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Silicon−Carbon Unsaturated Compounds. 61. Reactions of Silenes Produced Thermally from Acylpolysilanes with (Trimethylsilyl)acetylene

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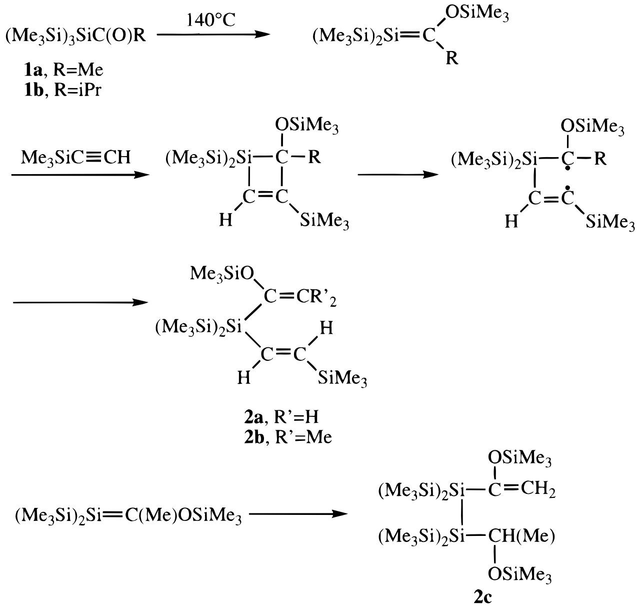
Summary: The cothermolysis of acetyl- and isopropionyltris(trimethylsilyl)silanes with (trimethylsilyl)acetylene afforded the ring-opened products derived from [2 + 2] cycloadducts, while a similar thermolysis of pivaloyl- and adamantoylpolysilanes produced [2 + 2] cycloadducts and the ring-opened products.

Introduction

It is well-known that acylpolysilanes are useful precursors for the synthesis of silenes. To date, numerous examples for the synthesis and reactions of silenes, which are produced by the photolysis[1−3] of acylpolysilanes or by way of a Peterson-type reaction of acylpolysilanes,[4−7] have been reported. Recently, however, it has been demonstrated that the thermolysis of acylpolysilanes also offers a convenient method for the synthesis of silenes.[8−12]

The first example of the thermal production of the silene from the acylpolysilane was reported by Brook et al.[8] They found that the cothermolysis of pivaloyltris(trimethylsilyl)silane with alcohols or phenylpropyne produced adducts that were derived from the reaction of the silene that was generated from the acylpolysilane with trapping agents. Recently, we have found that the thermolysis of various acylpolysilanes proceeds cleanly to give the respective silenes, and the silenes thus formed readily react with olefins, dienes, and carbonyl compounds to give adducts.[10,12] Brook et al. have also reported the thermolysis of α,β-unsaturated acylsilane that affords a siladiene intermediate.[11] In this paper we report the reactions of the silenes that are produced under thermal conditions with trimethylsilylacetylene.

Scheme 1



Results and Discussion

When a mixture of acetyltris(trimethylsilyl)silane (**1a**) and 3 equiv of (trimethylsilyl)acetylene was heated in a degassed, sealed tube at 140 °C for 24 h, (*E*)-1-{[1-(trimethylsiloxy)ethenyl]bis(trimethylsilyl)silyl}-2-(trimethylsilyl)ethene (**2a**) was produced in 51% yield, in addition to 31% of the unchanged starting compound **1a** (Scheme 1). In this reaction, product **2c**, which was probably produced from radical dimerization of the silenes that were generated thermally from **1a**, followed by disproportionation of the resulting carbon radicals, was obtained in 8% yield. It was reported that the thermolysis of **1a** in the absence of a trapping agent affords this dimer in high yields.[8,10] A similar reaction of isopropionyltris(trimethylsilyl)silane (**1b**) with 1.1 equiv of (trimethylsilyl)acetylene proceeded cleanly to give a product similar to **2a**, (*E*)-1-{[2-methyl-1-(trimethylsiloxy)-1-propenyl]bis(trimethylsilyl)silyl}-2-(trimethylsilyl)ethene (**2b**), in 60% yield, along with 31% of

