

Silicon–carbon unsaturated compounds. 62. Reactions of silenes produced thermally from pivaloyl- and adamantoyltris(trimethylsilyl)silane with mono(silyl)acetylenes

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Received 2 March 2000; accepted 30 March 2000

Abstract

Thermolysis of pivaloyltris(trimethylsilyl)silane (**1a**) with *tert*-butyldimethylsilylacetylene at 120°C gave 2-*tert*-butyl-3-*tert*-butyldimethylsilyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2a**). Similar treatment of adamantoyltris(trimethylsilyl)silane (**1b**) at 120°C produced 2-adamantyl-3-*tert*-butyldimethylsilyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2b**). Thermolysis of **1a** with *tert*-butyldimethylsilylacetylene at 160°C, however, gave 1-*tert*-butyl-1-(*tert*-butyldimethylsilyl)-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1,2-propadiene (**3a**), along with 1:2 adduct (**4a**). Similar reaction of **1b** gave 1-adamantyl-1-(*tert*-butyldimethylsilyl)-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1,2-propadiene (**3b**) similar to **3a**, together with 1:2 adduct (**4b**). Thermolysis of **1a** and **1b** in the presence of dimethylphenylsilylacetylene or triphenylsilylacetylene at 120°C produced [2 + 2] cycloadducts arising from the reaction of silenes generated thermally from **1a** and **1b** with mono(silyl)acetylenes analogous **2a** and **2b**, along with small amounts of 1:2 adducts. At 160°C, the similar treatment of **1a** and **1b** afforded propadiene derivatives arising from the ring opening reactions of [2 + 2] cycloadducts, in addition to 1:2 adducts. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silene; Acylpolysilane; Thermolysis; Silyl acetylene

1. Introduction

Acylpolysilanes are useful precursors for the synthesis of silenes, and many papers concerning the synthesis and reactions of silenes produced by the photolysis [1–3] of the acylpolysilanes have been published to date. It is also well-known that a Peterson-type reaction of the acylpolysilanes offers a convenient route to the synthesis of silenes [4–7].

We have found that the thermolysis of acyltris(trimethylsilyl)silanes readily affords silenes [8–13], and the silenes thus formed react with olefins [10], dienes [10], and carbonyl compounds [12] to give the respective adducts in high yields. The silenes produced thermally from acetyl- and isopropionyl-tris(trimethylsilyl)silane also react with trimethylsilylacetylene to give the ring-opened products derived from [2 + 2] cycloadducts [13].

Similar reactions of the silenes formed from pivaloyl- and adamantoyl-tris(trimethylsilyl)silane, however, produce [2 + 2] cycloadducts and the ring-opened products [13]. In a previous paper, we reported the [2 + 2] cycloadducts to be 2-*tert*-butyl- and 2-adamantyl-2-(trimethylsiloxy)-1,1,4-tris(trimethylsilyl)-1-silacyclobut-3-ene. However, this has turned out to be an erroneous structural assignment. Careful studies of the 500 MHz ¹H-NMR spectral data and also the chemical reaction indicated that these compounds must be regioisomers, 2-*tert*-butyl- and 2-adamantyl-2-(trimethylsiloxy)-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene.

In order to learn more about chemical behavior of [2 + 2] cycloadducts arising from the silenes produced thermally from acylpolysilanes with alkynes, we investigated the co-thermolysis of pivaloyl- and adamantoyl-tris(trimethylsilyl)silane with mono(silyl)acetylenes.

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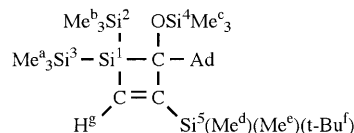
E-mail address: mishika@chem.kusa.ac.jp (M. Ishikawa).

2. Results and discussion

When the cothermolysis of pivaloyltris(trimethylsilyl)silane (**1a**) with *tert*-butyldimethylsilylacetylene was carried out in a sealed glass tube at 120°C for 12 h, 2-*tert*-butyl-3-*tert*-butyldimethylsilyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2a**) was obtained in 69% yield, along with a 23% yield of the starting compound **1a**. The ^{13}C -NMR spectrum of **2a** reveals resonances due to two methylsilyl carbons, three kinds of trimethylsilyl carbons, one quaternary sp^3 carbon, two kinds of olefinic carbons, as well as carbons attributed to two *tert*-butyl groups. Its ^{29}Si -NMR spectrum indicates the presence of five nonequivalent silicon atoms at -18.6 , -13.6 , -9.4 , -7.5 and 5.7 ppm. These results are wholly consistent with the structure proposed for **2a**. Product **2a** is rather unstable toward moisture and oxygen in air. Thus, when **2a** was allowed to stand in air for a long time, it gradually decomposed to give unidentified products.

A similar reaction of adamantoyltris(trimethylsilyl)silane (**1b**) with *tert*-butyldimethylsilylacetylene proceeded to give a product similar to **2a**, 2-adamantyl-3-*tert*-butyldimethylsilyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2b**) as white crystals, in 63% isolated yield, together with 35% of the starting compound **1b** (Scheme 1). No other volatile products were detected in the reaction mixture. The ^1H -NMR spectrum of **2b** shows the presence of two kinds of methylsilyl protons at 0.11 and 0.15 ppm, three kinds of trimethylsilyl protons at 0.22, 0.23 and 0.24 ppm, in addition to adamantyl protons at 1.64–2.04 ppm, *tert*-butyl protons at 0.97 ppm and olefinic protons at 7.05 ppm. The ^{29}Si -NMR spectrum of **2b** reveals five resonances at -18.2 , -13.6 , -10.6 , -7.6 , and 5.4 ppm as expected. Furthermore, we measured the ^1H - ^{29}Si COSY NMR spectrum to establish the structure of **2b**. Two trimethylsilyl protons at 0.22 and 0.24 ppm (Me^a , Me^b) couple with a ring silicon atom at -10.6 ppm (Si^1) and trimethylsilyl silicon atoms at -18.2 and -13.6 ppm (Si^2 , Si^3), while two methylsilyl protons at 0.11 and 0.15 ppm (Me^d , Me^e) and *tert*-butyl protons at 0.97 ppm couple with Si^5 at -7.6 ppm. The protons at

0.23 (Me^c) and 7.05 ppm (H^g) couple with Si^4 at 5.4 ppm and Si^1 at -10.6 ppm, respectively. These results are wholly consistent with the structure proposed for **2b**. In contrast to **2a**, product **2b** is stable to moisture and oxygen in air.

