Silicon−Carbon Unsaturated Compounds. 74. Thermal Behavior of 1-Silacyclobut-3-enes Generated from the Reaction of Acylpolysilanes with *tert*-Butylacetylene

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The thermolysis of 2-adamantyl-3-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2a**), obtained by the reaction of adamantoyltris(trimethylsilyl)silane with *tert*-butylacetylene, at 250 °C for 5 h gave two regioisomers, *trans*-4-adamantyl-2-*tert*-butyl- and *trans*-2-adamantyl-4-*tert*-butyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3a** and **4a**) in a ratio of 1.5:1, in 93% combined yield. The structure of **4a** was confirmed by X-ray crystallographic analysis. Similar thermolysis of 2,3-di-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2b**), formed by the reaction of pivaloyltris(trimethylsilyl)silane with *tert*-butylacetylene, however, afforded a single isomer, *trans*-2,4-di-*tert*-butyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3b**), in 93% yield. When **2a** was heated in a sealed tube at 190 °C for 5 h, 1-adamantyl-2-(*tert*-butyl)-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]cycloprop-1-ene (**5a**), which cleanly isomerized at 250 °C to give a mixture of **3a** and **4a**, was obtained in quantitative yield. Similarly, the thermolysis of **2b** at 190 °C for 5 h afforded 1,2-di-*tert*-butyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]cycloprop-1-ene (**5b**) in 90% yield, as the sole product. Treatment of **2a** with methanol in a sealed glass tube at 160 °C gave an alkene derivative (**7a**) with an *E* configuration, arising from addition of methanol to a silicon−carbon double bond in the 1-sila-1,3-butadiene generated from the ring opening of **2a**, in 84% yield. Similar treatment of **2b** with methanol afforded (*E*)-1,2-di-*tert*-butyl-2-[(methoxybis(trimethylsilyl)silyl)methyl]-1-(trimethylsiloxy)ethene (**7b**) in 83% yield. The co−thermolysis of **2a**,**b** with 2,3-dimethylbutadiene at 180 °C produced the respective silacyclohexene derivatives (**8a**,**b**), arising from [2 + 4] cycloaddition of the 1-sila-1,3-butadienes with the butadiene.

Introduction

It is well-known that acylpolysilanes are useful precursors for the synthesis of silenes. The photochemical reactions of the acylpolysilanes reported by Brook and co-workers afford various types of silenes, including rather stable ones.[1] The thermolysis and Peterson-type reactions of the acylpolysilanes also offer a convenient route to the synthesis of silenes.[2–8] Silenes are powerful reagents for synthesizing many types of silicon-containing compounds, and many papers concerning reactions of silenes with various substrates have been reported to date.[1–11] Recently, some silenes have also been used as silicon-based reagents for organic synthesis.[12]

The cycloaddition of alkynes to silenes proceeds cleanly and regiospecifically to give 1-silacyclobutenes in high yields. A study of the mechanism of formation and the ring-opening reactions of these compounds has become of interest in recent years. To verify the mechanism for these reactions, experimental and theoretical treatments have been extensively carried out. As a consequence, unambiguous evidence for the formation of the intermediates during addition of the silenes to alkynes and

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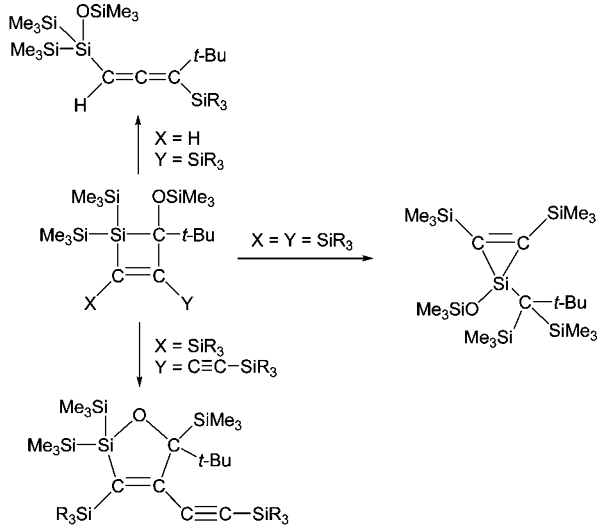
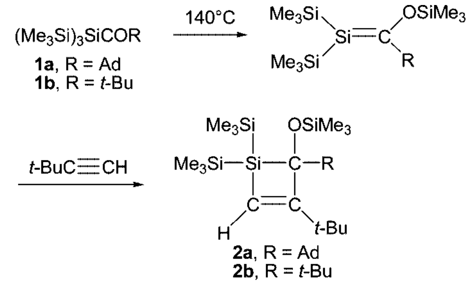
isomerization of the resulting 1-silacyclobutenes has been provided.[3g,11a,13,14]

