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Excited-State Reactions of an Isolable Silylene with Aromatic Compounds

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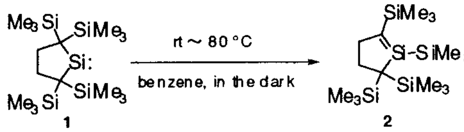
There have been very few reports of the excited-state reactions of divalent silicon compounds (silylenes) because of their intrinsic transient nature. While the photochemical isomerizations of dimethylsilylene,[1] di-*tert*-butylsilylene,[2] and silacyclopropenylidene[3] generated in low-temperature matrices have been investigated, no intermolecular reaction of excited-state silylenes has been reported so far. We wish herein to report the photochemical reactions of an isolable dialkylsilylene[4] with benzene derivatives that typically afford the corresponding silepins. The results constitute the first observation of the intermolecular reactions of the excited states of silylenes, indicating that the lifetime of the excited state is sufficient to allow bimolecular reactions with other reagents.

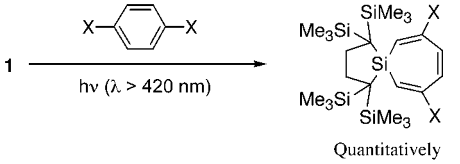
Whereas a diarylsilylene, Tbt(Mes)Si: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl), has been reported to add *thermally* to benzene and naphthalene by Suzuki, Tokitoh, and Okazaki,[5] silylene **1** did not react with the aromatic compounds, even at 80 °C in the dark, but isomerized to the corresponding silaethene **2** via the 1,2-trimethylsilyl migration, as reported in a previous paper (eq 1).[4]



(1)

In contrast, when a mixture of silylene **1** (96 mg, 0.26 mmol) and dry benzene (5 mL) in a sealed Pyrex tube (10 mm o.d.) was irradiated with light of wavelengths longer than 420 nm[6] for 6 h, the orange color of **1** disappeared. Evaporation of the benzene afforded white crystals of the corresponding silepin **3a** in quantitative yield.[7] The structure of **3a** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR, MS, and X-ray crystallography.[8,9] The molecular structure of **3a** is shown in Figure 1.

The photochemical insertion of silylene **1** into aromatic double bonds appears to be general; toluene, *m*- and *p*-xylenes, naphthalene, and various *p*-disubstituted-benzenes react similarly to afford the corresponding silepin derivatives in quantitative yields.[11] The photochemical reactions occurred regiospecifically at the unsubstituted double bonds in the substituted benzenes. As shown in eq 2,[11] in the reactions of **1** with *p*-disubstituted-benzenes, the corresponding 3,6-disubstituted-silepins **3b**−**e** were obtained in quantitative yields. As expected, the photoreaction of **1** in toluene gave an ca. 1:1 mixture of 2-methyl- and 3-methylsilepin derivatives, while a similar irradiation in *m*-xylene gave only the corresponding 3,5-dimethylsilepin.[11]



(2)

3a, X = H; **3b**, X = CH_3; **3c**, X = CH_3O;
3d, X = F; **3e**, X = CF_3

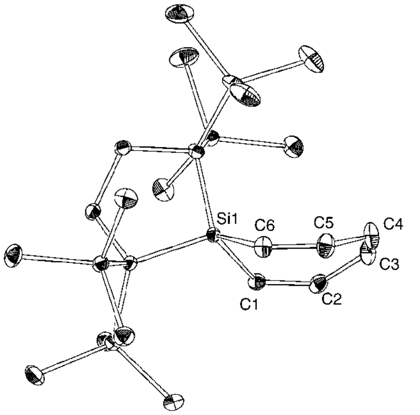
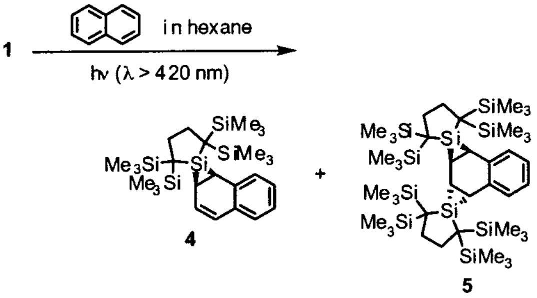
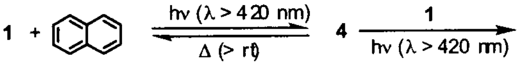


Figure 1. ORTEP drawing of silepin **3a**. Hydrogens are omitted for clarity. One of two crystallographically independent molecules in a unit cell is shown.

