Reactions of Silenes Produced Thermally from Pivaloyl- and Adamantoyltris(trimethylsilyl)silane with Bis(trimethylsilyl)butadiyne

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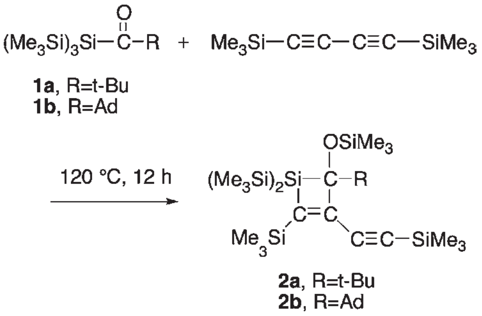
Thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane (**1a**) and (**1b**) with bis(trimethylsilyl)butadiyne at 120 °C gave the respective [2 + 2] cycloadducts. Similar thermolysis of **1a** and **1b** with bis(trimethylsilyl)butadiyne at 160 °C, however, afforded 2-oxa-1,1,3,5-tetrakis(trimethylsilyl)-4-trimethylsilylethynyl-1-silacyclopent-4-ene derivatives in high yields.

Recently, we have found that the thermolysis of acyltris(trimethylsilyl)silanes readily affords silenes, and the silenes thus formed react with olefins,[1] dienes,[1] carbonyl compounds,[2] and acetylenes[3] to give a wide variety of adducts in high yields. In order to learn more about chemical behavior of the silenes generated thermally from acylpolysilanes,[4] we investigated the cothermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane with bis(trimethylsilyl)butadiyne. We also report a novel isomerization of silacyclobutenes to oxasilacyclopentenes.

When the cothermolysis of pivaloyltris(trimethylsilyl)silane (**1a**)[5] with bis(trimethylsilyl)butadiyne was carried out in a sealed glass tube at 120 °C for 12 h, 2-tert-butyl-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-3-trimethylsilylethynyl-1-silacyclobut-3-ene (**2a**) was obtained regiospecifically in 85% yield, along with a 10% yield of the starting compound **1a**. The ^{13}C NMR spectrum of **2a** reveals resonances due to five kinds of trimethylsilyl carbons at -0.77, -0.45, 1.41, 1.78, and 4.24 ppm, three quaternary carbons at 94.31, 98.07, and 104.77 ppm, two kinds of olefinic carbons at 153.03 and 167.93 ppm, as well as carbons attributed to a tert-butyl group. Its ^{29}Si NMR spectrum indicates the presence of six nonequivalent silicon atoms at -18.2, -15.7, -15.6, -11.1, -5.6 and 8.8 ppm. IR spectra for **2a** show characteristic absorption at 2129 cm^{-1} due to the ethynyl structure. These results are wholly consistent with the structure proposed for **2a**.

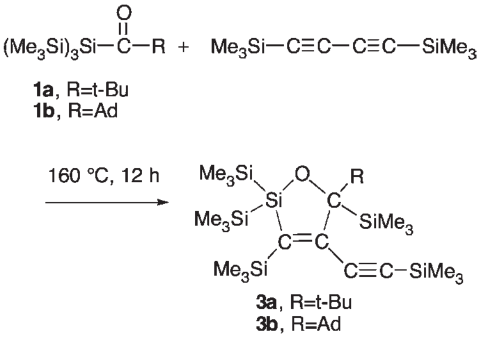
A similar reaction of adamantoyltris(trimethylsilyl)silane (**1b**)[6] with bis(trimethylsilyl)butadiyne proceeded to give a product analogous to **2a**, 2-adamantyl-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-3-trimethylsilylethynyl-1-silacyclobut-3-ene (**2b**), in 97% yield (Scheme 1). The location of the substituents on the silacyclobutene ring for **2b** was confirmed by NOE–FID difference experiments at 500 MHz. For example, irradiation of trimethylsilyl protons on C4 position of the silacyclobutene ring resulted in enhancement of the protons of two trimethylsilyl groups on the ring silicon atom. No other volatile products were detected in the reaction mixture.