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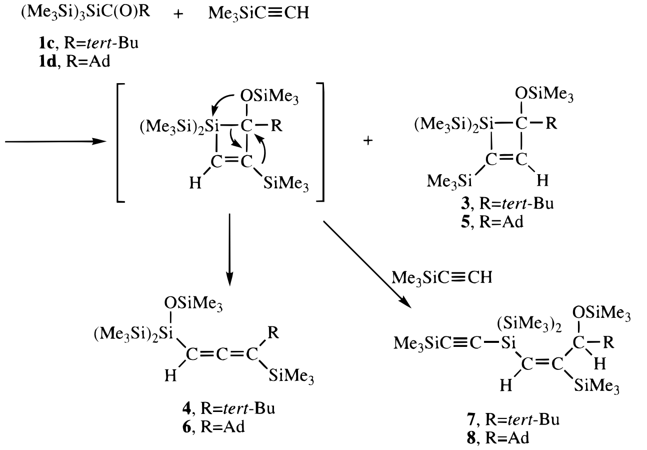
Scheme 2



the unreacted starting compound **1b**. No other volatile products were detected in the reaction mixture.

The structures of **2a** and **2b** were confirmed by spectrometric and elemental analysis (see Experimental Section). ^{13}C NMR spectra for **2a** and **2b** show four signals due to the sp^2-hybridized carbon atoms, indicating the presence of two ethenyl groups in the molecule. The proton coupling constants in the [2-(trimethylsilyl)ethenyl]silyl moieties for **2a** and **2b** were 22 and 23 Hz, respectively, showing that both **2a** and **2b** must have trans configurations.

The formation of products **2a** and **2b** can be understood best in terms of a [2 + 2] cycloaddition of the silenes that were produced thermally from acylpolysilanes **1a** and **1b** with (trimethylsilyl)acetylene, followed by the homolytic scission of a carbon−carbon bond in the silacyclobutene ring and then disproportionation of the resulting diradical. The fact that no regioisomers were detected in the reaction mixtures indicates that [2 + 2] cycloaddition of the silene and (trimethylsilyl)acetylene proceeds with high regiospecificity.

In contrast to **1a** and **1b**, the cothermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane, **1c** and **1d**, with (trimethylsilyl)acetylene produces two products, a [2 + 2] cycloadduct and ring-opened product. Thus, treatment of **1c** with an excess of (trimethylsilyl)acetylene at 140 °C for 24 h gave 2-*tert*-butyl-2-(trimethylsiloxy)-1,1,4-tris(trimethylsilyl)-1-silacyclobut-3-ene (**3**) and 1-*tert*-butyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1-(trimethylsilyl)-1,2-propadiene (**4**) in 42% and 33% yields, respectively, together with 15% of the unchanged starting compound **1c** (Scheme 2). In this reaction, a 7% yield of a 1:2 adduct (**7**) composed of one molecule of **1c** and two molecules of (trimethylsilyl)acetylene was produced. Products **3** and **4** are unstable toward moisture and oxygen, and the products gradually decompose on a recycling HPLC column. The purity of product **3** that was isolated by recycling HPLC was determined to be 80%, while product **4** was isolated as a 1.8:1 mixture composed of **4** and the 1:2 adduct **7**, which was assigned as (*E*)-3-*tert*-butyl-3-(trimethylsiloxy)-2-(trimethylsilyl)-1-[bis(trimethylsilyl)((trimethylsilyl)ethynyl)silyl]-1-propene by NMR spectrometric analysis. The DEPT NMR spectrum of **7** reveals the presence of two methine carbons at 84.0 and 134.6 ppm, and its COSY NMR spectrum shows that the protons at 4.93 and 5.71 ppm couple with the carbon atoms at 84.0 and 134.6 ppm, respectively. These results are wholly consistent with the structure proposed for **7**.

