Aluminum Chloride-Catalyzed Intramolecular Allyl-Migration Reaction of Allyl(chloromethyl)silanes and Trapping of the Intermediate with Allyltrimethylsilane

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Allyl(chloromethyl)diorganosilanes [$CH_2{=}CHCH_2SiR^1R^2(CH_2Cl)$, R^1 = Me, Ph; R^2 = Me, Ph, p-ClC_6H_4] in the presence of aluminum chloride undergo an allyl rearrangement reaction with allylic inversion to afford (3-butenyl)diorganochlorosilanes at room temperature. When allyltrimethylsilane was added to the reactions, the intermediate was trapped to give 1,1-dimethyl-3-(2-trimethylsilylmethyl-4-pentenyl)silacyclopentane (**4**) along with 3-(butenyl)-dimethylchlorosilane in 40% and 18% yields, respectively. The formation of **4** can be explained by the addition reaction of allyltrimethylsilane to 1-silacyclopent-3-yl cation produced by the intramolecular cyclization of (allyl)silylmethyl cation intermediate derived from the interaction of the chloromethyl group with aluminum chloride catalyst, followed by desilylation reaction.

Introduction

Organosilicon compounds containing alkenyl or chloroalkyl groups undergo a variety of interesting and useful reactions catalyzed by Lewis acids.[1,2] Examples include the allylsilylation of unsaturated hydrocarbons with allylsilanes,[1b,2b−f] the Friedel−Crafts alkylation[1a] of aromatic compounds with alkenylchlorosilanes[2a,g,h] and (chloroalkyl)chlorosilanes,[2i−m] and the 1,2-migration reaction of a vinyl or allyl group from silicon to an α-carbon atom of (chloromethyl)alkenylsilanes.[2h,3] In those rearrangement reactions, the alkenyl group migrates to the carbocation produced by the interaction of the chloromethyl group with aluminum chloride to afford rearrangement products. Ethylaluminum dichloride also is a good catalyst for the rearrangement of (chloromethyl)organosilanes.[3d]

We recently reported the alkylation and allylsilylation reactions of allylsilanes in the presence of aluminum chloride catalyst.[1] The reactivity and reaction modes of allylsilanes are variable, depending on the number (n) of chlorine substituent(s) on the silicon atom of the allylchlorosilanes ($CH_2{=}CHCH_2SiMe_{3-n}Cl_n$). Allylsilanes containing one or more chlorine substituents on the silicon atom readily react with aromatic compounds to give alkylation products, 2-aryl-1-silylpropanes.[1b,2a] However, allyltrimethylsilane, which has no chlorine atom on the silicon atom, in benzene solvent dimerizes to give the allylsilylation product 5-(trimethylsilyl)-4-(trimethylsilylmethyl)-1-pentene, but no alkylation products.[1a] On the basis of our previous studies described above, allyl(chloromethyl)silanes containing two reactive sites of chloromethyl and allyl groups on the same silicon atom should undergo two competing reactions of allylsilylation and allyl rearrangement from the silicon to the α-carbon atom in the presence of a Lewis acid catalyst. To study these reactions, a variety of allyl(chloromethyl)silanes **1** have been prepared and treated with aluminum chloride catalyst. Interestingly, only allyl rearrangement products were obtained as the major products, but no allylsilylation products were produced. Herein we report the results of allyl rearrangement reactions and the trapping reaction of the intermediates involved in the reactions using allyltrimethylsilane.

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Table 1. Conditions and Yields of Rearrangement Reactions of 1a

reaction conditions[a]			products (%)[c]	
solvent	$AlCl_3$[b] (mol %)	reaction time (min)	**2a**	**3a**
hexane	5	60	trace[d]	
hexane	10	20	82 (75)	10 (9)
hexane	20	10	58	17
hexane	100	10	46	18
CH_2Cl_2	10	10	19	34
CH_2Cl_2	20	10	2	43
neat	10	20	49	20

[a] The reaction was carried out at room temperature. [b] Amount of $AlCl_3$ used was based on reactant **1a**. [c] GLC yields (isolation yield in parentheses). [d] Reactant **1a** remained unreacted.