Irradiation of a mixture of **1** (0.17 mmol) and naphthalene (0.27 mmol) in hexane (5 mL) for 2 h at room temperature gave an ca. 1:1 mixture of mono(silylene) **4** and bis(silylene) adducts **5** as shown in eq 3.[11,12] When the product mixture was kept at 60 °C for 12 h in the dark, an NMR study showed that the amount of **4** decreased with an increase in the amount of **1**[13] but the amount of **5** was unchanged. The results indicate not only that **4** is thermally unstable at room temperature and dissociates into naphthalene and **1** but also that **5** is produced not thermally but via the photochemical reaction of **1** with **4** (eq 4).



(3)



(4)

Interestingly, a similar irradiation of silylene **1** in mesitylene did not give the corresponding silepin due to the severe steric hindrance

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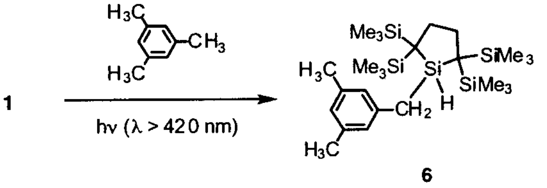
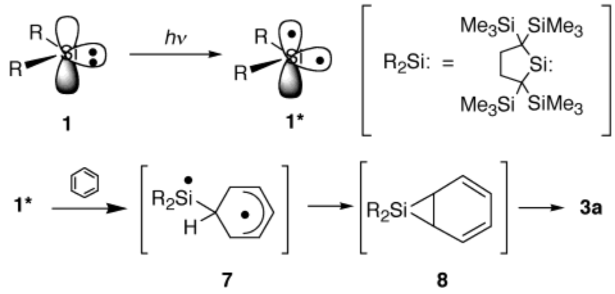
at C−C double bonds but gave instead **6** through the insertion to a benzylic C−H bond in high yield (eq 5).



(5)

All these features of the photoreactions of **1** with aromatics are compatible with the 1,1-biradical nature of the excited silylene. Since the homolytic aromatic addition of silyl radicals is a well-known process,[14] we may anticipate that the excited state of **1** (**1***) adds to benzene to give the 1,3-biradical intermediate **7**. Subsequent cyclization to the corresponding silanorcaradiene **8** followed by ring-opening leads to the final silepin **3a** (Scheme 1). The formation of **6** by the reaction shown in eq 5 is also explained by initial hydrogen abstraction of **1*** from mesitylene.[15]

Scheme 1



Discussions of the reactivity difference between Tbt(Mes)Si: and **1** in the ground state are interesting. Because a ground-state silylene has a high-lying lone-pair orbital and a low-lying vacant p-orbital, the silylene is ambiphilic and serves as both a nucleophile and an electrophile.[16] In the thermal reaction of a silylene with benzene as a π base, the interaction between the vacant p-orbital of the silylene and a benzene π HOMO (electrophilic approach) is more important than the interaction between the lone-pair orbital of the silylene and a benzene π LUMO (nucleophilic approach). The favorable electrophilic approach is probably achieved in the reaction of Tbt(Mes)Si: with benzene; however, it is prohibited in the reaction of **1** because the vacant p-orbital in **1** is sterically well protected by the helmet-like bidentate ligand.[4,17] In contrast, during the photoreaction of **1** with benzene, the less hindered in-plane orbital of the two singly occupied orbitals in **1*** may approach the benzene to accomplish the homolytic aromatic addition, as shown in Scheme 1. Further work is in progress to elucidate the electronic nature of **1***.

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Supporting Information Available: Texts describing physical data of **3a**−**3e**, **4**−**6**, and other products, experimental details of the photoreaction of **1** and **3a**, tables of crystal data, structure solution, and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, and ORTEP drawings for **3a** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

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(6) Details for selective irradiation of the n→p absorption band of **1** (λ_{max} 440 nm);[4] a 500-W high-pressure mercury arc lamp with a glass cutoff filter (L-42, Irie Co., Ltd.)

