Silicon−Carbon Unsaturated Compounds. 71. Thermolysis of 1,2-Bis(acyl)tetrakis(trimethylsilyl)disilane with Disubstituted Acetylenes

Joji Ohshita,*,[‡] Hidenobu Ohnishi,[†] Akinobu Naka,[†] Norihito Senba,[†] Junnai Ikadai,[‡]
Atsutaka Kunai,[‡] Hisayoshi Kobayashi,*,[#] and Mitsuo Ishikawa*,[†]

Department of Chemistry and Bioscience, Kurashiki University of Science and the Arts, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan, Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan, and Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

Received May 25, 2006

The thermolysis of 1,2-di(adamantoyl)tetrakis(trimethylsilyl)disilane (**1a**) with diphenylacetylene at 140 °C for 24 h afforded 1-[(*E*)-1,2-diadamantyl-2-(trimethylsiloxy)ethenyloxy]-2,3-diphenyl-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene (**2a**) and 3,4-diadamantyl-2,2-bis(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (**3a**) in 43% and 41% yields, respectively. Similarly, the cothermolysis of 1,2-di(pivaloyl)tetrakis(trimethylsilyl)disilane (**1b**) with diphenylacetylene gave 1-[(*E*)-1,2-di(*tert*-butyl)-2-(trimethylsiloxy)ethenyloxy]-2,3-diphenyl-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene (**2b**) in 52% yield, along with a mixture of unidentified products. The reaction of **1a** with bis(trimethylsilyl)acetylene under the same conditions produced 1-[(*E*)-1,2-diadamantyl-2-(trimethylsiloxy)ethenyloxy]-2,3-bis(trimethylsilyl)-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene and **3a** in 54% and 23% yield, while **1b** with bis(trimethylsilyl)acetylene gave 1-[(*E*)-1,2-di(*tert*-butyl)-2-(trimethylsiloxy)ethenyloxy]-2,3-bis(trimethylsilyl)-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene in 62% yield. The results of X-ray crystallographic analysis for the 1-silacycloprop-2-ene **2a** are described. Computational analyses for successive isomerization of a simplified model, 1,2-di(acetyl)tetra(silyl)disilane to a silylene intermediate, [(*E*)-1,2-dimethyl-2-siloxyethenyloxy]tri(silyl)silylsilylene via *trans*-3,4-dimethyl-3,4-di(siloxy)-1,2-di(silyl)-1,2-disilacyclobut-1-ene, are described. The results of the calculations for the real models having the same substituents as **1b** are also reported.

Introduction

It is well-known that acylpolysilanes can be used as convenient precursors for the synthesis of a wide variety of silenes.[1−3] The photolysis[4] and thermolysis[5] of the acylpolysilanes readily produce various types of silenes in high yields. The Peterson-type reactions of the acylpolysilanes also afford silenes.[6] Many papers concerning the reactions of the silenes thus formed with organic compounds have been published to date.[1−6] However, the acylpolysilanes reported so far involve only one acyl−Si bond in the molecules. Much less interest has been shown in the chemistry of the compounds bearing two or more acyl−Si bonds.

We have demonstrated that the reactions of acyltris(trimethylsilyl)silanes with silyllithium reagents proceed to give the corresponding lithium silenolates by elimination of a trimethylsilyl group, and the silenolates thus formed react with palladium dichloride to afford 1,2-bis(acyl)tetrakis(trimethylsilyl)disilanes involving the adamantoyl, pivaloyl, and mesitoyl groups as the acyl moieties.[7] We have also reported that the thermolysis of 1,2-di(adamantoyl)tetrakis(trimethylsilyl)disilane produces an isomer, 3,4-diadamantyl-1,1-bis(trimethylsiloxy)-2,2-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene, via a 2,3-disilabuta-1,3-diene intermediate.[8] In this paper we report the thermal reactions of 1,2-di(adamantoyl)- and 1,2-di(pivaloyl)tetrakis(trimethylsilyl)disilane with diphenylacetylene and bis-

---

* To whom correspondence should be addressed. E-mail: mishika@chem.kusa.ac.jp.

[†] Kurashiki University of Science and the Arts.

[‡] Hiroshima University.

[#] Kyoto Institute of Technology.

(1) (a) Brook, A. G. *J. Organomet. Chem.* **1986**, *300*, 21. (b) Brook, A. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 15.

(2) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

(3) Brook, A. G. In *The Chemistry of Organic Silicon Compounds, Vol. 2;* Rappoport, Z.; Apeloig, Y., Eds.; Wiley: Chichester, 1998; Chapter 21.

(4) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; Elsheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chan, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(5) (a) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Organometallics* **1996**, *15*, 3836. (b) Naka, A.; Ishikawa, M. Matsui, S.; Ohshita, J.; Kunai, A. *Organometallics* **1996**, *15*, 5759. (c) Naka, A. Ishikawa, M. *J. Organomet. Chem.* **2000**, *611*, 248. (d) Naka, A.; Ikadai, J.; Motoike, S.; Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Ishikawa, M. *Organometallics* **2002**, *21*, 2033. (e) Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Naka, A.; Ishikawa, M. *Organometallics* **2002**, *21*, 3271. (f) Ohshita, J.; Takayama, H.; Tamai, M.; Iida, T.; Kunai, A. *Organometallics* **2003**, *22*, 2338. (g) Naka, A.; Ohnishi, H.; Miyahara, I.; Hirotsu, K.; Shiota, Y.; Yoshizawa, K.; Ishikawa, M. *Organometallics* **2004**, *23*, 4277.

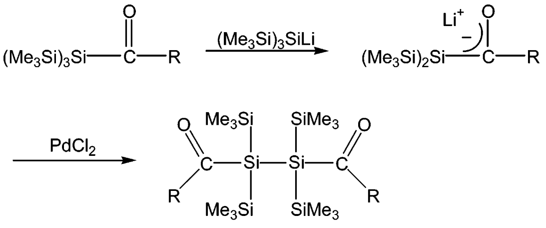
(6) (a) Brook, A. G.; Chiu, P.; McClenaghnan, J.; Lough, A. J. *Organometallics* **1991**, *10*, 3292. (b) Ohshita, J.; Masaoka, Y.; Ishikawa, M. *Organometallics* **1991**, *10*, 3775; **1993**, *12*, 876. (c) Bravo-Zhivotovskii, D.; Brande, V.; Stanger, A.; Kapon, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326. (d) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228. (e) Krempner, C.; Oehme, H. *J. Organomet. Chem.* **1994**, *464*, C7. (f) Krempner, C.; Reinke, H.; Oehme, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1615.

(7) Ohshita, J.; Masaoka, S.; Ishikawa, M. *Organometallics* **1996**, *15*, 2198.

(8) Ohshita, J.; Takayama, H.; Ishikawa, M.; Kunai, A. *J. Organomet. Chem.* **2003**, *672*, 72.

