

Preliminary communication

Thermolysis of 1,1-dimesityl-3-phenyl-2-trimethylsilyl-1-silacyclopropene: silylene transfer reactions to 1,4-bis(silyl)butadiynes

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Abstract

The cothermolysis of 1,1-dimesityl-3-phenyl-2-trimethylsilyl-1-silacyclopropene (**1**) with 1,4-bis(trimethylsilyl)- and 1,4-bis(triethylsilyl)butadiyne at 250°C for 24 h afforded 1,1-dimesityl-3-silyl-2-silylethynyl-1-silacyclopropenes (**3** and **5**) and dimesitylbis(silylethynyl)silanes (**4** and **6**), respectively. The thermolysis of silacyclopropene **3** under the same conditions cleanly produced an isomerization product **4**. © 1997 Elsevier Science S.A.

Keywords: Thermolysis; Silylene; Silacyclopropene

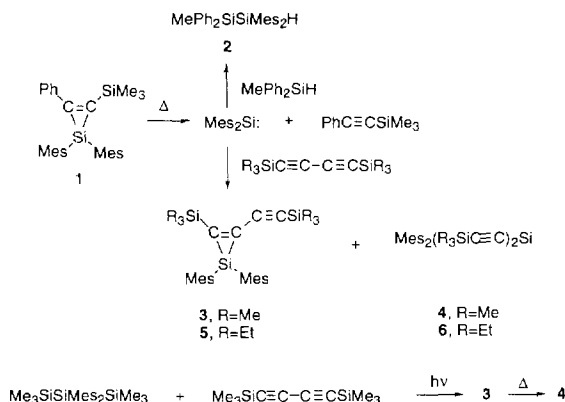
Silacyclopropenes undergo a wide variety of reactions, depending on the substituents on the silicon atom and the reaction conditions. It is also known that some silacyclopropenes extrude silylenes under thermal conditions. However, extrusion of the silylenes is always accompanied by isomerization or dimerization of the silacyclopropenes [1–13]. In this paper we report that the thermolysis of 1,1-dimesityl-3-phenyl-2-trimethylsilyl-1-silacyclopropene [14,15] (**1**) produces dimesitylsilylene and phenyl(trimethylsilyl)acetylene, and the silylene thus formed can be transferred into 1,4-bis(silyl)butadiyne. We also report a novel isomeriza-

tion of 1,1-dimesityl-3-silyl-2-silylethynyl-1-silacyclopropenes into dimesitylbis(silylethynyl)silane.

First, we carried out the cothermolysis of **1** with a hydrosilane. Thus, treatment of **1** with a 5-fold excess of methyl-diphenylsilane in a degassed sealed tube at 250°C for 24 h afforded a silylene insertion product, 2,2-dimesityl-1-methyl-1,1-diphenyldisilane (**2**), and phenyl(trimethylsilyl)acetylene in 31% and 32% yields, in addition to 68% of the starting silacyclopropene **1**. No other products were detected by GLC analysis of the reaction mixture. The result clearly indicates that dimesitylsilylene can be produced from the thermolysis of **1**.

When **1** was treated with 2 equiv of bis(trimethylsilyl)butadiyne under the same conditions, two silylene adducts, 1,1-dimesityl-3-trimethylsilyl-2-trimethyl-silylethynyl-1-silacyclopropene (**3**) and dimesitylbis(trimethylsilylethynyl)silane (**4**) were obtained in 17% and 42% yields, along with a 44% yield of phenyl(trimethylsilyl)acetylene and 41% of the starting compound **1**. The structures of product **3** and **4** were confirmed by spectrometric analysis, as well as by

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elemental analysis.^{1,2} The ²⁹Si NMR spectrum for **3** shows a resonance at $\delta -112.5$ ppm attributed to the silicon atom in the silacyclopropene ring, and two resonances at -17.7 and -8.8 ppm due to two nonequivalent trimethylsilyl silicons. Its ¹³C NMR spectrum reveals two resonances at $\delta 100.9$ and 114.0 ppm and at 163.3 and 176.1 ppm, due to *sp* carbons and *sp*² carbons, respectively. For compound **4**, the ²⁹Si NMR spectrum indicates two resonances at $\delta -64.0$ and -18.1 ppm, attributable to two trimethylsilylethynyl silicons and dimesityl silicon. The product **3** was also identified by preparing from an independent route. Thus, irradiation of 2,2-dimesitylhexamethyltrisilane with a low-pressure mercury lamp in the presence of a 9-fold excess of bis(trimethylsilyl)butadiyne in a hexane solution gave **3** in 50% yield, together with 13% of the starting trisilane. All spectral data for the product thus obtained were identical with those for **3** prepared from the cothermolysis of **1** with the butadiyne.

