Aluminum Chloride Catalyzed Stereoselective [3 + 2] Cycloaddition of Allylsilanes with Simple Conjugated Dienes

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Allyltrimethylsilane reacts with simple conjugated dienes in the presence of aluminum chloride catalyst to give stereoselective [3 + 2] cycloadducts of *trans*-vinylcyclopentanes in 29−72% yields at −10 °C. The same reactions give 1,4-allylsilylated compounds as the major products at −50 °C, which cyclize to the annulation products as the reaction mixture is allowed to warm to −10 °C. The reaction using (2-methyl-2-propenyl)trimethylsilane instead of allyltrimethylsilane does not give the annulation due to an unfavorable 1,2-silyl shift but, rather, allylsilylation products. The results are consistent with an initial 1,4-allylsilylation of the conjugated diene, followed by the intramolecular cyclization of the 1,4-allylsilylated alkene to the stereoselective *trans*-[3 + 2] cycloadduct, via a 1,2-silyl shift.

Introduction

A Lewis-acid-promoted [3 + 2] cycloaddition reaction in which an allylsilane serves as the three-carbon unit is an attractive approach to five-membered ring systems, which are found in a variety of important natural products.[1] Since the [3 + 2] cycloaddition of an allylsilane with an α,β-enone catalyzed by titanium chloride was first reported by Knölker and co-workers in 1990,[2] several examples of this [3 + 2] annulation of allylsilanes with other conjugated carbonyl compounds have been reported.[3−13]

We recently reported a novel aluminum chloride catalyzed addition reaction of allyltrimethylsilane with simple unactivated alkenes,[14] alkynes,[15] and diallylsilanes[16] to give regio- and stereoselective allylsilylation products. Yamamoto and co-workers reinvestigated allylsilylations of alkynes in the presence of $AlCl_3$ or $EtAlCl_2$.[17] The allylsilylation proceeds at temperatures as low as −47 °C, and yields are higher in the presence of Lewis acid catalysts in combination with chlorotrimethylsilane as an activator.[18,19] In order to extend this allylsilylation reaction, we examined the addition of allylsilanes to the simple conjugated dienes. Although allylsilylation and Diels−Alder-type [4 + 2] cycloaddition are possible from the reaction of allylsilane with electron-rich conjugated dienes, an unusual stereoselective [3 + 2] cycloaddition was observed. To the best of our knowledge, the [3 + 2] cycloaddition reaction of an allylsilane with conjugated dienes having no carbonyl groups is not known. We wish to report the first example of novel stereoselective [3 + 2] cycloadditions of allyltrimethylsilanes with conjugated dienes catalyzed by aluminum chloride in combination with chlorotrimethylsilane and provide a plausible mechanism for the annulation.

Results and Discussion

[3 + 2] Cycloaddition of Allyltrimethylsilane 1a with Conjugated Dienes (2a−2e). The typical reaction with conjugated dienes was carried out by adding **2** to **1a** in order to reduce the production of polymeric materials due to easy self-polymerization of dienes.[20,21] The [3 + 2] cycloaddition of 2,3-dimethylbutadiene **2a**

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(1) (a) Ramaiah, M. *Synthesis* **1984**, 529. (b) Hudlicky, T.; Rulin, F.; Lovelace, T. C.; Reed J. W. In *Studies in Natural Products Chemistry*; Attauer-Raman, T., Ed.; Elsevier Science: Sussex, U.K, 1989; p 3. (c) Ho, T.-L. *Carbocyclic Constructions in Terpene Synthesis*; VCH: New York, 1988.

(2) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1990**, 429.

(3) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B.; Weinkauf, A. *Synlett* **1991**, 147.

(4) Danheiser, R.-L.; Dixon, B.-R.; Gleason, R.-W. *J. Org. Chem.* **1992**, *57*, 6094.

(5) Yamaguchi, M.; Sehata, M.; Hayashi, A.; Hirama, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1708.

(6) (a)Knölker, H.-J.; Graf, R. ; Pannek, J.-B. *Tetrahedron* **1993**, *49*, 9955. (b) Knölker, H.-J.; Foitzik, N.; Goesmann, H.; Graf, R.; Jones, P.; Wanzl, G. *Chem. Eur. J.* **1997**, *3*, 538.

(7) Knölker, H.-J.; Foitzik, N.; Goesmann, H.; Graf, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1081.

(8) (a) Knölker, H.-J.; Graf, R. *Tetrahedron Lett.* **1993**, *34*, 4765. (b) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1994**, 131.

(9) Akiyama, T.; Ishikawa, K.; Ozaki, S. *Chem. Lett.* **1994**, 627.

(10) Akiyama, T.; Yasusa, T.; Ishikawa, K.; Ozaki, S. *Tetrahedron Lett.* **1994**, *35*, 8401.

(11) Stahl, A.; Steckhan, E.; Nieger, M. *Tetrahedron Lett.* **1994**, *35*, 7371.

(12) Kiyooka, S.; Shiomi, Y.; Kira, H; Kaneko, Y.; Tanimora, S. *J. Org. Chem.* **1994**, *59*, 1958.

