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1,5-Hydride Shift in the Aluminum Chloride Promoted Allylsilylation of 5-Silyl-1-alkenes

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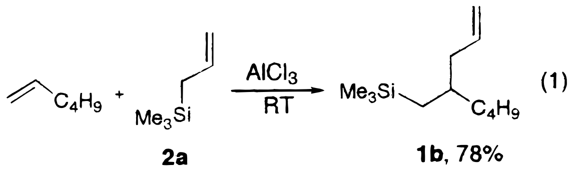
Linear 4-alkyl-5-silyl-1-alkenes **1a**−**c** react with allylsilanes **2a,b** in the presence of aluminum chloride catalyst at 40 °C to give unusual allylsilylation products **3a**−**d** derived from an intramolecular silyl group rearrangement in 23−57% yield. The reaction of cyclic 1-allyl-2-(trimethylsilyl)cycloalkanes **1d**,**e** with **2** gave the silyl-rearranged isomers of **1** in addition to the allylsilylation products **3e**,**f**. The results are consistent with silylenium ion formation and a 1,5-hydride shift in the allylsilylation and isomerization.

Introduction

Recently, we reported the novel aluminum chloride catalyzed addition of allyltrimethylsilane to simple unactivated alkenes,[1] diallylsilanes,[2] conjugated dienes,[3] and alkynes.[4] In the allylsilylation, the silyl group regiospecifically and stereospecifically adds to the terminal carbon and the allyl group to the inner carbon of terminal multiple bonds. The product yields were higher in the presence of the Lewis acid catalysts in combination with chlorotrimethylsilane as an activator.[2,3,5] The allylsilylation of carbon−carbon multiply bonded compounds proceeded at room temperature or below in the presence of a catalytic amount of aluminum chloride, in contrast to the requirement for more than stoichiometric quantities (1.2 equiv) of Lewis acid catalyst in the allylation of carbonyl compounds.[6−12]

Allyltrimethylsilane (**2a**) reacts with 1-hexene in the presence of anhydrous aluminum chloride catalyst to afford 4-((trimethylsilyl)methyl)-1-octene (**1b**) in 78% yield.[1] Since the allylsilylated products obtained from the allylsilylation of alkenes still have a double bond at the terminus, a continuous allylsilylation was expected to give polyallylsilylation products.

Surprisingly, as noted below, the unusual allylsilylation products were obtained as the major products in the aluminum chloride catalyzed reactions of 4-alkyl-5-silyl-1-alkenes **1a**−**f** with allylsilanes **2a**,**b**. A probable reaction mechanism for the allylsilylation and 1,5-hydride shift is discussed.



Results and Discussion

Reaction of 4-Linear Alkyl-5-silyl-1-pentenes (2a−c) with Allylsilanes (1a,b). The reaction of linear 4-alkyl-5-silyl-1-pentenes **1a**−**c**, prepared by the allylsilylation of terminal alkenes,[1] with 1.2 molar equiv of allylsilanes **2a**,**b** in the presence of anhydrous aluminum chloride catalyst and chlorotrimethylsilane activator in organic solvents or neat at 40 °C gave the unusual allylsilylation products 2-alkyl-8,8-dimethyl-4-((trimethylsilyl)methyl)-8-silanon-1-enes **3a**−**d**, as the major products, different from previously reported allylsilylation products,[1−3] along with polymeric materials. Compounds **3a**−**d** have a double bond on the carbon with the R^1 group but not on the carbon with R^2 (eq 2).

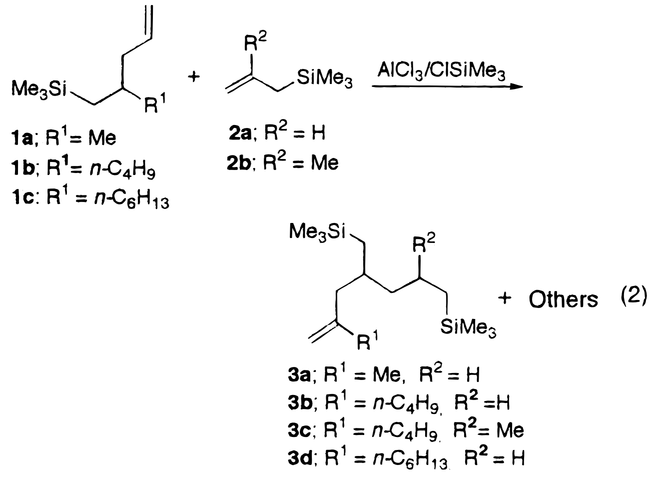


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Table 1. Aluminum Chloride Promoted Reaction of 5-Silyl-1-alkenes (1) with Allylsilanes (2)

entry nos.	reactants		reaction conditions		products (%)[b]	
	1[a]	2	time (h)	solvent	3	high boilers[c]
1	**1a** (41)	**2a**	4	hexane	**3a**, 23	46
2	**1b** (39)	**2a**	5	hexane	**3b**, 57	21
3	**1b** (42)	**2b**	10	CH_2Cl_2	**3c**, 36 (**4c**, 3)	45
4	**1c** (47)	**2a**	4	hexane	**3d**, 43	29

[a] Amount of **1** recovered after reaction. [b] Isolated yields based on **1** consumed. [c] Wt % of high boilers based on the amounts of **1** and **2** used.