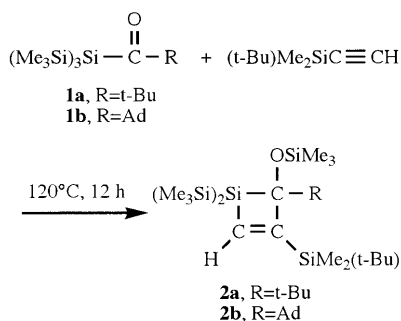


Recrystallization of **2b** from ethanol afforded a single crystal, and we carried out X-ray crystallographic analysis of this crystal. However, we could not obtain any information concerning the structure of **2b**, because **2b** probably decomposed by irradiating X-ray. Consequently, the structure of **2b** was verified by mass and NMR spectrometric analysis, as well as by elemental analysis.

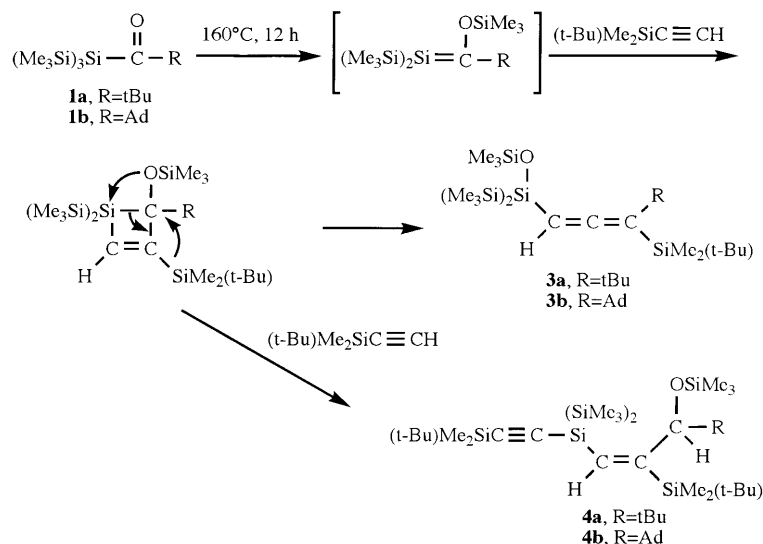
The formation of products **2a** and **2b** can be best understood in terms of [2 + 2] cycloaddition of the silenes produced thermally from the corresponding acylpolysilanes **1a** and **1b** with *tert*-butyldimethylsilylacetylene. The fact that no regioisomers were detected in the reaction mixture indicated that [2 + 2] cycloaddition of the silenes with the acetylene proceeded with high regiospecificity [3,14].

Next, we carried out the reaction of **1a** with *tert*-butyldimethylsilylacetylene at 160°C for 12 h. Thus, treatment of **1a** with *tert*-butyldimethylsilylacetylene at 160°C gave 1-*tert*-butyl-1-(*tert*-butyldimethylsilyl)-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1,2-propadiene (**3a**) and 1:2 adduct (**4a**) in 90 and 6% yields, respectively. The products **3a** and **4a** could readily be isolated by column chromatography (see Section 3). The structures of **3a** and **4a** were verified by mass, IR, and ^1H -, ^{13}C - and ^{29}Si -NMR spectrometry. Mass spectrometric analysis of **4a** showed that this molecule was formed from one molecule of **1a** and two molecules of *tert*-butyldimethylsilylacetylene. The formation of the 1:2 adduct similar to **4a** has been found in the reaction of the silenes produced from acylpolysilanes with trimethylsilylacetylene. Similarly, the reaction of **1b** with *tert*-butyldimethylsilylacetylene at 160°C for 12 h afforded 1-adamantyl-1-*tert*-butyldimethylsilyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1,2-propadiene (**3b**) and 1:2 adduct (**4b**) in 90 and 4% yield, respectively. IR spectra for **3a** and **3b** show characteristic absorptions at 1882 and 1889 cm^{-1} , respectively, due to the allenic structure. ^{13}C -NMR spectra reveal a signal at 209.20 ppm for **3a** and 209.80 ppm for **3b**, due to the central allenic carbon atoms. Products **3a** and **3b** may be formed via a 1,2-trimethylsiloxy shift in [2 + 2] cycloadducts **2a** and **2b** as shown in Scheme 2.

Indeed, when compound **2a** was heated at 160°C for 12 h in a sealed glass tube, it was found that **2a**



Scheme 1.



