Photochemical Generation of Halo(silyl)silylene: Spectroscopic Observation and Reactivity

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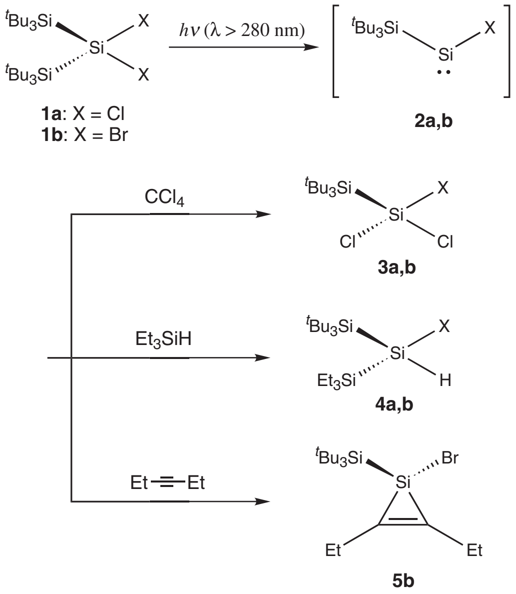
Dihalobis(tri-*tert*-butylsilyl)silanes (t-$Bu_3Si)_2SiX_2$ (**1a**: X = Cl, **1b**: X = Br) underwent photochemically α-elimination to produce halo(tri-*tert*-butylsilyl)silylenes, which were successively trapped by carbon tetrachloride, triethylsilane, and 3-hexyne. The halo(tri-*tert*-butylsily)silylenes were observed by UV–vis spectroscopy in a 3-methylpentane matrix at 77 K.

Divalent silylenes, the silicon analogues of the carbenes in organic chemistry, are examples of very important reactive intermediates.[1] These reactive species are generated by the thermal, photochemical, and alkali metal induced reactions of the appropriate organosilicon compounds. Recently, we have successfully observed triplet ground state bis(tri-*tert*-butylsilyl)silylene by the photochemical reaction of 2,3-diethyl-1,1-bis(tri-*tert*-butylsilyl)-1-silacycloprop-2-ene.[2] In contrast to the extensive studies of R_2Si: (R = alkyl, aryl, and silyl) in the condensed phase[1,3] and X_2Si: (X = F,[4] Cl,[5] Br[6]) in the gas phase at high temperature, only a few examples of the heteroleptic halosilylenes RXSi: (X = halogen) have been reported so far.[3] Photochemical interconversion of $ClHSi{=}CH_2$ to MeClSi: in an Ar matrix at 10 K was reported by Maier et al.[7] Lee et al. recently reported the reduction of tribromo[tris(trimethylsilyl)methyl]silane with two equiv of lithium naphthalenide to form bromo[tris(trimethylsilyl)methyl]silylene or silylenoid species, which were trapped by alcohols and diene derivatives.[8] Wiberg et al. reported the generation of bromo(tri-*tert*-butylsilyl)silylene by the thermolysis of dibromobis(tri-*tert*-butylsilyl)silane by heating at 160 °C, its formation being demonstrated by the trapping reaction with Et_3SiH and 1,3-butadiene.[9] In this paper, we report the photochemical generation of halo(tri-*tert*-butylsilyl)silylenes by the irradiation of dihalobis(tri-*tert*-butylsilyl)silane with light of wavelength longer than 280 nm and their first UV–vis spectroscopic observation in a 3-methylpentane (3-MP) matrix at 77 K.



1a: X = Cl
1b: X = Br
2a,b
3a,b
4a,b
5b

Scheme 1.

First, we examined the photochemical reaction of **1a** in the presence of carbon tetrachloride, a well-known trapping reagent of reactive silylene to give the halogen abstraction product.[10] A cyclohexane-d_{12} solution of bis(tri-*tert*-butylsilyl)dichlorosilane **1a** (53.3 mg, 0.11 mmol) and carbon tetrachloride (0.3 mL, 28 mmol) in a sealed quartz NMR tube was irradiated with light of wavelength longer than 280 nm. The progress of the photoreaction was monitored by NMR spectroscopy. In the ^1H NMR spectrum, new signals at 1.19 and 1.11 ppm, which can be assigned to **3a** and tri-*tert*-butylchlorosilane, respectively, grew up simultaneously with irradiation time, with a corresponding decrease of the signal at 1.37 ppm due to **1a**. The signal due to the starting material **1a** completely disappeared after 2.5 h irradiation. The photoreaction of **1a** proceeded cleanly to form the product **3a** (83%) together with tri-*tert*-butylchlorosilane (Scheme 1).[11] The photoreaction of **1b** in the presence of carbon tetrachloride also produced the similar product **3b** in 70% yield. In the presence of triethylsilane, products **4a** and **4b** were obtained in 52 and 49% yield, respectively (Scheme 1).[11] These results indicate that photochemical reaction of **1** leads to silylene t-$Bu_3Si(X)Si$: (**2**: X = Cl, Br) as well as t-Bu_3SiX, the intermediate existence of which was proven by the chlorine abstraction of carbon tetrachloride, as well as the insertion reaction into the Si–H bond of triethylsilane. The silacyclopropene derivative **5b** was formed in 89% yield when the photochemical reaction of **1b** was carried out in the presence of 3-hexyne.[12] Steric bulkiness around the central silicon atom, which causes the stretching of Si–Si bond and the widening of Si–Si–Si angle (e.g.: 2.4914(9) Å and 142.41(3)° for **1a**[13]), is crucial for the photochemical generation of the halogen-substituted silylenes. Indeed, dibromobis(triisopropylsilyl)silane was inert under the same conditions.