(13) Knölker, H.-J. *J. Prakt. Chem.* **1997**, 304.

(14) Yeon, S. H.; Lee, B. W.; Yoo, B. R.; Suk, M. Y.; Jung, I. N. *Organometallics* **1995**, *14*, 2361.

(15) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159.

(16) Cho, B. K.; Choi, G. M.; Jin, J.-I.; Yoo, B. R.; Jung, I. N. *Organometallics* **1997**, *16*, 3576.

(17) (a) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874. (b) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781.

(18) Kamigaito, M.; Sawamoto, M.; Hiagshimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1909.

(19) Peng, Y. X.; Shi, W. M. *Polym. Bull.* **1996**, *37*, 149.

(20) Kennedy, J. P. *Carbocation Polymerization*; John Wiley & Sons: New York, 1982; p 31.

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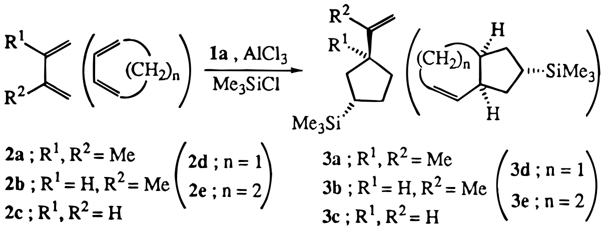
Table 1. [3 + 2] Annulation of Conjugated Dienes with Allyltrimethylsilane (1a)

entry no.	diene	mol ratio of $AlCl_3$ catalyst[a]	reaction time (min)	product	yield (%)[b]
1	**2a**	0.5	60	**3a**	67
2	**2b**	0.1	10	**3b**	29
3	**2c**	0.1	120	**3c**	38
4	**2d**[c]	0.1	10	**3d**	56[d]
5	**2e**	0.5	150	**3e**	72[e]

[a] Mole ratio with respect to **1a**. [b] Isolated yield. [c] Methylene chloride was used as a solvent. [d] A mixing solution of 1:1.5 of **1a** and **2d** was added. [e] Reaction temperature was increased to −10 °C after completing allylsilylation at −50 °C.

with **1a** in the presence of aluminum chloride as a catalyst and chlorotrimethylsilane as an activator in a −10 °C salt bath gave *trans*-1-isopropenyl-3-(trimethylsilyl)cyclopentane (**3a**) as the major product in 67% yield based on the amount of **1a** consumed. In addition, unidentified high-boiling compounds and unreacted **1a** (9%) were observed. The formation of the five-membered-ring product **3a** can be explained by the [3 + 2] cycloaddition of the allyl group of **1a** with a carbon−carbon double bond of **2a**, as shown in eq 1.



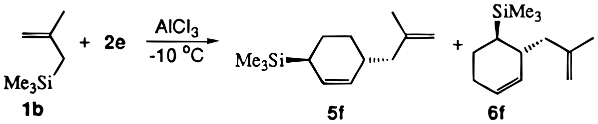
(1)

Lewis acids, such as boron trifluoride etherate,[22] titanium tetrachloride,[3−13] etc., have been known to be effective catalysts for the [3 + 2] cycloaddition of activated α,β-unsaturated ketones with allylsilanes. However, the [3 + 2] cycloaddition of dienes with allylsilanes did not occur with Lewis acid catalysts other than aluminum chloride, indicating the requirement of a strong Lewis acid for the allylsilylations.[14−16] When chlorotrimethylsilane was used as an acivator to the aluminum chloride catalyst, a higher yield and faster reaction rate were observed, consistent with the previous results obtained from the allylsilylation of diallylsilanes.[16] The results of the cycloadditions are summarized in Table 1.

As shown in Table 1, 2,3-dimethyl-1,3-butadiene (**2a**) or cyclic dienes **2d** and **2e** gave stereoselective [3 + 2] cycloadducts of *trans*-1-(trimethylsilyl)-3-vinylcyclopentanes **3a**, **3d**, and **3e**, respectively, in yields from 56 to 72% with less polymeric materials, while isoprene (**2b**) and butadiene (**2c**) gave **3b** (29%) and **3c** (38%), respectively, in lower yields, probably due to easy polymerization of the dienes.[20,21]

The structures and configurations of **3a**−**e** were determined by ^{1}H, ^{13}C, proton decoupling, 2D COSY, and NOE NMR techniques. Although all of the annulation products have two or three asymmetric centers, the ^{13}C NMR spectra of **3a**−**e** showed no diastereomers of the products,[14] indicating the regio- and stereoselectivity of the annulation. Analysis of the NMR spectra of the annulation products disclosed the regio- and stereoselective structures with both a trimethylsilyl group and a vinyl group located at the 1,3-carbon positions of the cyclopentane ring and arranged in a *trans* position. The regio- and stereoselectivity are consistent with the results from the allylsilylations of alkenes[14] and alkynes.[15,17]