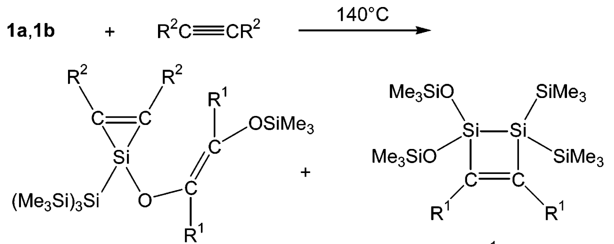
10.1021/om060458v CCC: $33.50

Scheme 1



1a, R = Ad
1b, R = *t*-Bu

Scheme 2



2a, R^1 = Ad, R^2 = Ph
2b, R^1 = *t*-Bu, R^2 = Ph
4a, R^1 = Ad, R^2 = Me_3Si
4b, R^1 = *t*-Bu, R^2 = Me_3Si

3a, R^1 = Ad

(trimethylsilyl)acetylene, which afford the respective 1-silacycloprop-2-ene derivatives, and computational analyses for these reactions. We also report the X-ray crystallographic analysis of the 1-silacycloprop-2-ene derivative obtained by the reaction of 1,2-di(adamantoyl)tetrakis(trimethylsilyl)disilane with diphenylacetylene.

Results and Discussion

Reactions of Bis(acyl)tetrakis(trimethylsilyl)disilanes with Diphenylacetylene. The starting compounds, 1,2-di(adamantoyl)- and 1,2-di(pivaloyl)tetrakis(trimethylsilyl)disilane (**1a** and **1b**), were prepared according to the method reported previously,[7] as shown in Scheme 1. When a mixture of **1a** and diphenylacetylene in benzene was heated in a sealed glass tube at 140 °C for 24 h, two products, a silacyclopropene derivative, 1-[(*E*)-1,2-diadamantyl-2-(trimethylsiloxy)ethenyloxy]-2,3-diphenyl-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene (**2a**), and an isomer of the starting compound **1a**, 3,4-diadamantyl-1,1-bis(trimethylsiloxy)-2,2-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (**3a**), were obtained in 43% and 41% isolated yields, respectively (Scheme 2). These two products could readily be isolated by silica gel column chromatography, and the product **2a** was obtained by recrystallization from hexane as colorless crystals. No geometrical isomer, 1-[(*Z*)-1,2-diadamantyl-2-(trimethylsiloxy)ethenyloxy]-2,3-diphenyl-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene, was detected in the reaction mixture by spectrometric analysis, indicating that the reaction proceeded with high stereospecificity to give **2a**.

The structure of **2a** was verified by mass and ^1H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis. Its ^{29}Si NMR spectrum shows four resonances at −131.1, −88.0, −8.8, and 12.6 ppm, due to the tetra(silyl)-substituted silicon, silacyclopropenyl ring silicon, trimethylsilyl silicon, and trimethylsiloxy silicon, respectively, which are consistent with the structure proposed for **2a**. It has been reported that the ^{29}Si NMR chemical shifts of the silicon atoms in the silacyclopropenes bearing the silyl substituent on the ring silicon atom appear at −143 to −187 ppm,[9] while the chemical shifts of the silacyclopropenes with the electron-withdrawing group on the ring silicon atom, such as 1-alkyl-1-trimethylsiloxy- and 1,1-diamino-1-silacyclopropene derivatives, appear at −94 to −97[10] and −100 ppm,[11] respectively.

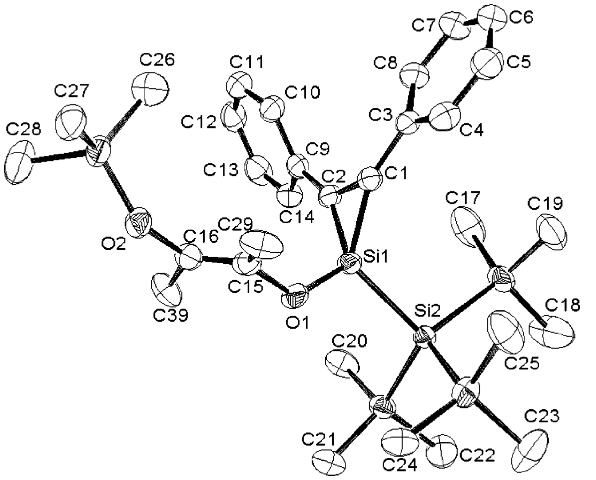


Figure 1. ORTEP drawing of compound **2a**. Adamantyl groups are represented by the respective quarter carbons, and protons are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. A disorder model was applied to solve the siloxyethene unit, using two sets of ethene carbons with occupancies of 0.79 and 0.21, respectively, and only that with higher occupancy is shown.

For **2a**, despite the presence of the silyl group on the ring silicon atom, its ^{29}Si chemical shift appears at −88.0 ppm. Such a large downfield shift may be ascribed to the existence of the ethenyloxy group on the ring silicon atom. The *E*-configuration for **2a** was confirmed by X-ray crystallographic analysis, and the ORTEP drawing is depicted in Figure 1.

Compound **3a** was identified as 3,4-diadamantyl-2,2-bis(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene by mass and ^1H, ^{13}C, and ^{29}Si NMR spectrometric analysis. All spectral data obtained for **3a** were identical with those of an authentic sample reported previously.[8]

Treatment of **1b** with diphenylacetylene under the same conditions again afforded the 1-silyl-1-silacycloprop-2-ene derivative, analogous to **2a**, 1-[(*E*)-1,2-di(*tert*-butyl)-2-(trimethylsiloxy)ethenyloxy]-2,3-diphenyl-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene (**2b**), in 52% isolated yield. The product **2b** was isolated by silica gel column chromatography, and its structure was verified by spectrometric analysis. As expected, ^1H, ^{13}C, and ^{29}Si NMR spectra for **2b** show signal patterns very similar to those of **2a**. For example, the ^1H NMR spectrum for **2b** displays two resonances at 0.05 and 0.22 ppm, due to the trimethylsiloxy and trimethylsilyl protons, and two resonances at 1.11 and 1.15 ppm, attributed to the two different kinds of *tert*-butyl protons, as well as the resonances due to the phenyl ring protons. The chemical shift of the ring silicon atom in the ^{29}Si NMR spectrum for the product **2b** again appears at −87.4 ppm, a very low magnetic field, as observed in that of **2a**.

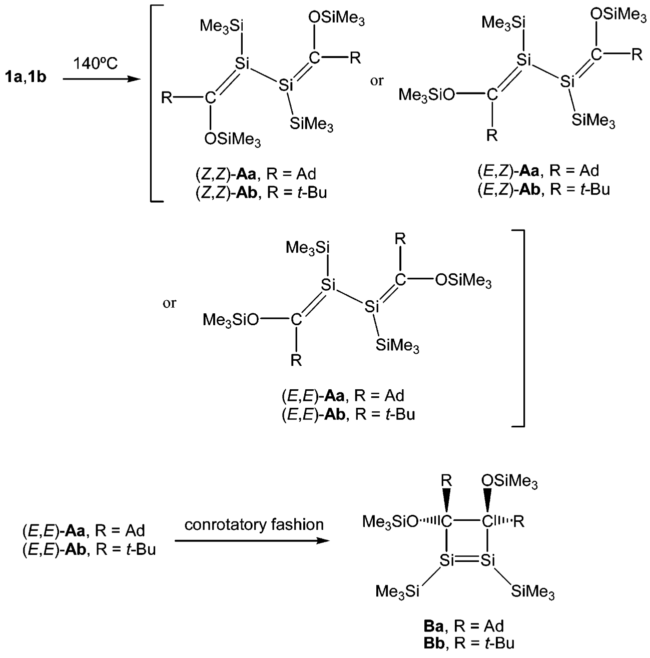
---

(9) (a) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3269. (b) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231. (c) Gaspar, P. P.; Beatty, A. M.; Chen, T.; Haile, T.; Lei, D.; Winchester, W. R.; Braddock-Wilking, J.; Rath, N. P.; Klooster, W. T.; Koetzle, T. F.; Mason, S. A.; Albinati, A. *Organometallics* **1999**, *18*, 3921. (d) Sekiguchi, A.; Tanaka, T.; Ichinohe, M.; Akiyama, K.; Tero-Kubota, S. *J. Am. Chem. Soc.* **2003**, *125*, 4962.