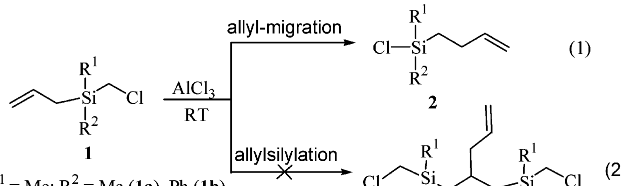
Table 2. Substituent Effects of 1 in $AlCl_3$-Catalyzed Reaction[a]

reactant **1** $CH_2{=}CHCH_2SiR^1R^2(CH_2Cl)$			reaction time (h)	products (%)[c]	
1[b]	R^1	R^2		**2**	**3**
1a (−)	Me	Me	0.3[d]	**2a** (75)	**3a** (9)
1b (−)	Me	Ph	1.5	**2b** (62)	**3b** (15)
1c (63)	Me	p-ClC_6H_4	4.0	**2c** (7)	**3c** (17)
1d (95)	Me	Cl	6.0	**2d** (−)	**3d** (−)
1e (−)	Ph	Ph	2.5	**2e** (59)	**3e** (5)
1f (99)	Cl	Cl	6.0	**2f** (−)	**3f** (−)

[a] The reaction was carried out in the presence of 10 mol % $AlCl_3$ in hexane at room temperature. [b] Unreacted **1** in parentheses. [c] Isolated yields. [d] Reaction time was 20 min.

Results and Discussion

Substituent Effects of Allyl(chloromethyl)silanes 1. As an example of allyl(chloromethyl)silanes, allyl(chloromethyl)dimethylsilane (**1a**) was treated with Lewis acids in organic solvents such as hexane and dichloromethane. The reaction gave the allyl rearrangement product 3-butenyldimethylchlorosilane (**2a**), as shown in eq 1. No allylsilylation product was detected (eq 2). In this reaction, the deallylation product, (chloromethyl)dimethylchlorosilane (**3a**), was formed as a minor product. This result is consistent with an intramolecular rearrangement reaction that is more favorable than the intermolecular allylsilylation. No reactions occurred when other Lewis acids such as $TiCl_4$, $HfCl_4$, $ZrCl_4$, and $SnCl_4$ were used under the same conditions. The results obtained in the reactions with **1a** in the presence of aluminum chloride catalyst are summarized in Table 1.



R^1 = Me; R^2 = Me (**1a**), Ph (**1b**),
p-PhCl (**1c**), Cl (**1d**)
R^1 = Ph; R^2 =Ph (**1e**)
R^1 = Cl; R^2 =Cl (**1f**)

As shown in Table 1, the compound **2a** was obtained as the major product in 82% GLC yield in the presence of 10 mol % aluminum chloride as a catalyst in hexane solvent along with the deallylation product **3a** (10%). The yield of **2a** decreased to 19% and 49% in dichloromethane and in the absence of solvents, respectively. The decomposition product **3a** increased to 34% and 20%, indicating that a nonpolar solvent favors the rearrangement reaction. Although dichloromethane was expected to stabilize the carbocation intermediates produced by the interaction of the chloromethyl group of **1a** and aluminum chloride, the deallylation occurred preferentially.

Regarding the amount of catalyst, the reaction was too slow in the presence of 5 mol % aluminum chloride, but gave the highest yield with 10 mol %. On increasing the quantity of catalyst to 20 mol % or more, the yield of **2a** decreased again and **3a** increased drastically. Thus, 10 mol % aluminum chloride and hexane solvent were used for the reaction of other allyl(chloromethyl)silanes. The results obtained from the rearrangement reaction of allyl(chloromethyl)silanes **1a**−**f** in the presence of aluminum chloride catalyst at room temperature are summarized in Table 2.