In 1994, we demonstrated that the thermolysis of acylpolysilanes proceeds to give silenes, and the silenes thus formed react with alkenes, dienes, and carbonyl compounds, to give the respective adducts in high yields.[3] We have also found that the cothermolysis of adamantoyl- and pivaloyltris(trimethylsilyl)silane with silyl-substituted acetylenes at 140 °C affords the 1-silacyclobut-3-ene derivatives, arising from formal [2 + 2] cycloaddition of the silenes to the silyl-substituted acetylenes.[3d,e] When the 1-silacyclobut-3-ene derivatives thus obtained are heated in a sealed glass tube at 160 °C, the ring-opened products 1-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-3-(silyl)propadienes are formed as the sole species.[3e] The thermolysis of 1-silacyclobut-3-enes generated from the reaction of adamantoyl- and pivaloyltris(trimethylsilyl)silane with bis(silyl)butadiynes, however, gives dihydrosilole derivatives.[3h] However, similar thermolysis of acylpolysilanes with bis(silyl)acetylenes affords the 2,3-bis(silyl)-1-(trimethylsiloxy)-1-silacyclopropene derivatives, probably via the formal [2 + 2] cycloadducts, 1-silacyclobut-3-ene intermediates.[3f]



The thermal behavior of the 1-silacyclobut-3-ene derivatives seems to be highly dependent upon the nature of the substituents on the sp^2-hybridized carbon atoms in the 1-silacyclobutenyl ring.[3e–h,14] It is of interest to us to investigate the thermal behavior of 1-silacyclobut-3-ene derivatives that have no silyl substituents on the sp^2-hybridized carbon atoms in the silacyclobutenyl ring. In a preliminary communication, we reported that the thermolysis of 2,3-di-*tert*-butyl-2- (trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene at 250 °C proceeds stereospecifically to give *trans*-2,4-di-*tert*-butyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene as the sole product.[3g] In this paper we report the thermal properties of the 1-silacyclobut-3-ene derivatives, prepared by the cothermolysis of adamantoyl- and pivaloyltris(trimethylsilyl)silane, with *tert*-butylacetylene in detail.

Scheme 1



Results and Discussion

Synthesis of 1-Silacyclobut-3-enes. The reaction of adamantoyltris(trimethylsilyl)silane (**1a**) with *tert*-butylacetylene in a sealed glass tube at 140 °C for 24 h proceeded to give a formal [2 + 2] cycloadduct, 2-adamantyl-3-(*tert*-butyl)-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2a**), in 95% yield,[3i] as shown in Scheme 1. In this reaction, no other isomers such as a regioisomer were detected by either spectrometric analysis or GLC analysis. Similar thermolysis of pivaloyltris(trimethylsilyl)silane (**1b**) with *tert*-butylacetylene again gave a 1:1 adduct, 2,3-di-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2b**), as the sole product in 94% yield, as reported previously.[3g]

The structures of **2a**,**b** were verified by spectrometric analysis, as well as by elemental analysis (see Experimental Section). To confirm the location of the substituents on the silacyclobutenyl ring for **2a**, we carried out NOE-FID difference experiments at 300 MHz. Thus, irradiation of the hydrogen atom on the sp^2-hybridized carbon in the silacyclobutenyl ring at δ 6.19 ppm led to a strong enhancement of the signal at 1.17 ppm, due to the *tert*-butyl protons on the sp^2-hybridized carbon in the ring, as well as the signals at 0.19 and 0.23 ppm, attributed to the two kinds of trimethylsilyl protons on the ring silicon atom. Furthermore, saturation of the *tert*-butyl protons on the sp^2-hybridized ring carbon at 1.17 ppm resulted in enhancement of the signals at 0.19 and 6.19 ppm, attributable to the trimethylsiloxy protons and olefinic proton, in addition to the adamantyl protons at 1.84−1.88 ppm. These results clearly indicate that the hydrogen on the olefinic carbon is located on the carbon atom at the 4-position in the 1-silacyclobutenyl ring.

Thermolysis of 2a,b. We initially thought that the thermolysis of **2a**,**b** might proceed to give the 1-silacyclo-1,3-butadiene derivatives with extrusion of hexamethyldisiloxane from the starting compounds and investigated their thermal reactions. The thermolysis of **2a** in a sealed tube at 250 °C for 5 h, however, afforded two regioisomers, *trans*-4-adamantyl-2-*tert*-butyl- and *trans*-2-adamantyl-4-*tert*-butyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3a** and **4a**), in 93% combined

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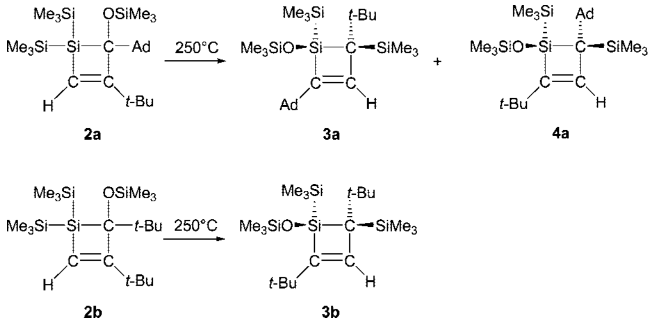
Scheme 2



yield (Scheme 2). The ratio of **3a** and **4a** was calculated to be 1.5:1 by ^{1}H NMR spectrometric analysis. Pure **3a** was separated from **4a** by recycling preparative HPLC. Neither product originated from elimination of hexamethyldisiloxane from the starting compound **2a** nor were stereoisomers of **3a** and **4a** detected in the reaction mixture by spectrometric analysis.