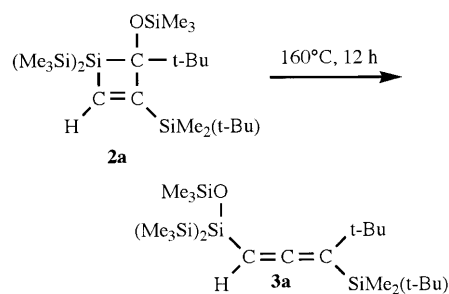
Scheme 2.

isomerized completely to give **3a**. In contrast to these results, we previously reported that the thermolysis of **1a** and **1b** with trimethylsilylacetylene at 140°C afforded [2 + 2] cycloadducts, 2-*tert*-butyl- and 2-adamantyl-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-1-silacyclobut-3-ene, in addition to ring-opened products and 1:2 adducts, analogous to **3a** and **4a**, respectively. We suspected that erroneous structure assignment had been made for the [2 + 2] cycloadducts produced from the reactions of **1a** and **1b** with trimethylsilylacetylene. Therefore, we reinvestigated the thermal properties of [2 + 2] cycloadducts obtained previously. Thus, when the [2 + 2] cycloadducts were heated in a sealed glass tube at 160°C , the ring-opened products, 1-*tert*-butyl- and 1-adamantyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1-trimethylsilyl-1,2-propadiene were obtained in almost quantitative yields. These results clearly indicate that a trimethylsilyl group should be on the C_3 position in the silacyclobutene ring, but not on the C_4 position as reported previously. Consequently, the structures of the [2 + 2] cycloadducts must be 2-*tert*-butyl- and 2-adamantyl-2-(trimethylsiloxy)-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene, analogous to **2a** and **2b** (Scheme 3).

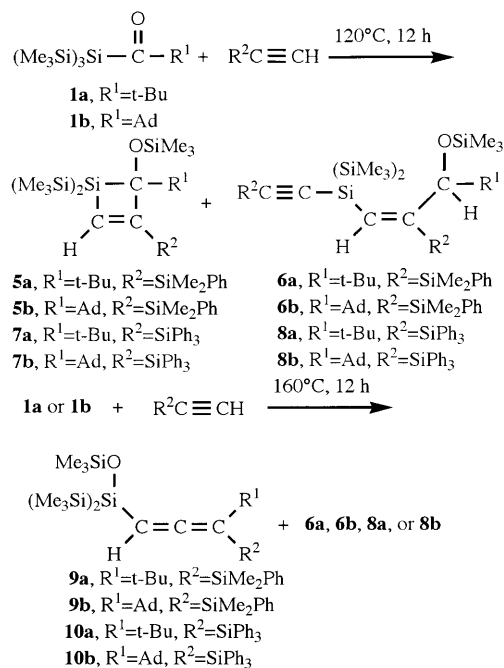
Phenyl-substituted silylacetylenes also react with the silenes formed thermally from **1a** and **1b**. Thus, the thermolysis of **1a** with dimethylphenylsilylacetylene at 120°C for 12 h afforded 2-*tert*-butyl-3-dimethylphenylsilyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**5a**) and 1:2 adduct (**6a**) in 52 and 20% yields, respectively. In this reaction 5% of the starting acylpolysilane **1b** was recovered unchanged. The similar reaction of **1b** with dimethylphenylsilylacetylene gave 2-adamantyl-3-dimethylphenylsilyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**5b**) and 1:2 adduct (**6b**) in 53 and 13% yields, along

with 10% of the starting compound **1b**. With triphenylsilylacetylene, **1a** reacted also at 120°C to give [2 + 2] cycloadduct, 2-*tert*-butyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-3-triphenylsilyl-1-silacyclobut-3-ene (**7a**) and 1:2 adduct (**8a**) in 40 and 9% yields, along with 41% of the unchanged **1a**, while **1b** reacted with triphenylsilylacetylene to give 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-3-triphenylsilyl-1-silacyclobut-3-ene (**7b**) and 1:2 adduct (**8b**) in 42 and 9% yields, together with 48% of the starting compound **1b**. The structures of products **5a**, **5b**, **6a**, **6b**, **7a**, **7b**, **8a** and **8b** were confirmed by mass, IR, and ^1H -, ^{13}C -, and ^{29}Si -NMR spectrometric analysis (Scheme 4).

At 160°C , **1a** and **1b** reacted with dimethylphenylsilylacetylene and triphenylsilylacetylene, respectively, to give the propadiene derivatives as main products. In all cases, no [2 + 2] cycloadducts were detected in the reaction mixtures. Presumably, the silacyclobutene derivatives once formed undergo isomerization to give the propadiene derivatives. Thus, the cothermolysis of **1a** with dimethylphenylsilylacetylene at 160°C gave 1-*tert*-butyl-1-dimethylphenylsilyl-3-[(trimethylsiloxy)bis-



Scheme 3.



Scheme 4.

(trimethylsilyl)silyl]-1,2-propadiene (**9a**) in 74% yield, along with an 11% yield of **6a**. A similar cothermolysis of **1b** with dimethylphenylsilylacetylene produced a propadiene derivative (**9b**) and **6b** in 72 and 11% yields, respectively.

Similar thermolysis of **1a** and **1b** with triphenylsilylacetylene at 160°C proceeded to give the propadiene derivatives and 1:2 adducts. Treatment of **1a** with triphenylsilylacetylene afforded 1-*tert*-butyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1-triphenylsilyl-1,2-propadiene (**10a**) and **8a** in 58 and 30% yields, while **1b** with triphenylsilylacetylene produced 1-adamantyl-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]-1-triphenylsilyl-1,2-propadiene (**10b**) in 43% yield, in addition to a 43% yield of **8b**. In the thermolysis of **1a** and **1b** in the presence of the silylacetylenes at 160°C, only propadiene derivatives and 1:2 adducts were obtained, but no other volatile products were detected in the reaction mixtures. The structures of **9a**, **9b**, **10a**, and **10b** were verified by mass, ¹H-, ¹³C- and ²⁹Si-NMR spectrometric analysis, as well as by elemental analysis.

In conclusion, the thermolysis of acylpolysilanes **1a** and **1b** with mono(silyl)acetylenes at 120°C proceeded to give [2 + 2] cycloadducts arising from the addition of the silenes produced thermally from acylpolysilanes to mono(silyl)acetylenes as main products. At 160°C, however, **1a** and **1b** reacted with mono(silyl)acetylenes to give the propadiene derivatives which were probably produced by the ring-opening reaction of the silacyclobut-3-enes.