As shown in Table 2, allyl(chloromethyl)diorganosilanes **1a**−**c**,**e** in the presence of aluminum chloride catalyst at room temperature underwent 1,2-allyl rearrangement reaction to give (3-butenyl)diorganosilanes **2a**−**c**,**e**, respectively, along with the deallylation products, (chlomethyl)diorganochlorosilanes **3a**−**c**,**e**. However, allyl(chloromethyl)silanes having chlorine atom(s) on the silicon atom, **1d** and **1f**, did not produce similar results, but slowly converted to polymeric materials. The formation of deallylation product **3** could be explained by the allylic Si−C bond cleavage[4] of **1** by a small amount of hydrogen chloride, which is formed from the reaction of anhydrous aluminum chloride with moisture possibly present in the reactants.[2b,5] These results clearly indicate that electron-withdrawing substituents such as chlorine or a chloroaryl group retard the reaction.

The reaction of (2-methyl-2-propenyl)dimethyl(chloromethyl)silane (**1g**) containing a methallyl group under the same reaction conditions as above was complete within 10 min to give (3-methyl-3-butenyl)dimethylchlorosilane (**2g**)[15] in 65% yield, as shown in eq 3. The reaction of **1g** is faster than that of **1a**, suggesting that an electron-donating methyl substituent on the second carbon of the allyl group of the reactant facilitates the allyl rearrangement reaction.

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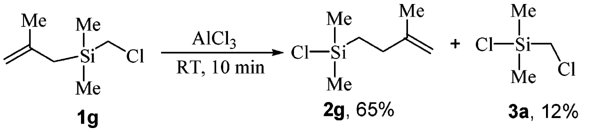
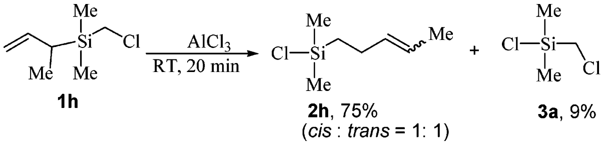


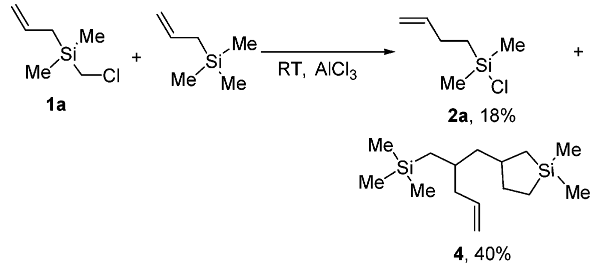
(3)

Allylic Inversion. (1-Methyl-2-propenyl)(chloromethyl)dimethylsilane (**1h**) underwent allyl rearrangement reaction in the presence of aluminum chloride catalyst at room temperature to give (3-pentenyl)dimethylchlorosilane (**2h**) with allylic inversion and the deallylation product **3a** in 75% and 9% isolated yields (eq 4), respectively. The formation of compound **2h** can be explained by a three-step reaction (Scheme 1): (1) An α-carbocation intermediate **A** is generated by the interaction of reactant **1h** with aluminum chloride. (2) An intramolecular electrophilic addition of the cation to the allyl group generates a β-carbocation intermediate via C−C bond formation. (3) Finally, a silicon−carbon bond cleavage reaction of the latter intermediate by a chloride ion occurs to give the product **2h**.



(4)

Trapping Reaction of the Intermediates with Allyltrimethylsilane. To trap the reaction intermediates involved in the 1,2-allyl rearrangement reaction of compounds **1**, allyltrimethylsilane was used as a trapping agent. When reactant **1a** was reacted with a 3-fold excess of allyltrimethylsilane at room temperature in the presence of aluminum chloride catalyst, a diastereoisomeric mixture of 1,1-dimethyl-3-(2-trimethylsilylmethyl-4-pentenyl)silacyclopentane (**4**) as the trapping products and (3-butenyl)dimethylchlorosilane as the allyl rearrangement product were obtained in 40% and 18% yields, respectively (eq 5).



