A Novel Reaction Mode in the Cycloaddition of Thermally Generated Silylenes with Conjugated Dienes

Nobuhiro Takeda,# Norihiro Tokitoh,*# and Renji Okazaki†‡

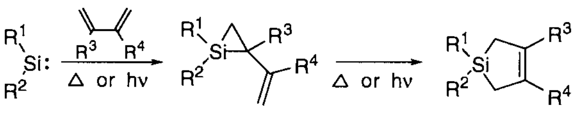
Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

†Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

(Received February 28, 2000; CL-000194)

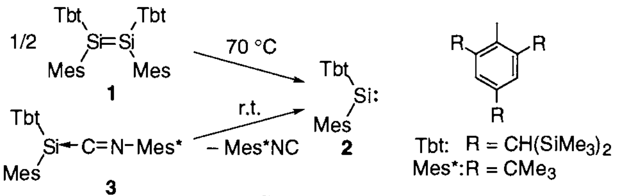
A thermally generated silylene bearing bulky substituents, Tbt(Mes)Si: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = 2,4,6-trimethylphenyl), reacted with isoprene at room temperature to give the corresponding 2-vinylsilirane, which thermally isomerized to the corresponding 3-silolene, while silylene underwent competitive [1+2] and [1+4] cycloadditions with 2,4-dimethyl-1,3-butadiene.

In recent decades, silylenes (silicon analogues of carbenes) have been extensively studied from the standpoints not only of fundamental chemistry but also of applied chemistry such as material science and organic syntheses.[1] Reactions of photochemically or thermally generated transient silylenes with 1,3-dienes giving the corresponding 3-silolenes (silacyclopent-3-enes) are known to be typical reactions for the detection of silylenes.[1] The mechanism of these reactions has been investigated in detail,[1,2] and it has been proposed that the reaction of silylenes with 1,3-dienes proceeds via the initial [1+2] cycloaddition to give 2-vinylsiliranes, followed by their isomerization into the corresponding 3-silolenes (Equation 1). However, the observation and isolation of the intermediary 2-vinylsiliranes have been limited to only a few reactions of photochemically generated silylenes with 1,3-dienes,[2] and there has been no report on the observation of 2-vinylsiliranes in the reactions of thermally generated silylenes with 1,3-dienes. The lability of intermediary 2-vinylsiliranes in the reactions of silylenes with 1,3-dienes is probably due to their ready isomerization into the corresponding 3-silolenes under the generation conditions of silylenes such as ultraviolet irradiation or heating at high temperature.



(1)

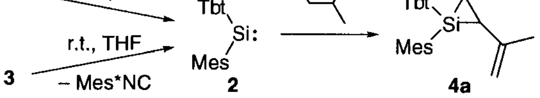
On the other hand, we have succeeded in the synthesis of an extremely hindered disilene **1** bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter)[3] and found that **1** is very stable with respect to oligomerization but thermally labile to give the corresponding silylene **2** under very mild conditions (Scheme 1).[4] In addition, we recently reported the synthesis of the first stable silylene– isocyanide complex **3**[5] by the reaction of **1** with a hindered isocyanide and its facile dissociation of **3** into silylene **2** and the corresponding isocyanide at room temperature (Scheme 1). In this paper, we describe the reaction of silylene **2**, generated from disilene **1** or complex **3** under very mild thermal conditions, with dienes, leading to the isolation of the corresponding 2-vinylsilirane intermediate and the occurrence of unusual direct [1+4] cycloaddition of silylene **2** to 2,3-dimethyl-1,3-butadiene.



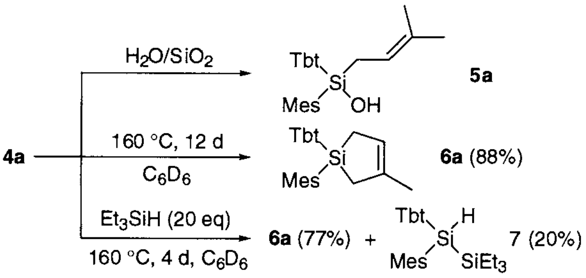
Scheme 1.