3. Experimental

All thermal reactions were carried out in a degassed sealed tube (1.0 cmØ × 15 cm). Yields for **2a**, **2b**, **3a**, **3b**, **4a**, **5a**, **5b**, **6a**, **6b**, **7a** and **7b** were determined by analytical GLC with the use of eicosane as an internal standard, on the basis of the acylpolysilanes used. Yields of the products **4b**, **8a**, **8b**, **9a**, **9b**, **10a** and **10b** were calculated on the basis of the isolated products. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low- and high-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Gel permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd.). Melting point were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). THF used as a solvent was distilled under nitrogen from sodium/benzophenone ketyls. Acylpolysilanes **1a** and **1b** were prepared according to the method reported by Brook et al. [8,15].

3.1. Preparation of triphenylsilylacetylene

In a 500 ml-three necked flask was placed a solution of ethynyl-Grignard reagent prepared from 0.10 mol of ethylmagnesium bromide and acetylene in 200 ml of THF. To this was added 30.13 g (0.10 mol) of chlorotriphenylsilane in 70 ml of THF through a dropping funnel over a period of 1 h. The mixture was refluxed for 3 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over magnesium sulfate. After the solvent was evaporated, triphenylsilylacetylene (19.878 g, 70%) was isolated by column chromatography: MS *m/z* 284 (M⁺); IR 3264, 3068, 3050, 3023, 2036, 1484, 1429, 1264, 1114, 740, 711, 696 cm⁻¹; ¹H-NMR δ(CDCl₃) 2.82 (s, 1H, HC), 7.41–7.49 (m, 9H, phenyl ring protons), 7.70–7.74 (m, 6H, phenyl ring protons); ¹³C-NMR δ(CDCl₃) 85.30, 97.77 (sp carbon), 128.03, 130.08, 132.78, 135.49 (phenyl ring carbons); ²⁹Si-NMR δ(CDCl₃) –28.9. Anal. Calc. for C₂₀H₁₆Si: C, 84.46; H, 5.67. Found: C, 84.37; H, 5.58%.

3.1.1. Thermolysis of **1a** with *tert*-butyldimethylsilylacetylene at 120°C

A mixture of 0.1679 g (0.506 mmol) of **1a** and 0.0700 g (0.500 mmol) of *tert*-butyldimethylsilylacetylene was heated in a sealed glass tube at 120°C for 12 h. The mixture was analyzed by GLC as being **2a** (69% yield), along with the starting compound **1a** (23%). Product **2a**

was isolated by column chromatography: MS m/z 472 (M^+); IR 2956, 2896, 2858, 1390, 1361, 1251, 1095, 1039, 898, 835, 754, 684, 624 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.10 (s, 3H, MeSi), 0.13 (s, 3H, MeSi), 0.20 (s, 18H, Me_3Si), 0.22 (s, 9H, Me_3Si), 0.95 (s, 9H, *t*-Bu), 1.07 (s, 9H, *t*-Bu), 7.06 (s, 1H, HC=C); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –3.80, –1.91 (MeSi), 1.21, 1.36, 3.04 (Me_3Si), 18.14 (CMe_3), 27.68 (Me_3C), 29.62 (Me_3C), 38.01 (CMe_3), 96.57 (CO), 153.07, 177.05 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –18.6, –13.6, –9.4, –7.5, 5.7; exact mass calc. for $\text{C}_{22}\text{H}_{52}\text{OSi}_5$ ($[M^+]$) 472.2865, found 472.2876.

3.1.2. Thermolysis of **1b** with *tert*-butyldimethylsilylacetylene at 120°C

A mixture of 0.1689 g (0.412 mmol) of **1b** and 0.0756 g (0.540 mmol) of *tert*-butyldimethylsilylacetylene was heated in a sealed glass tube at 120°C for 12 h. The mixture was analyzed by GLC as being **2b** (63% yield), along with the starting compound **1b** (35%). Product **2b** were isolated by column chromatography: MS m/z 550 (M^+); IR 2956, 2900, 2854, 1471, 1243, 1079, 831, 690, 624 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.11 (s, 3H, MeSi), 0.15 (s, 3H, MeSi), 0.22 (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.24 (s, 9H, Me_3Si), 0.97 (s, 9H, *t*-Bu), 1.64–2.04 (m, 15H, Ad), 7.05 (s, 1H, HC=C); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –3.56, –1.61 (MeSi), 1.37, 1.78, 3.50 (Me_3Si), 18.34 (CMe_3), 27.84 (Me_3C), 29.14, 36.75, 39.27, 39.63 (Ad), 98.99 (CO), 153.03, 176.38 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –18.2, –13.6, –10.6, –7.6, 5.4. Anal. Calc. for $\text{C}_{28}\text{H}_{58}\text{OSi}_5$: C, 61.01; H, 10.61. Found: C, 61.01; H, 10.60%.

3.1.3. Thermolysis of **1a** with *tert*-butyldimethylsilylacetylene at 160°C

A mixture of 0.1539 g (0.506 mmol) of **1a** and 0.0840 g (0.600 mmol) of *tert*-butyldimethylsilylacetylene was heated in a sealed glass tube at 160°C for 12 h. The mixture was analyzed by GLC as being **3a** (90% yield) and **4a** (6% yield). Products **3a** and **4a** were isolated by column chromatography. For **3a**: MS m/z 472 (M^+); IR 2956, 2896, 2858, 1882, 1471, 1390, 1361, 1253, 1052, 836, 767, 686 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.08 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 0.14 (s, 9H, Me_3Si), 0.18 (s, 3H, MeSi), 0.20 (s, 3H, MeSi), 0.94 (s, 9H, *t*-Bu), 1.12 (s, 9H, *t*-Bu), 4.54 (s, 1H, HC=C); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –2.49, –2.05 (MeSi), –1.17, –1.14, 2.25 (Me_3Si), 19.26 (CMe_3), 27.70 (Me_3C), 32.12 (Me_3C), 33.88 (CMe_3), 76.54 (HC=C), 95.70 (C=CH), 209.20 (C=C); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.2, –18.8, –12.1, 0.3, 7.8; exact mass calc. for $\text{C}_{22}\text{H}_{52}\text{OSi}_5$ ($[M^+]$) 472.2865, found 472.2880. For **4a**: MS m/z 612 (M^+); IR 2954, 2929, 2894, 2858, 2082, 1390, 1361, 1249, 1066, 894, 836, 773, 694 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$