Reaction with (2-Methyl-2-propenyl)trimethylsilane. The pathways for Lewis-acid-promoted [3 + 2] cycloadditions of allylsilanes with enones[2,6−9] and α-keto esters[10] have been explained assuming that allylsilanes are equivalent to 2-silyl-substituted 1,3-dipoles resulting from a 1,2-shift of a trimethylsilyl group. If this 1,2-silyl group shift applies to this cyclization of the conjugated diene, the cycloaddition would be less favorable with (2-methyl-2-propenyl)trimethylsilane than with allyltrimethylsilane due to the steric interactions between the methyl group on the middle carbon and the incoming trimethylsilyl group. To test whether steric hindrance retards or prevents the 1,2-silyl shift, a cyclization reaction of 1,3-cyclohexadiene with (2-methyl-2-propenyl)trimethylsilane was carried out for 25 min at −10 °C as described above. No cycloaddition product was detected, but *trans*-1,4- and 1,2-allylsilylation products 3-(2-methyl-2-propenyl)-6-(trimethylsilyl)cyclohexene (**5f**) and 3-(2-methyl-2-propenyl)-4-(trimethylsilyl)cyclohexene (**6f**) were obtained in a 15% and 3% yield, respectively (eq 2). These results clearly show that allylsilylation occurs before the cyclization and that a 1,2-silyl shift is involved in the cycloaddition.



(2)

To confirm the allylsilylation occuring prior to the cyclization, cyclohexadiene was reacted with **1a** at the lower reaction temperatures. Indeed, the 1,4-allylsilylated product, *trans*-3-allyl-6-(trimethylsilyl)cyclohexene (**5e**), was obtained as the predominant product along with the 1,2-allylsilylated product, *trans*-3-allyl-4-(trimethylsilyl)cyclohexene (**6e**), at −50 °C in a 97:3 ratio. A trace amount of the [3 + 2] cycloaddition product was observed after 1 h. When the reaction mixture was allowed to warm from −50 to −10 °C, the 1,4-allylsilylated compound was converted to the stereoselective [3 + 2] cycloaddition product **3e** as the major product and 3-(trimethylsilyl)propylbenzene (**4e**) as a byproduct while the 1,2-allylsilylated compound was polymerized.[24] The results indicate that [3 + 2] cycloaddition products are obtained from the intramolecular cyclization of 1,4-allylsilylated compounds in the reaction conditions.

From studies of the Cope rearrangement, it is known that the isomerization of allyl groups on the allylic position of olefins occurs through a thermal [3,3-sigmatropic] rearrangement.[23] To test whether the isomer-

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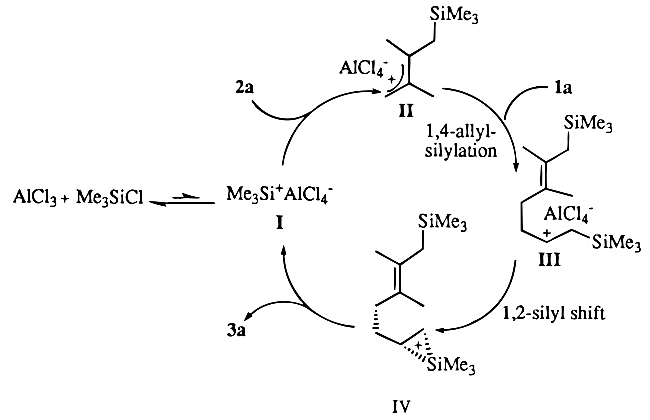
[21] Gaylord, N. G.; Matyska, B. *J. Polym. Sci., Part A-1* **1966**, *4*, 2493.

[22] Panek, J. S.; Jain, N. F. *J. Org. Chem.* **1993**, *58*, 2345.

[23] Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441.

[24] When the reactions with separated **5e** (22 mg, 0.11 mmol) and **6e** (10 mg, 0.05 mmol) in 0.2 mL of pentane in the presence of aluminum chloride (10 mol % based on the amount of **5e** and **6e** used) and chlorotrimethylsilane (50 mol % based on the amount of **5e** and **6e** used) were carried out at room temperature for 2 h in NMR tubes, respectively, **5e** gave 8*R*(*S*)-(trimethylsilyl)-1*R*(*S*),6*R*(*S*)-bicyclo[4.3.0]non-2-ene (**3e**; 31%) and 3-(trimethylsilyl)propylbenzene (**4e**; 13%) and **6e** gave polymeric materials. For **4e**, see ref 27.

Scheme 1



ization between the 1,4-allylsilylated product **5e** and 1,2-allylsilylated product **6e** occurs, purified **5e** or **6e** was placed under our reaction conditions[24] and heated to the reflux temperature (217 °C) of dodecane without aluminum chloride. In both cases, [3,3-sigmatropic] rearrangement was not observed.