A similar treatment of **1d** with the acetylene again gave two products analogous to **3** and **4**, 2-adamantyl-2-(trimethylsiloxy)-1,1,4-tris(trimethylsilyl)-1-silacyclobut-3-ene (**5**) and 1-adamantyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1-(trimethylsilyl)-1,2-propadiene (**6**), in 49% and 38% yields, respectively, along with 3% of the starting compound **1d**. A 1:2 adduct (**8**) that was assigned as (*E*)-3-adamantyl-3-(trimethylsiloxy)-2-(trimethylsilyl)-1-[bis(trimethylsilyl)((trimethylsilyl)ethynyl)silyl]-1-propene, similar to the structure of **7**, was also obtained in 7% yield. Products **5** and **6** are also unstable, but more stable than products **3** and **4**. Again, **5** and **6** decompose gradually on a HPLC column. The purities of the isolated products are calculated to be 87% for **5** and 89% for **6**. The structures of products **3**−**6** were verified by spectrometric analysis. The location of the substituents on the silacyclobutene ring for **3** and **5** was confirmed by NOE-FID difference experiments at 270 MHz. For **3**, irradiation of the *tert*-butyl protons at 1.05 ppm resulted in the enhancement of a proton (6.07 ppm) on the sp^2-ring carbon atom. Saturation of the proton at 6.07 ppm caused a positive NOE of the trimethylsiloxy protons at 0.12 ppm and the trimethylsilyl protons on the sp^2-hybridized carbon atom at 0.19 ppm, as well as the *tert*-butyl protons. Similar irradiation of a proton at 6.97 ppm on the silacyclobutene ring in product **5** led to an enhancement of the adamantyl, trimethylsilyl, and trimethylsiloxy protons. IR spectra for **4** and **6** show characteristic absorptions at 1888 and 1892 cm^{-1}, respectively, due to the allenic structure. ^{13}C NMR spectra reveal a signal at 208.2 ppm for **4** and 208.8 ppm for **6**, due to the central allenic carbon atoms. These results are wholly consistent with the structures proposed for **3**−**6**.

The formation of products **3**−**6** may be explained in terms of a nonregiospecific [2 + 2] cycloaddition of the silenes and (trimethylsilyl)acetylene. Thus, cycloaddition of the silenes that were generated from **1c** and **1d** with (trimethylsilyl)acetylene produces two types of regioisomers, 3-trimethylsilyl- and 4-trimethylsilyl-substituted silacyclobutenes as shown in Scheme 2. The 4-trimethylsilyl-substituted silacyclobutenes **3** and **5** are stable under the conditions used. In fact, no change was observed when compound **5** was heated in a degassed sealed tube at 140 °C for 24 h. Presumably, the 3-trimethylsilyl-substituted silacyclobutenes are thermally unstable and undergo a ring-opening reaction to give **4** and **6**. Unfortunately, evidence for the formation of 3-trimethylsilyl-substituted silacyclobutenes has not yet been obtained.

In contrast to the present results, it has been reported that the reactions of the silenes that are produced from reacting adamantoylmesitylbis(trimethylsilyl)silane with phenylacetylene and (trimethylsilyl)acetylene and reacting adamantoyl(2,4,6-triisopropylphenyl)bis(trimethylsilyl)silane with phenylacetylene proceed to give [2 + 2] cycloadducts with high regio- and stereospecificity.[3,13]

In conclusion, the silenes generated from **1a** and **1b** reacted with (trimethylsilyl)acetylene to give products **2a** and **2b**, presumably via ring-opening [2 + 2] cycloadducts that are produced regiospecifically, while similar reactions of the silenes from **1c** and **1d** with (trimeth-

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ylsilyl)acetylene proceeded with nonregiospecificity to give two types of [2 + 2] cycloadducts, and one of them underwent the ring-opening reaction to give an allene derivative.

Experimental Section

General Procedure. All reactions of acylpolysilanes with (trimethylsilyl)acetylene were carried out in a degassed, sealed glass tube (1.0 cm × 15 cm). Yields for **2**−**8** were determined by analytical GLC with the use of tridecane as an internal standard, on the basis of the acylpolysilanes used. NMR spectra were recorded on JEOL Model EX-270 and Bruker AMX-400 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. Gel permeation chromatographic separation was performed with a RI Model 504 Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd.).

Materials. Acylpolysilanes **1a**−**d** were prepared according to the method reported by Brook et al.[8,14,15] The benzene that was used as a solvent was dried over lithium aluminum hydride and distilled before use.

