Intramolecular Dimerization of Silylenes Leading to Novel Cyclic Disilenes[1]

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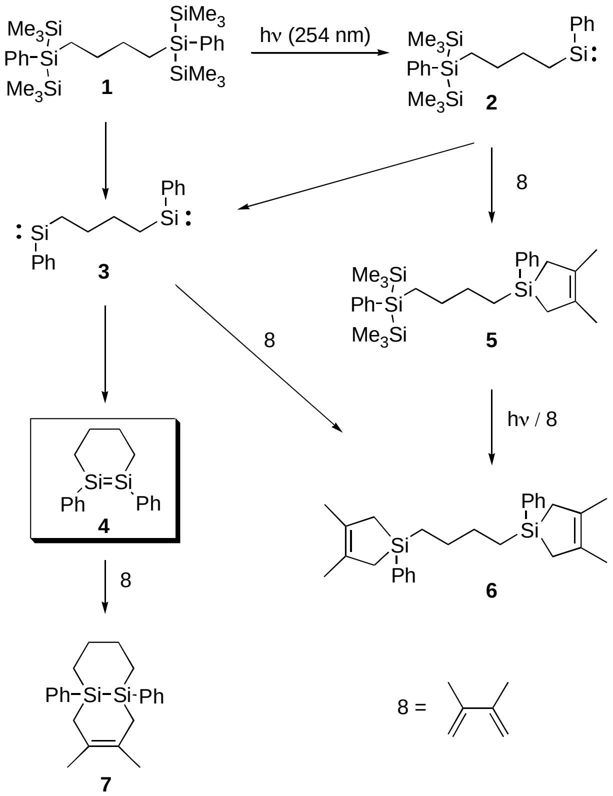
Photochemically generated 1,6-diphenyl-1,6-disilahexane-1,1,6,6-tetrayl (1,6-bissilylene) undergoes intramolecular dimerization to give 1,2-diphenyl-1,2-disilacyclohex-1-ene.

Silylenes, divalent silicon species, can dimerize to form disilenes, silicon-silicon double-bonded compounds.[2] West *et al.* thus obtained the first isolable disilene, tetramesityldisilene, in 1981.[3] Since then the chemistry of silicon-silicon doubly bonded compounds, disilenes, has enjoyed a few decades of explosive growth.[4] Intermolecular dimerization of silylenes has been utilized as one of the standard methods for generating kinetically stabilized disilenes. However, the intramolecular dimerization of remotely generated silylenes in a molecule has never been known up to date, except for an attempted generation of a related 1,2-bissilylene.[5] We report herein the first example of the generation and consecutive intramolecular dimerization of two silylenes in a molecule, 1,6-diphenyl-1, 6-disilahexane-1,1,6,6-tetrayl (**3**), to form a cyclic disilene, 1,2-diphenyl-1,2-disilacyclohex-1-ene (**4**).

In order to generate the requisite silylene, 1,6-diphenyl-1,6-disilahexane-1,1,6,6-tetrayl (1,6-bissilylene), a trisilane derivative **1** was synthesized as a photochemical precursor.[6] The precursors were photo-irradiated with a light of 254 nm at 77 K to generate silylenes and then the matrix was annealed to desired temperature (Scheme 1). The change of UV-Vis spectra was measured with a few minutes' intervals. A typical example of the observed time-dependent UV-Vis spectra at 90 K in 3-methylpentane matrix is shown in Figure 1. After photo-irradiation at 77 K, a peak at around 500 nm assignable to the n-p transition of the phenyl-substituted silylene appeared.[4a] However, when the matrix was annealed, a new peak at around 420 nm assignable to the π-π^* transition of 1,2-diphenyl-substituted disilenes started to grow.[7] Intensities of the absorption peak of the disilene increased gradually, while those of the silylenes decreased with the elapse of time. These changes suggest that the intramolecular dimerization of the silylenes to disilenes did occur. Strictly speaking, the change in the spectra could be accounted for the intermolecular dimerization as well but the matrix reaction from the very dilute solution suggested that the intramolecular rather than the intermolecular process occurred. The product studies support the conclusion as stated below.

To confirm the intramolecular dimerization of silylenes, the photolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene (**8**) in a sealed tube at 195 K for 2 h was examined.[8] The photolysis of **1** proceeded smoothly in 96% conversion under the conditions. The reaction gave an adduct **7** in addition to the expected silylene adducts **5** and **6** (Scheme 1). These products were characterized by GC-MS and further confirmed by comparing the spectroscopic data of authentic samples, independently prepared by the reaction of the corresponding chlorosilanes with **8** and magnesium.[9] Yields of **5**, **6** and **7** were 4.5, 32, and 0.76%, respectively,



Scheme 1.

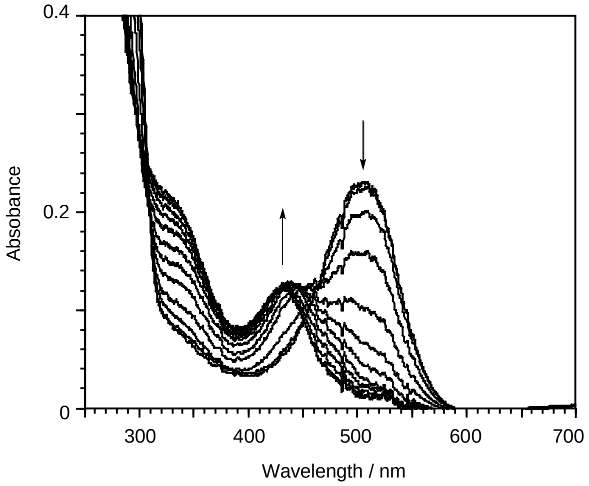


Figure 1. UV-Vis spectral change of **1** after photo-irradiation with 254 nm at 77 K followed by annealing to 90 K. The spectra were measured at 1 min intervals.

determined by GLC with a capillary column.