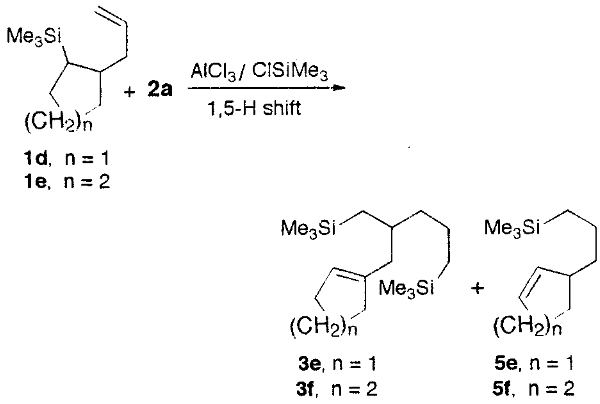
The results obtained from a series of these allylsilylations are summarized in Table 1. As shown in the table, the reaction of **1a**−**c** with simple allyltrimethylsilane (**2a**) gave 2,8,8-trimethyl-4-((trimethylsilyl)methyl)-9-silanon-1-ene (**3a**), 2-butyl-8,8-dimethyl-4-((trimethylsilyl)methyl)-8-silanon-1-ene (**3b**), and 8,8-dimethyl-2-hexyl-4-((trimethylsilyl)methyl)-8-silanon-1-ene (**3d**) in 23%, 57%, and 43% yields based on **1** consumed, respectively.

It has been well-known that regiospecific *trans*-addition and allylic inversion are characteristic of the allylsilylation of alkenes[1−3] and alkynes.[4,5] A new carbon−carbon bond formation occurs between the inner carbon of multiple bonds and the terminal carbon of allylsilanes. The bond between the allylic carbon and the silyl group of allylsilanes breaks to afford a new carbon−carbon double bond between the carbons α and β to the silicon of the allylsilanes. In light of these facts, **3a**−**c**, retaining the silyl group of **2a** but losing it from **1a**−**c**, are unusual allylsilylation products. The results suggest a silyl group rearrangement or an isomerization of the initial products of the allylsilylations.

The reaction of **1b** with **2b** which has a methyl group β to the silicon instead of **2a** in hexane solution did not proceed, indicating that the allylsilylation is sensitive to hindrance. When methylene chloride, known as an effective solvent[6−12] in Lewis acid-catalyzed reactions, was used, **3c** (36%) was obtained as the major product in a 10 h reaction along with 4,6-bis((trimethylsilyl)methyl)-2-methyl-1-undecene (**4c**, 3%). The lower yield and reactivity of bulky allylsilanes are consistent with other system previously reported.[1] Even though the yield of the normal allylsilylation product **4c** was only 3%, the product **4c** suggests that the same type of allylsilylated products as previously reported[1−4] also might have been obtained but that they isomerized to **3** or were further allylsilylated to polymeric materials. The distribution of the final products varies depending on the structures of the starting alkenes and allylsilanes in the allylsilylations.

The samples for characterization were purified by preparative GLC. Subsequent NMR spectral analyses such as ^{1}H, ^{13}C, 2D (^{1}H−^{1}H, ^{1}H−^{13}C correlation), DEPT, and NOE allowed the identification of the products. The compounds **3a**−**f** were identified on the basis of two singlets due to the vinylidenic protons in their ^{1}H NMR spectra near 4.7 ppm[13] and the peaks due to two vinylidenic carbons in their ^{13}C NMR spectra near 110 ppm (terminal carbon) and 150 ppm (inner carbon), while the typical peaks of the allyl group in the ^{1}H and ^{13}C NMR spectra of the normal allylsilylated product **4c** were observed.[1] Polymeric materials produced by the allylsilylation of **1a**−**c** consisted of a mixture of many products with low average molecular weights ranging from 700 to 1000 by GPC and showed very messy peaks in ^{1}H NMR spectra.

Reaction of 1-Allyl-2-(trimethylsilyl)cycloalkanes with 2a. The reaction of *trans*-1-allyl-2-(trimethylsilyl)cyclopentane (**1d**), prepared by the allylsilylation of cyclopentene,[1] with **2a** in the absence of solvent at 40 °C for 1.5 h also gave an unusual allylsilylation product, 7-cyclopent-1-enyl-2,2-dimethyl-4-((trimethylsilyl)methyl)-2-silaheptane (**3e**) and an isomer of **1d**, 3-(3-(trimethylsilyl)propyl))cyclopentene (**5e**), in 25% and 20% yield, respectively. Unreacted **1d** (16%) also was recovered. Similarly, in the allylsilylation of *trans*-1-allyl-2-(trimethylsilyl)cyclohexane (**1e**) with **2a** for 4 h, with 91% consumption of **1e**, 4-(cyclohex-1-enylmethyl)-2,2,8,8-tetramethyl-2,8-disilanonane (**3f**, 35%) was obtained as the major product along with 3-(3-(trimethylsilyl)propyl))cyclohexene (**5f**, 14%) as a minor product (eq 3). In contrast to the reaction with linear silylalkenes, the isomerization of **1d** and **1e** to **5e** and **5f**, respectively, occurred in the allylsilylations.



