Photoisomerization of Persilyl-Substituted Silacyclopropene: Formation of Stable Persilyl-Substituted 1-Silaallene, and Its Reactivity

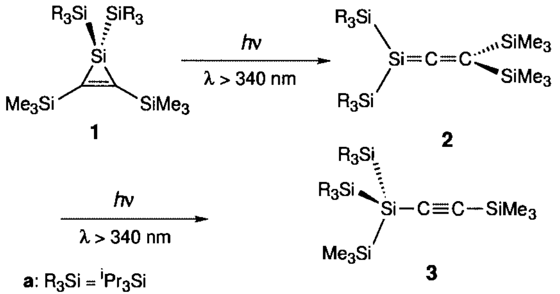
Masaaki Ichinohe, Takashi Tanaka, and Akira Sekiguchi*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

(Received July 27, 2001; CL-010715)

Persilyl-substituted silacyclopropenes, $(R_3Si)_2SiC_2(SiMe_3)_2$ (**1a**: R_3Si = $^iPr_3Si$, **1b**: R_3Si = $^tBu_2MeSi$), were photochemically isomerized to 1-silaallene derivatives, $(R_3Si)_2Si{=}C{=}C(SiMe_3)_2$ **2**, at wavelengths longer than 340 nm. These compounds subsequently photoisomerized to acetylene derivatives, $(R_3Si)_2(Me_3Si)Si–C{\equiv}C–SiMe_3$ **3**, as a final product. The existence of 1-silaallene **2** was demonstrated spectroscopically as well as by a trapping reaction with water.

Silacyclopropene, an unsaturated three-membered ring containing one silicon atom and one C=C double bond, is a highly strained molecule. Therefore, its preparation, structure, and reactivity have been extensively investigated.[1] Recently, we prepared 1,1-bis(trialkylsilyl)-2,3-bis(trimethylsilyl)silacycloprop-2-enes **1**, and found a new reaction of silacyclopropene to produce the corresponding bis(trialkylsilyl)dilithiosilanes by reaction with lithium metal in THF.[2] Silacyclopropene is also known to be a good photochemical precursor of silylene.[3] We examined the photoreaction of **1** to generate silylenes bearing bulky and electropositive trialkylsilyl substituents, which may be a triplet state silylene.[4] Instead of the generation of silylene, we found the sequential photochemical isomerization of **1** to 1-silaallene derivatives,[5,6] followed by rearrangement to silyl acetylene.

A benzene-d_6 solution of **1a** (0.25 mol/L, 0.4 mL) in a sealed NMR tube was irradiated by light of wavelength longer than 340 nm.[7] The reaction mixture turned bright yellow shortly after the commencement of irradiation, and then gradually decolorized. The yellow color completely disappeared after about 120-min irradiation. This photoreaction was monitored by NMR spectroscopy. In the ^1H NMR spectrum, new signals at 0.29 ppm (singlet) for Me_3Si, 1.22 ppm (doublet) $[(\mathit{CH}_3)_2HC]_3Si$, and 1.40–1.50 ppm (multiplet) for $[(CH_3)_2\mathit{H}C]_3Si$, which can be assigned to a photolabile intermediate **2a**,[8,9] grew with irradiation time. Upon continued irradiation, a second set of signals at 0.15 (s), 0.45 (s), 1.30 (d), and 1.45 (sept) ppm due to the acetylene derivative **3a**[10] increased, while the first set of signals due to **2a** simultaneously decreased. Eventually, the signals due to the starting material **1a** and the photolabile intermediate **2a** completely disappeared. The photoreaction of **1a** proceeded cleanly, and the final product **3a** was isolated in 56% yield by HPLC separation (Scheme 1). The amount of photolabile intermediate **2a** in the reaction mixture reached a maximum after 20-min irradiation: the molar ratio of **1a**/**2a**/**3a** was estimated as 40/30/30 from the ^1H NMR spectrum. The similar two-step photoisomerization of **1b** to **3b** via **2b**[11] could also be monitored by NMR spectroscopy. The silaallenes **2a** and **2b** are very sensitive to oxygen, but stable to moisture. Separation of **2** from the reaction mixture was unsuccessful.