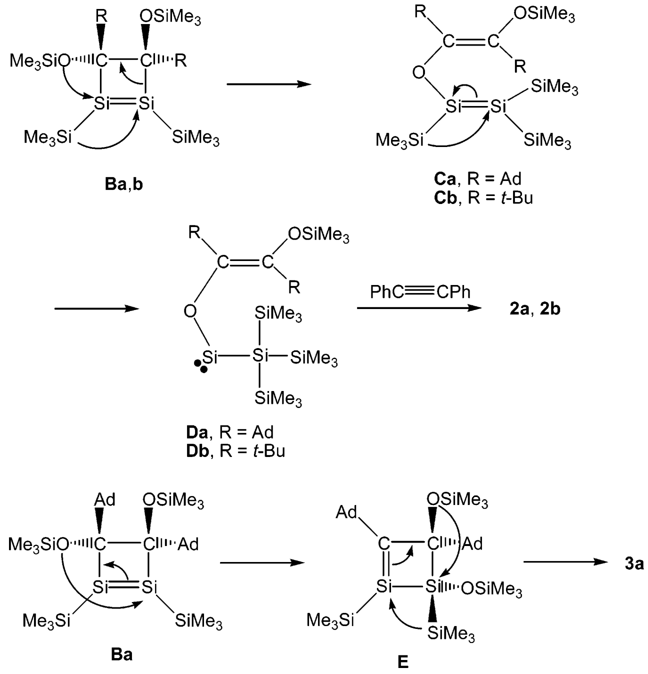
(10) Naka, A.; Ishikawa, M. *Organometallics* **2000**, *19*, 4921.

(11) Sakamoto, K.; Tsutsui, S.; Sakurai, H.; Kira, M. *Bull. Soc. Chem. Jpn.* **1997**, *70*, 253.

Scheme 3



Scheme 4



The fact that the product **2b** also has an *E*-configuration was confirmed by NOE-FID difference experiments at 300 MHz. Thus, saturation of the resonance at 0.05 ppm due to the trimethylsiloxy protons resulted in a strong enhancement of the signals at 1.11 and 1.15 ppm, attributable to the two kinds of *tert*-butyl protons, indicating that **2b** must have the *E*-configuration. Again, no *Z*-isomer was detected in the reaction mixture by spectrometric analysis. Although the formation of small amounts of other products was observed in this reaction, all attempts to isolate the product analogous to **3a** were unsuccessful. However, mass spectrometric analysis of this mixture showed the presence of the molecular ion at *m*/*z* 518, corresponding to the calculated molecular weight for $C_{22}H_{54}O_2Si_6$.

In contrast to **2a**, compound **2b** has been found to decompose on storing over a period of a few months. However, the rate of decomposition of this compound is very slow. In fact, when the crystals of **2b** were allowed to stand in a small flask at room temperature, no change was observed for one or two weeks, but a couple of months later, the crystals changed to oily substances. Evaporation of the products under reduced pressure gave diphenylacetylene as the sole volatile product, along with nonvolatile substances.

Recently, we have reported that the thermolysis of **1a** in the absence of a trapping agent produces **3a** as the major product.[8] We have proposed the transient formation of 1,4-diadamantyl-1,4-bis(trimethylsiloxy)-2,3-bis(trimethylsilyl)-2,3-disila-1,3-butadiene, which would undergo cyclization to give 3,4-diadamantyl-3,4-bis(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1,2-disilacyclobut-1-ene, as a key intermediate for the formation of **3a**. For the 2,3-disila-1,3-butadiene intermediate, three isomers with different configurations, (*E*,*E*)-**Aa**, (*E*,*Z*)-**Aa**, and (*Z*,*Z*)-**Aa**, are thought to be produced in the thermolysis of **1a** (Scheme 3). However, theoretical calculations shown below indicated that the (*E*,*E*)-isomer was found to be the most important species among these isomers, in accord with the experimental results. If this is true, the ring closure of (*E*,*E*)-**Aa** with the conrotatory process would afford the *trans*-1,2-disilacyclobut-1-ene intermediate (**Ba**), which undergoes isomerization to give **2a** and **3a**, respectively.

The formation of **2a** and **2b** may be best explained in terms of isomerization of the intermediates **Ba,b** with trans configurations, as shown in Scheme 4. Presumably, the oxygen atom of a trimethylsiloxy group on the ring carbon in the 1,2-disilacyclobut-1-enes **Ba**,**b** plays an important role for isomerization, leading to the products **2a**,**b**. Namely, a sequence of isomerization may be initiated by attack of the trimethylsiloxy oxygen to the sp^2-hybridized silicon atom in the 1,2-disilacyclobut-1-ene ring, and the trimethylsilyl group on this ring silicon migrates to the adjacent sp^2-hybridized silicon atom. Subsequently, a shift of the trimethylsilyl group on the oxygen onto the ring silicon and ring opening takes place to give the (*E*)-ethenyloxydisilene derivatives (**Ca**,**b**). The disilenes **Ca**,**b** thus formed undergo isomerization to give silyl-substituted silylenes (**Da**,**b**), which can add readily to a triple bond in alkynes, giving the final products, **2a** and **2b**. The transformation of the silyl-substituted silylenes into the disilenes has been observed to date.[12] In the present reactions, no products arising from the reaction of the disilenes **Ca**,**b** with diphenylacetylene were detected in the resulting mixture. It seems likely that the low reactivity of the disilenes **Ca**,**b** may be ascribed to the steric hindrance owing to the bulky substituents around the silicon−silicon double bond. Furthermore, the theoretical calculations indicate that the energy of the disilene **Cb** is less stable than that of the silyl-substituted silylene intermediate **Db**.

A similar role of the oxygen in the trimethylsiloxy group for the skeletal rearrangement has been found in the thermolysis of the trimethylsiloxy-substituted silacyclobutene derivatives.[5d,g] For example, the thermolysis of 2-*tert*-butyl-3-(trimethylsilylethynyl)-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-1-silacyclobut-3-ene affords an oxygen insertion product, a dihydrooxasilole derivative.[5g]

As reported previously,[8] the formation of **3a** can be understood by the successive migrations of two trimethylsiloxy groups and a trimethylsilyl group. A 1,3-shift of one of two trimethylsiloxy groups in **Ba** onto the sp^2-hybridized silicon atom in the 1,2-disilacyclobut-1-ene ring gives 3,4-diadamantyl-1,4-bis-

---

[12] (a) Sakurai, H.; Sakaba, H.; Nakadaira, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6156. (b) Sakurai, H.; Nakadaira, Y.; Sakaba, H. *Organometallics* **1983**, *2*, 1484. (c) Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 1320. (d) Sanji, T.; Mori, T.; Sakurai, H. *J. Organomet. Chem.* **2006**, *691*, 1169.

