Silylenes

The Singlet Excited State of a Stable Dialkylsilylene Is Responsible for Its Photoreactions**

Mitsuo Kira, Shintaro Ishida, Takeaki Iwamoto, Armin de Meijere, Mamoru Fujitsuka, and Osamu Ito*

Silylenes (divalent silicon species)[1] as well as other heavier Group 14 element divalent species are usually singlet at the ground state ($^1A_1$) and should have two low-lying excited states, $^1B_1$ and $^3B_1$, with singlet and triplet 1,1-diradical nature,

---

[*] Prof. Dr. M. Kira, Dr. S. Ishida, Dr. T. Iwamoto
Department of Chemistry
Graduate School of Science
Tohoku University
Aoba-ku, Sendai 980-8578 (Japan)
Fax: (+81) 22-217-6589
E-mail: mkira@si.chem.tohoku.ac.jp
Prof. Dr. A. de Meijere
Instutut für Organische und Biomolekulare Chemie
Georg-August-Universität Göttingen
Tammannstrasse 2, 37077 Göttingen (Germany)
Dr. M. Fujitsuka, Prof. Dr. O. Ito
Institute of Multidisciplinary Research for Advanced Materials
Tohoku University
1-1, Katahira 2-chome, Aoba-ku, Sendai 980-8577 (Japan)

[**] This work was supported by the Japanese Ministry of Education, Culture, Sports, Science, and Technology [Grant-in-Aid for Scientific Research on Priority Areas (No. 14078203), “Reaction Control of Dynamic Complexes”] (for M.K.) and the Fonds der Chemischen Industrie (for A.d.M.).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460317

respectively (Figure 1). Little is known, however, about the properties of the excited states of silylenes.[2]

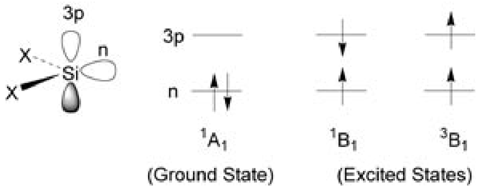
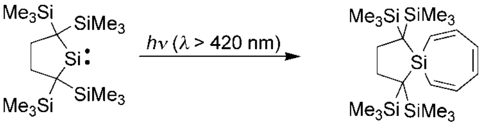


Figure 1. Important electronic states of silylene.

We have recently reported the first intermolecular reactions of an excited silylene with benzene and its derivatives to afford the corresponding adducts.[3] Typically, irradiation of the stable silylene **1**[4] in benzene gave the corresponding silepin in quantitative yield [Eq. (1)].

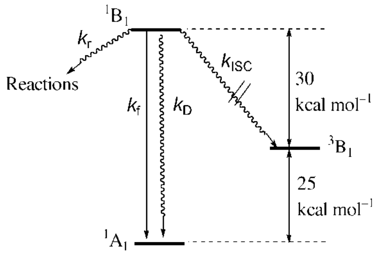


(1)

1 **2** (quant.)

Although all the features of the photoreactions of **1** with benzene derivatives are compatible with a 1,1-diradical nature of the excited silylene, the true multiplicity of the reacting excited state so far could not be proven experimentally. Herein we report that the excited state responsible for the photoreactions of **1** with benzenes and alkenes is a $^1B_1$ state on the basis of the fluorescence quenching behavior of excited **1** by benzene. It is noteworthy that in contrast, similar $^1B_1$ states are rarely encountered in carbene chemistry. The photoreactions should be stepwise but the ring-closure reactions of the intermediate 1-silatrimethylene-1,3-diyl diradicals were estimated to be very fast with rates of more than $10^9\,s^{-1}$ according to the photoaddition modes of silylene **1** to bicyclopropylidene[5] and (*E*)- and (*Z*)-2-butenes.