Scheme 1.

The structure of **2** was deduced from the NMR spectra observed for a reaction mixture of **1**, **2**, and **3**, and from a trapping experiment with water. In the ^{13}C NMR spectrum, two characteristic signals at 129.6 and 268.3 ppm were observed for **2a**, together with signals from the carbon atoms of Me_3Si and $^iPr_3Si$ substituents. The former can be assigned to the terminal carbon atom of the 1-silaallene skeleton, and the latter to the central carbon atom. The ^{29}Si NMR spectrum showed signals at 18.5, –8.2, and –64.5 ppm, with the former two signals being assigned to silyl substituents. The ^{29}Si NMR chemical shift of the sp^2 silicon atom in **2a** is assigned to –64.5 ppm, which is the most upfield-shifted signal of the known Si=C double bond species.[12] To date, four stable 1-silaallene derivatives have been reported by West et al.[6] Their ^{29}Si NMR chemical shift of a terminal silicon is highly dependent on the substituents, ranging from +55.1 to +13.1 ppm. To confirm the assignment of the ^{13}C and ^{29}Si NMR signals, we calculated the chemical shifts for the model compound $(H_3Si)_2Si{=}C{=}C(SiH_3)_2$ **2c** by an ab initio method.[13] Model compound **2c**, optimized at B3LYP/6-31G(d) level without any symmetry, has nearly C_2 symmetry with a linear allene skeleton, and the terminal silicon and carbon atoms have planar three-coordinate geometry. The calculated chemical shifts for the allene skeleton atoms at GIAO/B3LYP/6-311+G(2df,p) level are –50.8 ppm for the terminal silicon atom, 292.6 ppm for the central carbon atom, and 125.7 ppm for the terminal carbon atom, which are very close to the observed values. Photoreaction of **1a** (0.18 mmol/L hexane solution) could also be monitored by UV–vis spectroscopy (Figure 1). New absorption bands with maxima at 333 and 405 nm due to **2a** increased at first and then decreased,[14] similar to the observation for **2a** by ^1H NMR spectroscopy.

Ishikawa et al. have reported the photolysis of 1-mesityl-2-phenyl-1,3-bis(trimethylsilyl)silacycloprop-2-ene to produce the 1-silaallene derivative as a reactive intermediate, which was confirmed only by a trapping reaction with methanol.[15] In our system, photolabile but thermally stable 1-silaallene **2** could be spectroscopically observed due to steric protection by the bulky trialkylsilyl groups.

The polarity of the Si=C double bond in 1-silaallenes is

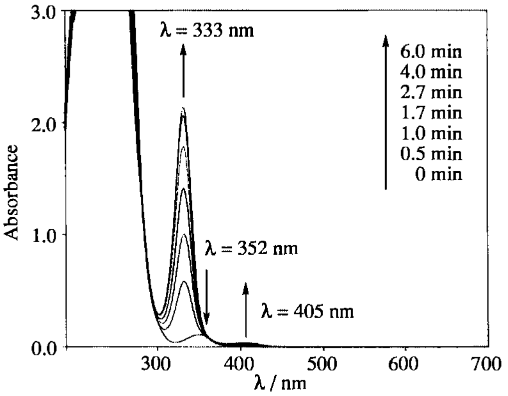
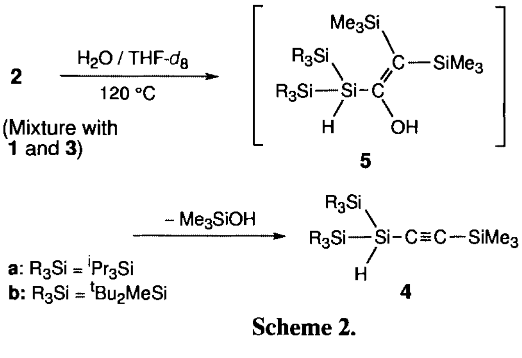


Figure 1. Photoreaction of silacyclopropene **1a** monitored by UV–Vis spectroscopy in hexane.