(3)

To confirm that the isomerization was occurring in an acidic medium, the representative compound **1d** was reacted under the same reaction conditions in the absence of **2a**. After a 30 min reaction time, 12% of **1d** was converted to give **5e** in 11% yield. After a 1.5 h reaction, 12% of **5e** was obtained with 14% consumption of **1e**, suggesting that the isomerization reaction of **1d** under these reaction conditions is slower than that occurring in the allylsilylation of **2a**.[14] It seems reasonable that the first step in the isomerization is the addition of a silyl species bearing a full or partial positive charge to the carbon−carbon double bond of **1d** or **1e**, followed by a 1,5-hydride shift to give a carbocation on a ring carbon β to the silyl group and then the regeneration of the positive silyl species from the ring to form a double bond on the other side of the branched carbon.[1−4] The regiospecific isomerization cannot be

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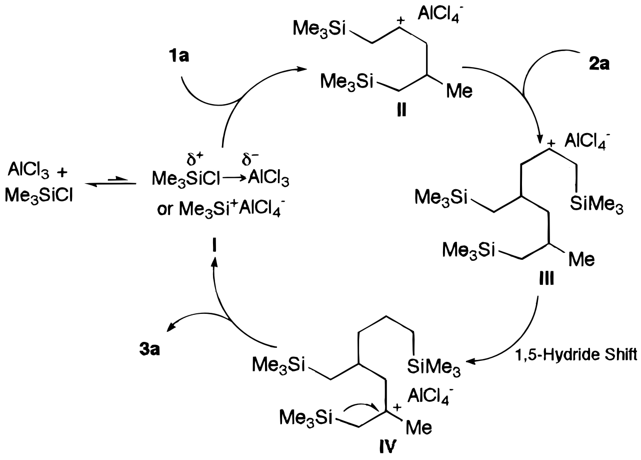
(14) An isomerization reaction of **1d** (220 mg, 1.21 mmol) to **6e** was tested in the presence of anhydrous aluminum chloride (16 mg, 0.12 mmol) and chlorotrimethylsilane (66 mg, 0.60 mmol) and with decane (100 mg) as an internal standard. The progress of the reaction was monitored by GLC.

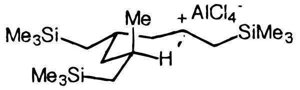
Scheme 1. Catalytic Recycle for the Allylsilylation of 1a and 1,5-Hydride Rearrangement to 3a



explained by an alternative mechanism involving a dehydrosilylation and a rehydrosilylation.[15]

Reaction Mechanism. On the basis of the analogy to the previously reported allylsilylations of alkenes,[1] diallylsilanes,[2] conjugated dienes,[3] and alkynes,[4] we propose a possible mechanism for the intramolecular hydride shifted allylsilylation of **1** to **3**. The reaction pathway of **1a** with **2a** to **3a** as a representative is illustrated in Scheme 1. A silyl intermediate **I** is formed at the beginning stage of the reaction from aluminum chloride and chlorotrimethylsilane[2,3] or from the protodesilylation of allyltrimethylsilane by acids resulting from the reaction of anhydrous aluminum chloride with adventitious water in the reaction mixture.[2,16–18] When the intermediate **I** interacts with **1a**, the trimethylsilyl cation can add to the terminal carbon–carbon double bond of **1a** to generate a new intermediate **II** which is stabilized by the hyperconjugative β stabilization effect of the silyl group.[2,16–18] When the intermediate **II** interacts with the double bond of **2a** to form a new carbon–carbon bond, the secondary carbonium intermediate **III** would be generated. The latter rearranges to more the stable tertiary carbonium intermediate **IV** by means of a 1,5-hydride shift.[18] Finally, **3a** can be produced by the elimination of the silyl cation.

The formation of **3a** as the major product is consistent with the higher stability of the tertiary carbonium intermediate **IV** than the secondary carbonium **III** through a convenient six-membered transition state.[20–22] Although the same stabilization from the secondary to the tertiary carbonium ion will be obtained by a 1,3-hydride shift, no product due to a 1,3-hydride shift was observed. The 1,5-hydride shift through a six-membered transition state is also consistent with the sensitivity of the allylsilylations to the steric hindrance previously observed.



6-Membered-ring transition state

In summary, the reaction of 4-linear alkyl-5-silyl-1-alkenes **1a**–**c** with allyltrimethylsilane (**2a**) in the presence of aluminum chloride catalyst at 40 °C gives the unusual allylsilylation product **3** in moderate yields ranging from 31% to 57% based on **1** used through the intramolecular 1,5-hydride rearrangement reaction on the normal allylsilylated products. When (2-methylallyl)silane (**2b**) was used, normal allylsilylated products as minor products were observed along with the unusual allylsilylation products. The results suggest that the route from allylsilanes to high molecular weight material involves repeated allylsilylations and intramolecular hydrogen rearrangement isomerizations.