Broad absorption and fluorescence band maxima of **1** arising from transitions between $^1B_1$ and $^1A_1$ states were observed at 440 nm (ε 500)[4] and 610 nm, respectively, both in hexane and in benzene at room temperature. The spectral features are similar to those for dimethylsilylene, the absorption and fluorescence maxima of which were observed at 450 nm and 650 nm, respectively, at 77 K in a 3-methylpentane glass matrix.[6] As the intersection point of the mirror image absorption and fluorescence spectra, the 0–0 transition energy of **1**, that is, energy gap between $^1A_1$ and $^1B_1$ is estimated to be 55 kcal mol^{-1},[7] the value of which is in excellent agreement with the calculated value for dimethylsilylene at the CISD + Q/DZ(d)//SCF/DZ(d) level of theory (54.2 kcal mol^{-1}).[8] The state diagram for **1** should be similar to that for dimethylsilylene, and hence, can be drawn as shown in Figure 2 using the theoretical energy gap between $^1A_1$ and $^3B_1$ for dimethylsilylene (25.1 kcal mol^{-1});[8] the energy gap between the $^1B_1$ and $^3B_1$ states (ΔE_{ST}) is estimated to be roughly 30 kcal mol^{-1}.



1

Figure 2. Schematic state energy diagram for silylene **1**.

Time-resolved fluorescence spectra of **1** (excited at 440 nm and observed at 610 nm)[7,9] in hexane showed that the fluorescence decay obeyed a first-order rate law with a lifetime of 80.5 ns (τ_0). The fluorescence lifetime in a benzene–hexane mixture (τ) depended on the concentration of benzene according to Equation (2), indicating the effective quenching of the fluorescence by benzene. From the slope of the plot of τ_0/τ versus [benzene] and the τ_0 value, the quenching rate constant k_q was determined as $9.4\times 10^6\,s^{-1}\,mol^{-1}\,dm^3$.[7] The k_q value would be adequate for the rate constant for the addition of the highly reactive $^1B_1$ state of **1** having a singlet 1,1-biradical nature to benzene, because the rate constant is only twenty times larger than that for the addition of triethylsilyl radical to benzene ($4.6\times 10^5\,s^{-1}\,mol^{-1}\,dm^3$).[10]

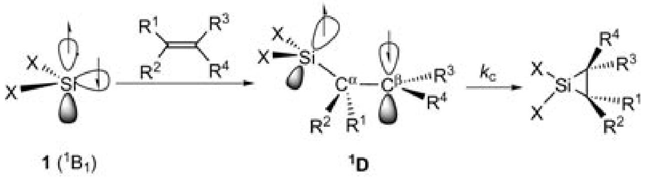
$$\tau_0/\tau = 1 + k_q\,\tau_0\,[\text{benzene}] \tag{2}$$

These results imply that though the $^3B_1$ state is more stable than $^1B_1$ (Figure 2), the intersystem crossing of **1** from $^1B_1$ to $^3B_1$ is too slow to compete with other processes such as fluorescence, radiationless decay, and reactions. Neither phosphorescence nor any ESR signals due to the $^3B_1$ state were observed during the irradiation of **1** in a 3-methylpentane glass matrix at 77 K.

No formation of $^3B_1$ from $^1B_1$ is rationalized in terms of the electronic configurations of $^1B_1$ and $^3B_1$ states and ΔE_{ST} in **1**.[11] Because the $^1B_1 \rightarrow {}^3B_1$ transition must involve either a 3p or an n electron spin inversion (Figure 1), the transition should be forbidden according to the El-Sayed rule.[12] In addition, the large ΔE_{ST} value should reduce the rate for the intersystem crossing from $^1B_1$ to $^3B_1$.