Thermolysis of 1a with (Trimethylsilyl)acetylene. A mixture of 139 mg (0.5 mmol) of **1a** and 140 mg (1.4 mmol) of (trimethylsilyl)acetylene in 0.5 mL of benzene was heated in a sealed tube at 140 °C for 24 h. The mixture was analyzed by GLC and was found to be **2a** (51% yield), a dimer **2c** (8% yield), and 31% of the starting compound **1a**. Products **2a** and **2c** were isolated by MPLC. For **2a**: MS *m/z* 373 ($M^+ - Me$); IR 2956, 2856, 1579, 1246, 1003, 837, 700 cm^{-1}; ^1H NMR δ (C_6D_6) 0.15 (s, 9H, Me_3Si), 0.25 (s, 9H, Me_3Si), 0.34 (s, 18H, Me_3Si), 4.74 (d, 1H, olefinic proton, $J = 1$ Hz), 5.02 (d, 1H, olefinic proton, $J = 1$ Hz), 6.94 (d, 1H, olefinic proton, $J = 22$ Hz), 6.99 (d, 1H, olefinic proton, $J = 22$ Hz); ^{13}C NMR δ (C_6D_6) −1.6 (Me_3Si), −0.5 (Me_3Si, 2C), 0.6 (Me_3Si), 105.0 ($\mathit{C}H_2{=}C$), 144.6, 154.4 ($\mathit{C}H{=}\mathit{C}H$), 164.2 ($\mathit{C}{=}CH_2$); ^{29}Si NMR δ (C_6D_6) −48.1 ($\mathit{Si}(SiMe_3)_2$), −15.7 ($SiMe_3$, 2Si), −7.8 ($SiMe_3$), 15.9 ($OSiMe_3$). Anal. Calcd for $C_{16}H_{40}OSi_5$: C, 49.41; H, 10.37. Found: C, 49.41; H, 10.30. All spectral data obtained for **2c** were identical with those reported in the literature.[10]

Thermolysis of 1b with (Trimethylsilyl)acetylene. Heating a mixture of 192 mg (0.6 mmol) of **1b** and 106 mg (1.1 mmol) of (trimethylsilyl)acetylene in 0.6 mL of benzene in a sealed tube at 140 °C for 24 h gave **2b** in 60% yield, in addition to 29% of the starting compound **1b**. Product **2b** was isolated by MPLC: MS *m/z* 401 ($M^+ - Me$); IR 2954, 2905, 1617, 1248, 1126, 841 cm^{-1}; ^1H NMR δ (C_6D_6) 0.19 (s, 9H, Me_3Si), 0.26 (s, 9H, Me_3Si), 0.31 (s, 18H, Me_3Si), 1.68 (s, 3H, Me), 1.76 (s, 3H, Me), 6.81 (d, 1H, olefinic proton, $J = 23$ Hz), 7.06 (d, 1H, olefinic proton, $J = 23$ Hz); ^{13}C NMR δ (C_6D_6) −1.4 (Me_3Si), 0.6 (Me_3Si, 2C), 1.7 (Me_3Si), 19.0, 22.7 (Me), 128.5 ($\mathit{C}Me_2{=}C$), 145.6 ($\mathit{C}{=}CMe_2$) 147.1, 152.5 ($\mathit{C}H{=}\mathit{C}H$); ^{29}Si NMR δ (C_6D_6) −51.1 ($\mathit{Si}(SiMe_3)_2$), −14.7 ($SiMe_3$, 2Si), −7.8 ($SiMe_3$), 14.5 ($OSiMe_3$). Anal. Calcd for $C_{18}H_{44}OSi_5$: C, 51.85; H, 10.64. Found: C, 51.84; H, 10.60.