The formation of **5** and **6** is a clear evidence for the formation of transient silylenes, **2** and **3**, upon photolysis, which undergo cycloaddition with **8**, indicating the stepwise generations of the silylenes. The photoreaction of **5** with **8** to give **6** is also possible under a set of conditions. In addition to these compounds, the notable product **7** was obtained from the photolysis of **1**. The most reasonable pathway for the formation of **7** is the intramolecular dimerization of the silylene **3** to form a cyclic disilene, 1,2-diphenyl-1,2-disilacyclohex-1-ene **4**, which undergoes the Diels-Alder reaction with **8**.

The reaction of **5** should give the corresponding silylene, which might undergo the Si-C insertion reaction to give **7**. However, an independent reaction of **5** in the presence of **8** (**5** : **8** = 1 : 5) did not give **7** at all, while a considerable amount of **6** was detected (31%).

The mechanism shown in Scheme 1 involves stepwise formation of **3** and **4** from **2** and if this is the case, the product ratio should depend on the relative amount of the precursor and the trapping reagent. In fact, the ratio of **5**, **6**, and **7** depends upon the relative amount of **1** to **8**, supporting the stepwise reaction from **2** to **4**. As described above, at a higher ratio of [**1**]/[**8**] (1/5), the ratio of **5**, **6**, and **7** was 5.9 : 42 : 1, while at a lower ratio of [**1**]/[**8**] (1/2), the ratio was 2.0 : 8.0 : 1 (4.1, 16, and 2.0% yield, respectively, in 97% conversion). At a lower ratio of the trapping reagent, the monosilylene **2** should undergo the second silylene forming reaction more preferably than the trapping reaction in a relative sense. Then the chance of the intramolecular silylene dimerization should increase. Thus the yield of **7** increased, while those of **5** and **6** decreased.

These results demonstrate the first example of the intramolecular dimerization of the remotely generated silylenes in a molecule to form cyclic disilenes. This strategy may open a new synthetic route to cyclic disilenes.

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References and Notes

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6 Spectral data of **1**: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.125 (s, 36H), 1.01-1.04 (m, 4H), 1.46-1.55 (m, 4H), 7.24-7.48 (m, 10H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ -0.3, 10.1, 31.2, 127.7, 129.1, 134.9, 136.9; ^{29}Si NMR (CDCl$_3$, 59.6 MHz) δ -42.0, -16.0; MS (70 eV) m/z (%) 408 (40.3), 335 (7.55), 258 (100): HRMS m/z Calcd for $C_{28}H_{54}Si_6$ 558.2841, Found 558.2805.

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8 A typical experiment is as follows. A solution of **1** (20 mg, 0.036 mmol), **8** (14.8 mg, 0.18 mmol), and 3-methylpentane (3 ml) were placed in a quartz tube and degassed by freeze-pump-thaw cycles. The solution was cooled to 195 K and irradiated with a low-pressure mercury arc lamp (125 W) for 2 h. Then the reaction mixture was analyzed by GLC with a capillary column. The yield of **5**, **6**, and **7** were determined to be 4.5, 32, and 0.76%, respectively.

9 Spectral data of **5**: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.17 (s, 18H), 0.97-1.020 (m, 4H), 1.50-1.75 (m, 10H), 7.18-7.40 (m, 10H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ -0.34, 10.2, 12.9, 19.3, 23.3, 28.6, 30.5, 128.2, 130.7, 133.6, 133.9, 134.9, 136.7, 138.1; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ -21.5, 16.0, 7.13; GC-MS (70 eV) m/z (%) 345 (36), 344 (100), 289 (44), 271 (32), 194 (21), 73 (14); HRMS m/z Calcd for $C_{28}H_{46}Si_4$ 494.2677, Found 494.2630. **6**: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.93-1.03 (m, 8H), 1.57-1.62 (m, 8H), 1.74 (s, 12H) 7.24-7.25 (m, 6H), 7.52-7.53 (m, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 12.9, 19.3, 23.3, 27.8, 127.7, 128.9, 130.7, 133.9, 138.1; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ 7.09; GC-MS (70 eV) m/z (%) 430 (22, M$^+$), 352 (17), 264 (84), 204 (58), 186 (100), 166(44); HRMS m/z Calcd for $C_{28}H_{38}Si_2$ 430.2512, Found 430.2509. **7**: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.99-1.12 (m, 8H), 1.61-1.67 (m, 4H), 1.82 (s, 6H), 7.18-7.39 (m, 10H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 13.6, 22.7, 23.0, 26.3 124.2, 127.5, 128.6, 134.9, 137.4; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ -27.8; GC-MS (70 eV) m/z (%) 348 (100, M$^+$), 324 (9.8), 270 (22), 186 (35); HRMS m/z Calcd for $C_{22}H_{28}Si_2$ 348.1730, Found 348.1720.