(5)

The formation of **4** can be explained by the successive addition reaction of two molecules of allyltrimethylsilane to the 1-silacyclopent-3-yl cation intermediate (**B** in Scheme 1) arising from the intramolecular cyclization of (allyl)silylmethyl cation (**A**), followed by desilylation as described in previously reported allylsilylation reactions.[1]

Mechanism for the Formation of 2 from 1. On the basis of our results, we propose a mechanism for the formation of **2** through the trapping reaction of the reaction intermediate **B** by allyltrimethylsilane in the presence of aluminum chloride catalyst as outlined in Scheme 1. In this mechanism, the reactant **1a** is described as a representative compound among allyl(chloromethyl)silanes. Aluminum chloride interacts with **1a** to give a α-carbocation intermediate **A**. The intermediate **A** is intramolecularly cyclized to give the more stable secondary carbocation intermediate **B** in which the β-carbocation is stabilized by the electron-donating silyl group through the $\sigma-\pi$ conjugation known as β-stabilization.[8−11] This carbocation intermediate **B** undergoes a Si−C bond-cleavage reaction to give compound **2** or electrophilic attack to the π-bond of the allyltrimethylsilane to generate new carbocation intermediate **C**. The intermediate **C** participates in another electrophilic addition to allyltrimethylsilane to form a new carbocation intermediate **D**, followed by a desilylation reaction to give compound **4** and trimethylchlorosilane and regenerate aluminum chloride. Aluminum chloride is recycled as a catalyst in this reaction system. The interaction between a carbocation and allylsilane in allylsilylation reactions to form a new C−C bond has been well documented in our previous report.[1]

Other ω-Alkenyl(chloromethyl)silanes. This rearrangement reaction was extended to ω-alkenyl(chloromethyl)silanes such as (chloromethyl)dimethyl(vinyl)silane and 3-butenyl(chloromethyl)dimethylsilane. Each compound was stirred under the same reaction conditions using 10 mol % aluminum chloride, but a rearrangement reaction did not take place, in contrast to the previous report.[6] It is well known that (alkyl- or aryl-substituted vinyl)(chloromethyl)dimethylsilanes containing an alkyl-substituted vinyl group give a vinyl group-migrated product of (alkyl- or aryl-substituted allyl)dimethylchlorosilanes and/or cyclopropyldimethylchlorosilanes.[7]

Experimental Section

General Procedures. 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. Aluminum chloride and allyltrimethylsilane were purchased from Aldrich Chemical Co. and used without further purification. Allyl(chloromethyl)silanes such as allyl(chloromethyl)dimethylsilane (**1a**),[12] allyl(chloromethyl)methylphenylsilane (**1b**),[11,12] allyl(chloromethyl)(*p*-chlorophenyl)methylsilane (**1c**),[13] allyl(chloromethyl)methylchlorosilane (**1d**),[14] allyl(chloromethyl)diphenylsilane (**1e**), allyl(chloromethyl)dichlorosilane (**1f**), and allyl(chloromethyl)silanes **1g**[15] and **1h**[16,17] were prepared by Grignard reaction, starting from (chloromethyl)trichlorosilane. Hexane was dried by distillation from sodium benzophenone ketyl prior to use. The reaction products were analyzed by gas liquid chromatography (GLC) using a packed column (10% SE-30 or SE-54 on 80−100 mesh chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. The progress of the reactions was monitored by GLC in the time interval of 10 min. Samples for characterization were purified by preparative GLC using a Donam system series DS 6200 gas chromatograph with a thermal conductivity detector and a 4 m by 1/8 in. stainless steel column packed with 20% OV-101 on 80−100 mesh chromosorb P/AW. NMR spectra were recorded on a Varian Gem 300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C) or a Bruker Avance 300 spectrometer in CDCl$_3$ solvent. Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS. Elemental analyses were performed by the Chemical Analysis Center at the Korea Institute of Science and Technology.

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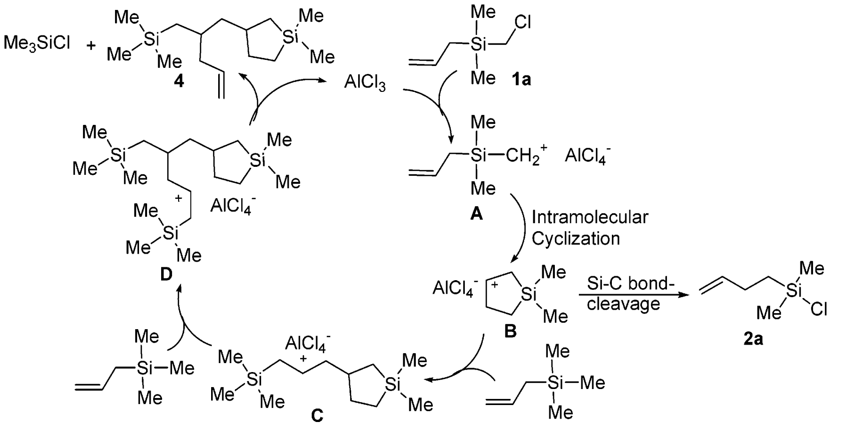
Scheme 1. Mechanism for the Formation of 2a and Trapping Reaction with Allyltrimethylsilane