(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1,2-disilacyclobut- 2-ene (**E**), as shown in Scheme 4. A 1,2-shift of a trimethylsiloxy group on the ring carbon at the 4 position onto the sp^3-hybridized silicon atom in the intermediate **E** and simultaneously a 1,2-trimethylsilyl shift from the resulting silicon to the adjacent sp^2-hybridized silicon affords the product **3a**.

Reactions of 1a and 1b with Bis(trimethylsilyl)acetylene. When a benzene solution of **1a** and bis(trimethylsilyl)acetylene was heated in a sealed glass tube at 140 °C for 24 h, two products, **3a** and a silacyclopropene derivative, 1-[(*E*)-1,2-diadamantyl-2-(trimethylsiloxy)ethenyloxy]-2,3-bis(trimethylsilyl)-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene (**4a**), were obtained in 23% and 54% yield, respectively. Similarly, treatment of **1b** with bis(trimethylsilyl)acetylene in benzene under the same conditions produced 1-[(*E*)-1,2-di(*tert*-butyl)-2-(trimethylsiloxy)ethenyloxy]-2,3-bis(trimethylsilyl)-1-[tris(trimethylsilyl)silyl]-1-silacycloprop-2-ene (**4b**) in 62% yield. Although mass spectrometric analysis of the reaction mixture indicated the presence of the molecular ion at *m*/*z* 518, corresponding to the calculated molecular weight for the isomer of **1b**, all attempts to isolate this product were unsuccessful. Both **4a** and **4b** are stable at room temperature and can be stored in atmospheric oxygen without decomposition.

The structures of **4a** and **4b** were confirmed by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section). The *E*-configuration for these compounds was verified by NOE-FID difference experiments at 300 MHz. For example, irradiation of a signal at 0.27 ppm attributed to the trimethylsiloxy protons on the terminal sp^2-hybridized carbon in **4b** led to enhancement of the signals at 1.35 and 1.38 ppm due to the two kinds of *tert*-butyl protons. This result clearly indicates that **4b** must have the *E*-configuration. The formation of **4a** and **4b** may be explained in terms of addition of the silylsilylene intermediates **Da**,**b** into a triple bond in bis(trimethylsilyl)acetylene, in analogy with those observed in the reactions of **1a** and **1b** with diphenylacetylene.

To learn more about thermal behavior of the 2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene derivatives, we investigated the thermolysis of **4a** in the absence of a trapping agent. Thus, when **4a** was heated in a sealed glass tube at 250 °C for 5 h, bis(trimethylsilyl)acetylene was obtained as the sole volatile product. No ring-opened product arising from a 1,2-trimethylsilyl shift from the sp^2-hybridized carbon to the ring silicon atom was detected, which is well-known in the thermolysis of the 2,3-bis(silyl)-1-silacycloprop-2-ene.[13] Presumably, the thermal decomposition of the 1-silacycloprop-2-enes bearing bulky substituents on the ring silicon atom, such as **4a**, proceeds to give the corresponding acetylenes and silylenes.[13a,14]

X-ray Crystallographic Analysis for 2a. Compound **2a** is the first silacyclopropene derivative with an alkoxy substituent on the ring silicon atom, whose structure is solved by a single-crystal X-ray diffraction study. Cell dimensions, data collections, refinement parameters, and selected bond lengths and angles for **2a** are summarized in Tables1 and 2. As can be seen in Figure 1, compound **2a** has a highly crowded silacyclopropene ring. Two phenyl groups are a little twisted with respect to the silacyclopropene ring, like the crystal structure of 2,3-diphenylsilacyclopropene reported previously.[14a] The Si−C (1.823(5) and 1.804(5) Å) and C═C (1.349(7) Å) bond lengths in the three-membered ring are typical of silacyclopropenes, indicating that the alkoxy substituent little affects the crystal structure[14a,15] This is in marked contrast to the structure of 1,1-diaminosilacyclopropene reported by Kira et al., in which elongation of the C═C bond (1.371(2) Å) is observed, presumably arising from the enhanced $\sigma^*-\pi$ interaction by the electronegative amino substituents on the ring silicon.[16] In the present case, the existence of a highly electron-donating tris(trimethylsilyl)silyl group may compensate the effect of the alkoxy substituent.

Table 1. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for Compound 2a

mol formula	$C_{48}H_{76}O_2Si_6$
mol wt	853.64
space group	$P2_1/a$ (#14)
cell dimens	
a, Å	18.2410(4)
b, Å	13.0428(3)
c, Å	21.3729(6)
β, deg	92.7966(8)
V, Å^3	5078.9(2)
Z	4
D_{cacld}, Mg/m^3	1.116
F_{000}	1856.00
cryst size, mm^3	0.40 × 0.20 × 0.20
cryst color	colorless
μ, cm^{-1}	1.99
radiation	Mo Kα (λ = 0.71069 Å)
temp, K	100
2*θ* max.	55.0
no. of unique reflns	11 596
no. of obsd reflns ($I \geq 3\sigma(I)$)	6457
reflns/param	10.74
corrections	Lorentz-polarization absorption
abs range	0.9007−1.0730
R	0.056
R_w[a]	0.073

[a] Weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 2a with Their esd's in Parentheses

Si1	Si2	2.323(2)	Si1	O1	1.652(4)
Si1	C1	1.823(5)	Si1	C2	1.804(5)
O1	C15	1.411(8)	O2	C16	1.410(9)
C1	C2	1.349(7)	C1	C3	1.463(7)
C2	C9	1.468(7)	C15	C16	1.32(1)
C15	C29	1.563(9)	C16	C39	1.58(1)

O1	Si1	Si2	110.2(1)	C1	Si1	Si2	119.9(2)
C2	Si1	Si2	124.8(2)	C2	Si1	C1	43.7(2)
C1	Si1	O1	123.8(2)	C2	Si1	O1	120.0(2)
Si1	O1	C15	127.6(4)	Si1	C1	C2	67.4(3)
Si1	C1	C3	154.8(4)	C3	C1	C2	136.5(4)
Si1	C2	C1	68.9(3)	Si1	C2	C9	154.0(4)
C1	C2	C9	137.0(4)	O1	C15	C16	117.0(7)
O1	C15	C29	119.4(5)	O2	C16	C15	116.6(7)
O2	C16	C39	115.9(6)				

An alternative explanation is based on the fact that the Si(ring)−O and Si(ring)−Si bonds are not exactly parallel to the C═C *π*-orbital, as indicated by an interplane angle of 83.982° between the silacyclopropene and O−Si(ring)−Si planes, although the twisting is small.