Experimental Section

All reactions and manipulations were carried out under prepurified nitrogen using Schlenk techniques. Glassware was flame dried before use. Dried solvents were employed in all reactions. Allyltrimethylsilane was purchased from Gelest, Inc., and used without further purification. (2-Methylallyl)-trimethylsilane[23] and crotyltrimethylsilane[19] were prepared by the methods described in the literature. Anhydrous aluminum chloride was obtained from Aldrich Chemical Co. Other simple chemicals were purchased and used without further purification. To analyze products, gas chromatographic analyses were performed using a Varian 3300 chromatograph equipped with a packed column (10% OV-101 on Chromosorb, W/AW-DMCS 1.5 m × $^{1}/_{8}$ in. o.d.) in conjunction with a flame ionization detector. Proton and carbon-13 NMR spectra were obtained using Verian Gemini 300 or Verian unity Plus 600 proton. In proton spectra, the reference material was $CHCl_3$ in $CDCl_3$ solvent at 7.27 ppm downfield from TMS. In carbon-13 spectra, the reference material was $CDCl_3$ at 77.0 ppm. 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. Gel permeation chromatography (GPC) was carried out on a Waters Millipore gel permeation chromatograph with Ultrastyragel GPC column series (in sequence, 100, 500, 10^3, and 10^4 Å columns) using toluene solvent as an eluent. Molecular weights were calibrated by polystyrene standards. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by the Korea Basic Science Institute, Seoul, Korea. Elemental analyses were performed by the Chemical Analysis Laboratory of the Korea Institute of Science and Technology.

Synthesis of 1a. To a 25 mL sealed stainless steel bomb was introduced 2.36 g (56.1 mmol) of propene, 2.56 g (22.4 mmol) of **2a**, 0.30 g (2.25 mmol) of anhydrous aluminum chloride, and dried *n*-hexane (6 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The reaction solution was washed with 10 mL of ice–water. The upper layer was separated and dried over

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(15) One of the reviewers suggested an alternative mechanism involving a dehydrosilylation and a rehydrosilylation reactions for the isomerization of **1d** to **5e**. This mechanism was ruled out because the expected products, 1-allyl-1-cycloalkene and 3-(trimethylsilyl)propyl-1-cycloalkene, were not observed.

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anhydrous magnesium sulfate. The solvent and unreacted **2a** (1.03 g, 40%) were distilled out. The remained reaction mixture was distilled under vacuum to give **1a** (2.09 g, 13.4 mmol) in 60% yield based on **2a** consumed. Several other byproducts were identified as 0.09 g of **1f** and 0.47 g of unidentified high boilers and polymeric materials.

Allylsilylation of 1a with 2a. To a stirred solution of anhydrous aluminum chloride (0.11 g, 0.82 mmol), chlorotrimethylsilane (0.44 g, 4.10 mmol), and **1a** (1.28 g, 8.19 mmol) in *n*-hexane (7 mL) at 40 °C was added **2a** (1.12 g, 9.80 mmol) during 1 h and stirred for another 3 h. The progress of the reaction was monitored by a GLC at 30 min time intervals. After **2a** had been consumed, 5 mL of water or aqueous sodium bicarbonate was added. Extraction with ether, drying with anhydrous magnesium sulfate, concentration, and fractional distillation (bp 51−53 °C/0.2 mmHg) gave **3a** (0.30 g, 1.11 mmol) in 23% yield based on **1a** consumed. Other byproducts were identified as 6,6-dimethyl-4-((trimethylsilyl)methyl)-6-silahept-1-ene[1] (**1f**, 0.22 g), hexamethyldisiloxane (0.32 g), and 1.10 g of unidentified high boilers and polymeric materials. Unreacted **1a** (0.52 g, 41%) was recovered. Data for **3a**: ^{1}H NMR δ 0.04 (s, 9H), 0.06 (s, 9H) ($\mathrm{SiC}H_3$), 0.48−0.50 (m, 2H, $\mathrm{SiC}H_2\mathrm{CH_2}$), 0.54 (dd, $J = 6.1, 15.1$ Hz, 1H), 0.57 (dd, $J = 7.3, 15.1$ Hz, 1H) ($\mathrm{SiC}H_2\mathrm{CH}$), 1.26−1.35 (m, 4H, $\mathrm{CHC}H_2\mathrm{C}H_2$), 1.62−1.72 (m, 1H, $\mathrm{C}H$), 1.72 (s, 3H, $\mathrm{C}H_3$), 1.93 (dd, $J = 7.2, 13.2$ Hz, 1H), 2.05 (dd, $J = 7.2, 13.5$ Hz, 1H) ($=\mathrm{CC}H_2$), 4.68 (s, 1H), 4.79 (s, 1H) ($=\mathrm{C}H_2$); ^{13}C NMR δ −1.58, −0.47 ($\mathrm{Si}C\mathrm{H_3}$), 16.97 ($\mathrm{Si}C\mathrm{H_2CH_2}$), 20.67 ($C\mathrm{H_3}$), 21.55 ($\mathrm{Si}C\mathrm{H_2CH}$), 22.24 ($\mathrm{CH}C\mathrm{H_2CH_2}$), 31.80 ($C\mathrm{H}$), 40.49 ($\mathrm{CHCH_2}C\mathrm{H_2}$), 46.18 ($=\mathrm{C}C\mathrm{H_2}$), 111.54 ($=C\mathrm{H_2}$), 145.05 ($=C$); mass spectra [*m*/*e* (relative intensity)] 270 (1, (M)$^+$), 255 (1, (M − $\mathrm{CH_3}$)$^+$), 215 (8, (M − $\mathrm{CH_2{=}CMeCH_2}$)$^+$), 127 (26), 99 (29), 73 (100), 59 (12); HRMS (*m*/*e*) calcd for $\mathrm{C_{15}H_{34}Si_2}$ (M)$^+$ 270.2199, found 270.2220. Anal. Calcd for $\mathrm{C_{15}H_{34}Si_2}$: C, 66.58; H, 12.66. Found: C, 66.64; H, 12.75.