0.09 (s, 3H, MeSi), 0.10 (s, 6H, Me_2Si), 0.12 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 0.23 (s, 3H, MeSi), 0.93 (s, 9H, *t*-Bu), 0.94 (s, 18H, *t*-Bu), 4.94 (s, 1H, HCO), 5.81 (s, 1H, HC=C); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –4.69 (MeSi), –4.64 (MeSi), –2.30 (MeSi), –0.60 (Me_3Si), –0.40 (Me_3Si), –0.19 (MeSi), 1.27 (Me_3Si), 16.57 (CMe_3), 18.88 (Me_3C), 26.08 (Me_3C), 27.29 (CMe_3), 28.54 (Me_3C), 36.56 (CMe_3), 85.37 (CO), 110.25, 119.14 (sp carbons), 136.88, 166.26 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –73.0, –14.0, –13.7, –9.6, –1.7, 14.4. Anal. Calc. for $\text{C}_{30}\text{H}_{68}\text{OSi}_6$: C, 58.74; H, 11.17. Found: C, 58.50; H, 11.27%.

3.1.4. Thermolysis of **1b** with *tert*-butyldimethylsilylacetylene at 160°C

A mixture of 0.1455 g (0.355 mmol) of **1b** and 0.0730 g (0.521 mmol) of *tert*-butyldimethylsilylacetylene was heated at 160°C for 12 h. The mixture was analyzed by GLC as being **3b** (90% yield). Products **3b** and **4b** (0.0099 g, 4%) were isolated by column chromatography. For **3b**: MS m/z 550 (M^+); IR 2955, 2904, 2850, 1889, 1407, 1251, 1054, 836, 757, 682 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.10 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 0.14 (s, 3H, MeSi), 0.15 (s, 9H, Me_3Si), 0.22 (s, 3H, MeSi), 0.94 (s, 9H, *t*-Bu), 1.63–1.98 (m, 15H, Ad), 4.55 (s, 1H, HC=C); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –2.14, –1.90 (MeSi), –1.14, –1.10, 2.30 (Me_3Si), 19.24 (CMe_3), 27.75 (Me_3C), 29.36, 36.90, 44.13, 45.39 (Ad), 76.56 (HC=C), 96.55 (C=CH), 209.80 (C=C); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.22, –19.17, –12.1, –0.1, 7.8. Anal. Calc. for $\text{C}_{28}\text{H}_{58}\text{OSi}_5$: C, 61.01; H, 10.61. Found: C, 61.06; H, 10.82. For **4b**: MS m/z 690 (M^+); IR 2954, 2931, 2902, 2854, 2085, 1471, 1249, 1081, 1056, 890, 838, 769, 692 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.09 (s, 3H, MeSi), 0.098 (s, 3H, MeSi), 0.101 (s, 3H, MeSi), 0.12 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 0.22 (s, 3H, MeSi), 0.95 (s, 9H, *t*-Bu), 1.55–1.95 (m, 15H, Ad), 4.75 (s, 1H, HCO), 5.81 (s, 1H, HC=C); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –4.64 (Me_2PhSi), –2.32 (MePhSi), –0.63 (Me_3Si), –0.43 (Me_3Si), –0.27 (MePhSi), 1.31 (Me_3Si), 16.54, 18.91 (CMe_3), 26.09, 28.63 (Me_3C), 28.68, 37.21, 38.16, 38.70 (Ad), 85.77 (CO), 110.43, 119.26 (sp carbons), 136.73, 165.66 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –72.9, –14.0, –13.9, –9.5, –1.9, 14.5. Anal. Calc. for $\text{C}_{36}\text{H}_{74}\text{OSi}_6$: C, 62.53; H, 10.79. Found: C, 62.83; H, 10.67%.

3.1.5. Thermolysis of **2a** at 160°C

Compound **2a** (0.1009 g, 0.214 mmol) was heated in a sealed glass tube at 160°C for 12 h. The reaction mixture was analyzed by GLC as being **3a** (96%). All spectral data obtained for **3a** were identical with those of an authentic sample obtained from the above reaction.

3.1.6. Thermolysis of 2-*tert*-butyl-2-(trimethylsiloxy)-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene at 160°C

2-*tert*-Butyl-2-(trimethylsiloxy)-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene (0.1950 g, 0.453 mmol) was heated in a sealed glass tube at 160°C for 12 h. The resulting reaction mixture was analyzed by ^1H - and ^{13}C -NMR spectrometry. The results indicated that the starting silacyclobutene was transformed completely into a propadiene derivative in quantitative yield. All spectral data for the product were identical with those of the authentic sample reported previously [13].

3.1.7. Thermolysis of 2-adamantyl-2-(trimethylsiloxy)-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene at 160°C

2-Adamantyl-2-(trimethylsiloxy)-1,1,3-tris(trimethylsilyl)-1-silacyclobut-3-ene (0.1580 g, 0.311 mmol) was heated in a sealed glass tube at 160°C for 12 h. The mixture was analyzed by ^1H - and ^{13}C -NMR spectrometry, indicating that the starting silacyclobutene was transformed into a propadiene derivative in quantitative yield. All spectral data for the product were identical with those of the authentic sample [13].