The reaction rates of allylsilylation and [3 + 2] annulation were accelerated by chlorotrimethylsilane addition aluminum chloride, as reported in other allylsilylations.[18,19] When chlorodimethylethylsilane was used instead of chlorotrimethylsilane as an activator in the cyclization of **5e** to **3e**, the annulation product **3e′** having the dimethylethylsilyl group was obtained as a major product and **3e** as a minor product. This result suggests that the reactions were initiated by the trialkylsilyl cation, generated from the reaction of aluminum chloride with chlorotrialkylsilane as described in a previous report.[16]

Reaction Mechanism. On the basis of the results obtained in this study and in analogy to the allylsilylation of alkenes,[14] alkynes,[15] and diallylsilanes,[16] we propose the mechanism for stereoselective [3 + 2] cycloaddition of allyltrimethylsilane with conjugated dienes illustrated in Scheme 1. A silyl cation intermediate **I** is formed at the beginning of the reaction directly from aluminum chloride and chlorotrimethylsilane, although the protodesilylation of allyltrimethylsilane by acids is not ruled out in the absence of chlorotrimethylsilane.[25,26] When the intermediate **I** interacts with **2a**, the trimethylsilyl cation can add to the terminal carbon−carbon double bond of **2a** to generate a new intermediate **II**, which is stabilized by the resonance effect of the allylic cation. The intermediate **II** interacts with the double bond of **1a** to give carbon−carbon bond formation and intermediate **III**. In the allylic cationic intermediate **II**, 1,2-allylsilylation is disfavored because of steric repulsion between the bulky trimethylsilyl group and the incoming allyltrimethylsilane. Intermediate **III** should undergo a 1,2-silyl shift[4] to intermediate **IV** at higher reaction temperatures, even though it is thermodynamically less favorable. Finally, the product **3a** is formed by the cyclization of **IV** to give a five-membered ring through the intramolecular nucleophilic attack of the carbon−carbon double bond on the carbocation of **IV**, followed by the elimination of a silyl cation.

In summary, it is found that the [3 + 2] cycloaddition of conjugated dienes with allylsilanes involves stepwise reactions; the allylsilylation of conjugated dienes with allysilanes gives 1,4-allylsilylated products, followed by intramolecular cyclization to regio- and stereoselective [3 + 2] cycloaddition products with the *trans* configuration of the trimethylsilyl and vinylic groups, via a 1,2-silyl shift.

Experimental Section

All reactions and manipulations were carried out under prepurified dinitrogen using Schlenk techniques. Glassware was flame dried before use. Dried solvents were employed in all reactions. Allyltrimethylsilane, chlorotrimethylsilane, the diene compounds, and anhydrous aluminum chloride were obtained from Aldrich Chemical Co. All chemicals were dried over calcium chloride or molecular sieves (4 Å) and distilled prior to use. Reaction products were analyzed by GLC using a capillary column (SE-30, 30 m) or a packed column (10% OV-101 on 80−100 mesh Chromosorb W/AW, $^1/_8$ in. × 1.5 m) on a Varian 3300 gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. NMR spectra were recorded on a Varian Unity Plus 600, Varian Gemini 300, or Bruker AMX 500 spectrometer in $CDCl_3$ solvent. A small amount of $CHCl_3$ in the NMR solvent was used as a reference material (7.26 ppm in the proton spectra and 77.0 ppm in the carbon-13 spectra). GC/MS data were obtained using a Hewlett Packard 5890 II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm i.d. × 30.0 m, film thickness 0.25 μm) connected to a Hewlett-Packard 5972A mass-selective detector. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by Korea Basic Science Institute, Seoul, Korea. Elemental analyses were performed by the Chemical Analysis Laboratory of the Korea Institute of Science and Technology.

Typical Procedure for [3 + 2] Cycloaddition Reaction of 2a with 1a. To a suspended solution of anhydrous aluminum chloride (1.20 g, 9.0 mmol), dried pentane (6.2 mL), chlorotrimethylsilane (9.76 g, 90.0 mmol), and **1a** (2.05 g, 18.0 mmol) in a −10 °C salt bath was added dropwise 2,3-dimethyl-1,3-butadiene (**2a**; 1.50 g, 18.3 mmol) for 60 min and stirred for another 60 min. The reaction mixture was then quenched with a water solution saturated with sodium hydrogen carbonate. The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated. Purification with silica gel chromatography using hexane as an eluent gave *trans*-1-isopropenyl-1-methyl-3-(trimethylsilyl)cyclopentane (**3a**; 2.15 g, 67%, based on the amount of **1a** consumed) and 1.05 g of unidentified high-boiling compounds. Unreacted **1a** (0.19 g, 9%) was recovered. Data for **3a**: ^{1}H NMR δ −0.02 (s, 9H, $SiCH_3$), 1.13 (quint, $J = 12$ Hz, 1H, Si*CH*), 1.07−1.11 (m, 1H), 1.92 (dd, $J = 8, 12$ Hz, 1H, $CHCH_2C$), 1.10, 1.77 (s, 3H, CH_3), 1.37 (ddd, $J = 5, 8$, and 12 Hz, 1H), 1.86 (dt, $J = 7$ and 12 Hz, 1H, $CHCH_2CH_2$), 1.43−1.50 (m, 1H), 1.71−1.79 (m, 1H, $CHCH_2CH_2$), 4.73−4.75 (m, 2H, $=CH_2$); ^{13}C NMR δ −3.04 ($SiCH_3$), 20.00, 25.25, 26.80, 27.53, 39.60, 39.92, 48.77 (CH_3, CH_2, *C*H), 108.03 ($=CH_2$), 152.42 ($=CH$). HRMS (*m*/*e*): calcd for $C_{12}H_{24}Si$ (M^+), 196.1647; found, 196.1647. Anal. Calcd for $C_{12}H_{24}Si$: C, 73.38; H, 12.32. Found: C, 73.31; H, 12.45.