Thermolysis of 1c with (Trimethylsilyl)acetylene. A mixture of 330 mg (1.0 mmol) of **1c** and 105 mg (1.1 mmol) of (trimethylsilyl)acetylene in 1.0 mL of benzene was heated in a sealed tube at 140 °C for 24 h. The mixture was analyzed by GLC and was found to be **3** (42% yield), **4** (33% yield), **7** (7% yield), and 15% of the starting compound **1c**. Products **3**, **4**, and **7** were separated by recycling HPLC. For **3**: MS *m/z* 430 (M^+); IR 2950, 2898, 1246, 1096, 1041, 833 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.12 (s, 9H, Me_3Si), 0.18 (s, 18H, Me_3Si), 0.19 (s, 9H, Me_3Si), 1.05 (s, 9H, Me_3C), 6.97 (s, 1H, olefinic proton); ^{13}C NMR δ ($CDCl_3$) 0.4 (Me_3Si), 0.9 (Me_3Si), 1.2 (Me_3Si), 3.0 (Me_3Si), 29.5 (Me_3C), 37.8 ($\mathit{C}Me_3$), 94.9 (COSi), 150.9 ($\mathit{C}H{=}C$), 178.3 ($Me_3Si{-}\mathit{C}{=}C$); ^{29}Si NMR δ (C_6D_6) −18.9 ($SiMe_3$), −13.6 ($SiMe_3$), −13.2 ($SiMe_3$), −9.4 ($\mathit{Si}(SiMe_3)_2$), 6.4 ($OSiMe_3$); exact mass calcd for $C_{19}H_{46}OSi_5$ ([M^+]) 430.2392, found 430.2335. For **4**: MS *m/z* 430 (M^+); IR 2954, 2897, 1888, 1247, 1097, 1041, 836 cm^{-1}; ^1H NMR δ (C_6D_6) 0.22 (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 0.30 (s, 9H, Me_3Si), 0.34 (s, 9H, Me_3Si), 1.28 (s, 9H, Me_3C), 4.77 (s, 1H, $HC{=}C{=}C$); ^{13}C NMR δ (C_6D_6) −1.13 (Me_3Si), −1.11 (Me_3Si), 1.8 (Me_3Si), 2.4 (Me_3Si), 32.0 (Me_3C), 36.9 ($\mathit{C}Me_3$), 76.0 ($\mathit{C}H{=}C{=}C$), 97.5 ($\mathit{C}{=}C{=}CH$), 208.2 ($C{=}\mathit{C}{=}C$); ^{29}Si NMR δ (C_6D_6) −19.0 ($SiMe_3$), −18.7 ($SiMe_3$), −10.9 ($\mathit{Si}(SiMe_3)_2$), −6.0 ($SiMe_3$), 8.0 ($OSiMe_3$); exact mass calcd for $C_{19}H_{46}OSi_5$ ([M^+]) 430.2392, found 430.2299; calcd for $C_{18}H_{43}OSi_5$([$M^+ - Me$]) 415.2158, found 415.2130. For **7**: MS *m/z* 513 ($M^+ - Me$); ^1H NMR δ ($CDCl_3$) 0.10 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 0.150 (s, 9H, Me_3Si), 0.154 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.91 (s, 9H, Me_3C), 4.93 (d, 1H, HC−C, $J = 1$ Hz), 5.71 (d, 1H, $HC{=}C$, $J = 1$ Hz); ^{13}C NMR δ ($CDCl_3$) −0.8 (Me_3Si), −0.5 (Me_3Si), −0.1 (Me_3Si), 1.0 (Me_3Si), 2.0 (Me_3Si), 27.2 (Me_3C), 36.5 ($\mathit{C}Me_3$), 84.0 (CO), 109.5, 120.8 (sp carbons), 134.6 ($\mathit{C}H{=}C$), 168.4 ($\mathit{C}{=}CH$); ^{29}Si NMR δ (C_6D_6) −72.3 ($\mathit{Si}(SiMe_3)_2$), −14.8 ($SiMe_3$), −14.4 ($SiMe_3$), −6.4 ($SiMe_3$, 2Si), 14.7 ($OSiMe_3$); exact mass calcd for $C_{23}H_{53}OSi_6$ ([$M^+ - Me$]) 513.2712, found 513.2715.