3.1.8. Thermolysis of **1a** with dimethylphenylsilylacetylene at 120°C

A mixture of 0.2068 g (0.621 mmol) of **1a** and 0.1207 g (0.753 mmol) of dimethylphenylsilylacetylene was heated at 120°C for 12 h. The mixture was analyzed by GLC as being **5a** (52% yield) and **6a** (20% yield), along with the starting compound **1a** (5%). Products **5a** and **6a** were isolated by column chromatography. For **5a**: MS m/z 492 (M^+); IR 2958, 2898, 1411, 1363, 1253, 1060, 840, 755, 700 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.03 (s, 9H, Me_3Si), 0.038 (s, 9H, Me_3Si), 0.039 (s, 9H, Me_3Si), 0.21 (s, 3H, MePhSi), 0.33 (s, 3H, MePhSi), 0.77 (s, 9H, *t*-Bu), 6.93 (s, 1H, HC=C), 7.16–7.17 (m, 3H, phenyl ring protons), 7.38–7.40 (m, 2H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –1.98, –0.09 (Me₂PhSi), 1.00, 1.19, 3.00 (Me₃Si), 29.37 (Me₃C), 37.86 (CMe₃), 95.28 (CO), 127.44, 128.53, 134.11, 139.42 (phenyl ring carbons), 153.37, 175.68 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.1, –18.7, –13.4, –9.4, 6.25; exact mass calc. for $\text{C}_{24}\text{H}_{48}\text{OSi}_5$ ($[\text{M}^+]$) 492.2552, found 492.2566. For **6a**: MS m/z 652 (M^+); IR 3018, 2954, 2898, 2088, 1427, 1359, 1249, 1216, 1110, 1066, 894, 836, 817, 759 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.13 (s, 18H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.39 (s, 3H, MePhSi), 0.41 (s, 3H, MePhSi), 0.42 (s, 3H, MePhSi), 0.52 (s, 3H, MePhSi), 0.89 (s, 9H, *t*-Bu), 5.01 (d, 1H, HCO, $J=0.6$ Hz), 5.83 (d, 1H, HC=C, $J=0.6$ Hz), 7.29–7.39 (m, 6H phenyl ring protons), 7.54–7.75 (m, 2H phenyl ring protons), 7.63–7.65 (m, 2H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –0.91 (MePhSi), –0.81 (MePhSi), –0.82 (Me₃Si), –0.45 (Me₃Si), 0.41 (MePhSi), 1.10 (Me₃Si), 1.96 (MePhSi), 27.17 (Me₃C), 36.59 (CMe₃),

84.38 (CO), 111.87, 118.57 (sp carbons), 127.42, 127.73, 128.34, 129.30, 133.72, 134.14, 139.92, 137.89, 141.04, 165.12 (phenyl ring and olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –72.1, –23.2, –13.9, –10.0, 15.0. Anal. Calc. for $\text{C}_{34}\text{H}_{60}\text{OSi}_6$: C, 62.50; H, 9.26. Found: C, 62.28; H, 9.41%.

3.1.9. Thermolysis of **1b** with dimethylphenylsilylacetylene at 120°C

A mixture of 0.3083 g (0.750 mmol) of **1b** and 0.1283 g (0.800 mmol) of dimethylphenylsilylacetylene was heated at 120°C for 12 h. The resulting mixture was analyzed by GLC as being **5b** (53% yield) and **6b** (13% yield), along with the starting compound **1b** (10%). Product **5b** and **6b** were isolated by column chromatography. For **5b**: MS m/z 570 (M^+); IR 3068, 2954, 2904, 2850, 1452, 1249, 1083, 894, 836, 732, 701 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.34 (s, 9H, Me_3Si), 0.37 (s, 9H, Me_3Si), 0.38 (s, 9H, Me_3Si), 0.50 (s, 3H, MePhSi), 0.67 (s, 3H, MePhSi), 1.55–2.03 (m, 15H, Ad), 7.20 (s, 1H, HC=C), 7.22–7.29 (m, 3H, phenyl ring protons), 7.63–7.65 (m, 2H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –2.10, 0.24 (MePhSi), 1.44, 1.75, 3.56 (Me₃Si), 29.41, 36.87, 39.59, 40.04 (Ad), 97.62 (CO), 127.80, 128.94, 134.52, 139.56 (phenyl ring carbons), 153.35, 175.45 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –18.8, –18.6, –13.3, –10.3, 6.4; exact mass calc. for $\text{C}_{30}\text{H}_{54}\text{OSi}_5$ ($[\text{M}^+]$) 570.3021, found 570.3013. For **6b**: MS m/z 730 (M^+); IR 2954, 2904, 2848, 2086, 1249, 1051, 836, 773, 698 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.12 (s, 9H, Me_3Si), 0.13 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.38 (s, 3H, MePhSi), 0.41 (s, 6H, Me₂PhSi), 0.51 (s, 3H, MePhSi), 1.47–1.87 (m, 15H, Ad), 4.83 (br s, 1H, HCO), 5.81 (br s, 1H, HC=C), 7.29–7.37 (m, 6H, phenyl ring protons), 7.54–7.65 (m, 4H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –0.80 (2C) (Me₃Si, Me₂PhSi), –0.49 (Me₃Si), 0.33 (MePhSi), 1.14 (Me₃Si), 1.83 (MePhSi), 28.56, 37.14, 38.18, 38.75 (Ad), 84.94 (CO), 111.94, 118.68 (sp carbons), 127.37, 127.74, 128.33, 129.32, 133.71, 134.23, 136.88, 137.66, 141.04, 164.58 (phenyl ring and olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –72.1, –23.2, –14.0, –13.9, –10.2, 15.0. Anal. Calc. for $\text{C}_{40}\text{H}_{66}\text{OSi}_6$: C, 65.68; H, 9.09. Found: C, 65.32; H, 9.31%.