When disilene **1** was allowed to react with isoprene at 70 °C in THF, the [1+2] adduct **4a**[6] of silylene **2** with the diene was isolated as an air-stable colorless powder in 89% yield (Scheme 2). Also, vinylsilirane **4a** was isolated by the reaction of silylene–isocyanide complex **3** with isoprene at room temperature in 84% yield. These results indicate that these reactions proceed via silylene **2** as an intermediate. The ^{29}Si NMR spectrum of **4a** showed a characteristic signal (δ_{Si} = –88.5) attributable to that of a silicon atom in a three-membered ring.[2] The isopropenyl group in **4a** is presumed to lie on the same side as the Mes group for a steric reason, and the exclusive formation of **4a** is most likely interpreted in terms of the severe steric repulsion among bulky substituents on the silicon atom and the methyl group of isoprene. Although **4a** was stable in the solid state even on exposure to the air, it underwent hydrolysis on silica gel to give the corresponding silanol **5a**[7] (Scheme 3). The stability of **4a** to air is in sharp contrast to that of less hindered 2-vinylsiliranes which readily react with methanol,[8] indicating the effective steric protection in the strained silirane ring of **4a** by the combination of bulky Tbt and Mes groups.

Thermolysis of **4a**, however, proceeded at 160 °C for 12 days in C_6D_6 to give a formal [1+4] cycloadduct **6a**[9] in 88% yield, as monitored by ^{29}Si NMR spectroscopy (Scheme 3).



Scheme 2.

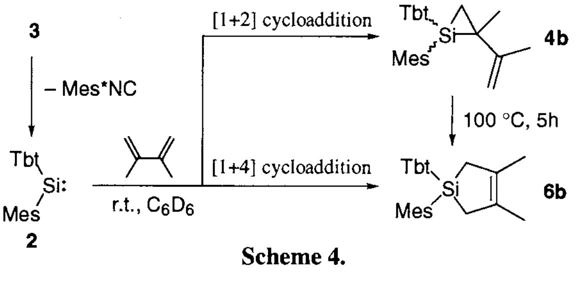


Scheme 3.

The isolation of **4a** and its thermal ring expansion leading to the formation of **6a** is the first experimental demonstration for the stepwise formation of a 3-silolene via a 2-vinylsilirane intermediate in the reaction of a thermally generated silylene with a 1,3-diene, although the existence of this type of intermediary [1+2] cycloadducts has already been evidenced by NMR spectroscopy for the cycloaddition reaction of photochemically generated silylenes to 1,3-dienes.[2a] The isolation of **4a** in the present study is certainly due to the very mild conditions for the generation of **2**. The formation mechanism of **6a** from **4a** may be explained by the direct [1+4] cycloaddition of silylene **2** regenerated from **4a** to isoprene because thermolysis of **4a** in the presence of triethylsilane gave the silylene adduct **7**[4c] (20%) together with **6a** (77%) (Scheme 3),[10] although other mechanistic possibilities can not be ruled out.