Theoretical Calculations. To clarify the mechanism for a series of isomerizations of **1a**,**b** leading to the [(*E*)-ethenyloxy]-

---

(13) (a) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147. (b) Kabe, Y.; Ohkubo, K.; Ishikawa, H.; Ando, W. *J. Am. Chem. Soc.* **2000**, *122*, 3775.

(14) (a) Ohshita, J.; Honda, N.; Nada, K.; Iida, T.; Mihara, T.; Matsuo, Y.; Kunai, A.; Naka, A.; Ishikawa, M. *Organometallics* **2003**, *22*, 2436. (b) Kunai, A.; Mihara, T.; Matsuo, Y.; Ohshita, J.; Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **1997**, *545−546*, 611.

(15) (a) Hirotsu, K.; Higuchi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726. (b) Hojo, F.; Sekigawa, S.; Nakayana, N.; Shimizu, T.; Ando, W. *Organometallics* **1993**, *12*, 803. (c) Kunai, A.; Matsuo, Y.; Ohshita, J.; Ishikawa, M.; Aso, Y.; Otsubo, T.; Ogura, F. *Organometallics* **1995**, *14*, 1204. (d) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3629.

(16) Tsutsui, S.; Sakamoto, K.; Kabuto, C.; Kira, M. *Organometallics* **1998**, *17*, 3819.

silylsilylene intermediates **Da**,**b** via the 1,2-disilacyclobut-1-ene derivatives **Ba**,**b**, we carried out density functional theory (DFT) calculations. The Becke-three-parameter−Lee-Yang-Parr hybrid functional[17] available in the Gaussian03 program package[18] was employed. Two types of models, the simplified models, in which all methyl groups in **1b** are replaced by the hydrogen atoms, and the real models bearing the same substituents as compound **1b** used in the experiments, are adopted. The 6-31G and 6-31G(d,p) basis sets were used for the simplified models. For the real models, the 6-31G (d,p) basis set was employed only for the silicon atom, and the 6-31G basis set for other atoms.

Calculations are carried out as follows: (1) The transition states (TSs) on the potential energy surface are characterized by using the simplified models with the 6-31G basis set; (2) the intrinsic reaction coordinate (IRC) analysis for each TS is evaluated for both sides. To save calculation time, the IRC analysis is restricted to the neighbor of the TS, and full optimization is carried out at the end point of the IRC. Thus, two local minima (LMs) are located in the reactant and product sides. The energies of all the LMs and TSs are evaluated again with the 6-31G(d,p) basis set optimization. The calculations for the simplified models with *E*- and *Z*-configurations indicate that both models afford almost the same energies. In such a case, the optimization is repeated by using the real models and the 6-31G/6-31G(d,p) mixed basis set.

The reaction path for the isomerization of the 1,2-diacyldisilane **1b** leading to the silylsilylene intermediate **Db** via the 1,2-disilacyclobut-1-ene derivative **Bb** was divided into three parts, i.e., from **1b** to **Bb** (path a), from **Bb** to **Cb** (path b), and from **Cb** to **Db** (path c). The simplified compounds of **1b** and **Bb** are named as LM-1 and LM-4.0, respectively, and two simplified compounds which are found between LM-1 and LM-4.0 are (*E*)-LM-2 and (*E*,*E*)-LM-3. Compounds (*E*)-LM-2 and (*E*,*E*)-LM-3 correspond to (*E*)-1-acetyldi(silyl)silyl-2-methyl-2-siloxy-1-silyl-1-silene and the simplified model of *s-cis*-**Ab** with *E*,*E*-configuration, respectively. Four LMs are separated by three TSs [(*E*)-TS-1, (*E*,*E*)-TS-2, and TS-3]. Thus, the reaction proceeds in the order of LM-1(**1b**), (*E*)-TS-1, (*E*)-LM-2, (*E*,*E*)-TS-2, (*E*,*E*)-LM-3(**Ab**), TS-3, and LM-4.0(**Bb**). The geometries of these compounds are shown in Figure 2. The TS structures were confirmed by a single negative eigenvalue of the energy second derivative and the leading components among the internal coordinates characterizing the reaction coordinate. (*E*)-TS-1 represents a 1,3-SiH_3 shift from the Si atom to the adjacent carbonyl oxygen in LM-1, and (*E*,*E*)-TS-2 shows a 1,3-silyl shift similar to the carbonyl oxygen in (*E*)-LM-2 thus formed. TS-3 indicates the conrotatory ring closure of (*E*,*E*)-LM-3, and thus LM-4.0 is formed.

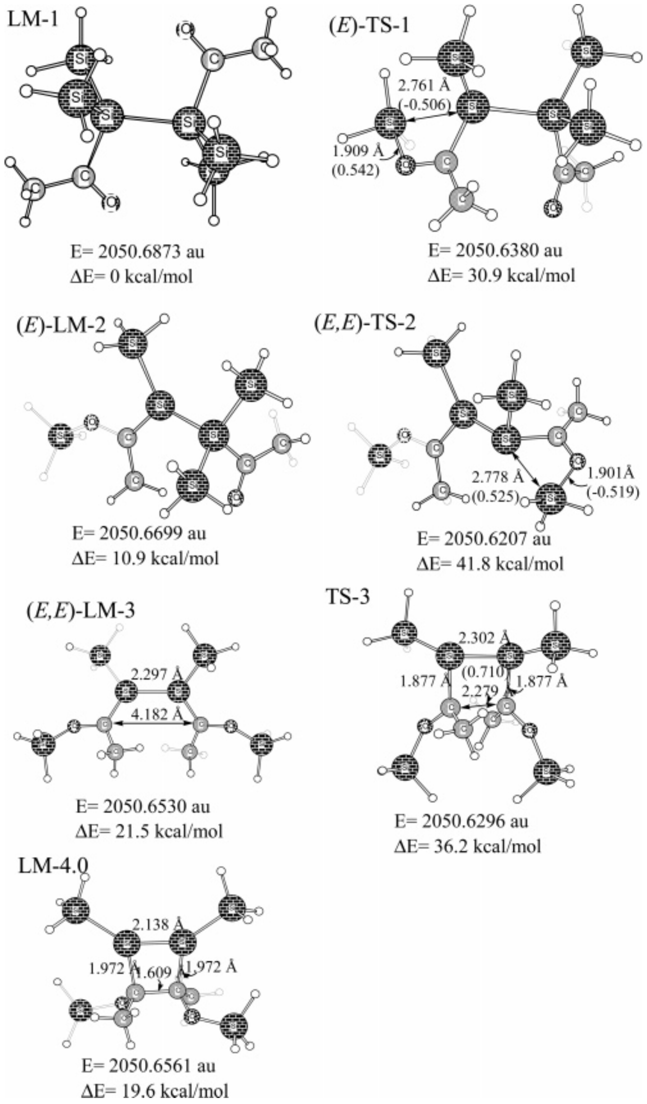


Figure 2. Optimized geometries of the simplified models, LM-1, (*E*)-TS-1, (*E*)-LM-2, and (*E*,*E*)-TS-2, (*E*,*E*)-LM-3, TS-3, and LM-4.0 at the level of the 6-31G(d,p) basis set. Total energy and the relative energy in which LM-1 is taken as the reference are shown. For TSs, the leading components among the internal coordinates characterizing the reaction coordinate are shown in parentheses together with bond lengths.