3.1.10. Thermolysis of **1a** with triphenylsilylacetylene at 120°C

A mixture of 0.1230 g (0.370 mmol) of **1a** and 0.1165 g (0.410 mmol) of triphenylsilylacetylene was heated at 120°C for 12 h. Products **7a** (0.0923 g, 40% yield), **8a** (0.0298 g, 9% yield) and the starting compound **1a** (0.0498 g, 41%) were isolated by column chromatography. For **7a**: MS m/z 616 (M^+); IR 3072, 3048, 2954, 2923, 2898, 1427, 1245, 1205, 1078, 836 cm^{-1} ; ^1H -

NMR $\delta(\text{CDCl}_3)$ 0.14 (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.24 (s, 9H, Me_3Si), 0.95 (s, 9H, *t*-Bu), 7.34 (s, 1H, HC=C), 7.33–7.41 (m, 9H, phenyl ring protons), 7.63–7.65 (m, 6H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ 1.19, 1.32, 2.93 (Me_3Si), 29.68 (Me_3C), 31.77 (CMe_3), 96.46 (CO), 127.34, 129.02, 135.44, 136.86 (phenyl ring carbons), 158.91, 171.56 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –23.0, –18.0, –13.3, –9.4, 6.6. Anal. Calc. for $\text{C}_{34}\text{H}_{52}\text{OSi}_5$: C, 66.16; H, 8.49. Found: C, 66.04; H, 8.60. For **8a**: MS m/z 900 (M^+); IR 3068, 3050, 2954, 2871, 2084, 1429, 1245, 1112, 1105, 1068, 1027, 887, 836, 781, 738, 698 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ –0.12 (s, 9H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.31 (s, 9H, Me_3Si), 0.77 (s, 9H, *t*-Bu), 5.11 (s, 1H, HCO), 6.07 (s, 1H, HC=C), 7.34–7.76 (m, 15H phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –0.59 (Me_3Si), –0.22 (Me_3Si), 0.95 (Me_3Si), 27.82 (Me_3C), 36.85 (CMe_3), 84.78 (CO), 115.59, 115.72 (sp carbons), 127.17, 127.85, 128.87, 129.85, 133.35, 135.64, 136.64, 137.07, 141.13, 162.35 (phenyl ring and olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –71.3, –30.3, –12.8, –12.5, –11.9, 15.8. Anal. Calc. for $\text{C}_{54}\text{H}_{68}\text{OSi}_6$: C, 71.93; H, 7.60. Found: C, 72.01; H, 7.63%.

3.1.11. Thermolysis of **1b** with triphenylsilylacetylene at 120°C

A mixture of 0.1201 g (0.293 mmol) of **1b** and 0.1346 g (0.474 mmol) of triphenylsilylacetylene was heated at 120°C for 12 h. Product **7b** (0.0858 g, 42% yield), **8b** (0.0260 g, 9% yield) and the starting compound **1b** (0.0581 g, 48%) were isolated by column chromatography. For **7b**: MS m/z 694 (M^+); IR 3068, 3050, 2904, 2848, 1429, 1251, 1105, 1014, 908, 890, 836, 736, 703 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.11 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 1.40–1.78 (m, 15H, Ad), 7.25 (s, 1H, HC=C), 7.27–7.37 (m, 9H, phenyl ring protons), 7.58–7.62 (m, 6H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ 1.37, 1.72, 3.37 (Me_3Si), 28.88, 36.35, 39.12, 39.90 (Ad), 98.61 (CO), 127.34, 128.97, 135.51, 136.96 (phenyl ring carbons), 159.26, 170.18 (olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –22.1, –17.6, –13.3, –10.2, 6.4. Anal. Calc. for $\text{C}_{40}\text{H}_{58}\text{OSi}_5$: C, 69.10; H, 8.41. Found: C, 69.00; H, 8.46. For **8b**: MS m/z 978 (M^+); IR 3068, 3048, 2904, 2848, 2082, 1429, 1247, 1105, 1081, 1052, 838, 781, 736, 700 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ –0.14 (s, 9H, Me_3Si), 0.22 (s, 9H, Me_3Si), 0.28 (s, 9H, Me_3Si), 1.31–1.97 (m, 15H, Ad), 4.89 (br s, 1H, HCO), 6.08 (br s, 1H, HC=C), 7.33–7.74 (m, 30H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –0.61, –0.24, 0.95 (Me_3Si), 28.48, 36.95, 38.51, 39.20 (Ad), 85.25 (CO), 115.59, 115.72 (sp carbons), 127.14, 127.83, 128.81, 129.85, 133.33, 135.63, 136.64, 137.10, 141.13, 161.65 (phenyl ring and olefinic carbons); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –71.2, –13.0, –12.5, –12.1, 15.8. Anal. Calc. for $\text{C}_{60}\text{H}_{74}\text{OSi}_6$: C, 73.55; H, 7.61. Found: C, 73.50; H, 7.68%.