Next, we examined the photolysis of **1** by UV–vis spectroscopy in a glass matrix at low temperature. Upon irradiation with light (λ > 280 nm) of the 3-MP glass matrix containing **1a** or **1b** at 77 K, the glass matrix turned yellow and produced two weak UV–vis absorption bands with maxima at 291, 518 nm, or 312, 512 nm, respectively (Figure 1).[14] The absorption bands observed at 518 and 512 nm were assigned to the HOMO–LUMO transition of **2a** and **2b**, respectively, corresponding to the $n(Si) \rightarrow 3p(Si)$ transition. The absorption maxima of 518 nm for **2a** and 512 nm for **2b** are at appreciably longer wavelengths

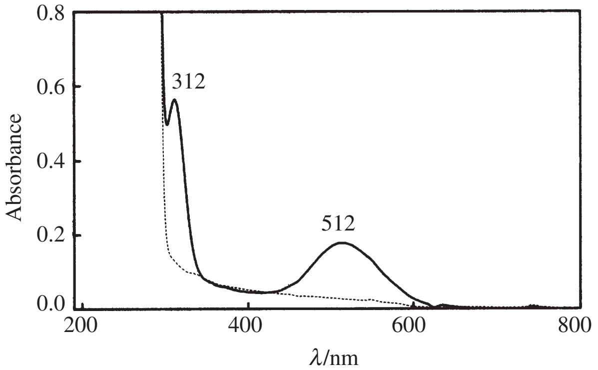
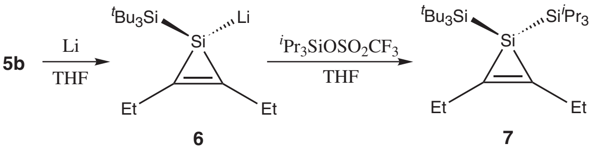


Figure 1. UV–vis spectra obtained during photolysis of **1b** in 3-MP: (a) before irradiation (-----); (b) after 7 min irradiation at 77 K (——).

than those of F_2Si: (321 nm, in the gas phase),[4c] Cl_2Si: (317 nm, in the gas phase),[5] and MeClSi: (407 nm, Ar matrix, 10 K).[7] These substituent effects can be attributed to the σ-electron donating ability of the electropositive t-Bu$_3$Si group, which raises the energy level of the n(Si) orbital significantly. Since the electronegative substituent lowers the energy level of the n(Si) orbital,[15] it is expected that the n(Si) $\rightarrow$ 3p(Si) transition in **2a** would shift to shorter wavelength compared with **2b**.[16] However, the silylene **2a** showed an unexpected small red shift relative to **2b**. The reason is not clear at this moment. In the presence of a Lewis base, the absorption band was observed at 344 nm for **2a** and 354 nm for **2b** during the photolysis of **1** in the glass matrix of 3-MP/2-Me-THF (99:1) at 77 K. It is considered that the 2-Me-THF interacts with the vacant 3p(Si) orbital to appreciably stabilize the singlet silylene **2**.[17]



Scheme 2.

A halosilylene should lead to novel silicon chemistry because of its synthetic utility. For example, as mentioned in the reaction with 3-hexyne, silacyclopropene derivative **5b** having a halogen atom was successfully prepared (Scheme 1). Compound **5b** is a promising precursor to the unprecedented silacyclopropenylide ion. Actually, compound **5b** was treated with lithium in THF to produce the corresponding silacyclopropenyllithium **6**,[18] which was trapped with triisopropylsilyltriflate to produce silacyclopropene **7** (Scheme 2).[19] The further synthetic application of the halosilylene will be reported elsewhere.

References and Notes

1 For reviews on silylene, see: a) P. P. Gaspar and G. S. Hammond, "Carbenes," ed. by R. A. Moss and M. Jones, Jr., Wiley, New York (1975), Vol. II. b) Y. Apeloig, "The Chemistry of Organic Silicon Compounds," ed. by S. Patai and Z. Rappoport (1989), Part 1, Chap. 2. c) M. Haaf, T. A. Schmedake, and R. West, *Acc. Chem. Res.*, **33**, 704 (2000). d) P. P. Gaspar and R. West, "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig (1998), Vol. 2, Chap. 43.