Allylsilylation of 1b with 2a. As described in the reaction of **1a** with **2a**, the reaction of 2.96 g (14.9 mmol) of **1b** with 2.04 g (17.9 mmol) of **2a** and 0.81 g (7.50 mmol) of chlorotrimethylsilane using 0.20 g (1.50 mmol) of anhydrous aluminum chloride in *n*-hexane at 40 °C for 5 h gave 2-butyl-8,8-dimethyl-4-((trimethylsilyl)methyl)-8-silanon-1-ene (**3b**) (1.57 g, 5.52 mmol; bp 75−77 °C/0.2 mmHg) in 57% yield based on **1b** consumed. Other byproducts were 0.54 g of 6,6-dimethyl-4-((trimethylsilyl)methyl)-6-silahept-1-ene (**1f**), 0.08 g of **3a**, and 1.04 g of unidentified high boilers and polymeric materials. Unreacted **1b** (1.15 g, 39%) was recovered. Data for **3b**: ^{1}H NMR δ 0.02 (s, 18H), 0.05 (s, 9H) ($\mathrm{SiC}H_3$), 0.47−0.50 (m, 2H, $\mathrm{SiC}H_2\mathrm{CH_2}$), 0.52 (dd, $J = 7.2, 15.0$ Hz, 1H), 0.57 (dd, $J = 6.0, 15.0$ Hz, 1H) ($\mathrm{SiC}H_2\mathrm{CH}$), 0.95 (t, $J = 7.2$ Hz, 3H, $\mathrm{C}H_3$), 1.26−1.39 (m, 6H, $\mathrm{SiC}H_2\mathrm{C}H_2$, $\mathrm{CH_3C}H_2$), 1.44 (quin, $J = 7.2$ Hz, 2H, $\mathrm{CH_3CH_2C}H_2$), 1.69−1.72 (m, 1H, $\mathrm{C}H$), 1.92 (dd, $J = 6.9, 13.8$ Hz, 1H), 2.05 (dd, $J = 7.3, 13.8$ Hz, 1H) ($=\mathrm{CC}H_2\mathrm{CH}$), 2.00 (t, $J = 7.8$ Hz, 2H, $=\mathrm{CC}H_2$), 4.70 (s, 1H), 4.78 (s, 1H) ($=\mathrm{C}H_2$); ^{13}C NMR δ −0.52, −0.40 ($\mathrm{Si}C\mathrm{H_3}$), 14.01 ($C\mathrm{H_3}$), 16.97 ($\mathrm{Si}C\mathrm{H_2CH_2}$), 20.71 ($C\mathrm{H_2}$), 21.69 ($\mathrm{Si}C\mathrm{H_2CH}$), 22.53 ($C\mathrm{H_2}$), 30.06 ($C\mathrm{H_2CH_2CH_3}$), 31.87 ($C\mathrm{H}$), 35.41 ($=\mathrm{C}C\mathrm{H_2CH}$), 40.55 ($C\mathrm{H_2}$), 44.39 ($=\mathrm{C}C\mathrm{H_2}$), 110.34 ($=C\mathrm{H_2}$) 148.97 ($=C$); mass spectra [*m*/*e* (relative intensity)] 312 (2, (M)$^+$), 255 (2), 197 (78), 155 (6), 127 (33), 99 (4), 73 (100, $\mathrm{SiMe_3}$), 59 (6); HRMS (*m*/*e*) calcd for $\mathrm{C_{18}H_{40}Si_2}$ (M)$^+$ 312.2669, found 312.2670. Anal. Calcd for $\mathrm{C_{18}H_{40}Si_2}$: C, 69.14; H, 12.89. Found: C, 69.34; H, 13.01.