The structures of the products **3a** and **4a** were verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis. The ^{1}H$-$^{29}Si COSY NMR spectrum for **3a** reveals that the trimethylsilyl protons on the ring carbon atom at 0.10 ppm couple with the silicon atom at 1.2 ppm, while the trimethylsiloxy protons at 0.15 ppm couple with the silicon atom at 5.9 ppm. Similarly, the trimethylsilyl protons on the ring silicon atom at 0.23 ppm couple with the signals at -27.9 and -20.0 ppm. The location of the substituents on the 1-silacyclobutenyl ring for **3a** was confirmed by NOE-FID difference experiments at 300 MHz. Thus, irradiation of the trimethylsilyl protons at 0.10 ppm on the sp^3-hybridized carbon atom in the four-membered ring resulted in a strong enhancement of the signals at 0.15 and 1.01 ppm, due to the trimethylsiloxy protons on the ring silicon and *tert*-butyl protons on the sp^3-hybridized ring carbon, as well as the olefinic proton at 6.43 ppm. Similar irradiation of the trimethylsilyl protons on the ring silicon atom at 0.23 ppm showed enhancement of the signals at 0.15, 1.01, and 1.67 ppm, due to the trimethylsiloxy protons, *tert*-butyl protons, and adamantyl protons, respectively. Furthermore, saturation of the olefinic proton at 6.43 ppm led to enhancement of the signals at 0.10 and 1.01 ppm, attributed to the trimethylsilyl protons and *tert*-butyl protons on the same ring carbon, in addition to the adamantyl protons at 1.67 ppm. These results are wholly consistent with the structure proposed for **3a**.

The structure for **4a** was confirmed by X-ray crystallographic analysis, as well as by spectrometric analysis. An ORTEP representation of the molecular structure for **4a** is shown in Figure 1.

In contrast to the case for **2a**, the thermolysis of **2b** under the same conditions proceeded with stereospecificity, to give a single isomer, *trans*-2,4-di-*tert*-butyl-1-(trimethysiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3b**), in quantitative yield. Again, the structure of **3b** was verified by spectrometric analysis, as well as by elemental analysis. The configuration of the product **3b** was confirmed by NOE-FID difference experiments at 300 MHz, as reported previously.[3g]

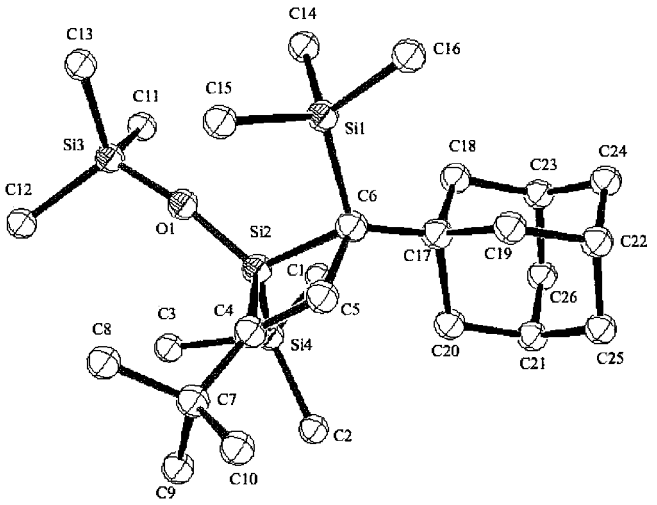
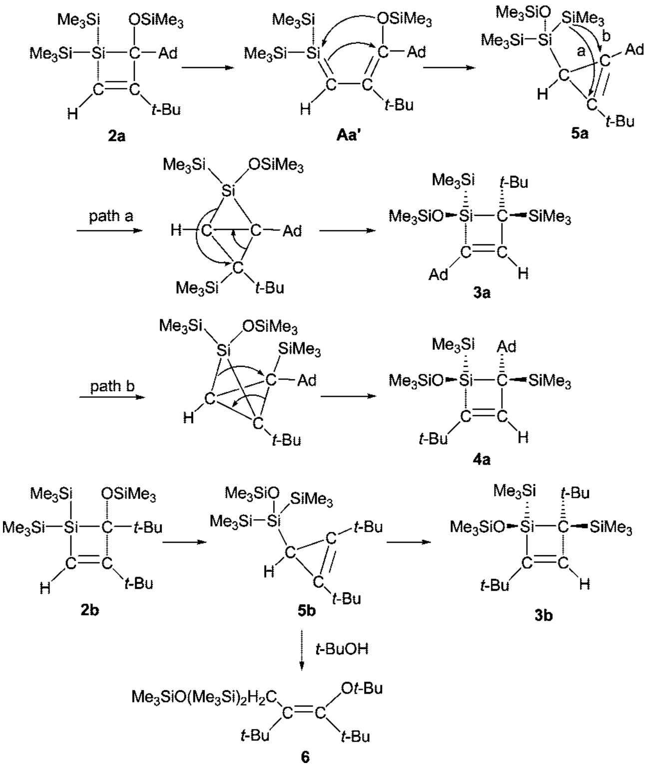