The energies of the *s-cis*- and *s-trans*-2,3-disila-1,3-butadienes with *E*,*E*-, *E*,*Z*-, and *Z*,*Z*-configurations were compared by using the simplified models at the level of the 6-31G(d,p) basis set. The energy differences between the most stable species and the most unstable one in these systems are calculated to be 1.0 and 1.3 kcal/mol, respectively. Furthermore, similar calculations for the real models having the *s-cis* structure with *E*,*E*-, *E*,*Z*-, and *Z*,*Z*-configurations indicate that the energy increases in the order of *Z*,*Z*-, *E*,*Z*-, and *E*,*E*-isomers, but the difference between *E*,*E*- and *Z*,*Z*-isomers is found to be only 1.3 kcal/mol. These results clearly indicate that the stabilization energy difference among the *E*,*E*-, *E*,*Z*-, and *Z*,*Z*-isomers is too small to control the product distribution. Therefore, we carried out calculations for the TS-1 structure, using the simplified models with the 6-31G(d,p) basis set and the real models with the 6-31G/6-31G(d,p) mixed basis set. In the former case, both (*E*)- and (*Z*)-TS-1 structures can be optimized, and the stabilization energy of (*Z*)-TS-1 is found to be slightly higher than (*E*)-TS-1 by 0.2 kcal/mol. In the real model, (*E*)-TS-1 can readily be

---

(17) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 319.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

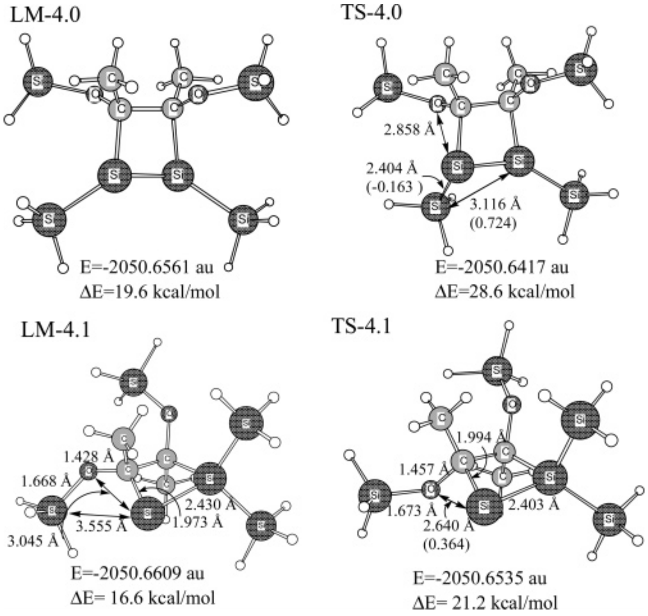


Figure 3. Optimized geometries of the simplified models, LM-4.0, TS-4.0, LM-4.1, and TS-4.1, at the level of the 6-31G(d,p) basis set. The geometry of LM-4.0 is the same as that shown in Figure 2.

obtained, but the corresponding (*Z*)-TS-1 cannot, although (*Z*)-TS-1 with the simplified structure is used as the initial geometry. The absence of (*Z*)-TS-1 in the real models may be ascribed to steric hindrance due to the presence of the bulky *t*-Bu and Me$_3$Si groups. Consequently, the formation of (*E*)-TS-1 as a single species seems to control the stereochemistry in the present reactions.

The latter half of the DFT calculations cover the reaction pathway from **Bb** to **Db**, which corresponds to path b and path c in this paper. Path b is divided into four steps as follows: (1) a 1,2-shift of a silyl group on the ring silicon in LM-4.0 (**Bb**) onto the adjacent ring silicon to give LM-4.1 via TS-4.0; (2) attack of the oxygen atom in the siloxy group on the ring carbon to the adjacent ring silicon in LM-4.1 (in this attack, however, the Si−C bond in the four-membered ring is still retained and the three-membered ring consisting of the oxygen, silicon, and carbon atoms is formed, leading to TS-4.1, and then LM-4.2); (3) migration of the silyl group on the oxygen in the three-membered ring onto the ring silicon atom in LM-4.2, leading to TS-4.2 and LM-4.3; and (4) elongation of the Si−C bond in the four-membered ring of LM-4.3 and skeletal rearrangement involving the cleavage of this bond and the Si−C bond in the three-membered ring to produce TS-4.3 and LM-5(**Cb**). The optimized geometries for LMs and TSs are shown in Figures3 and 4. Relative energies for all LMs and TSs are shown in Figure 6, where the energy of LM-1 is taken as the reference.

We have examined the alternative reaction sequence to the four-step reactions shown in path b. Thus, in the first step, an attack of the siloxy group on the ring carbon atom to the adjacent ring silicon in LM-4.0 occurs to produce the three-membered ring consisting of O, C, and Si atoms, and then, the silyl group on this ring silicon migrates to the adjacent ring silicon. The TS in the latter reaction was obtained by calculations with the 6-31G basis set. However, all attempts to optimize this TS structure using the 6-31G (d,p) basis set were unsuccessful. The opening of the three-membered ring always occurred to regenerate the starting LM-4.0. Thus, the results of calculations suggest that migration of both silyl and siloxy groups could occur at the beginning of the reaction in path b, but at first the migration of the silyl group on the ring silicon seems to be important in a series of reactions leading to the product LM-5(**Cb**).

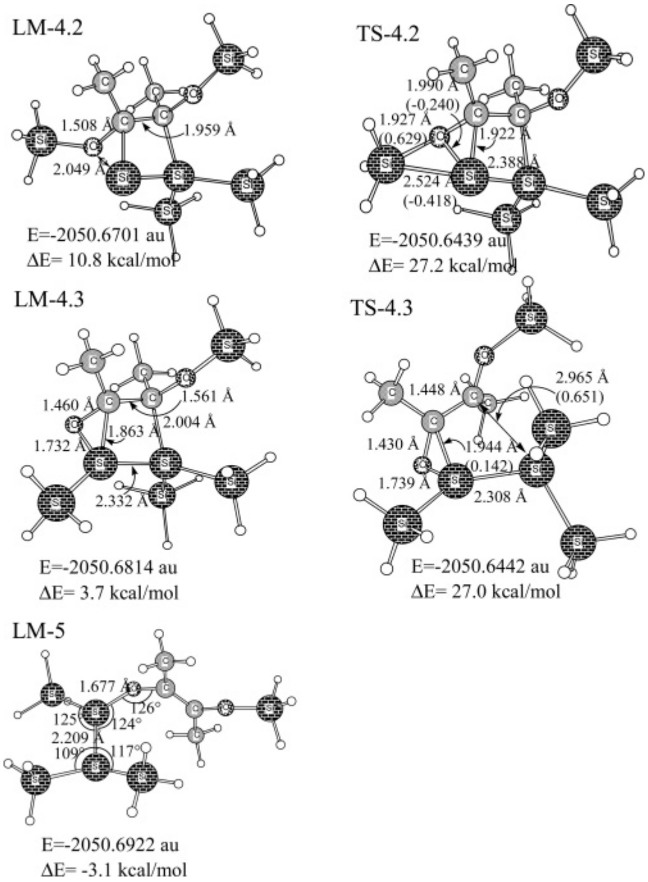


Figure 4. Optimized geometries of the simplified models, LM-4.2, TS-4.2, LM-4.3, TS-4.3, and LM-5, at the level of the 6-31G(d,p) basis set.