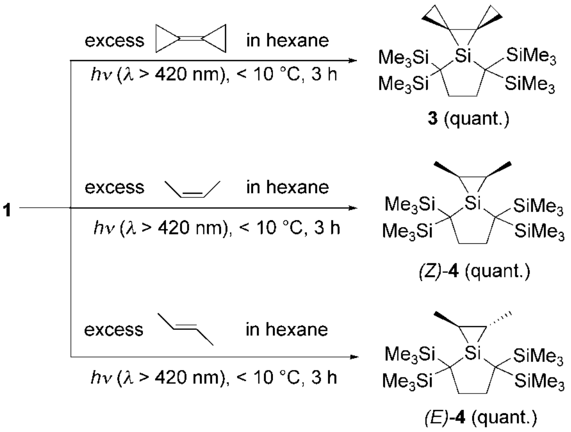
Silyl radicals are known to add to alkenes faster than to benzene; the second-order rate constant for the addition of triethylsilyl radical to (*E*)-3-hexene is $9.6\times 10^5\,s^{-1}\,mol^{-1}\,dm^3$.[10] Consequently, the addition of **1** in its $^1B_1$ state to an alkene is much faster than the intersystem crossing to the $^3B_1$ state, and hence, should give a singlet 1,3-biradical ^{1}**D**, the ring closure of which will give the corresponding silacyclopropanes as shown in Scheme 1. The reaction profile is in agreement with that derived theoretically for the addition of the $^1B_1$ state of H_2Si: to ethylene.[13]

To estimate the rates for the ring closure (k_c), the photochemical reactions of **1** with bicyclopropylidene[5] and (*E*)- and (*Z*)-2-butenes were investigated. Irradiation ($\lambda >$ 420 nm) of a mixture of **1** and excess bicyclopropylidene in



Scheme 1. Stepwise addition of $^1B_1$ silylene to an alkene.

hexane at < 10 °C gave the corresponding silacyclopropane **3** quantitatively (Scheme 2). Similarly, photoreactions of **1** in (*E*)- and (*Z*)-2-butene at < 10 °C afforded the corresponding (*E*)- and (*Z*)-2,3-dimethylsilacyclopropanes (*E*)-**4** and (*Z*)-**4**, respectively, in quantitative yields (Scheme 2). The excited state of **1** should be responsible for these reactions, because no reactions of **1** with these alkenes took place in the dark at < 10 °C.



Scheme 2. Photoadditions of silylene **1** to various alkenes.

The stereospecificity of the addition of a carbene to alkenes has often been used to determine whether the added carbene reacted as a singlet or a triplet species (Skell's rule).[14] However, since Skell's rule is usually applied for the discrimination between $^1A_1$ and $^3B_1$ carbenes, which prefer the stereospecific concerted addition and the two-step addition involving the intermediary formation of a 1,3-diradical followed by ring closure, respectively, this rule may not a priori be used to diagnose the multiplicity of the excited states of silylenes responsible for the addition.

The exclusive formation of **3** in the photoaddition of **1** to bicyclopropylidene as well as the stereospecific photoaddition of **1** to (*E*)- and (*Z*)-2-butenes indicates that the rate constant for the cyclization from $\mathbf{^1D}$ (k_c) should be more than ten times larger than the rate constants for other competitive processes such as the cyclopropane ring-opening of $\mathbf{^1D}$ produced in the former reaction and the rotation around the $C^\alpha{-}C^\beta$ bond of $\mathbf{^1D}$ in the latter reactions. The rate constant for the ring opening of cyclopropylmethyl radical to 3-butenyl radical as a radical clock has been determined to be $1.3 \times 10^8\ s^{-1}$.[5,15] The rate constants for the rotation around C−C σ bonds are estimated to be larger than $10^8\ s^{-1}$ at 10 °C, if we assume the activation energy for the rotation is less than 6 kcal mol^{-1} with an A factor of $10^{13}\ s^{-1}$.[16] Therefore, the k_c value should be larger than $10^9\ s^{-1}$.