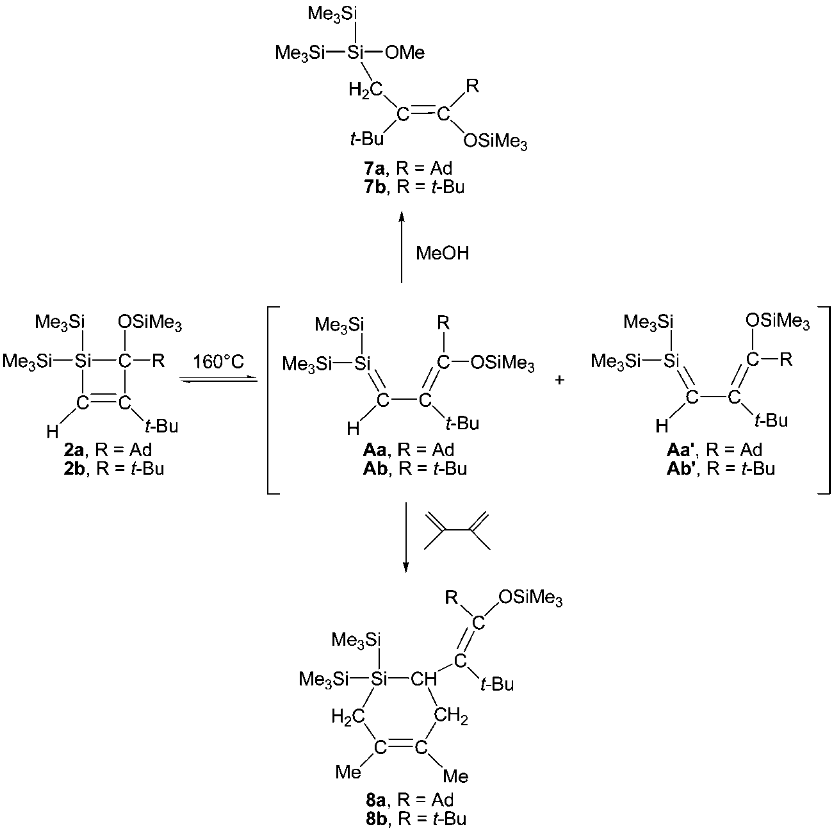
Figure 1. ORTEP drawing of compound **4a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 3



When compound **2a** was heated in a sealed glass tube in the absence of a trapping agent at 190 °C for 5 h, a silylcyclopropene derivative, 1-adamantyl-2-*tert*-butyl-3-[(trimethylsiloxy)-bis(trimethylsilyl)silyl]cycloprop-1-ene (**5a**), was produced in quantitative yield. The result indicates that the isomerization of **2a** to the products **3a** and **4a** proceeds through the silyl-substituted cyclopropene **5a**. In fact, when the silylcyclopropene **5a** thus formed was heated at 250 °C for 24 h, two products, **3a** and **4a**, were obtained in almost quantitative yield. The isomerization of **5a** leading to the two products **3a** and **4a** can be best understood in terms of a 1,3-trimethylsilyl shift from the silicon atom on the sp^3-hybridized carbon to one of the two sp^2-hybridized carbon atoms in the cyclopropenyl ring. The 1,3-trimethylsilyl shift to the *tert*-butyl-substituted carbon atom in the cyclopropenyl ring produces **3a**, probably via the silabicyclobutane intermediate[3g,k] (path a), as shown in Scheme 3, while the 1,3-silyl shift to the adamantly substituted carbon affords **4a** (path b). As can be expected, the thermolysis of **2b** at 190 °C for 5 h quantitatively afforded 1,2-di-*tert*-butyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]cycloprop-1-ene (**5b**), analogous to **5a**, and the **5b** thus formed underwent further isomerization, via the silabicyclobutane intermediate at 250 °C, to give the

Scheme 4



product **3b** as the sole isomerization product, in agreement with results reported previously.[3g]

The silyl-substituted cyclopropene derivatives **5a**,**b** are unstable in air. On exposure to atmospheric oxygen at room temperature, **5a**,**b** decompose immediately to give nonvolatile substances. However, they are stable under an inert atmosphere and can be stored without decomposition. The structures of **5a**,**b** were confirmed by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis. Furthermore, as reported previously,[3g] the fact that the thermolysis of **2b** with *tert*-butyl alcohol in a sealed tube at 210 °C gives (*Z*)-1-*tert*-butoxy-1,2-di-*tert*-butyl-2-[(trimethylsiloxy)bis(trimethylsilyl)silylmethyl]ethene (**6**) in 35% yield, in addition to a 44% yield of **3b**, is wholly consistent with the structure proposed for **5b**.

In order to get more information about the reactive intermediates, which might be involved in a series of isomerizations of the 1-silacyclobutenes **2a**,**b**, leading to the products **3a** and **4a** and to **3b**, we carried out the thermolysis of **2a** in the presence of methanol, which is more reactive than *tert*-butyl alcohol, at much lower temperature. Thus, when **2a** was heated with methanol in a sealed glass tube at 160 °C for 24 h, (*E*)-1-adamantyl-2-*tert*-butyl-2-[(methoxy)bis(trimethylsilyl)silyl]methyl-1-(trimethylsiloxy)ethene (**7a**) was obtained in 84% yield, as shown in Scheme 4. No other regio- and stereoisomers were detected in the reaction mixture. The structure of **7a** was verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section). Its *E* configuration was readily confirmed by NOE-FID difference experiments at 500 MHz. Thus, saturation of the trimethylsiloxy protons on the terminal olefinic carbon atom at 0.19 ppm led to a strong enhancement of the signals at 1.04 and 1.85 ppm, due to the *tert*-butyl protons and adamantyl protons. Irradiation of the *tert*-butyl protons at 1.04 ppm resulted in enhancement of the signals at 0.10, 0.19, and 2.08 ppm, attributable to the trimethylsilyl protons, trimethylsiloxy protons, and methylene protons, as well as the methoxy protons at 3.36 ppm. These results are wholly consistent with the structure proposed for **7a**.

