 6900 instead of the previously reported ca. 9000.^{6a}

Kinetics of the Isomerization of 3 to 4. The rates of the isomerization of **3** to **4** were determined UV-vis spectroscopically in hexane at various temperatures. Typically, a hexane solution of silylene **3** in a sealed quartz cuvette was placed in a cell holder with a Peltier device and a temperature controller. Temperature was controlled within ± 0.3 K. The solution was allowed to warm up for 5–10 min and then variation of the absorbance at 440 nm was monitored with time. Kinetic plots at various temperatures are shown in Supporting Information.

Photochemical Isomerization of Silene 4 to Alkenylsilane 11. A mixture of silene **4** (ca. 50 mg) and benzene-*d*₆ (0.6 mL) in a sealed NMR sample tube was irradiated using a 500 W high pressure mercury arc lamp with a glass cutoff filter (L-32, Irie Co, Ltd.). The pale yellow color of the solution disappeared after 6 h. Quantitative formation of compound **11** was confirmed by NMR spectroscopy. **11**: a colorless oil; ¹H NMR (C₆D₆, δ) 0.11 (s, 9H, SiMe₃), 0.13 (s, 9H, SiMe₃), 0.20 (s, 9H, SiMe₃), 0.32 (s, 9H, SiMe₃), 2.65 (ddd, ²*J* = 19.3 Hz, ³*J* = 2.6 Hz, ⁴*J* = 3.8 Hz, 1H), 2.69 (ddd, ²*J* = 19.3 Hz, ³*J* = 2.6 Hz, ⁴*J* = 2.1 Hz, 1H), 4.61–4.71 (m, 1H, SiH, ¹*J*(Si–H) = 165 Hz), 6.86 (td, ³*J* = 2.6, ⁴*J* = 1.0 Hz, 1H, C=CH); ¹³C NMR (C₆D₆, δ) 0.2 (SiMe₃), 0.3 (SiMe₃), 0.9 (SiMe₃), 1.4 (SiMe₃), 5.9 (C), 43.3 (CH₂), 140.1 (C), 160.8 (CH); ²⁹Si NMR (C₆D₆, δ) -18.2, -8.0, -6.7, 3.0, 3.9; MS (EI, 70 eV) *m/z* (%) 372 (2, M⁺), 357 (11), 298 (100), 283 (31), 239 (21), 225 (37), 73 (15); IR ν (Si–H) 2060 cm⁻¹; HRMS calcd for C₁₆H₄₀Si₅, 372.1977, found, 372.2005.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan [Specially Promoted Research (No. 17002005), M.K. and T.I.].

Supporting Information Available: Figures and text discussing the time-course of ¹H NMR of silylene **3** in C₆D₆ at room temperature and kinetic analysis for the isomerization of **3** to **4**, tables and a scheme discussing the theoretical calculations for the reactions of **5**, **7**, and **9** giving **6**, **8**, and **10**, and figures showing the magnified parts of ¹H NMR of **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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