Synthesis of 1e. To a stirred solution of (chloromethyl)trichlorosilane (8.0 g, 43.5 mmol) in diethyl ether (40 mL) was added dropwise phenylmagnesium chloride diluted to 2 M in THF (87 mmol, 43.5 mL) for 30 min. The reaction mixture was stirred for 3 h at room temperature. Then allylmagnesium chloride was diluted to 2 M in THF (22 mL, 44 mmol) and added to the reaction mixture over a 5 min period. The reaction mixture was stirred another 2 h at room temperature. Next, distilled water (2 mL) was added. Solvents were removed by evaporation under reduced pressure, and the residue was dissolved in diethyl ether (150 mL) and water (200 mL). The organic layer was separated and combined with diethyl ether (two 20 mL portions) used for extracting product from the water layer. The reaction mixture was fractionally distilled under reduced pressure to give product **1e** (8.0 g, bp 144 °C/0.5 mmHg) in 67% yield. Data for **1e**: ^{1}H NMR (300 MHz) δ 2.35, 2.38 (d, $J = 7.9$ Hz, 2H, SiCH_2), 3.39 (s, 2H, CH_2Cl), 5.01−5.14 (m, 2H, =CH_2), 5.87−6.01 (m, 1H, =CH), 7.43−7.67 (m, 10H, phenyl-*H*); ^{13}C NMR (75 MHz) δ 18.80 (SiCH_2), 27.04 (CH_2Cl), 115.38 (=CH_2), 132.63 (allylic-*C*H), 127.97, 130.03, 132.71, 135.02 (phenyl-*C*). Anal. Calcd for $C_{16}H_{17}ClSi$: C, 70.43; H, 6.28. Found: C, 70.47; H, 6.34.

General Procedure for the Allyl-Migration Reaction. To a stirred solution of 2.34 g (16 mmol) of **1a** and 20 mL of dried *n*-hexane in a 50 mL two-necked round-bottomed flask equipped with a reflux condenser and gas inlet tube at room temperature was added 0.21 g (1.6 mmol) of anhydrous aluminum chloride under dry nitrogen. The mixture was stirred for 20 min at room temperature, and the solution was quenched with 1.22 g (8 mmol) of phosphorus oxychloride. The $POCl_3$−$AlCl_3$ complexed salt was removed by filtration. The filtrate was bulb-to-bulb distilled under vacuum. The mixture was distilled under vacuum to give 3-butenylchlorodimethylsilane, **2a** (1.75 g, bp 128−130 °C), in 75% yield. Other byproducts were also obtained by vacuum distillation and identified as (chloromethyl)chlorodimethylsilane (12%) and unidentified high boiling and polymeric material (10%). The spectroscopic data of **2a** are identical to those reported in the literature.[18]

Allyl-Migration Reaction of 1b. Using the reaction procedure described above, 3-butenylmethylphenylchlorosilane (**2b**, bp 80−84 °C/10 Torr, 1.24 g; 62% yield) was obtained from the reaction of 2.0 g (9.5 mmol) of **1b** using 0.13 g (0.97 mmol) of anhydrous aluminum chloride in *n*-hexane. Another byproduct was identified as **3b** (11%). Data for **2b**:[19] ^{1}H NMR (300 MHz) δ 0.68 (s, 3H, SiCH_3), 1.15−1.26 (m, 2H, SiCH_2CH$_2$), 2.16−2.23 (m, 2H, SiCH$_2$$CH_2$), 4.91−5.04 (m, 2H, =$CH_2$), 5.80−5.94 (m, 1H, =$CH$), 7.40−7.63 (m, 5H, phenyl-H); ^{13}C NMR (75 MHz) δ 0.42 (SiCH_3), 17.14 (SiCH_2CH$_2$), 26.99 (SiCH$_2$$CH_2$), 113.97 (=$CH_2$), 130.35 (=$CH$), 128.09, 133.33, 135.19, 140.09 (phenyl-C).