The reaction of **2b** with methanol at 160 °C for 24 h proceeded to give a product similar to **7a**, (*E*)-1,2-di-*tert*-butyl-2-[(methoxy)bis(trimethylsilyl)silyl]methyl-1-(trimethylsiloxy)ethene (**7b**), in 83% yield. Again, no other isomers were detected in the reaction mixture. The ^{1}H, ^{13}C, and ^{29}Si NMR spectrum for **7b** revealed patterns very similar to those of **7a**. The *E* configuration of **7b** was also confirmed by NOE-FID difference experiments at 500 MHz.

The formation of **7a**,**b** may be best understood by the reaction of the 1-sila-1,3-butadienes, generated from the ring-opening reaction of the 1-silacyclobutenes **2a**,**b**, with methanol. Theoretical calculations on the ring opening of the 1-silacyclobutenes reported to date indicate that the reaction proceeds in a conrotatory fashion, leading to two stereoisomers of 1-sila-1,3-butadienes, for example, **Aa** and **Aa′** in the ring opening of **2a**, as shown in Scheme 4, and the formation of **Aa** is a dominant process.[3h,13,14] The fact that the thermolysis of **2a**,**b** with methanol gives the adducts **7a**,**b**, respectively, arising from addition of methanol to a silicon−carbon double bond in **Aa** and **Ab**, but not **Aa′** and **Ab′**, is in good agreement with the results of the theoretical treatments.

The formation of the silyl-substituted cyclopropene derivatives **5a,b** may be understood in terms of a 1,4-trimethylsiloxy shift in the 1-sila-1,3-butadiens **Aa′** and **Ab′**, but not in **Aa** and **Ab**, because of the favorable orientation of the siloxy group in **Aa′** and **Ab′**. The isomerization of **Aa′** and **Ab′**, leading to **5a,b**, presumably proceeds in a concerted manner as follows. At an initial step, a lone pair of electrons on the oxygen in the trimethylsiloxy group of the 1-sila-1,3-butadienes would attack the sp^{2} silicon atom of the silene moiety, and then skeletal rearrangement takes place to give **5a**,**b**. On the basis of the theoretical calculations, a direct pathway to **5a**,**b** from the starting 1-silacyclobutenes, which involves a 1,2-trimethylsiloxy shift in **2a**,**b**, is also possible.[13,14]

To learn more about the formation of (*E*)-1-sila-1,3-butadienes **Aa** and **Ab**, we have examined the thermal reactions of **2a**,**b** with 2,3-dimethylbutadiene. Thus, the cothermolysis of **2a** with 2,3-dimethylbutadiene at 180 °C for 24 h gave 2-[(*E*)-2-adamantyl-1-(*tert*-butyl)-2-(trimethylsiloxy)ethenyl]-4,5-dimethyl-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene (**8a**), arising from formal [2 + 4] cycloaddition of a silicon−carbon double bond in the intermediate **Aa** with the butadiene, in 65% yield. Similar thermolysis of **2b** with 2,3-dimethylbutadiene under the same conditions again afforded a formal [2 + 4] cycloadduct with an *E* configuration, 2-[(*E*)-1,2-di-*tert*-butyl-2-(trimethylsiloxy)-ethenyl]-4,5-dimethyl-1,1-bis(trimethylsilyl)-1-silacyclohexene (**8b**), in 72% yield. No other isomers were detected in both thermolyses by spectrometric analysis.

The structures of **8a**,**b** were verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, and their *E* configurations were confirmed by NOE-FID difference experiments at 500 MHz. For example, in the NOE-FID difference experiments for **8a**, saturation of the trimethylsilyl protons at 0.30 ppm caused a positive NOE of the *tert*-butyl protons at 1.21 ppm and adamantyl protons at 1.74−1.80 ppm. Irradiation of the *tert*-butyl protons at 1.12 ppm led to enhancement of the trimethylsilyl protons and trimethylsiloxy protons at 0.10 and 0.30 ppm, as well as the ring protons at 2.61 and 3.09 ppm.