Finally, in path c, a 1,2-SiH$_3$ shift to the terminal sp^2-hybridized silicon in the disilene LM-5 leads to the formation of LM-6.0 slightly exothermically ($\Delta H = -1.6$ kcal/mol), through TS-5, as shown in Figures 5 and 6 for their energies. Silylsilylene LM-6.0 exhibits a rather congested geometry between one of the silyl groups and the ethenyloxy unit located closeby. Therefore, silylene LM-6.0 may further isomerize to more stable conformational isomers LM-6.1 and LM-6.2, although no TSs for the interconversion between these isomers are provided (the difference between LM-6.0 and LM-6.1 or LM-6.2 is due to the conformation, and the bonding topology is exactly the same). Calculations for the real model were also carried out to give the optimized geometries of **Cb** and **Db**, having frameworks similar to LM-5 and LM-6.1, respectively. The results of the real model calculations again suggest that silylsilylene **Db** is slightly more stable than disilene **Cb** by 1.7 kcal/mol. One might consider the possibility of silylene LM-7, which would be formed by a 1,2-shift of a silyl group on the terminal sp^2-hybridized silicon atom in LM-5 onto the internal sp^2-silicon atom. However, LM-7 is less stable than LM-6.0−LM-6.2 by 16−19 kcal/mol, indicating that this process is much less favorable even if it is present (Figure 5). In LM-6.0−LM-6.2, it seems reasonable to assume that the lone pair orbital of the adjacent oxygen interacts with the vacant 3p orbital of the silylene center, and this may stabilize the silylene species.

The relative stability between LM-1 and LM-5 (and also LM-6.0 to LM-6.2) seems to be strange. In the simplified models, LM-5 is more stable than LM-1 by 3.1 kcal/mol (Figure 6); however, in the real models for LM-1 and LM-5, the reverse

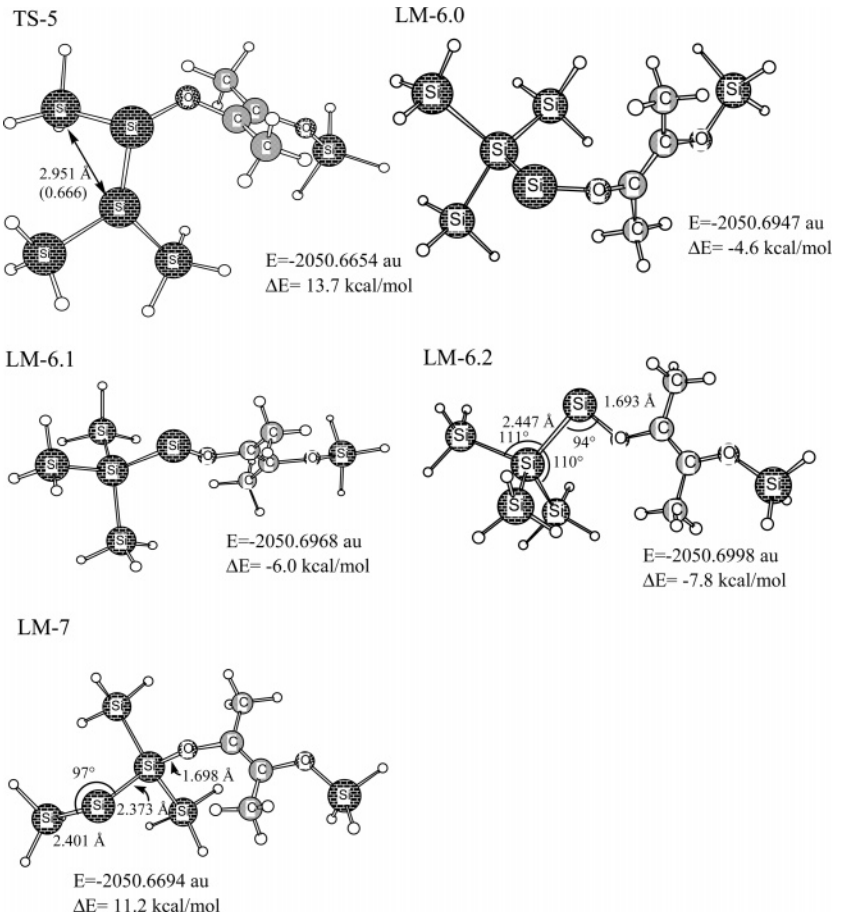


Figure 5. Optimized geometries of the simplified models, TS-5, LM-6.0, LM-6.1, LM-6.2, and LM-7, at the level of the 6-31G(d,p) basis set.

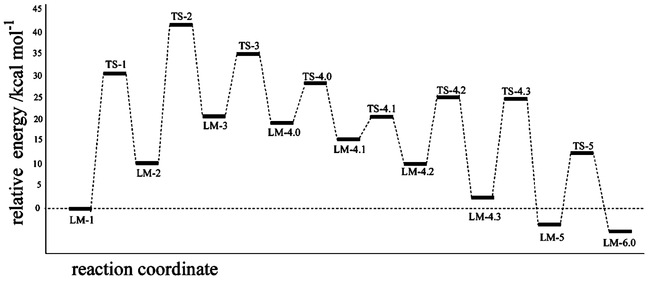


Figure 6. Energy change along the whole reaction path from LM-1 to LM-6.0. Labels (*E*) and (*E*,*E*) are omitted for clarity.

result is obtained. In fact, the total energies are calculated to be −2758.0433 au for the real model of LM-1 and −2758.0394 au for that of LM-5, respectively. Thus, in contrast with the simplified models, the real model for LM-1 is more stable than that of LM-5 by 2.4 kcal/mol. Presumably, the presence of the bulky *tert*-butyl and trimethylsilyl groups is responsible for this inversion. Consequently, the theoretical calculations successfully reproduce the complicated processes for a series of isomerizations of **1a**,**b** to the silylsilylene intermediates **Da**,**b**.

In conclusion, the cothermolysis of **1a** and **1b** with diphenylacetylene at 140 °C gave the respective 1-silacycloprop-2-enes **2a** and **2b**, arising from the reaction of the silylene intermediates with diphenylacetylene. In the former reaction, the isomer of the starting compound, the 1,2-disilacyclobut-3-ene derivative **3a**, was also obtained. Similar thermolysis of **1a** and **1b** with bis(trimethylsilyl)acetylene also afforded the respective 1-silacycloprop-2-enes **4a** and **4b**. The thermolysis of **4a** gave bis(trimethylsilyl)acetylene as the sole volatile product. The results of the theoretical calculations for the stereochemical formation of [(*E*)-ethenyloxy]silylsilylenes, using the simplified models of **1b** and also real models bearing the same substituents as **1b**, were consistent with experimental observations.