Allyl-Migration Reaction of 1c. Using the reaction procedure described above, 3-butenyl-*p*-chlorophenyl(methyl)chlorosilane (**2c**, 0.14 g, 7%) was obtained from the reaction of **1c** (2.0 g, 8.2 mmol) using 0.13 g (0.97 mmol) of anhydrous aluminum chloride in *n*-hexane. Another byproduct was identified as **3c** (17%). Data for **2c**: bp 62 °C/0.12 Torr; ^{1}H NMR (300 MHz) δ 0.67 (s, 3H, SiCH_3), 1.13−1.18 (m, 2H, SiCH_2CH$_2$), 2.14−2.21 (m, 2H, SiCH$_2$$CH_2$), 4.91−5.04 (m, 2H, =$CH_2$), 5.77−5.92 (m, 1H, =$CH$), 7.38 (m, 2H), 7.54 (m, 2H, phenyl-H); ^{13}C NMR (75 MHz) δ 0.42 (SiCH_3), 17.05 (SiCH_2), 26.90 (SiCH$_2$$CH_2$), 113.84 (=$CH_2$), 130.35 128.38, (=$CH$), 133.49, 134.72, 136.81, 139.82 (=CH, phenyl-*C*). Anal. Calcd for $C_{11}H_{14}Cl_2Si$: C, 53.88; H, 5.75. Found: C, 53.61; H, 5.82.

Allyl-Migration Reaction of 1e. Using the reaction procedure described above, 3-butenylchlorodiphenylsilane, **2e**[20] (1.18 g, bp 110−114 °C/10 Torr, 59% yield), was obtained from the reaction of 2.0 g (7.3 mmol) of **1e** using 0.09 g (0.73 mmol) of anhydrous aluminum chloride in *n*-hexane. Another byproduct was identified as **3e** (12%). Data for **2e**: ^{1}H NMR (300 MHz) δ 1.44−1.49 (m, 2H, SiCH_2CH$_2$), 2.21−2.29 (m, 2H, SiCH$_2$$CH_2$), 4.92−5.06 (m, 2H, =$CH_2$), 5.84−5.97 (m, 1H, =$CH$), 7.41−7.75 (m, 10H, phenyl-H); ^{13}C NMR (75 MHz) δ 16.01 (SiCH_2CH$_2$), 27.37 (SiCH$_2$$CH_2$), 114.07 (=$CH_2$), 128.58, 131.02, 131.77, 133.86, 134.77 (=CH, phenyl-C).

Allyl-Migration Reaction of 1g. Using the reaction procedure described above, (3-methyl-3-butenyl)dimethylchlorosilane, **2g**[15] (1.3 g; bp 125−127 °C, 65%), was obtained from the reaction of 2.0 g (12.2 mmol) of **1g** using 0.16 g (1.2 mmol) of anhydrous aluminum chloride in *n*-hexane. Another byproduct was identified as **3a** (11%). Data for **2g**: ^{1}H NMR (300 MHz) δ 0.42 (s, 6H, Si(CH_3)$_2$), 0.94−1.00 (m, 2H, SiCH_2CH$_2$), 1.73 (s, 3H, =CCH_3), 2.07−2.13 (m, 2H, SiCH$_2$$CH_2$), 4.70−4.71 (m, 2H, =$CH_2$); ^{13}C NMR (75 MHz) δ 1.61 (Si(CH_3)$_2$), 17.06 (SiCH_2CH$_2$), 22.14 (SiCH$_2$$CH_2$), 30.88 (=C$CH_3$), 109.10 (=$CH_2$), 147.12 (=$CCH_3$).