The results of the trapping experiments indicate that the 1-sila-1,3-butadiene intermediates **Aa** and **Ab** and also **Aa′** and **Ab′** are produced at the initial step of the thermolysis of **2a**,**b**. In the presence of methanol and 2,3-dimethylbutadiene, **Aa** and **Ab** react with the trapping agent to give adducts, such as **7a**,**b** and **8a**,**b**. In the absence of the trapping agent, 1-sila-1,3-butadienes **Aa′** and **Ab′** undergo isomerization to produce the silylcyclopropene derivatives **5a**,**b**.[13,14]

Recently, it has been reported that the reactions of various silenes with 1,3-butadienes afford many kinds of silacyclohexene derivatives, arising from [2 + 4] cycloaddition, and the reactions can be employed to provide a novel method for the organic synthesis.[12]

In conclusion, the thermolysis of **2a** at 250 °C gave two regioisomers of the rearranged silacyclobutenes **3a** and **4a**, while the thermolysis of **2b** afforded **3b** as the sole product. The thermolysis of **2a**,**b** with methanol at 160 °C proceeded with high stereospecificity to give the respective adducts **7a**,**b**, arising from addition of methanol to a silicon−carbon double bond in the 1-sila-1,3-butadienes **Aa** and **Ab**. With 2,3-dimethylbutadiene, **Aa** and **Ab** reacted to give the 1-silacyclohexene derivatives, derived from [2 + 4] cycloaddition of the butadiene to a silicon−carbon double bond in **Aa** and **Ab**. When **2a**,**b** were heated in the absence of a trapping agent at 190 °C, the silyl-substituted cyclopropenes **5a**,**b**, probably via isomerization of **Aa′** and **Ab′**, were obtained. Heating the product **5a** at 250 °C resulted in clean isomerization to produce **3a** and **4a**, while **5b** afforded **3b**, quantitatively.

Experimental Section

General Procedures. Thermal reactions were carried out in a degassed sealed tube (1.0 cm i.d. × 15 cm). Yields of the products were calculated on the basis of the isolated products. NMR spectra were recorded on a JNM-LA 300 spectrometer and JNM-500 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). Gel permeation chromatographic separation was carried out with the use of a Model LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.).

Materials. Acylpolysilanes **1a**,**b** were prepared according to the method reported by Brook et al.[2] For **2a**, the preparation and analytical data are described in a previous paper.[3i] Benzene used as a solvent was dried over sodium metal under a nitrogen atmosphere and distilled just before use.

Synthesis of 1-Silacyclobut-3-ene 2b. A mixture of 2.772 g (8.33 mmol) of pivaloyltris(trimethylsilyl)silane and 2.203 g (26.82 mmol) of *tert*-butylacetylene in 3 mL of benzene was heated in a sealed tube at 140 °C for 24 h. Benzene and the excess *tert*-butylacetylene were evaporated off in vacuo, and the residue was chromatographed on a silica gel column, with hexane as eluent, to give 3.250 g (94% yield) of **2b**. Anal. Calcd for $C_{20}H_{46}OSi_4$: C, 57.89; H, 11.17. Found: C, 57.70; H, 11.14. Mp: 69−70 °C. MS: *m*/*z* 414 (M^+). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 0.20 (s. 9H. Me_3Si), 1.12 (s, 9H, *t*-Bu), 1.15 (s, 9H, *t*-Bu), 6.19 (s, 1H, HC═C). ^{13}C NMR ($CDCl_3$): δ 1.07, 1.30, 3.11 (Me_3Si), 31.66 (Me_3C) (2C), 37.72 (CMe_3) (2C), 96.04 (CO), 129.05, 174.74 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −24.5, −18.3, −13.5, 4.9.

Thermolysis of 2a at 250 °C. A solution of 0.181 g (0.368 mmol) of **2a** in 0.5 mL of benzene in a sealed glass tube was heated at 250 °C for 5 h. After evaporation of the solvent benzene, a mixture of compounds **3a** and **4a** was obtained in a ratio of 1.5:1 in 93% yield. Pure **3a** and **4a** were isolated by preparative HPLC. Data for **3a** are as follows. Anal. Calcd for $C_{26}H_{52}OSi_4$: C, 63.34; H, 10.63. Found: C, 63.30; H, 10.70. Mp: 134−135 °C. MS: *m*/*z* 492 (M^+). ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 0.23 (s. 9H. Me_3Si), 1.01 (s, 9H, *t*-Bu), 1.67−1.97 (m, 15H, Ad), 6.43 (s, 1H, HC═C). ^{13}C NMR ($CDCl_3$): δ 0.38, 3.06, 3.74 (Me_3Si), 28.78 (Ad), 32.13 (Me_3C), 34.59 (CMe_3), 35.69 (Ad), 37.01 (Ad), 43.64 (Ad), 49.26 (CO), 138.73, 165.32 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −27.9, −20.0, 1.2, 5.9. Data for **4a** are as follows. Anal. Calcd for $C_{26}H_{52}OSi_4$: C, 63.34; H, 10.63. Found: C, 63.10; H, 10.59. Mp: 138−139 °C. MS: *m*/*z* 492 (M^+). ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 0.25 (s. 9H. Me_3Si), 1.08 (s, 9H, *t*-Bu), 1.67−1.97 (m, 15H, Ad), 6.52 (s, 1H, HC═C). ^{13}C NMR ($CDCl_3$): δ 0.49, 3.06, 3.97 (Me_3Si), 29.16 (Ad), 31.11 (Me_3C), 33.71 (CMe_3), 35.70 (Ad), 36.95 (Ad), 43.31(Ad), 51.07 (ring sp^3-C), 138.08, 165.48 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −28.6, −19.7, 0.7, 5.9.