reduced compared with that in silenes because of the contribution of the characteristic charge distribution in the allene skeleton.[5] The reactivity of the Si=C double bond in 1-silaallene is therefore lower than that in silenes.[14] However, all known transient and stable 1-silaallene derivatives, except for one extremely stable derivative reported by West et al.,[6a] react with alcohol or water to give (vinyl)alkoxysilane or (vinyl)hydroxysilane derivatives, respectively.[6,15] This regioselectivity can be explained by the polarity of the Si=C double bond ($Si^{\delta+}=C^{\delta-}$) caused by the difference in the electronegativity of Si and C atoms. On the other hand, 1-silaallene **2** reacts very slowly with water on heating (Scheme 2). A mixture of **1a**, **2a**, and **3a** was allowed to react with water at 120 °C in a sealed tube for 24 h in THF-d_8. The yellow color due to **2a** gradually disappeared, and acetylene derivative **4a**[16] was formed in 94% yield (by NMR) based on **2a** as a mixture with **1a** and **3a**, which are stable to water under the reaction conditions. Reaction of **2b** with water in THF-d_8 at 120 °C also cleanly gave **4b**.[17] The formation of **4** could be explained by addition of a hydroxy group and hydrogen atom to the central carbon and silicon atoms of **2**, respectively, to give the (hydrosilyl)vinylalcohol intermediate **5** followed by β-elimination of trimethylsilanol to produce the acetylene derivative **4**. The regioselectivity of the addition of water to the Si=C double bond in **2** is opposite to that observed with an isolated Si=C double bond, due to the charge distribution $Si^{\delta-}=C^{\delta+}$ caused by the electron donating effect of the trialkylsilyl groups on the terminal sp^2 Si atom. This reversed polarity of the Si=C double bond in **2** is confirmed by ab initio calculations. Thus, for the model compound **2c**, the calculated Mulliken atomic charges on the terminal Si and on the central C are –0.24 and +0.33, respectively, compared with +0.09 and –0.17 in $H_2Si=C=CH_2$ at the B3LYP/6-311+G(2df,p) level.[18]



Scheme 2.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 B. J. Ayllett and A. C. Sullivan, “Comprehensive Organometallic Chemistry II,” ed. by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1995), Vol. 2, p 45.

2 a) A. Sekiguchi, M. Ichinohe, and S. Yamaguchi, *J. Am. Chem. Soc.*, **121**, 10231 (1999). b) M. Ichinohe, Y. Arai, A. Sekiguchi, N. Takagi, and S. Nagase, *Organometallics*, **20**, 4141 (2001).

3 For the generation of silylenes by the photolysis of silacycloprop-2-enes, see: a) M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Am. Chem. Soc.*, **99**, 245 (1977). b) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *J. Am. Chem. Soc.*, **99**, 3879 (1977). c) S. Tsutsui, K. Sakamoto, and M. Kira, *J. Am. Chem. Soc.*, **120**, 9955 (1998).

4 M. C. Holthausen, W. Koch, and Y. Apeloig, *J. Am. Chem. Soc.*, **121**, 2623 (1999) and references cited there in.

5 For reviews of 1- and 2-silaallenes, see: T. Müller, W. Ziche, and N. Auner, “The Chemistry of Organic Silicon Compounds,” ed. by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1998), Vol. II, p 857.

6 For stable 1-silaallene derivatives, see: a) G. E. Miracle, J. L. Ball, D. R. Powell, and R. West, *J. Am. Chem. Soc.*, **115**, 11598 (1993). b) M. Trommer, G. E. Miracle, B. E. Eichler, D. R. Powell, and R. West, *Orgamnometallics*, **16**, 5737 (1997).

7 Photolysis of **1** with light shorter than 340 nm (λ > 280 nm or λ = 254 nm) gave a product arising from silylene as the minor process, which was trapped by *cis*-2-butene, with the formation of **2**.