Allyl-Migration Reaction of 1h. A reaction procedure similar to that above was applied except that yields were determined by GLC using *n*-dodecane internal standard. The reaction of 0.5 g (3.1 mmol) of **1h** using 0.04 g (0.3 mmol) of anhydrous aluminum chloride and *n*-dodecane (0.1 g) in *n*-hexane for 20 min gave a 1:1 isomeric mixture of *cis*- and *trans*-(3-pentenyl)dimethylchlorosilane (**2h**) and **3a** in 75% and 9% yields.

Data for the mixture of both isomeric *cis*- and *trans*-**2h** (chemical shifts of *trans*-**2h** are given in parentheses): ^{1}H NMR (300 MHz) δ 0.40 (0.41) (s, 6H, SiCH_3); 0.87−0.92 (m, 2H, SiCH_2), 1.60−1.64 (m, 3H, CH$_3$), 2.06−2.20 (m, 2H, allylic-

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CH_2), 5.38−5.45 (m, 2H, =CH); ^{13}C NMR (75 MHz) δ 1.79 (SiCH$_3$), 12.64 (17.75) (CH$_3$), 19.04 (18.85) (SiCH$_2$), 20.28 (25.91) (allylic-CH$_2$), 1,23.34 (124.20), 132.15 (132.79) (=CH); HRMS for both isomers (*m*/*z*), calcd for $C_7H_{15}ClSi$ (M^+), 162.0632; found, 162.0634. Anal. Calcd for $C_7H_{15}ClSi$: C, 51.66; H, 9.29. Found: C, 51.43; H, 9.30.

Reactions of Allyl(chloromethyl)chlorosilanes 1d and 1f. Under the same reaction conditions described above, the 5% and 2% consumption of compounds **1d** and **1f** occurred but gave decomposed compounds methyl(chloromethyldichlorosilane (4%) and (chloromethyltrichlorosilane (1%), respectively, from the analysis of GLC data. Allyl rearrangement products were not observed.

Reaction of 1a with Allytrimethylsilane. Using the reaction procedure described above, the reaction of **1a** (1.0 g, 6.7 mmol) with allyltrimethylsilane (2.26 g, 20.0 mmol) in the presence of aluminum chloride (0.09 g, 0.67 mmol) at room temperature for 2.5 h gave 1,1-dimethyl-3-(2-trimethylsilylmethyl-4-pentenyl)silacyclopentane (**4**, 0.72 g, 40%), **2a** (0.18 g), and **3a**, (12%). A major product of two diastereomeric components **4** was isolated by column chromatography on alumina (3.0 × 100.0 cm) using *n*-hexane eluent. Data for **4**: ^{1}H NMR (600 MHz) δ −0.03 (s, 6H, Si(CH_3)$_2$), −0.02 (s, 9H, Si(CH_3)$_3$), 0.36−0.40 (dd, *J* = 12.03 Hz, 1H), 0.70−0.76 (m, 1H) (ring-SiCH_2), 0.66−0.69 (m, 2H, ring-SiCH_2), 0.52−0.53 (dd, *J* = 6.77 Hz, 2H, SiCH_2), 1.27−1.30 (m, 1H), 1.74−1.77 (m, 1H) (ring-CH_2), 1.48−1.60 (overlapped with allylic-CH_2, 2H, 2CH), 0.89−0.95 (m, 1H), 1.60−1.62 (overlapped with 2CH, 1H) (allylic-CH_2), 1.96−2.00 (m, 2H, CH_2), 4.93−4.98 (m, 2H, =CH_2), 5.71−5.75 (m, 1H, =CH); ^{13}C NMR (150 MHz) δ −1.63, −1.31 (ring-Si(CH$_3$)$_2$), −0.73 (Si(CH$_3$)$_3$), 13.26, 23.18 (ring-SiCH$_2$), 32.77 (ring-CH$_2$), 27.45 (SiCH$_2$), 35.21, 38.63 (CH), 46.59, 47.69 (allylic-CH$_2$, CH$_2$), 115.48 (=CH$_2$), 137.79 (=CH); HRMS (*m*/*z*) calcd for $C_{15}H_{32}Si_2$ (M^+), 268.2043; found, 268.2040. Anal. Calcd for $C_{15}H_{32}Si_2$: C, 67.08; H, 12.01. Found: C, 67.20; H, 12.39.

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