Thermolysis of 2b at 250 °C. A solution of 1.170 g (2.82 mmol) of **2b** in 1.5 mL of benzene in a sealed glass tube was heated at 250 °C for 5 h. After evaporation of the solvent benzene, compound **3b** was obtained in 93% yield. Anal. Calcd for $C_{20}H_{46}OSi_4$: C, 57.89; H, 11.17. Found: C, 57.81; H, 11.21. Mp: 135−136 °C. MS: *m*/*z* 414 (M^+). ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H, Me_3Si), 0.15 (s, 9H, Me_3Si), 0.22 (s. 9H. Me_3Si), 1.02 (s, 9H, *t*-Bu), 1.08 (s, 9H, *t*-Bu), 6.45 (s, 1H, HC═C). ^{13}C NMR ($CDCl_3$): δ 0.30, 3.05, 3.72 (Me_3Si), 31.07, 32.13 (Me_3C), 33.64, 34.59 (CMe_3), 48.84 (ring sp^3-C), 139.33, 165.07 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −27.8, −20.0, −1.5, 6.1.

Thermolysis of 2a at 190 °C. A solution of 0.103 g (0.209 mmol) of **2a** in 0.6 mL of dry deuteriobenzene in a sealed glass tube was heated at 190 °C for 5 h. The resulting product was analyzed by NMR spectrometry as being **5a** (quantitative yield). Exact mass: *m*/*z* calcd for $C_{26}H_{52}OSi_4$ [M^+], 492.3095; found, 492.3076. MS: *m*/*z* 492 (M^+). ^{1}H NMR (C_6D_6): δ 0.31 (s, 9H, Me_3Si), 0.39 (s, 18H, Me_3Si), 1.04 (s, 1H, CH), 1.30 (s, 9H, *t*-Bu), 1.77−2.04 (s, 15H, Ad). ^{13}C NMR (C_6D_6): δ 0.34, 2.81 (Me_3Si), 11.40 (CH), 28.70 (Me_3C), 31.17 (CMe_3), 29.44, 33.40, 37.12, 41.86 (Ad), 116.43, 116.78 (olefinic carbons). ^{29}Si NMR (C_6D_6): δ −20.9, 1.4, 5.3.

Thermolysis of 5a at 250 °C. In an NMR tube, there were placed 0.10 g (0.21 mmol) of **2a** and 0.6 mL of dry deuteriobenzene. The tube was thoroughly degassed by freeze−pump−thaw cycles and heated at 190 °C for 5 h. The ^{1}H NMR spectrum for the reaction mixture indicated that **5a** was produced, quantitatively. The tube was again heated at 250 °C for 5 h, and the contents were analyzed by NMR spectrometry as being **3a** and **4a** in the ratio of 1.5:1. ^{1}H, ^{13}C, and ^{29}Si NMR spectral data for **3a** and **4a** were identical with those of the authentic samples.

Thermolysis of 2b at 190 °C. A solution of 0.102 g (0.246 mmol) of **2b** in 0.6 mL of dry deuteriobenzene in a sealed glass tube was heated at 190 °C for 5 h. The resulting product was analyzed by NMR spectrometry as being **5b** (90% yield) and the starting compound **2b** (10%). Data for **5b** are as follows. Exact mass: *m/z* calcd for $C_{20}H_{46}OSi_4[M^+]$, 414.2626; found, 414.2598. MS: *m/z* 414 (M^+). ^{1}H NMR (C_6D_6): δ 0.28 (s, 9H, Me_3Si), 0.36 (s, 18H, Me_3Si), 1.18 (s, 1H, CH), 1.27 (s, 18H, *t*-Bu). ^{13}C NMR (C_6D_6): δ 0.28, 2.75 (Me_3Si), 14.27 (CH), 29.38 (Me_3C), 31.16 (CMe_3), 116.73 (olefinic carbons). ^{29}Si NMR (C_6D_6): δ −20.8, 1.4, 5.4.

Thermolysis of 5b at 250 °C. In a NMR tube, there were placed 0.100 g (0.25 mmol) of **2b** and 0.6 mL of dry deuteriobenzene. The tube was thoroughly degassed by freeze−pump−thaw cycles and heated at 190 °C for 5 h. The ^{1}H NMR spectrum of the reaction mixture indicated that **5b** was produced, quantitatively. The tube was again heated at 250 °C for 5 h and analyzed by NMR spectrometry as being **3b**, which was produced in quantitative yield. ^{1}H, ^{13}C, and ^{29}Si NMR spectral data for **3b** were identical with those of the authentic sample.

Thermolysis of 2b with *tert*-Butyl Alcohol at 210 °C. A mixture of 0.100 g (0.24 mmol) of **2b** and 0.3875 g (5.23 mmol) of *tert*-butyl alcohol in a sealed glass tube was heated at 210 °C for 36 h. The excess *tert*-butyl alcohol was evaporated off in vacuo, and the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.044 g (44% yield) of **3b** and 0.041 g (35% yield) of (*Z*)-1-*tert*-butoxy-1,2-di-*tert*-butyl-2-[(trimethylsiloxy)-bis(trimethylsilyl)silylmethyl]ethane (**6**).[3g]

Thermolysis of 2a with Methanol. A mixture of 0.085 g (0.17 mmol) of **2a** and 0.010 g (0.31 mmol) of methanol was heated in a sealed glass tube at 160 °C for 24 h. Product **7a** (0.076 g, 84% yield) was isolated by using column chromatography. Anal. Calcd for $C_{27}H_{56}O_2Si_4$: C, 61.76; H, 10.75. Found: C, 61.49; H, 10.71. MS: *m/z* 524 (M^+);. IR: 2919, 2850, 1596, 1243, 1189, 1168, 1116, 1020, 875, 835 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 18H, Me_3Si), 0.19 (s, 9H, Me_3Si), 1.04 (s, 9H, *t*-Bu), 1.55−1.90 (m, 15H, Ad), 2.08 (s, 2H, CH_2), 3.36 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$): δ 0.52, 3.43 (Me_3Si), 18.85 (CH_2), 29.12, 30.67, 35.53, 36.88, 40.48, 41.25 (*t*-Bu and Ad), 53.54 (OMe), 124.50, 150.67 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −17.9, 8.5, 13.2.