The cothermolysis of **1** with bis-(triethylsilyl)butadiyne at 250°C for 24 h again afforded three products, 3-triethylsilyl-2-triethylsilylethynyl-1,1-dimesityl-1-silacyclopropene (**5**), dimesitylbis(triethylsilylethynyl)silane (**6**), and phenyl(trimethyl-

silyl)acetylene in 22%, 55%, and 77% yields, respectively, in addition to 19% of the starting compound **1**. Products **5** and **6** were identified by spectrometric analysis and elemental analysis.^{3,4}

The formation of the products **3** and **5** can be best understood in terms of a silylene transfer reaction from **1** to bis(silyl)butadiynes. In order to learn more about the mechanism for the formation of the product **4** and **6**, we carried out the thermolysis of silacyclopropene **3**. Heating compound **3** in a sealed glass tube at 250°C for 24 h cleanly afforded an isomerization product **4** in 80% yield, along with 10% of the starting compound **3**. No other volatile products were detected by GLC analysis. The isomerization of this type is of considerable interest, because the thermolysis of the silacyclopropenes bearing a silyl group on a carbon atom in the silacyclopropene ring gives ring-opened isomers produced from a 1,2-shift of the silyl group to the ring silicon atom [16]. In the thermolysis of the silacyclopropenes **3** and **5**, a migrating group is the silylethynyl group, but not the silyl group. Compounds **3** and **5** are air-stable and can be handled under atmospheric oxygen without decomposition.

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¹ Compound **3**: MS *m/z* 460 (*M*⁺); IR ν 2956, 2923, 2835, 2119, 1603, 1247, 841 cm^{-1} ; ¹H NMR (δ in C₆D₆) 0.03 (s, 9H, Me₃Si), 0.07 (s, 9H, Me₃Si), 2.08 (s, 6H, *p*-Me), 2.61 (s, 12H, *o*-Me), 6.68 (s, 4H, ring protons); ¹³C NMR (δ in C₆D₆) -0.6 , 0.0 (Me₃Si), 21.1 (*p*-Me), 23.8 (*o*-Me), 100.9 , 114.0 (ethynyl carbons), 128.7 , 131.3 , 139.5 , 144.3 (mesityl ring carbons), 163.3 , 176.1 (olefinic carbons); ²⁹Si NMR (δ in C₆D₆) -112.5 (SiMe₂), -17.7 , -8.8 (SiMe₃). Anal. Calcd for C₂₈H₄₀Si₃: C, 72.97; H, 8.75. Found: C, 72.70; H, 8.75.

² Compound **4**: MS *m/z* 460 (*M*⁺); IR ν 2958, 2853, 1663, 1563, 1538, 1460, 1400, 1249, 845, 767, 638 cm^{-1} ; ¹H NMR (δ in C₆D₆) 0.09 (s, 18H, Me₃Si), 2.09 (s, 6H, *p*-Me), 2.79 (s, 12H, *o*-Me), 6.75 (s, 4H, ring protons); ¹³C NMR (δ in C₆D₆) -0.7 (Me₃Si), 21.0 (*p*-Me), 24.6 (*o*-Me), 112.7 , 117.9 (ethynyl carbons), 127.2 , 130.0 , 139.6 , 144.7 (mesityl ring carbons); ²⁹Si NMR (δ in C₆D₆) -64.0 (SiMe₂), -18.1 (SiMe₃). Anal. Calcd for C₂₈H₄₀Si₃: C, 72.97; H, 8.75. Found: C, 72.68; H, 8.67.

³ Compound **5**: MS *m/z* 544 (*M*⁺); IR ν 3068, 2959, 2159, 1756, 1490, 1367, 1215, 1170, 1106, 905 cm^{-1} ; ¹H NMR (δ in C₆D₆) 0.75–1.17 (m, 30H, Et), 2.08 (s, 6H, *p*-Me), 2.63 (s, 12H, *o*-Me), 6.70 (s, 4H, ring protons); ¹³C NMR (δ in C₆D₆) δ 4.7, 5.0 (CH₂Si), 7.9 (2C, CH₃CH₂), 21.2 (*p*-Me), 23.9 (*o*-Me), 102.5, 111.8 (ethynyl carbons), 128.8, 131.6, 139.6, 144.4 (mesityl ring carbons), 165.4, 173.3 (olefinic carbons); ²⁹Si NMR (δ in C₆D₆) -114.7 (SiMe₂), -6.9 , -1.4 (SiEt₃); Exact mass calcd for C₃₃H₄₉Si₃ (*M*⁺–CH₃) 529.3140, found 529.3171, calcd for C₃₂H₄₇Si₃ (*M*⁺–C₂H₅) 515.2981, found 515.3032.

⁴ Compound **6**: MS *m/z* 544 (*M*⁺); IR ν 2960, 2908, 1644, 1558, 1452, 1412, 1254, 1104, 793 cm^{-1} ; ¹H NMR (δ in C₆D₆) 0.60 (q, 12H, CH₂Si, *J* = 7.6 Hz), 1.06 (t, 18H, CH₃CH₂, *J* = 7.6 Hz), 2.09 (s, 6H, *p*-Me), 2.77 (s, 12H, *o*-Me), 6.73 (s, 4H, ring protons); ¹³C NMR (δ in C₆D₆) 4.5 (CH₂Si), 7.7 (CH₃CH₂), 21.0 (*p*-Me), 24.6 (*o*-Me), 114.4, 115.5 (ethynyl carbons), 129.3, 129.9, 139.5, 144.6 (mesityl ring carbons); ²⁹Si NMR (δ in C₆D₆) -57.2 (SiMe₂), -0.2 (SiEt₃). Anal. Calcd for C₃₄H₅₂Si₃: C, 74.93; H, 9.62. Found: C, 74.65; H, 9.41.

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