Allylsilylation of 1b with 2b. As described in the reaction of **1a** with **2a**, the reaction of 2.96 g (14.9 mmol) of **1b** and 2.30 g (18.0 mmol) of **2b** and 0.81 g (7.50 mmol) of chlorotrimethylsilane, using 0.20 g (1.50 mmol) of anhydrous aluminum chloride in methylene chloride at 40 °C for 10 h, gave 2-butyl-8,8-dimethyl-6-methyl-4-((trimethylsilyl)methyl)-8-silanon-1-ene (**3c**) (1.02 g, 3.12 mmol; bp 81−83 °C/0.2 mmHg) in 36% yield based on **1b** consumed and 6-butyl-8,8-dimethyl-2-methyl-4-((trimethylsilyl)methyl)-silanon-1-ene (**4c**) (0.09 g, 0.28 mmol; bp 79−81 °C/0.2 mmHg) in 3% yield. Other byproducts were 0.18 g of 2,4,4,6,6-pentamethyl-6-silahept-1-ene[1] and 2.34 g of unidentified high boilers and polymeric materials. Unreacted **1b** (1.23 g, 42%) was recovered. Data for **3c** (two mixed diastereomers): ^{1}H NMR δ 0.00 (s, 27H), 0.01 (s, 9H) ($\mathrm{SiC}H_3$), 0.35 (dd, $J = 1.9, 14.7$ Hz, 1H), 0.37 (dd, $J = 10.4, 14.7$ Hz, 1H), 0.37 (dd, $J = 1.4, 14.7$ Hz, 1H), 0.58 (dd, $J = 5.2, 14.7$ Hz, 1H) ($\mathrm{SiC}H_2$), 0.46 (dd, $J = 7.1, 14.7$ Hz, 1H), 0.52 (dd, $J = 6.2, 14.7$ Hz, 1H), 0.57 (dd, $J = 4.7, 14.7$ Hz, 1H), 0.63 (dd, $J = 4.7, 14.7$ Hz, 1H) ($\mathrm{SiC}H_2$), 0.85 (d, $J = 6.6$ Hz, 3H), 0.90 (d, $J = 6.2$ Hz, 3H) ($\mathrm{CHC}H_3$), 0.90 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.3$ Hz, 3H) ($\mathrm{CH_2C}H_3$), 1.05 (ddd, $J = 6.2, 7.6, 13.7$ Hz, 1H), 1.08 (ddd, $J = 5.7, 8.1, 13.7$ Hz, 1H), 1.14−1.19 (m, 2H) ($\mathrm{CHC}H_2\mathrm{CH}$), 1.29−1.35 (m, 4H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.37−1.48 (m, 4H, $\mathrm{CH_3CH_2C}H_2$), 1.64−1.72 (m, 4H, $\mathrm{C}H$), 1.76 (dd, $J = 8.1, 13.7$ Hz, 1H), 2.08 (dd, $J = 6.2, 13.7$ Hz, 1H), 1.91 (br d, 2H) ($=\mathrm{CCH_2C}H$), 1.95 (br t, 4H, $=\mathrm{CC}H_2$), 4.66−4.67 (m, 2H), 4.73−4.74 (m, 2H) ($=\mathrm{C}H_2$); ^{13}C NMR δ (chemical shifts for one of the diastereomers are given in parentheses) −0.54 (−0.43), −0.35 (−0.16) ($\mathrm{Si}C\mathrm{H_3}$), 13.98 ($\mathrm{CH_2}C\mathrm{H_3}$), 22.00 (22.16) ($\mathrm{CH}C\mathrm{H_3}$), 22.53, 22.87 (23.11), 25.64 (25.72), 26.83 (27.00), 29.65 (29.77), 30.02 ($C\mathrm{H_2}$, $C\mathrm{H}$), 35.42 ($\mathrm{C}C\mathrm{H_2CH_2}$), 44.48 (44.72) ($\mathrm{C}C\mathrm{H_2CH}$), 48.61 (48.71) ($\mathrm{CH}C\mathrm{H_2CH}$), 110.46 ($=C\mathrm{H_2}$), 148.84 (148.93) ($=C$); mass spectra [*m*/*e* (relative intensity)] 311 (1, (M − $\mathrm{CH_3}$)$^+$), 229 (7), 155 (2), 115 (26), 99 (14), 73 (100), 59 (10); HRMS (*m*/*e*) calcd for $\mathrm{C_{19}H_{42}Si_2}$ (M)$^+$ 326.2825, found 326.2838. Anal. Calcd for $\mathrm{C_{19}H_{42}Si_2}$: C, 69.85; H, 12.96. Found: C, 70.00; H, 13.15. Data for **4c**: ^{1}H NMR δ 0.04 (s, 18H), 0.05 (s, 9H), 0.06 (s, 9H) ($\mathrm{SiC}H_3$), 0.45 (dd, $J = 6.8, 14.7$ Hz, 2H), 0.49 (dd, $J = 6.8, 15.6$ Hz, 2H), 0.53 (dd, $J = 6.8, 14.7$ Hz, 2H), 0.58 (dd, $J = 6.8, 15.6$ Hz, 2H) ($\mathrm{SiC}H_2$), 0.89−0.96 (m, 6H, $\mathrm{C}H_3$), 1.01 (dd, $J = 6.8, 13.7$ Hz, 1H), 1.21 ($J = 7.2, 13.7$ Hz, 1H), 1.05−1.16 (m, 2H), 1.19−1.35 (m, 12 H) ($\mathrm{C}H_2$), 1.71 (s, 6H, allylic $\mathrm{C}H_3$), 1.53−1.61 (m, 2H, $\mathrm{CH_2C}H\mathrm{CH_2}$), 1.71−1.75 (m, 2H, $=\mathrm{CCH_2C}H$) 1.86 (dd, $J = 7.8, 13.8$ Hz, 1H), 1.92 (dd, $J = 7.2, 13.8$ Hz, 1H), 1.97 (dd, $J = 7.8, 13.8$ Hz, 1H), 2.09 (dd, $J = 6.6, 13.8$ Hz, 1H) ($=\mathrm{CC}H_2$), 4.68 (m, 2H), 4.78 (m, 2H) ($=\mathrm{C}H_2$); ^{13}C NMR δ (chemical shifts for two diastereomers are given in parentheses) −0.51, (−0.37), −0.17, (0.00) ($\mathrm{Si}C\mathrm{H_3}$), 14.17 (14.23) ($\mathrm{CH_2}C\mathrm{H_3}$), 22.02 (22.10) ($\mathrm{C}C\mathrm{H_3}$), 22.25 (22.53), 23.12, 28.41 (28.60), 29.42 (29.52), 45.04 (45.16) ($C\mathrm{H_2}$), 46.28 (46.51) ($=\mathrm{C}C\mathrm{H_2}$), 31.27 (31.39), 36.08 (36.22) ($C\mathrm{H}$), 111.75 ($C\mathrm{H}{=}$), 144.83 (144.93) ($C{=}$); mass spectra [*m*/*e* (relative intensity)] 311 (1) (M − $\mathrm{CH_3}$)$^+$, 271 (4, (M − $\mathrm{CH_2{=}CMeCH_2}$)$^+$), 157 (14), 99 (10), 73 (100), 59 (10); HRMS (*m*/*e*) calcd for $\mathrm{C_{18}H_{39}Si_2}$ (M − $\mathrm{CH_3}$)$^+$ 311.2590, found 311.2594. Anal. Calcd for $\mathrm{C_{19}H_{42}Si_2}$: C, 69.85; H, 12.96. Found: C, 70.09; H, 13.04.