Thermolysis of 2b with Methanol. A mixture of 0.123 g (0.30 mmol) of **2b** and 0.014 g (0.44 mmol) of methanol was heated in a sealed glass tube at 160 °C for 24 h. Product **7b** (0.110 g, 83% yield) was isolated by using column chromatography. Anal. Calcd for $C_{21}H_{50}O_2Si_4$: C, 56.43; H, 11.28. Found: C, 56.35; H, 11.26. MS: *m/z* 446 (M^+). IR: 2952, 2900, 2825, 1573, 1481, 1390, 1361, 1253, 1174, 1124, 1078, 910, 836 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 18H, Me_3Si), 0.18 (s, 9H, Me_3Si), 1.06 (s, 9H, *t*-Bu), 1.12 (s, 9H, *t*-Bu), 1.93 (s, 2H, CH_2), 3.34 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$): δ 0.58, 3.13 (Me_3Si), 18.57 (CH_2), 30.61, 31.60 (Me_3C), 35.26, 37.70 (C Me_3), 53.36 (OMe), 123.56, 150,50 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −17.8, 9.0, 13.2.

Thermolysis of 2a with 2,3-Dimethylbutadiene. A mixture of 0.109 g (0.22 mmol) of **2a** and 0.047 g (0.58 mmol) of 2,3-dimethylbutadiene was heated in a sealed glass tube at 180 °C for 24 h. Product **8a** (0.083 g, 65% yield) was isolated by using column chromatography. Anal. Calcd for $C_{32}H_{62}OSi_4$: C, 66.82; H, 10.86. Found: C, 66.66; H, 10.70. MS: *m/z* 574 (M^+). IR: 2956, 2915, 2850, 1452, 1365, 1251, 1066, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H, Me_3Si), 0.14 (s, 9H, Me_3Si), 0.30 (s, 9H, Me_3Si), 1.12 (d, 1H, CH, J = 16 Hz), 1.21 (s, 9H, *t*-Bu), 1.56 (s, 3H, Me), 1.75 (s, 3H, Me), 1.65−2.00 (m, 17H, Ad and CH_2), 2.61 (br t, 1H, CH, J = 15 Hz), 3.09 (dd, 1H, CH, J = 13 Hz, 4 Hz). ^{13}C NMR ($CDCl_3$): δ 0.90, 1.55, 3.45 (Me_3Si), 20.40 (CH_2), 21.10, 24.24 (Me), 27.31 (CH), 29.22, 31.99, 35.67, 36.90, 40.53, 42.06 (*t*-Bu and Ad), 45.94 (CH_2), 126.61, 128.33, 131.84, 153.25 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −41.0, −17.7, −12.8, 8.7.

Thermolysis of 2b with 2,3-Dimethylbutadiene. A mixture of 0.265 g (0.64 mmol) of **2b** and 0.087 g (1.06 mmol) of 2,3-dimethylbutadiene was heated in a sealed glass tube at 180 °C for 24 h. Product **8b** (0.229 g, 72% yield) was isolated by using chromatography. Anal. Calcd for $C_{26}H_{56}OSi_4$: C, 62.83; H, 11.36. Found: C, 62.66; H, 11.26. MS: *m/z* 496 (M^+). IR: 2956, 2906, 1554, 1481, 1392, 1336, 1253, 1132, 1066, 838 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 1.16 (d, 1H, CH, J = 17 Hz), 1.20 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu), 1.56 (s, 3H, Me), 1.75 (s, 3H, Me), 1.62 (d, 1H, CH, J = 17 Hz), 1.94 (br d, 1H, CH, J = 18 Hz), 2.60 (br t, 1H, CH, J = 15 Hz), 2.92 (dd, 1H, CH, J = 13 Hz, 4 Hz). ^{13}C NMR ($CDCl_3$): δ 0.93, 1.53, 3.28 (Me_3Si), 19.96 (CH_2), 21.10, 24.13 (Me), 27.23 (CH), 31.92, 32.16 (Me_3C), 35.56, 38.18 (CMe_3), 45.09 (CH), 126.55, 128.25, 130.59, 152.86 (olefinic carbons). ^{29}Si NMR ($CDCl_3$): δ −41.1, −17.3, −13.0, 8.8.

X-ray Crystallographic Analysis of 4a. Data collection was performed on a Riga RAXIS-RAPID imaging plate system. The structure was solved by direct methods[15] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically.[16] Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure crystallographic software package.[17,18]

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Supporting Information Available: A CIF file giving crystallographic data for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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