When complex **3** was allowed to react with 2,3-dimethyl-1,3-butadiene in C_6D_6 in a sealed tube at room temperature for 2.5 h (Scheme 4), the original deep blue solution of **3** turned greenish yellow. The ^{29}Si NMR spectrum of the mixture showed three peaks (–76.3, –72.9, and –5.3 ppm with the peak height ratio of ca. 2 : 6 : 3) besides the peaks for the trimethylsilyl groups of Tbt group. The former three peaks are most reasonably assignable to that for [1+4] cycloadduct **6b**[4c] (δ_{Si} = –5.3) and those for the geometric isomers of [1+2] cycloadducts **4b** (δ_{Si} = –76.3, –72.9). Since heating the reaction mixture at 50 °C for 7 h resulted in no change as judged by NMR spectroscopy, it is considered that silylene **2** undergoes both [1+2] and [1+4] cycloaddition reactions with the 1,3-diene competitively. This result is very interesting because this is the first unambiguous evidence for the occurrence of unusual direct [1+4] cycloaddition of a silylene to a 1,3-diene moiety as far as we know. Since it is theoretically predicted that [1+4] cycloaddition of silylenes to dienes more easily occurs in the reaction of triplet silylenes than in that of singlet silylenes, the experimental results obtained here may imply some triplet character for silylene **2**. However, this is probably not the case; the occurrence of the direct [1+4] cycloaddition in this reaction is better explained as below. The [1+2] cycloaddition may be suppressed by the steric repulsion among the methyl groups of the diene and the bulky substituents on the silicon atom of **2**, while the effect of the steric repulsion in the [1+4] cycloaddition is smaller than that in the [1+2] cycloaddition. Therefore, the [1+4] cycloaddition, which is normally considered to be much slower reaction than the [1+2] cycloaddition, would occur competitively with the [1+2] cycloaddition. This interpretation is in keeping with the absence of [1+4] cycloadduct **6a** in the reaction with isoprene. Thus, the results here obtained indicate that silylenes bearing very bulky substituents may undergo direct [1+4] cycloaddition to dienes.

Further heating the reaction mixture containing **4b** and **6b** at 100 °C for 5 h led to the complete isomerization of initially formed **4b** into **6b**.



Scheme 4.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 11133247) from the Ministry of Education, Science, Sports and Culture, Japan. We are grateful to Central Glass, Shin-Etsu Chemical, and Tosoh Akzo Co., Ltds. for the generous gifts of tetrafluorosilane, chlorosilanes, and alkyllithiums, respectively.

References and Notes

\# Present address: Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

‡ Present address: Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, 2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan.

1 For recent reviews on silylenes, see: a) P. P. Gaspar and R. West, in "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig, John Wiley & Sons, New York (1998), Vol. 2, Part 3, pp. 2463-2568. b) J. Hermanns and B. Schmidt, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 2209.

2 a) S. Zhang and R. T. Conlin, *J. Am. Chem. Soc.*, **113**, 4272 (1991). b) M. Weidenbruch, E. Kroke, H. Marsmann, S. Pohl, and W. Saak, *J. Chem. Soc., Chem. Commun.*, **1994,** 1233. c) E. Kroke, S. Willms, M. Weidenbruch, W. Saak, S. Pohl, and H. Marsmann, *Tetrahedron Lett.*, **37**, 3675 (1996).

3 a) R. Okazaki, M. Unno, and N. Inamoto, *Chem. Lett.*, **1987**, 2293. b) R. Okazaki, N. Tokitoh, and T. Matsumoto in "Synthetic Methods of Organometallic and Inorganic Chemistry," ed. by W. A. Herrmann, Vol. ed. by N. Auner and U. Klingebiel, Thieme, New York (1996), Vol. 2, pp. 260-269.

4 a) N. Tokitoh, H. Suzuki, R. Okazaki, and K. Ogawa, *J. Am. Chem. Soc.*, **115**, 10428 (1993). b) H. Suzuki, N. Tokitoh, R. Okazaki, J. Harada, K. Ogawa, S. Tomoda, and M. Goto, *Organometallics*, **14**, 1016 (1995). c) H. Suzuki, N. Tokitoh, and R. Okazaki, *Bull. Chem. Soc. Jpn.*, **68**, 2471 (1995).