2 A. Sekiguchi, T. Tanaka, M. Ichinohe, K. Akiyama, and S. Tero-Kubota, *J. Am. Chem. Soc.*, **125**, 4962 (2003).

3 For the reactivity of halogen-substituted silylenes, see: a) R. L. Jenkins, A. J. Vanderwielen, S. P. Ruis, S. R. Gird, and M. A. Ring, *Inorg. Chem.*, **12**, 2968 (1973). b) E. E. Siefert, R. A. Ferrieri, O. F. Zeck, and Y.-N. Tang, *Inorg. Chem.*, **17**, 2802 (1978). c) J. Heinicke, B. Gehrhus, and S. Meinel, *J. Organomet. Chem.*, **474**, 71 (1994). d) S. Konieczny and P. P. Gaspar, *J. Organomet. Chem.*, **307**, 151 (1986). e) W. L. Lee, C. F. Shieh, and C. S. Liu, *J. Organomet. Chem.*, **302**, 23 (1986). f) C. S. Liu and T. L. Hwang, *J. Am. Chem. Soc.*, **100**, 2577 (1978). g) T. L. Hwang, Y. M. Pai, and C. S. Liu, *J. Am. Chem. Soc.*, **102**, 7519 (1980). h) S. R. Church, C. G. Davies, R. Lümen, P. A. Mounier, G. Saint, and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, **1996**, 227.

4 a) V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, **43**, 2557 (1965). b) V. M. Khanna, G. Besenbruch, and J. L. Margrave, *J. Chem. Phys.*, **46**, 2310 (1967). c) J. A. Dagata, D. W. Squire, C. S. Dulcey, D. S. Y. Hsu, and M. C. Lin, *Chem. Phys. Lett.*, **134**, 151 (1986).

5 B. P. Ruzsicska, A. Jodhan, I. Safarik, O. P. Strausz, and T. N. Bell, *Chem. Phys. Lett.*, **113**, 67 (1985).

6 I. Hargittai, G. Schulz, J. Tremmel, N. D. Kagramanov, A. K. Maltsev, and O. M. Nefedov, *J. Am. Chem. Soc.*, **105**, 2895 (1983).

7 a) H. P. Reisenauer, G. Mihm, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, **21**, 854 (1982). b) G. Maier, G. Mihm, H. P. Reisenauer, and D. Littmann, *Chem. Ber.*, **117**, 2369 (1984).

8 M. E. Lee, H. M. Cho, M. S. Ryu, C. H. Kim, and W. Ando, *J. Am. Chem. Soc.*, **123**, 7732 (2001).

9 N. Wiberg and W. Niedermayer, *J. Organomet. Chem.*, **628**, 57 (2001).

10 S. Ishida, T. Iwamoto, C. Kabuto, and M. Kira, *Chem. Lett.*, **2001**, 1102.

11 The products were identified by comparison with the reported spectral data (see Ref. 9).

12 Spectral data for **5b**: ^{1}H NMR (C_6D_6, δ) 1.14 (t, $J = 7.6$ Hz, 6 H), 1.26 (s, 27 H), 2.40 (dq, $J = 15.2$, 7.6 Hz, 2 H), 2.50 (dq, $J = 15.2$, 7.6 Hz, 2 H); ^{13}C NMR (C_6D_6, δ) 13.6, 22.7, 24.1, 31.5, 156.8; ^{29}Si NMR (C_6D_6, δ) -14.6, -105.2.

13 N. Wiberg, W. Niedermayer, H. Nöth, J. Knizek, W. Ponikwar, K. Polborn, D. Fenske, and G. Baum, *Z. Anorg. Allg. Chem.*, **627**, 594 (2001).

14 When the matrix was warmed up to 90 K, the absorption bands of the silylene disappeared immediately and four new absorption bands at 313, 370, 441, 498 nm appeared in the case of **2b**. The silylene **2b** probably dimerized upon the annealing of the matrix, however, the structure of the product is unclear at this moment.

15 a) M. Kira, T. Maruyama, and H. Sakurai, *Chem. Lett.*, **1993**, 1345. b) S. G. Bott, P. Marshall, P. E. Wagenseller, Y. Wang, and R. T. Conlin, *J. Organomet. Chem.*, **499**, 11 (1995).

16 G. Maier, G. Glatthaar, and H. P. Reisenauer, *J. Organomet. Chem.*, **686**, 341 (2003).

17 a) G. R. Gillette, G. H. Noren, and R. West, *Organometallics*, **6**, 2617 (1987). b) W. Ando, A. Sekiguchi, K. Hagiwara, A. Sakakibara, and H. Yoshida, *Organometallics*, **7**, 558 (1988). c) M. Kira, T. Maruyama, and H. Sakurai, *Heteroat. Chem.*, **5**, 305 (1994).

18 Spectral data for **6**: ^{1}H NMR (THF-d_8, δ) 1.13 (s, 27 H), 1.16 (t, $J = 7.4$ Hz, 6 H), 2.45 (dq, $J = 15.2$, 7.4 Hz, 2 H), 2.65 (dq, $J = 15.2$, 7.4 Hz, 2 H); ^{13}C NMR (THF-d_8, δ) 15.3, 25.1, 26.0, 33.2, 141.3; ^{29}Si NMR (THF-d_8, δ) -2.2, -153.9.

19 P. Jiang and P. P. Gaspar, *J. Am. Chem. Soc.*, **123**, 8622 (2001).

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