Thermolysis of 1d with (Trimethylsilyl)acetylene. A mixture of 410 mg (1.0 mmol) of **1d** and 98 mg (1.0 mmol) of (trimethylsilyl)acetylene in 1.0 mL of benzene was heated in a sealed tube at 140 °C for 24 h. The mixture was analyzed by GLC and was found to be **5** (49% yield), **6** (38% yield), **8** (7% yield), and 3% of the starting compound **1d**. Products **5**, **6**, and **8** were isolated by recycling HPLC. For **5**: MS *m/z* 508 (M^+); IR 2955, 2905, 1247, 1084, 1018, 836 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.14 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.22 (s, 9H, Me_3Si), 1.63−2.03 (m, 15H, Ad), 6.97 (s, 1H, olefinic proton); ^{13}C NMR δ ($CDCl_3$) 0.6 (Me_3Si), 1.1 (Me_3Si), 1.6 (Me_3Si), 3.4 (Me_3Si), 29.2, 36.9, 37.3, 39.5 (Ad), 96.9 (COSi), 150.9 ($\mathit{C}H{=}C$), 177.4 ($Me_3Si{-}\mathit{C}{=}C$); ^{29}Si NMR δ (C_6D_6) −18.6 ($SiMe_3$), −13.5 ($SiMe_3$), −13.1 ($SiMe_3$), −10.2 ($\mathit{Si}(SiMe_3)_2$), 6.6 ($OSiMe_3$); exact mass calcd for $C_{24}H_{49}OSi_5$ ([$M^+ - Me$]) 493.2628, found 493.2679. For **6**: MS *m/z* 508 (M^+); IR 2955, 2904, 1892, 1249, 1055, 839 cm^{-1}; ^1H NMR δ (C_6D_6) 0.22 (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 0.30 (s, 9H, Me_3Si), 0.35 (s, 9H, Me_3Si), 1.74−2.04 (m, 15H, Ad), 4.80 (s, 1H, $HC{=}C{=}C$); ^{13}C NMR δ (C_6D_6) −1.1 (Me_3Si), −1.0 (Me_3Si), 2.1 (Me_3Si), 2.5 (Me_3Si), 29.7, 36.6, 37.2, 44.4 (Ad), 76.1 ($\mathit{C}H{=}C{=}C$), 98.4 ($\mathit{C}{=}C{=}CH$), 208.8 ($C{=}\mathit{C}{=}C$); ^{29}Si NMR δ (C_6D_6) −19.0 ($SiMe_3$), −18.9 ($SiMe_3$), −11.0 ($\mathit{Si}(SiMe_3)_2$), −7.0 ($SiMe_3$), 8.2 ($OSiMe_3$); exact mass calcd for $C_{25}H_{52}OSi_5$ ([M^+]) 508.2862, found 508.2878. For **8**: MS *m/z* 591 ($M^+ - Me$); ^1H NMR δ ($CDCl_3$) 0.09 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 0.148 (s, 9H, Me_3Si), 0.154 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 1.56−1.95 (m, 15H, Ad), 4.76 (s, 1H, HC−C), 5.71 (s, 1H, $HC{=}C$); ^{13}C NMR δ ($CDCl_3$) −0.8 (Me_3Si), −0.6 (Me_3Si), −0.1 (Me_3Si), 1.0 (Me_3Si), 1.9 (Me_3Si), 28.6, 37.3, 38.0, 38.8 (Ad), 84.5 (CO), 109.5, 120.8 (sp carbons), 134.3 ($\mathit{C}H{=}C$), 167.7 ($\mathit{C}{=}CH$); ^{29}Si NMR δ (C_6D_6) −72.4 ($\mathit{Si}(SiMe_3)_2$), −14.8 ($SiMe_3$), −14.4 ($SiMe_3$), −6.6 ($SiMe_3$, 2Si), 14.8 ($OSiMe_3$); exact mass calcd for $C_{29}H_{59}OSi_6$ ([$M^+ - Me$]) 591.3182, found 591.3134.

Thermolysis of 5. Compound **5** (83 mg, 0.16 mmol) in 0.3 mL of benzene-d_6 was heated in a sealed NMR tube at 140 °C for 24 h and analyzed by ^1H and ^{13}C NMR spectrometry. The results indicated that no change occurred.

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Supporting Information Available: ^1H, ^{13}C, and ^{29}Si NMR spectra of products **3**−**8** (18 pages). Ordering information is given on any current masthead page.

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