8 Compound **2a** (in the reaction mixture with **1a** and **3a**): ^{1}H NMR (C_6D_6, δ) 0.29 (s, 18 H), 1.22 (d, *J* = 4.6 Hz, 36 H), 1.40–1.50 (m, 6 H); ^{13}C NMR (C_6D_6, δ) 0.4, 13.6, 20.2, 129.6, 268.3; ^{29}Si NMR (C_6D_6, δ) –64.5, –8.2, 18.5; UV–vis (hexane) λ_{max}/nm 333, 405.

9 For the transient 1-silaallene by thermolysis of silacycloprop-2-ene derivative, see: M. Ishikawa, T. Horio, Y. Yuzuriha, A. Kunai, T. Tsukihara, and H. Naitou, *Organometallics*, **11**, 597 (1992).

10 Compound **3a**: Mp 103–105 °C; ^{1}H NMR (C_6D_6, δ) 0.15 (s, 9 H), 0.45 (s, 9 H), 1.30 (d, *J* = 7.0 Hz, 36 H), 1.45 (sept, *J* = 7.0 Hz, 6 H); ^{13}C NMR (C_6D_6, δ) –0.3, 2.3, 15.5, 20.8, 114.2, 120.9; ^{29}Si NMR (C_6D_6, δ) –107.2, –20.7, –10.5, 8.7; HRMS *m/z*: calcd for $C_{26}H_{60}Si_5$, 512.3541; found, 512.3533.

11 Compound **2b** (in the reaction mixture with **1b** and **3b**): ^{1}H NMR (C_6D_6, δ) 0.17 (s, 6 H), 0.26 (s, 18 H), 1.15 (s, 36 H); ^{13}C NMR (C_6D_6, δ) –5.4, 0.7, 21.9, 30.8, 129.9, 267.8; ^{29}Si NMR (C_6D_6, δ) –55.0, –6.6, 18.7; UV–vis (hexane) λ_{max}/nm 332, 407.

12 A. G. Brook and M. A. Brook, “Multiply Bonded Main Group Metals and Metalloids,” ed. R. West and F. G. S. Stone, Academic Press Inc., San Diego (1996).

13 For ab initio calculations of parent 1-silaallene, $H_2Si=C=CH_2$, see: a) K. Krogh-Jesperson, *J. Comput. Chem.*, **3**, 571 (1982). b) G. Trinquier and J. P. Malrieu, *J. Am. Chem. Soc.*, **109**, 5303 (1987).

14 UV absorption bands were observed for $Me_2Si=C=C(SiMe_3)_2$ at 275 nm and 325 nm using a laser flash photolysis techniques, see: C. Kerst, C. W. Rogers, R. Ruffolo, and W. J. Leigh, *J. Am. Chem. Soc.*, **119**, 466 (1997).

15 J. Ohshita, Y. Isomura, and M. Ishikawa, *Organometallics*, **8**, 2050 (1989).

16 Compound **4a**: ^{1}H NMR (C_6D_6, δ) 0.14 (s, 9 H), 1.24 (d, *J* = 7.1 Hz, 18 H), 1.28 (d, *J* = 7.1 Hz, 18 H), 1.36–1.41 (m, 6 H), 4.11 (s, 1 H); ^{13}C NMR (C_6D_6, δ) –0.3, 13.6, 20.07, 20.11, 110.2, 120.3; ^{29}Si NMR (C_6D_6, δ) –109.6, –19.8, 7.3; HRMS *m/z*: calcd for $C_{23}H_{52}Si_4$, 440.3146; found, 440.3149.

17 Compound **4b**: ^{1}H NMR (C_6D_6, δ) 0.14 (s, 9 H), 0.21 (s, 6 H), 1.12 (s, 18 H), 1.26 (s, 18 H), 4.11 (s, 1 H); ^{13}C NMR (C_6D_6, δ) –6.1, –0.4, 21.4, 21.9, 29.1, 29.5, 111.5, 121.3; ^{29}Si NMR (C_6D_6, δ) –103.4, –19.7, 8.0; HRMS *m/z*: calcd for $C_{23}H_{52}Si_4$, 440.3146; found, 440.3140.

18 For Mulliken atomic charges of parent 1-silaallene, see: ref 13a (+0.17 on the terminal Si, –0.10 on the central C).