Experimental Section

General Procedures. All reactions were carried out in a degassed sealed tube (1.0 cm ϕ × 15 cm). Yields of the products were calculated on the basis of the isolated products. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Mass spectra were measured on a JEOL Model JMS-700 instrument. Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). 1,2-Bis(acyl)tetrakis(trimethylsilyl)disilanes **1a** and **1b** were prepared by the method reported previously.[7]

Thermolysis of 1a with Diphenylacetylene. A mixture of 113.3 mg (0.17 mmol) of **1a** and 105.4 mg (0.59 mmol) of diphenylacetylene in 0.5 mL of dry benzene was heated in a sealed glass tube at 140 °C for 24 h. The mixture was chromatographed on a silica gel column, with hexane as eluent, to give **2a** (61.4 mg, 43% yield) and **3a** (46.2 mg, 41% yield). The product **2a** was recrystallized from hexane. Anal. Calcd for $C_{48}H_{76}O_2Si_6$: C, 67.54; H, 8.97. Found: C, 67.20; H, 8.00. Mp 195.0−195.5 °C; MS *m/z* 852 (M^+); IR 2904, 1444, 1242, 1149, 1115, 1097, 1047, 985, 945, 920, 837, 692 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.13 (s, 9H, Me_3Si), 0.23 (s, 27H, Me_3Si), 1.61−1.88 (m, 30H, Ad), 7.22−7.36 (m, 10H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) 2.69, 2.80 (Me_3Si), 28.77, 29.05, 36.74, 36.77, 38.38, 39.18, 40.20, 40.29 (adamantyl carbons), 127.58, 128.02, 129.02 (two carbons) (phenyl ring carbons), 135.09, 143.48, 145.46 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −131.1, −88.0, −8.8, 12.6. For **3a**, all spectral data were identical with those of an authentic sample reported previously.[8]

Thermolysis of 1b with Diphenylacetylene. A mixture of 100.5 mg (0.19 mmol) of **1b** and 108.2 mg (0.61 mmol) of diphenylacetylene in 0.5 mL of benzene was heated in a sealed glass tube at 140 °C for 24 h. The resulting mixture was chromatographed on a silica gel column with hexane as eluent to give the product **2b** (70.7 mg, 52% yield). The product **2b** was recrystallized from hexane. Anal. Calcd for $C_{36}H_{64}O_2Si_6$: C, 62.00; H, 9.25. Found: C, 62.00; H, 9.00. Mp 123.0−123.5 °C; MS *m*/*z* 696 (M^+); IR 2954, 1479, 1360, 1255, 1159, 1136, 939, 837, 760, 690 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.05 (s, $9H_i$ Me_3Si), 0.22 (s, 27H, Me_3Si), 1.11 (s, 9H, t-Bu), 1.15 (s, 9H, t-Bu), 7.21−7.31 (m, 8H, phenyl ring protons), 7.52−7.54 (m, 2H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) 2.25, 2.72 (Me_3Si), 29.53 (Me_3C), 30.76 (Me_3C), 35.92 (CMe_3), 37.06 (CMe_3), 127.46, 128.08, 128.67, 135.28 (phenyl ring carbons), 142.79, 144.61, 163.99 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −131.0, −87.4, −8.9, 12.7.

Thermolysis of 1a with Bis(trimethylsilyl)acetylene. A mixture of 90.9 mg (0.13 mmol) of **1a** and 105.8 mg (0.62 mmol) of bis(trimethylsilyl)acetylene in 1.0 mL of benzene was heated in a sealed tube at 140 °C for 24 h. The reaction mixture was chromatographed on a silica gel column with hexane as eluent, to give **4a** (64.1 mg, 54% yield) and **3a** (21.7 mg, 23% yield). The product **4a** was recrystallized from hexane. Anal. Calcd for $C_{42}H_{84}O_2Si_8$: C, 59.64; H, 10.01. Found: C, 59.42; H, 9.84. Mp 173.0−174 °C; MS *m*/*z* 844 (M^+); IR 2952, 2904, 2850, 1452, 1299, 1243, 1186, 1153, 1114, 1103, 978, 917, 836, 752 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.235 (s, 9H, Me_3Si), 0.237 (s, 27H, Me_3Si), 0.27 (s, 9H, Me_3Si), 0.28 (s, 9H, Me_3Si), 1.61−2.05 (m, 30H, Ad); ^{13}C NMR δ ($CDCl_3$) 1.56, 2.95, 3.02 (Me_3Si), 28.79, 28.99, 36.74, 36.77, 38.63, 39.36, 40.27, 40.48 (adamantyl carbons), 143.93, 145.22, 200.99, 204.43 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −128.0, −99.4, −13.2, −13.0, −9.0, 12.0. For **3a**, all spectral data were identical with those of an authentic sample reported previously.[8]

Thermolysis of 1b with Bis(trimethylsilyl)acetylene. A mixture of 104.7 mg (0.20 mmol) of **1b** and 121.3 mg (0.71 mmol) of bis(trimethylsilyl)acetylene in 1.0 mL of benzene was heated in a sealed tube at 140 °C for 24 h. The reaction mixture was chromatographed on a silica gel column with hexane as eluent, to give **4b** (85.8 mg, 62% yield). The product **4b** was recrystallized from hexane. Anal. Calcd for $C_{30}H_{72}O_2Si_8$: C, 52.25; H, 10.52. Found: C, 51.90; H, 10.54. Mp 114.0−115.0 °C; MS *m*/*z* 688 (M^+); IR 2983, 2910, 1429, 1292, 1191, 1112, 1105, 973, 842, 674 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.27 (s, 9H, Me_3Si), 0.37 (s, 27H, Me_3Si), 0.43 (s, 18H, Me_3Si), 1.35 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu); ^{13}C NMR δ ($CDCl_3$) 1.55, 2.77, 3.24 (Me_3Si), 30.12, 31.63 (Me_3C), 36.10, 37.33 (CMe_3), 143.05, 144.60, 202.67 (2C) (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −128.4, −99.6, −13.0, −9.0, 11.3.

Thermolysis of 4a at 250 °C. Compound **4a** (105.0 mg, 0.124 mmol) was heated in a sealed tube at 250 °C for 5 h. The reaction mixture was analyzed by GC-MS and NMR spectrum as being bis(trimethylsilyl)acetylene, along with nonvolatile products.

X-ray Crystallographic Analysis of 2a. Data collection was performed on a Rigaku RAXIS-RAPID imaging plate system. The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure crystallographic software package.[21,22] A disorder model was applied for the olefin unit of the alkoxy substituent on the ring silicon, by locating two sets of olefin carbons with occupancies of 0.79 and 0.21, respectively.

Acknowledgment. This work was supported by a Grant-in Aid for Scientific Research (Nos. 14750687 and 15550038) from the Ministry of Education, Science, Sports, and Culture of Japan, to which our thanks are due. We thank Sumitomo Chemical Co., Ltd. and Hokko Chemical Industry Co., Ltd. for financial support.

Supporting Information Available: A full ORTEP drawing of compound **2a** and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060458V

---

(19) Sheldrick, G. M. *SHELX97*; 1997.

(20) Beurskens, P. T.; Admiraal, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1999.

(21) *Crystal Structure 3.10*: Crystal Structure Analysis Package; Rigaku and Rigaku/MSC, 2000−2002.

(22) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, UK, 1996.