[3 + 2] Cycloaddition of 2b with 1a. As described in the reaction of **2a** with **1a**, the reaction of isoprene **2b** (1.50 g, 18.3 mmol) with **1a** (2.05 g, 18.0 mmol) in the presence of anhydrous aluminum chloride (0.24 g, 1.80 mmol) and chlorotrimethylsilane (9.76 g, 90.0 mmol) in pentane solvent (6.2 mL) gave *trans*-1-isopropenyl-3-(trimethylsilyl)cyclopentane (**3b**, 0.12 g, 29%) and 1.67 g of unidentified high-boiling products. Unreacted **1a** (1.37 g, 67%) was recovered. Data

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(25) Jenkins, P. R.; Gut, R.; Wetter, H.; Eschenmoser, A. *Helv. Chim. Acta* **1979**, *62*, 1922.

(26) Fleming, I.; Marchi, D.; Patel, K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2518.

(27) Musolf, M. C.; Speier, J. L. *J. Org. Chem.* **1964**, *29*, 2519.

(28) Doucet, A. *Ann. Sci. Univ. Besancon, Chim.* **1979**, 3; *Chem. Abst.* **1981**, *95*, 150745x.

for **3b**: ^{1}H NMR δ −0.02 (s, 9H, SiCH_3), 1.09 (tt, J = 8 and 11 Hz, 1H, SiCH), 1.29−1.37 (m, 1H), 1.80−1.86 (m, 1H, SiCHCH_2-CH$_2$), 1.42−1.50 (m, 1H), 1.80−1.86 (m, 1H, SiCHCH$_2$CH_2), 1.60−1.66 (m, 2H, SiCHCH_2CH), 1.75 (s, 3H, CH_3), 2.43 (quint, J = 8 Hz, 1H, CH), 4.68 (m, 1H), 4.71 (m, 1H, ═CH_2); ^{13}C NMR δ −3.07 (SiCH$_3$), 21.19 (SiCH), 24.82, 28.39, 32.15, 33.38 (CH$_3$, CH$_2$), 47.77 (CH), 107.91 (═CH$_2$), 149.31 (═CH). HRMS (m/e): calcd for $C_{11}H_{22}Si$ (M$^+$), 182.1491; found, 182.1491. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.46; H, 12.27.

[3 + 2] Cycloaddition of 2c with 1a. As described in the reaction of **2a** with **1a**, the reaction of 1,3-butadiene (**2c**, 0.99 g, 18.3 mmol) with **1a** (2.05 g, 18.0 mmol) in the presence of anhydrous aluminum chloride (0.24 g, 1.80 mmol) and chlorotrimethylsilane (9.76 g, 90.0 mmol) in pentane solvent (6.2 mL) gave *trans*-1-(trimethylsilyl)-3-vinylcyclopentane (**3c**, 1.02 g, 38%), 4-((trimethylsilyl)methyl)-1,5-hexadiene (**4c**, 0.48 g, 18%), 3-(2-(trimethylsilyl)ethyl)cyclopentane (**5c**, 0.20 g, 7.5%), and 0.93 g of unidentified high-boiling compounds. Unreacted **1a** (0.23 g, 11%) was recovered. Data for **3c**: ^{1}H NMR δ −0.01 (s, 9H, SiCH_3), 1.08 (m, 1H, SiCH), 1.29−1.41 (m, 2H), 1.79−1.87 (m, 2H, SiCHCH_2CH_2), 1.53−1.65 (m, 2H, CHCH_2CH), 2.48 (dt, J = 7 and 15 Hz, 1H, CH), 4.89 (ddd, J = 1, 2 and 10 Hz, 1H), 4.98 (ddd, J = 1, 2, and 17 Hz, 1H, ═CH_2), 5.83 (ddd, J = 7, 10, and 17 Hz, 1H, ═CH); ^{13}C NMR δ −3.05 (SiCH$_3$), 24.62 (SiCH), 28.15, 33.84, 34.71 (CH$_2$), 44.75 (CH), 111.92 (═CH$_2$), 143.83 (═CH). HRMS (m/e): calcd for $C_{10}H_{20}Si$ (M$^+$), 168.1334; found, 168.1335. Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 71.45; H, 12.09. Data for **4c**: ^{1}H NMR δ −0.00 (s, 9H, SiCH_3), 0.58 (dd, J = 9.0 and 14.8 Hz, 1H), 0.70 (dd, J = 4.9 and 14.8 Hz, 1H, SiCH_2), 2.06−2.09 (br m, 2H, CH_2), 2.17−2.21 (m, 1H, CH), 4.91−5.01 (m, 4H, ═CH_2), 5.63 (dt, J = 8.8 and 18.1 Hz, 1H, ═CHCH), 5.67−5.79 (m, 1H, ═CHCH$_2$); ^{13}C NMR δ −0.61 (SiCH$_3$), 22.44 (SiCH$_2$), 40.23 (CH$_2$), 43.08 (CH), 112.98, 115.67 (═CH$_2$), 137.19, 144.62 (═CH). HRMS (m/e): calcd for $C_9H_{17}Si$ ((M − CH$_3$)$^+$), 153.1100; found, 153.1101. Data for **5c**: ^{1}H NMR δ −0.02 (s, 9H, SiCH_3), 0.50 (t, J = 8.7 Hz, 2H, SiCH_2), 1.22−1.44 (m, 2H, CH_2), 1.22−1.44 (m, 1H), 2.02 (ddt, J = 5.0, 8.2, and 12.9 Hz, 1H, ring-CH_2), 2.20−2.39 (br m, 2H, allylic-CH_2), 2.56−2.65 (br m, 1H, CH), 5.71 (br s, 2H, ═CH); ^{13}C NMR δ −1.71 (SiCH$_3$), 14.58 (SiCH$_2$), 29.35, 30.08, 32.05 (CH$_2$), 48.76 (CH), 130.22, 135.23 (═CH). HRMS (m/e): calcd for $C_{10}H_{20}Si$ (M$^+$), 168.1334; found, 168.1334.