In conclusion, the $^1B_1$ state generated by the irradiation of **1** reacts directly with benzene derivatives and alkenes to give the corresponding singlet 1,3-diradicals $\mathbf{^1D}$ with the addition rates of around $10^6\ mol^{-1}\,s^{-1}\,dm^3$, and then the ring closures of $\mathbf{^1D}$ to the corresponding silacyclopropanes occur with rate constants larger than $10^9\ s^{-1}$, while faster radical clocks are required to determine the ring-closure rates more acculately. The $^3B_1$ state of **1** does not participate in the reactions because of the strongly forbidden nature of the intersystem crossing from $^1B_1$ to $^3B_1$ of **1**.

Received: May 14, 2004 [Z460317]

Keywords: carbene homologues · laser spectroscopy · photochemistry · reaction mechanisms · silicon

---

[1] For a recent review, see: P. P. Gaspar, R. West in *The Chemistry of Organic Silicon Compounds, Vol. 2, Part 3* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, Chapter 43, p. 2463.

[2] For reviews on the photochemistry of silylenes, see: a) A. G. Brook in *The Chemistry of Organic Silicon Compounds, Vol. 2, Part 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, Chapter 21, p. 1233; b) M. Kira, T. Miyazawa in *The Chemistry of Organic Silicon Compounds, Vol. 2, Part2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, Chapter 22, p. 1311.

[3] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2002**, *124*, 3830.

[4] M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722.

[5] a) A. de Meijere, S. I. Kozhushkov, T. Späth, *Org. Synth.* **2000**, *78*, 142–151; for reviews see: b) A. de Meijere, S. I. Kozhushkov, *Eur. J. Org. Chem.* **2000**, 3809; c) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Top. Curr. Chem.* **2000**, *207*, 89.

[6] a) T. J. Drahnak, J. Michl, R. West, *J. Am. Chem. Soc.* **1979**, *101*, 5427; b) C. A. Arrington, K. A. Klingensmith, R. West, J. Michl, *J. Am. Chem. Soc.* **1984**, *106*, 525.

[7] See the Supporting Information for experimental details.

[8] R. S. Grev, H. F. Schaefer III, *J. Am. Chem. Soc.* **1986**, *108*, 5804.

[9] K. Yamanaka, M. Fujitsuka, Y. Araki, O. Ito, T. Aoshima, T. Fukushima, T. Miyashi, *J. Phys. Chem. A* **2004**, *108*, 250.

[10] a) C. Chatgilialoglu, K. U. Ingold, J. C. Scaiano, *J. Am. Chem. Soc.* **1983**, *105*, 3292; b) C. Chatgilialoglu, *Chem. Rev.* **1995**, *95*, 1229.

[11] N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., Menlo Park, California, **1978**.

[12] a) M. A. El-Sayed, *J. Chem. Phys.* **1962**, *36*, 573; b) M. A. El-Sayed, *J. Chem. Phys.* **1963**, *38*, 2834; c) M. A. El-Sayed, *J. Chem. Phys.* **1964**, *41*, 2462; d) M. A. El-Sayed, *Acc. Chem. Res.* **1968**, *1*, 8; e) S. K. Lower, M. A. El-Sayed, *Chem. Rev.* **1966**, *66*, 199.

[13] C. Lennartz, H. M. Hildebrandt, B. Engels, *J. Phys. Chem. A* **1977**, *101*, 10053.

[14] P. S. Skell, R. C. Woodworth, *J. Am. Chem. Soc.* **1956**, *78*, 4496. See also: P. P. Gaspar, G. S. Hammond in *Carbenes*, *Vol. 2* (Eds.: R. A. Moss, M. Jones Jr), Wiley, New York, **1975**, Chapter 6.

[15] a) B. Maillard, D. Fonest, K. U. Ingold, *J. Am. Chem. Soc.* **1976**, *98*, 7024; b) D. Griller, K. U. Ingold, *Acc. Chem. Res.* **1980**, *13*, 317.

[16] T. Kawamura, P. Meakin, J. K. Kochi, *J. Am. Chem. Soc.* **1972**, *94*, 8065, and references therein.