The formation of products **2a** and **2b** can be best understood in terms of [2 + 2] cycloaddition of the silenes produced thermally from **1a** and **1b** across a triple bond in bis(silyl)butadiyne.[3] The fact that no regioisomers are detected in the reaction mixture indicates that [2 + 2] cycloaddition of the silenes to the acetylene proceeds with high regiospecificity.



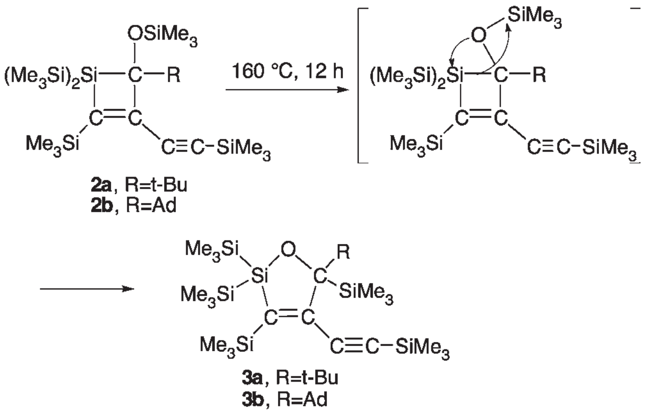
Scheme 1.

Next, we carried out the reaction of **1a** with bis(trimethylsilyl)butadiyne at higher temperature. To our surprise, when **1a** with bis(trimethylsilyl)butadiyne at 160 °C for 12 h, 3-*tert*-butyl-1,1,3,5-tetrakis(trimethylsilyl)-4-trimethylsilylethynyl-2-oxa-1-silacyclopent-4-ene (**3a**) was obtained in 93% yield.[7,8] The reaction of **1b** with bis(trimethylsilyl)butadiyne under the same conditions afforded 3-adamantyl-1,1,3,5-tetrakis(trimethylsilyl)-4-trimethylsilylethynyl-2-oxa-1-silacyclopent-4-ene (**3b**) in 92% yield.[7,8] The structures of **3a** and **3b** were verified by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometry, as well as by elemental analysis.[9] ^{29}Si NMR spectra show six resonances at -19.7, -18.8, -18.4, -10.1, 1.2 and 37.8 ppm for **3a** and six resonances at -20.2, -18.8, -18.4, -10.2, 0.7, 38.0 ppm for **3b**. IR spectra for **3a** and **3b** show characteristic absorption at 2138 and 2140 cm^{-1}, respectively, due to the ethynyl structure. In both cases, no [2 + 2] cycloadducts were detected in the reaction mixtures.



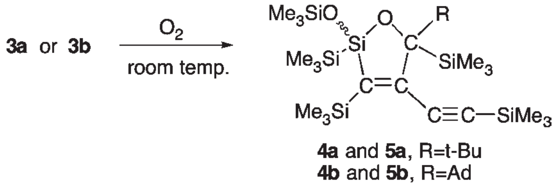
Scheme 2.

In order to get more information concerning the formation of products **3a** and **3b**, we have investigated the thermal behavior of [2 + 2] cycloadducts, **2a** and **2b**. Interestingly, when compound **2a** was heated in a sealed glass tube at 160 °C for 12 h, isomerization took place to give **3a** as the sole product. The similar reaction of **2b** at 160 °C afforded an oxasilacyclopentene derivative **3b** in 97% yield. These results clearly indicate that the silacyclobutene derivatives once formed undergo thermal isomerization to give the oxasilacyclopentene derivatives. This isomerization is of considerable interest to us, because thermolysis of silacyclobutenes formed from the reactions of **1a** and **1b** with silyl-substituted acetylenes always give the products originated from a 1,2-trimethylsiloxy shift from carbon to silicon in four-membered ring.[3c,d] Furthermore, it has also been found that the cothermolysis of **1a** and **1b** with carbonyl compounds affords the products arising from a 1,2-trimethylsiloxy shift in the silaoxetane intermediates.[2]



Scheme 3.