[3 + 2] Cycloaddition of 2d with 1a. To a suspension solution of anhydrous aluminum chloride (1.20 g, 9.0 mmol), chlorotrimethylsilane (9.76 g, 90.0 mmol), and methylene chloride (6.2 mL) in a −10 °C salt bath was added dropwise a mixed solution of **1a** (2.05 g, 18.0 mmol) and **2d** (1.50 g, 18.3 mmol) in methylene chloride (5.1 mL) for 10 min under a dry nitrogen atmosphere. Using the general work-up procedure above, *R*(*S*)-(trimethylsilyl)-1*R*(*S*),6*R*(*S*)-bicyclo[3.3.0]oct-3-ene (**3d**; 1.80 g, 56%), *trans*-3-allyl-4-(trimethylsilyl)cyclopentene (**4d**; 0.32 g, 10%), and 1.53 g of unidentified high-boiling compounds were obtained. Data for **3d**: ^{1}H NMR δ −0.05 (s, 9H, SiCH_3), 0.82 (tt, J = 6 and 13 Hz, 1H, SiCH), 1.31 (dt, J = 9 and 13 Hz, 1H), 1.37−1.47 (m, 1H, SiCHCH_2CHCH═), 1.37−1.47 (m, 2H, SiCHCH_2CHCH$_2$), 1.90 (ddt, J = 3, 5, and 17 Hz, 1H), 2.60 (ddd, J = 2, 10, and 17 Hz, 1H, ═CHCH_2), 2.68−2.73 (m, 1H, CH), 3.17 (br t, 1H, CH), 5.37 (m, 1H), 5.57 (m, 1H, ═CH); ^{13}C NMR δ −2.78 (SiCH$_3$), 23.58 (SiCH), 34.38, 38.02, 40.73, 42.38, 52.14 (CH$_2$, CH), 130.69, 134.20 (═CH). HRMS (m/e): calcd for $C_{11}H_{20}Si$ (M$^+$), 180.1334; found, 180.1332. Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.02; H, 11.38. Data for **4d**: ^{1}H NMR δ −0.02 (s, 9H, SiCH_3), 0.99 (dt, J = 6.7 and 10.1 Hz, 1H, SiCH), 2.02 (dt, J = 7.8 and 13.6 Hz, 1H), 2.15−2.26 (m, 1H, allylic-CH_2), 2.15−2.26 (m, 1H), 2.50−2.59 (m, 1H, ring-CH_2), 2.66 (br m, 1H, CH), 4.99−5.05 (m, 2H, ═CH_2), 5.65−5.69 (m, 2H, CH═CH), 5.73−5.85 (m, 1H, ═CH); ^{13}C NMR δ −3.05 (SiCH$_3$), 27.89 (SiCH), 34.48, 41.68 (CH$_2$), 47.54 (CH), 115.56 (═CH$_2$), 130.34, 134.44, 137.46 (═CH). HRMS (m/e): calcd for $C_{11}H_{20}Si$ ((M − CH$_3$)$^+$), 165.1100; found, 165.1097.