Allylsilylation of 1c with 2a. As described in the reaction of **1a** with **2a**, the reaction of 0.80 g (3.53 mmol) of 4-((trimethylsilyl)methyl)-1-octene (**1c**), and 0.48 g (4.21 mmol) of **2a**, and 0.19 g (1.77 mmol) of chlorotrimethylsilane using 0.05 g (0.35 mmol) of anhydrous aluminum chloride in methylene chloride at 40 °C for 10 h gave 2-hexyl-8,8-dimethyl-4-((trimethylsilyl)methyl)-8-silanon-1-ene (**3d**) (0.27 g, 0.79 mmol; bp 94−96 °C/0.2 mmHg) in 43% yield based on **1c** consumed. Other byproducts were 0.16 g of **1f** and 0.37 g of unidentified high boilers and polymeric materials. Unreacted **1c** (0.38 g, 48%) was recovered. Data for **3d**: ^{1}H NMR δ −0.02 (s, 9H), 0.01 (s, 9H) ($\mathrm{SiC}H_3$), 0.42−0.52 (m, 4H, $\mathrm{SiC}H_2\mathrm{CH_2}$, $\mathrm{SiC}H_2\mathrm{CH}$), 0.87−0.91 (m, 3H, $\mathrm{C}H_3$), 1.29 (m, 10H, $\mathrm{SiCH_2C}H_2\mathrm{C}H_2$, $\mathrm{CH_3C}H_2\mathrm{C}H_2\mathrm{C}H_2$), 1.36−1.41 (m, 2H, $=\mathrm{CCH_2C}H_2$), 1.62−1.67 (m, 1H, $\mathrm{C}H$), 1.84−2.05 (m 4H, $=\mathrm{CC}H_2\mathrm{CH}$, $=\mathrm{CC}H_2$), 4.67 (s, 1H), 4.74 (s, 1H) ($=\mathrm{C}H_2$); ^{13}C NMR δ −1.65, −0.45 ($\mathrm{Si}C\mathrm{H_3}$), 14.11 ($C\mathrm{H_3}$), 16.96 ($\mathrm{Si}C\mathrm{H_2CH_2}$), 20.71 ($C\mathrm{H_2}$), 21.67 ($\mathrm{Si}C\mathrm{H_2CH}$), 22.65, 27.27, 29.15 ($C\mathrm{H_2}$), 31.85 ($C\mathrm{H}$), 35.71 ($=\mathrm{C}C\mathrm{H_2CH}$), 40.54 ($C\mathrm{H_2}$), 44.37 ($=\mathrm{C}C\mathrm{H_2}$), 110.31 ($=C\mathrm{H_2}$) 149.08 ($=C$); mass spectra [*m*/*e* (relative intensity)] 215 (2, (M − $\mathrm{CH_2{=}CMe(CH_2)_5CH_3}$)$^+$), 183 (2), 127 (29), 99 (22), 85 (2), 73 (100), 59 (10). Anal. Calcd for $\mathrm{C_{20}H_{44}Si_2}$: C, 70.53; H, 13.03. Found: C, 70.44; H, 13.18.

Allylsilylation of 1d with 2a. As described in the reaction of **1a** with **2a**, the reaction of 0.96 g (5.26 mmol) of *trans*-1-