3.1.12. Thermolysis of **1a** with dimethylphenylsilylacetylene at 160°C

A mixture of 0.5148 g (1.55 mmol) of **1a** and 0.2970 g (1.85 mmol) of dimethylphenylsilylacetylene was heated at 160°C for 12 h. The mixture was analyzed by GLC as being **9a** (74% yield), along with **6a** (11% yield). Products **6a** and **9a** were isolated by column chromatography. For **9a**: MS m/z 492 (M^+); IR 3070, 2958, 2900, 1887, 1693, 1429, 1253, 1064, 840, 755 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.13 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Si), 0.41 (s, 3H, MePhSi), 0.52 (s, 3H, MePhSi), 1.03 (s, 9H, *t*-Bu), 4.76 (s, 1H, HC=C), 7.34–7.36 (m, 3H, phenyl ring protons), 7.60–7.62 (m, 2H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –1.28 (Me_3Si), –1.26 (Me_3Si), –0.27 (MePhSi), 0.40 (MePhSi), 2.25 (Me_3Si), 31.97 (Me_3C), 34.27 (CMe_3), 76.12 (HC=C), 96.27 (C=CH), 127.58, 128.67, 134.03, 140.38 (phenyl ring carbons), 208.54 (=C=); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.1, –18.8, –11.7, 7.9; exact mass calc. for $\text{C}_{24}\text{H}_{48}\text{OSi}_5$ ($[\text{M}^+]$) 492.2552, found 492.2565. All spectral data for **6a** were identical with those of an authentic sample obtained from the above reaction.

3.1.13. Thermolysis of **1b** with dimethylphenylsilylacetylene at 160°C

A mixture of 0.5104 g (1.24 mmol) of **1b** and 0.2001 g (1.25 mmol) of dimethylphenylsilylacetylene was heated at 160°C for 12 h. The mixture was analyzed by GLC as being **9b** (72% yield), along with **6b** (11% yield). Products **6b** and **9b** were isolated by column chromatography. For **9b**: MS m/z 570 (M^+); IR 2964, 2906, 2850, 1891, 1685, 1251, 1064, 840, 754, 700 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ 0.11 (s, 9H, Me_3Si), 0.14 (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.42 (s, 3H, MePhSi), 0.49 (s, 3H, MePhSi), 1.59–1.93 (m, 15H, Ad), 4.74 (s, 1H, HC=C), 7.32–7.37 (m, 3H, phenyl ring protons), 7.55–7.58 (m, 2H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –1.29 (Me_3Si), –1.27 (Me_3Si), –0.01 (MePhSi), 0.56 (MePhSi), 2.26 (Me_3Si), 29.16, 36.76, 43.89, 51.94 (Ad), 76.23 (HC=C), 96.95 (C=CH), 127.51, 128.59, 134.03, 140.67 (phenyl ring carbons), 209.00 (=C=); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.2, –19.1, –12.1, –11.7, 7.9; exact mass calc. for $\text{C}_{30}\text{H}_{54}\text{OSi}_5$ ($[\text{M}^+]$) 570.3021, found 570.2999. All spectral data for **6b** were identical with those of an authentic sample obtained from the above reaction.

3.1.14. Thermolysis of **1a** with triphenylacetylene at 160°C

A mixture of 0.1631 g (0.491 mmol) of **1a** and 0.1745 g (0.614 mmol) of triphenylsilylacetylene was heated at 160°C for 12 h. Products **8a** (0.1330 g, 30% yield) and **10a** (0.1750 g, 58% yield) were isolated by column chromatography. For **10a**: MS m/z 616 (M^+); IR 3070, 3050, 2958, 2898, 1886, 1429, 1253, 1043, 842, 700 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ –0.18 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 1.04 (s, 9H, *t*-Bu),

4.56 (s, 1H, HC=C), 7.32–7.38 (m, 9H, phenyl ring protons), 7.69–7.73 (m, 6H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –1.58, –1.29, 2.38 (Me_3Si), 31.77 (Me_3C), 34.44 (CMe_3), 77.97 (HC=C), 93.57 (C=CH), 127.52, 129.08, 135.73, 136.61 (phenyl ring carbons), 210.78 (=C=); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.2, –18.9, –16.1, –11.3, 8.4. Anal. Calc. for $\text{C}_{34}\text{H}_{52}\text{OSi}_5$: C, 66.16; H, 8.49. Found: C, 66.09; H, 8.50%. All spectral data for **8a** were identical with those of an authentic sample obtained from the above reaction.

3.1.15. Thermolysis of **1b** with triphenylsilylacetylene at 160°C

A mixture of 0.1100 g (0.268 mmol) of **1b** and 0.1240 g (0.437 mmol) of triphenylsilylacetylene was heated at 160°C for 12 h. Products **8b** (0.1111 g, 43% yield) and **10b** (0.0789 g, 43% yield) were isolated by column chromatography. For **10b**: MS m/z 694 (M^+); IR 3070, 3048, 2954, 2904, 2848, 1891, 1429, 1251, 1106, 1045, 842, 738, 700 cm^{-1} ; ^1H -NMR $\delta(\text{CDCl}_3)$ –0.20 (s, 9H, Me_3Si), 0.09 (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 1.42–1.81 (m, 15H, Ad), 4.54 (s, 1H, HC=C), 7.29–7.39 (m, 9H, phenyl ring protons), 7.66–7.71 (m, 6H, phenyl ring protons); ^{13}C -NMR $\delta(\text{CDCl}_3)$ –1.60 (Me_3Si), –1.30 (Me_3Si), 2.42 (Me_3Si), 29.19, 36.53, 36.66, 43.51 (Ad), 78.04 (HC=C), 94.17 (C=CH), 127.46, 129.05, 135.91, 136.67 (phenyl ring carbons), 211.17 (=C=); ^{29}Si -NMR $\delta(\text{CDCl}_3)$ –19.3, –19.2, –16.4, –11.4, 8.35. Anal. Calc. for $\text{C}_{40}\text{H}_{58}\text{OSi}_5$: C, 69.10; H, 8.41. Found: C, 69.10; H, 8.42%. All spectral data for **8b** were identical with those of an authentic sample obtained from the above reaction.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas 'The Chemistry of

Inter-element Linkage' (No. 11120260) from Ministry of Education, Science, Sports and Culture of Japan and by Research for the Future Program (JSPS-PFTF96P00206), to which our thanks are due. We also express our appreciation to Sumitomo Electric Industry, and Tokuyama for financial support.

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