[3 + 2] Cycloaddition of 2e with 1a. To a suspension solution of anhydrous aluminum chloride (1.20 g, 9.0 mmol), chlorotrimethylsilane (9.76 g, 90.0 mmol), pentane (6.2 mL), and **1a** (2.05 g, 18.0 mmol) at −50 °C was added dropwise **2e** (1.47 g, 18.4 mmol) for 60 min. The mixture was allowed to warm to −10 °C from −50 °C for 30 min and stirred for another 65 min. Using the general work-up procedure above, 8*R*(*S*)-(trimethylsilyl)-1*R*(*S*),6*R*(*S*)-bicyclo[4.3.0]non-2-ene (**3e**; 2.52 g, 72% based on the amount of **1a** consumed) was obtained along with (3-(trimethylsilyl)propyl)benzene (**4e**; 0.34 g, 9.8%) and *trans*-3-allyl-6-(trimethylsilyl)cyclohexene (**5e**; 0.02 g, 0.6%) as byproducts. Unidentified high-boiling products (0.58 g) were obtained. For **3e**: ^{1}H NMR δ −0.04 (s, 9H, SiCH_3), 1.09 (quint, J = 10 Hz, 1H, SiCH), 1.36−1.58 (m, 6H, CH_2), 1.83−1.89 (m, 1H), 1.93−1.99 (m, 1H, allylic-CH_2), 2.04−2.09 (m, 1H), 2.34−2.36 (br m, 1H, CH), 5.54 (ddt, J = 2, 5, and 10 Hz, 1H), 5.63 (ddt, J = 2, 4, and 10 Hz, ═CH); ^{13}C NMR δ −3.02 (SiCH$_3$), 22.54, 22.75, 24.75, 32.52, 34.05, 38.04, 40.14 (CH$_2$, CH), 126.71, 131.36 (═CH). HRMS (m/e): calcd for $C_{12}H_{22}Si$ (M$^+$), 194.1491; found, 194.1493. Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 73.77; H, 11.64. Data for **4e:** see ref 27. Data for **5e:** ^{1}H NMR δ −0.04 (s, 9H, SiCH_3), 0.73 (ddd, J = 3.6, 5.4, and 8.4 Hz, 1H, SiCH), 1.45 (dddd, J = 6.0, 6.6, 8.4, and 13.4 Hz, 1H), 1.70 (dddd, J = 3.6, 5.4, 6.6, and 13.4 Hz, 1H, SiCHCH_2), 1.85−1.90 (m, 2H, SiCHCH$_2$CH_2), 2.06−2.11 (br m, 1H, CH), 2.00−2.05 (m, 1H), 2.12−2.17 (m, 1H, allylic-CH_2), 4.93−4.97 (m, 2H, ═CH_2), 5.58 (ddt, J = 2, 4, and 10 Hz, 1H), 5.64−5.67 (m, 1H, ring-CH_2), 5.71 (ddt, J = 7, 10, and 18 Hz, 1H, ═CH); ^{13}C NMR δ −1.62 (SiCH$_3$), 21.85, 25.13, 25.22, 35.43, 40.73 (CH$_2$, CH), 116.00 (CH$_2$), 127.25, 131.70, 137.39 (═CH). HRMS (m/e): calcd for $C_{11}H_{19}Si$ ((M − CH$_3$)$^+$), 179.1256; found, 179.1256. Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.38; H, 11.51.

Allylsilylation of 2e with 1a. This was performed as described in the reaction of **2a** with **1a**. To a suspension solution of anhydrous aluminum chloride (1.41 g, 10.6 mmol), chlorotrimethylsilane (14.3 g, 131.7 mmol), pentane (10 mL), and **1a** (3.0 g, 26.2 mmol) at −50 °C was added dropwise **2e** (4.2 g, 52.4 mmol) for 60 min and stirred for another 3.5 h. Using the general work-up procedure above, **3e** (0.25 g, 5%) was obtained along with **4e**[27] (0.05 g, 1%), **5e** (4.13 g, 81%), and *trans*-3-allyl-4-(trimethylsilyl)cyclohexene (**6e**; 0.41 g, 8%). Unidentified high-boiling compounds (0.25 g) were obtained. Data for **6e**: ^{1}H NMR δ −0.08 (s, 9H, SiCH_3), 1.07 (ddt, J = 2, 9, and 12 Hz, 1H), 1.72−1.77 (m, 1H, SiCHCH_2), 1.29−1.36 (m, 1H, SiCH), 1.72−1.77 (m, 1H), 1.97−2.00 (m, 1H, SiCHCH$_2$CH_2), 1.72−1.77 (m, 1H, CH), 1.97−2.00 (m, 2H, allylic-CH_2), 4.94 (dd, J = 3 and 10 Hz, 1H), 4.96 (dd, J = 3 and 17 Hz, 1H, ═CH_2), 5.47−5.57 (m, 2H, ring-═CH), 5.75 (ddt, J = 7, 10, and 17 Hz, 1H, ═CH); ^{13}C NMR δ −3.41 (SiCH$_3$), 23.13, 26.25, 29.62, 35.23, 40.86 (CH$_2$, CH), 115.67 (═CH$_2$), 127.99, 129.90 (ring-═CH), 137.34 (═C). HRMS (m/e): calcd for $C_{12}H_{22}Si$ (M$^+$), 194.1491; found, 194.1491. Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.03; H, 11.42.