(7) In the thermal reaction of Tbt(Mes)Si: with benzene, the corresponding 2:1 adduct [bis(silylene) adduct] was obtained probably via the further addition of the silylene to the corresponding silepin. In contrast, during the irradiation of **1** in benzene, no bis(silylene) adduct formed. The irradiation of a 1:1 mixture of silepin **3a** and **1** in benzene for 1 h afforded the corresponding bis(silylene) adduct in 83% yield, while **3a** did not react with **1** thermally. See the Supporting Information for details.

(8) **3a**: colorless crystals; mp 86 °C; ^{1}H NMR (C_6D_6) δ 0.24 (s, 36H), 1.98 (s, 4H), 6.11 (dd, J = 7.4 Hz, 14.8 Hz, 2H), 6.19 (d, J = 14.8 Hz, 2H), 6.65 (m, 2H); ^{13}C NMR (C_6D_6) δ 4.8 ($SiMe_3$), 14.6 (C), 34.4 (CH_2), 132.4 (CH), 134.4 (CH), 141.0 (CH); ^{29}Si NMR (C_6D_6) δ 2.7 ($SiMe_3$), 6.1 (Si); MS (EI, 70 eV) *m/z* (%) 450 (6, M^+), 435 (5), 372 (11), 313 (6), 299 (32), 73 (100). Anal. Calcd for $C_{22}H_{46}Si_5$: C, 58.59; H, 10.28. Found: C, 58.44; H, 10.13.

(9) Crystal data for silepin **3a**: MF = $C_{22}H_{46}Si_5$, monoclinic, $P2_1/c$, a = 11.5559(6) Å, b = 30.045(1) Å, c = 16.8501(7) Å, β = 110.3786(4)°, V = 5484.1(4) Å^3, Z = 8, D_{calc} = 1.092 g/cm^3, T = 150 K, R = 0.042, R_w = 0.141, GOF = 1.12. Among a few known *C*-unsubstituted silepins,[10] **3a** is the first compound analyzed by X-ray crystallography. Like other cycloheptatrienes, the ring system of **3a** has a folded boat conformation with a diherdal angle between plane (C1−C2−C5−C6) and plane (C2−C3−C4−C5) of 24.4°, being in good accord with the angle estimated for a silepin in solution by NMR spectroscopy.[10] No appreciable decomposition of **3a** was observed after keeping the solution of **3a** in benzene-d_6 at 80 °C for 3 days, while **3a** decomposed completely as the solution was heated at 100 °C for 9 days to give benzene, silene **2**, and unidentified products, probably via silylene extrusion from **3a**.[5,10]

(10) (a) Nakadaira, Y. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; Chapter 14. (b) Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* **1991**, *10*, 435.

(11) For characterization of the photoproducts, see the Supporting Information.

(12) Bis(silylene) adduct **5** was stable enough to be isolated. The structure of **5** was confirmed by X-ray crystallography. Mono(silylene) adduct **4** was not isolated but identified using the NMR spectra of the mixture of **4** and **5**. See the Supporting Information for details. In contrast, in the thermal reaction of Tbt(Mes)Si: with naphthalene, the corresponding bis(silylene) adduct has been reported to be isolated without detection of the intermediary mono(silylene).[5]

(13) Since **1** isomerized to **2** under these conditions (eq 1), the amount of **1** was estimated as that of **2**.

(14) (a) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Son: New York, 1973; Vol. II. (b) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229. See also: Kira, M.; Sugiyama, H.; Sakurai, H. *J. Am. Chem. Soc.* **1983**, *105*, 6436.

(15) Although abstraction of a benzylic hydrogen by a silyl radical will be endothermic, and hence, a less favorable process, the hydrogen abstraction of a 1,1-silandiyl in the excited state would be exothermic. The intramolecular hydrogen abstraction of triplet bis(silyl)silylenes has been reported recently: (a) Jiang, P.; Gaspar, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 8622. (b) Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217. (c) Wiberg, N.; Niedermayer, W. *J. Organomet. Chem.* **2001**, *628*, 57.

(16) For a discussion of the ambiphilic nature of silylene **1** in the reactions with haloalkanes, see: Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Chem. Lett.* **2001**, 1102.

(17) Whereas the coordination of Lewis bases such as ethers and amines to silylenes is well established, no interaction has been observed between **1** and THF.[18]

(18) Kira, M.; Ishida, S.; Iwamoto, T.; Yauchibara, R.; Sakurai, H. *J. Organomet. Chem.* **2001**, *636*, 144.

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