5 N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, and S. Nagase, *J. Am. Chem. Soc.*, **119**, 1456 (1997).

6 Spectral data for **4a**: colorless powder, mp 172–175 °C (dec); ^{1}H NMR (500 MHz, C_6D_6, 75 °C) δ 0.01 (s, 18H), 0.14 (s, 9H), 0.15 (s, 9H), 0.28 (s, 18H), 1.41–1.49 (m, 3H), 1.86 (s, 3H), 2.04 (s, 3H), 2.44–2.47 (m, 1H), 2.67 (s, 6H), 2.89 (br s, 2H), 4.32 (s, 1H), 4.43 (s, 1H), 6.57 (s, 2H), 6.70 (s, 2H); ^{13}C NMR (125 MHz, C_6D_6, 75 °C) δ 1.0 (q), 1.2(q), 2.1 (q), 11.9 (t), 21.0 (q), 25.0 (q), 26.5 (q), 29.3 (d), 29.9 (d), 31.3 (d), 103.7 (t), 125.8 (s), 128.3 (d), 128.6 (s), 128.7 (d), 139.6 (s), 145.4 (s), 145.6 (s), 145.7 (s), 153.5 (s); ^{29}Si NMR (99 MHz, C_6D_6, 75 °C) δ –88.5, 2.6. Anal. Calcd for $C_{41}H_{78}Si_7 \cdot H_2O$: C, 62.68; H, 10.26%. Found: C, 62.59; H, 10.07%.

7 Spectral data for **5a**: colorless powder, mp 175–177 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C) δ -0.12 (s, 18H), 0.06 (s, 18H), 0.09 (s, 18H), 1.32 (s, 1H), 1.37 (s, 3H), 1.60 (s, 3H), 1.94 (s, 1H), 1.97 (dd, 1H, ^2J = 14 Hz, ^3J = 8 Hz), 2.19 (dd, 1H, ^2J = 14 Hz, ^3J = 9 Hz), 2.21 (s, 3H), 2.23 (br s, 2H), 2.36 (br s, 6H), 4.95 (dd, 1H, ^3J = 8 and 9 Hz), 6.28 (br s, 1H), 6.37 (br s, 1H), 6.68 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 60 °C) δ 0.9 (q), 1.0 (q), 1.9 (q), 17.7 (q), 20.9 (q), 24.5 (q), 25.7 (q), 26.3 (t), 27.4 (d×2), 30.6 (d), 119.9 (d), 123.1 (d), 128.1 (d), 129.3 (d), 130.6 (s), 131.7 (s), 134.0 (s), 138.5 (s), 143.3 (s), 144.3 (s), 151.1 (s×2); ^{29}Si NMR (99 MHz, $CDCl_3$, 60 °C) δ –6.5, 1.6, 1.7, 2.35, 2.41. Anal. Calcd for $C_{41}H_{80}OSi_7$: C, 62.68; H, 10.26%. Found: C, 62.65; H, 9.97%.

8 a) M. Ishikawa, F. Ohi, and M. Kumada, *J. Organomet. Chem.*, **86**, C23 (1975). b) M. Ishikawa, K. Nakagawa, and M. Kumada, *J. Organomet. Chem.*, **178**, 105 (1979).

9 Spectral data for **6a**: colorless powder, mp 159–161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.09 (s, 9H), –0.08 (s, 9H), –0.02 (s, 9H), –0.01 (s, 9H), 0.04 (s, 18H), 1.28 (s, 1H), 1.78 (s, 3H), 1.78–1.84 (m, 1H, CH_2CH), 1.88 (d, 1H, ^2J = 19 Hz, CH_2CMe), 2.02 (d, 1H, ^2J = 19 Hz, CH_2CMe), 2.06 (s, 1H), 2.09–2.15 (m, 1H, CH_2CH), 2.16 (s, 1H), 2.21 (s, 3H), 2.37 (s, 6H), 5.56 (m, 1H), 6.24 (s, 1H), 6.37 (s, 1H), 6.74 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.89 (q), 0.93 (q), 1.1 (q), 1.2 (q), 1.4 (q), 1.5 (q), 20.8 (q), 22.4 (q), 25.6 (q), 26.0 (t), 27.6 (d), 27.9 (d), 29.4 (t), 30.3 (d), 122.8 (d), 125.4 (d), 128.0 (d), 128.9 (s), 129.4 (d), 137.1 (s), 138.2 (s), 140.0 (s), 143.2 (s), 143.5 (s), 151.6 (s),151.8 (s); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 1.7, 2.2, 2.4, 2.6. Anal. Calcd for $C_{41}H_{78}Si_7$: C, 64.15; H, 10.24%. Found: C, 64.14; H, 10.15%.

10 No change was observed in thermolysis of **6a** at this temperature in the presence of triethylsilane.