(trimethylsilyl)-2-allylcyclopentane (**1d**) with 0.72 g (6.33 mmol) of **2a** and 0.29 g (2.64 mmol) of chlorotrimethylsilane using 0.07 g (0.53 mmol) of anhydrous aluminum chloride in the absence of solvent at 40 °C for 1 h gave 4-(cyclopent-1-enylmethyl)-2,2,8,8-tetramethyl-2,8-disilanonane (**3e**) (0.33 g, 1.11 mmol; bp 67−69 °C/0.2 mmHg) in 25% yield based on **1d** consumed. Other byproducts were 0.18 g (20%) of 3-(cyclopent-2-enyl)-1-(trimethylsilyl)propane (**5e**) (bp 24−26 °C/0.2 mmHg) and 0.86 g of unidentified high boilers and polymeric materials. Unreacted **1d** (0.15 g, 16%) was recovered. Data for **3e**: ^{1}H NMR δ −0.02 (s, 9H), −0.00 (s, 9H) (SiCH$_3$), 0.44−0.46 (m, 2H, SiC*H*$_2$CH$_2$), 0.51 (d, *J* = 6.7 Hz, 2H, SiC*H*$_2$CH), 1.20−1.24, 1.25−1.32 (m, 2H, CHC*H*$_2$CH$_2$), 1.25−1.32 (m, 2H, CHCH$_2$C*H*$_2$), 1.62−1.68 (m, 1H, C*H*), 1.82−1.87 (m, 2H, =CCH$_2$C*H*$_2$), 1.93 (dd, *J* = 6.3, 14.2 Hz, 1H), 2.06 (dd, *J* = 7.5, 14.2 Hz, 1H) (=CC*H*$_2$CH), 2.15−2.23 (m, 2H, =CHC*H*$_2$), 2.29−2.31 (m, 2H, =CC*H*$_2$CH$_2$), 5.32 (br s, 1H, =CH); ^{13}C NMR δ −1.57, −0.47 (Si*C*H$_3$), 16.98, 20.82, 21.96, 23.59, 32.40, 32.49, 35.11, 39.24, 40.85 (*C*H, *C*H$_2$), 124.87 (=*C*H), 143.93 (=*C*); mass spectra [*m*/*e* (relative intensity)] 281 (1, (M − CH$_3$)$^+$), 215 (10), 127 (29), 99 (27), 73 (100), 58 (12). Anal. Calcd for $C_{17}H_{36}Si_2$: C, 68.83; H, 12.23. Found: C, 69.09; H, 12.51. Data for **5e**: ^{1}H NMR δ −0.01 (s, 9H, SiCH$_3$), 0.50−0.53 (m, 2H, SiC*H*$_2$), 1.25−1.46 (m, 4H) (SiCH$_2$C*H*$_2$C*H*$_2$), 1.25−1.46 (m, 1H), 2.03 (ddt, *J* = 4.9, 8.4, 12.6 Hz, 1H) (=CHCHC*H*$_2$), 2.23−2.35 (m, 2H, =CHC*H*$_2$), 2.62−2.65 (m, 1H, C*H*), 5.66−5.73 (m, 2H, C*H*=C*H*); ^{13}C NMR δ −1.64 (Si*C*H$_3$), 16.95 (Si*C*H$_2$), 22.32, 29.88, 31.97, 40.20, 45.43 (*C*H, *C*H$_2$), 129.93, 135.43 (=*C*H); mass spectra [*m*/*e* (relative intensity)] 182 (1), 167 (3), 139 (8), 108 (19), 99 (4), 73(100), 67 (25), 59 (15); HRMS (*m*/*e*) calcd for $C_{11}H_{22}Si$ (M)$^+$ 182.1491, found, 182.1492.

Allylsilylation of 1e with 2a. As described in the reaction of **1a** with **2a**, the reaction of 0.48 g (2.44 mmol) of *trans*-1-(trimethylsilyl)-2-allylcyclohexane (**1e**) with 0.34 g (2.94 mmol) of **2a** and 0.13 g (1.22 mmol) of chlorotrimethylsilane using 0.033 g (0.24 mmol) of anhydrous aluminum chloride in the absence of solvent at 40 °C for 4 h gave 4-(cyclohex-1-enylmethyl)-2,2,8,8-tetramethyl-2,8-disilanonane (**3f**) (0.24 g, 0.77 mmol; bp 87−89 °C/0.2 mmHg) in 35% yield based on **1e** consumed. Other byproducts were 0.06 g (0.32 mmol; 13%) of 3-(cyclohex-2-enyl)-1-(trimethylsilyl)propane[1] (**5f**) and 0.60 g of unidentified high boilers and polymeric materials. Unreacted **1e** (0.043 g, 9%) was recovered. Data for **3f**: ^{1}H NMR δ −0.04 (s, 9H), −0.01 (s, 9H) (SiCH$_3$), 0.41−0.44 (m, 2H, SiC*H*$_2$CH$_2$), 0.47 (dd, *J* = 2.4, 6.7 Hz, 2H, SiC*H*$_2$CH), 1.15−1.20, 1.23−1.31 (m, 2H, CHC*H*$_2$CH$_2$), 1.23−1.29 (m, 2H, CHCH$_2$C*H*$_2$), 1.51−1.56 (m, 2H, =CHCH$_2$C*H*$_2$), 1.58−1.63 (m, 3H) (C*H*, =CCH$_2$C*H*$_2$), 1.79 (dd, *J* = 6.7, 13.4 Hz, 1H), 1.87 (dd, *J* = 7.3, 13.4 Hz, 1H) (=CC*H*$_2$CH), 1.84−1.89 (m, 2H, =CC*H*$_2$CH$_2$), 1.98−1.99 (m, 2H, =CHC*H*$_2$CH$_2$), 5.35 (br s, 1H, =C*H*); ^{13}C NMR δ −1.54, −0.45 (Si*C*H$_3$), 16.98, 20.76, 21.70, 23.13, 25.38, 28.36, 31.75, 40.58, 46.56 (*C*H, *C*H$_2$), 122.55 (=*C*), 136.90 (=*C*H); mass spectra [*m*/*e* (relative intensity)] 295 (1, (M − CH$_3$)$^+$), 215 (10), 153 (2), 127 (31), 99 (27), 73 (100), 58 (13); HRMS (*m*/*e*) calcd for $C_{18}H_{38}Si_2$ (M)$^+$ 310.2512, found 310.2512. Anal. Calcd for $C_{18}H_{38}Si_2$: C, 69.59; H, 12.33. Found: C, 69.41; H, 12.38.

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Supporting Information Available: Figures showing NMR spectra and a HRMS for **3b** (6 pages). Ordering information is given on any current masthead page.

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