Intramolecular Cyclization of 5e in the Presence of Chlorodimethylethylsilane. Reaction of **5e** (22 mg, 0.11 mmol) with chlorodimethylethylsilane (7 mg, 0.06 mmol), and dodecane (5 mg), as an internal standard, in the presence of aluminum chloride (1.5 mg, 0.01 mmol) in hexane solvent (0.4 mL) afforded 8*R*(*S*)-((trimethylethyl)silyl)-1*R*(*S*), 6*R*(*S*)-bicyclo-[4.3.0]non-2-ene (**3e′**; 34%), 3-(dimethylethylsilyl)propylbenzene[28] (**4e′**; 14%), **3e** (5%), and **4e** (2%). Data for **3e′**: ^{1}H NMR δ −0.08 (s, 6H, SiCH_3), 0.48 (q, J = 8 Hz, 2H, SiCH_2), 0.93 (t, J = 8 Hz, 3H, CH_3), 1.19 (quint, J = 10 Hz, 1H, SiCH), 1.39−1.68 (m, 6H, CH_2), 1.89−2.07 (m, 2H, allylic-CH_2), 2.09−2.11 (m, 1H), 2.41 (br s, 1H, CH), 5.58−5.71 (m, 2H, ═CH); ^{13}C NMR δ −5.40 (SiCH$_3$), 6.14 (Si CH$_2$), 7.56 (CH$_3$), 21.48, 22.52, 24.71, 32.58, 34.11, 37.97, 40.06 (CH$_2$, CH), 126.72, 131.40 (═CH). HRMS (m/e): calcd for $C_{13}H_{24}Si$ (M$^+$), 208.1647;

found, 208.1648. Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 75.15; H, 11.67. Data for **4e′**: see ref 28.

Reaction of 2e with 1b. As described in the reaction of **2a** with **1a**, the reaction of **2e** (0.24 g, 3.03 mmol) with (2-methyl-2-propenyl)trimethylsilane (**1b**; 0.38 g, 2.97 mmol) in the presence of anhydrous aluminum chloride (0.20 g, 1.50 mmol) and chlorotrimethylsilane (1.61 g, 14.80 mmol) in pentane solvent (5 mL) gave *trans*-3-(2-methyl-2-propenyl)-6-(trimethylsilyl)cyclohexene (**5f**; 0.09 g, 15%), *trans*-3-(2-methyl-2-propenyl)-4-(trimethylsilyl)cyclohexene (**6f**; 0.03 g, 3%), and 0.38 g of unidentified high-boiling compounds. Data for **5f**: ^1H NMR δ −0.01 (s, 9H, $SiCH_3$), 0.78 (dt, J = 4 and 7 Hz, 1H), 1.91−1.98 (m, 1H, $SiCHCH_2CH_2$), 1.53 (ddt, J = 6, 7, and 13 Hz, 1H) 1.75−1.81 (m, 1H, $SiCHCH_2$), 1.71 (s, 3H, CH_3), 1.91−1.98 (m, 1H, SiC*H*), 1.91−1.98 (m, 1H), 2.17 (dd, J = 7 and 13 Hz, 1H, allylic-CH_2), 2.22 (br m, 1H, C*H*), 4.67 (dd, J = 1 and 2 Hz, 1H), 4.77 (dd, J = 1 and 2 Hz, 1H, ═CH_2), 5.64−5.67 (m, 2H, ring-═C*H*); ^{13}C NMR δ −1.80 ($SiCH_3$), 21.23, 22.20, 25.01, 25.26, 32.93, 45.00 (CH_3, CH_2, *C*H), 112.09 (═CH_2), 126.83, 131.62 (ring-═*C*H), 144.21 (═*C*). HRMS (*m*/*e*): calcd for $C_{13}H_{24}Si$ (M^+), 208.1647; found, 208.1646. Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 75.09; H, 11.75. Data for **6f**: ^1H NMR δ −0.01 (s, 9H, $SiCH_3$), 1.07−1.44 (m, 1H, SiC*H*), 1.32−1.49 (m, 2H), 1.77−1.83 (m, 2H, $SiCHCH_2CH_2$), 1.72 (s, 3H, CH_3), 1.91−2.03 (m, 2H, allylic-CH_2), 2.18−2.20 (br m, 1H, C*H*), 4.69 (s, 1H), 4.76 (s, 1H, ═CH_2), 5.52 (dt, J = 2 and 10 Hz, 1H), 5.63 (ddd, J = 2, 3, and 10 Hz, 1H, ring-═C*H*); ^{13}C NMR δ −3.36 ($SiCH_3$), 22.31, 23.10, 26.35, 29.87, 33.05, 45.10 (CH_3, CH_2, *C*H), 111.51 (═CH_2), 127.75, 130.03 (ring-═CH_2), 144.24 (═*C*). HRMS (*m*/*e*): calcd for $C_{13}H_{24}Si$ (M^+), 208.1647; found, 208.1648. Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.98; H, 11.66.

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Supporting Information Available: Figures of the ^1H and ^{13}C NMR, HOMO COSY, 1D-NOE, and HRMS results for **3a** (6 pages). Ordering information is given on any current masthead page.

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