Compound **3a** and **3b** is gradually oxidized in air at room temperature. The reaction of **3a** with oxygen in 5 ml of hexane at room temperatrure for 48 h afforded two isomers of **4a** and **5a** quantitatively (Scheme 4). The ratio of the isomers was calculated to be approximately 1.1 : 1 by ^{1}H NMR spectrometric analysis. We identified two isomers as *cis*- and *trans*-3-*tert*-butyl-2-oxa-1-trimethylsiloxy-1,3,5-tris(trimethylsilyl)-4-trimethylsilylethynyl-1-silacyclopent-4-ene formed from insertion of oxygen into one of two Si-Si bonds on the ring silicon atom in **3a** by NMR spectrometric analysis.[10] Similar treatment of **3b** with oxygen at room temperature for 36 h gave *cis* and *trans* isomers, **4b** and **5b** quantitatively. The ratio of the isomers in this case was calculated to be approximately 1.2 : 1 by ^{1}H NMR spectrometric analysis. The structures of **4b** and **5b** were verified by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometry. Compounds **3a** and **3b** would be produced by the photochemical reaction with oxygen in air. In fact, absorption spectra for **3a** and **3b** show that their absorption edge reaches to the visible region.



Scheme 4.

UV absorption spectra for compound **2a**, **2b**, **3a**, **3b**, **4a**, **5a**, **4b** and **5b** have been observed and their peak positions are listed in Table 1. The absorption maxima for **3a** and **3b** appear at longer (about 70 nm) wavelength than that of **4a**, **5a** and **4b**, **5b**.

Table 1. UV-Vis spectral data for **2–5** in cyclohexane

Compound	$\lambda_{\mathrm{max,Abs}}$/nm	ε
2a	296	7900
2b	298	7000
3a	329	5100
3b	328	6200
4a, **5a**	255	10500
4b, **5b**	262	8000

Further studies concerning the mechanism of isomerization and UV absorption are in progress and will be reported elsewhere.

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8 Some oxasilacyclopentene derivatives have been reported, and their chemical shift are similar to those of **3a** and **3b**.

9 Spectroscopic data for **3a**; MS 526 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 0.17, 0.18, 0.19, 0.20, 0.22 (s, 9H, Me$_3$Si), 1.07 (s, 9H, t-Bu); ^{13}C NMR (CDCl$_3$): δ −0.61 (2C), 0.65, 1.00, 1.40 (Me$_3$Si), 28.37 (Me$_3$C), 41.03 (CMe$_3$), 99.18 (CO), 103.56, 105.60 (sp carbons), 150.71, 151.71 (olefinic carbons). Anal. Calcd for $C_{24}H_{54}OSi_6$: C, 54.68; H, 10.32%. Found: C, 55.06; H, 10.47%. For **3b**; MS 604 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 0.16 (s, 9H, Me$_3$Si), 0.18 (br.s, 27H, Me$_3$Si), 0.21 (s, 9H, Me$_3$Si), 1.64–1.94 (m, 15H, Ad); ^{13}C NMR (CDCl$_3$): δ −0.63, −0.57, 0.48, 0.98, 1.55 (Me$_3$Si), 28.81, 37.23, 38.82, 43.48 (Ad), 99.60 (CO), 103.67, 105.69 (sp carbons), 150.61, 150.79 (olefinic carbons). Anal. Calcd for $C_{30}H_{60}OSi_6$: C, 59.53; H, 9.99%. Found: C, 59.50; H, 9.90%.

10 Spectroscopic data for **4a** and **5a**; MS 542 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 0.10 (s, 9H, Me$_3$Si), 0.12 (s, 18H, Me$_3$Si), 0.14, 0.15, 0.16 (s, 9H, Me$_3$Si), 0.18 (s, 18H, Me$_3$Si), 0.20, 0.21 (s, 9H, Me$_3$Si), 1.03 (s, 9H, t-Bu), 1.07 (s, 9H, t-Bu).