Selective Formation of Rearranged Silenes from Polysilylenones via 1,3- and 1,5-Silyl Migration

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Supporting Information

Experimental Details

General. All reactions were carried out in dry nitrogen. THF and toluene were distilled from sodium and stored over activated molecular seives until use. NMR spectra were recorded on a JEOL model LA-400 spectrometer. Low-resolution MS were measured on a Shimadzu model QP-5050A spectrometer, while high-resolution MS were obtained by a JEOL model SX-107 spectrometer. IR spectra were measured on a Shimadzu model FTIR-8700 spectrometer. t-Butyl(phenyl)propynone was prepared as reported in the literature (Cox, R. J.; Ritson, D. J.; Dane, T. A.; Berge, J.; Charmant, J.; Kantacha, A. Chem. Commun. 2005, 1037). The usual work up mentioned below includes separation of the organic layer, extraction of the aqueous layer with ether, drying the combined organic layer and the extracts with anhydrous magnesium sulfate, and evaporation of the solvent, in this order.

Preparation of E-1a. To a suspension of 1.72 g (9.03 mol) of CuI in 9 mL of THF was added a solution of (TMS)$_3$SiLi (18.1 mmol) in 90 mL of THF/ether = 1/1 at 0°C to prepare [(TMS)$_3$Si]$_2$CuLi. After being stirred for 1 h, the mixture was added dropwise to a solution of 1.53 g (8.21 mmol) of t-butyl(phenyl)propynone in 12 mL of THF at -80°C. The resulting mixture was stirred at this temperature for 1 h then was
hydrolyzed with water/THF = 1/1. After the usual work up, the residue was subjected to silica gel column chromatography eluting with hexane/ethyl acetate = 15/1 to give a crude product, which was further purified by recycling preparative GPC eluting with benzene to give **E-1a** in 21% yield as a colorless solid: mp 60.6-62.5 °C; MS m/z 434 (M⁺); ¹H NMR (δ, C₆D₆) 0.20 (s, 27H, SiMe₃), 1.05 (s, 9H, t-Bu), 7.00-7.12 (m, 6H, olefin and Ph); ¹³C NMR (δ, CDCl₃) 1.20 (SiMe₃), 26.37 (Me₃C), 43.42 (CMe₃), 124.79, 125.58, 128.07, 133.59 (aromatic ring carbons), 145.60, 161.24 (C=O). Anal. Calcd for C₂₂H₄₂O₄Si₄: C, 60.76; H, 9.73. Found: C, 60.71; H, 10.02.

**Preparation of Z-1b.** Quenching the anionic species obtained by the reaction of [(TMS)₃Si]₂CuLi with t-butyl(phenyl)propynone as above with Mel, followed by hydrolysis with water and the usual work up gave the residue containing **Z-1b** and **1c** as the major products. The residue was subjected to silica gel column chromatography eluting with hexane then to recycling preparative GPC eluting with benzene to give **Z-1b** and **1c** as colorless solids in 11% and 41% yields, respectively. Data for **Z-1b**: mp 97.4-99.0 °C; MS m/z 375 (M⁺-SiMe₃); ¹H NMR (δ, C₆D₆) 0.26 (s, 27H, SiMe₃), 1.10 (s, 9H, t-Bu), 1.66 (s, 3H, Me), 6.75-6.78, 6.99-7.01 (m, 5H, Ph); ¹³C NMR (δ, C₆D₆) 2.69 (SiMe₃), 19.20 (Me), 27.28 (CH₃-C), 43.36 (C-CH₃), 125.41, 126.06, 128.69, 141.60 (aromatic ring carbons), 147.85, 164.82 (C=O); Exact MS Calcd for C₂₂H₄₀O₄Si₄ (M⁺-Me): 433.2234; Found: 433.2215. Data for **1c**: mp 89.9-91.3 °C; DIMS m/z 375 (M⁺-SiMe₃); ¹H NMR (δ, C₆D₆) 0.29 (s, 27H, SiMe₃), 1.26 (s, 9H, t-Bu), 3.39 (s, 3H, OMe), 6.95-7.03, 7.49-7.51 (m, 5H, Ph); ¹³C NMR (δ, C₆D₆) 2.05 (SiMe₃), 28.35 (CH₃-C), 34.91 (C-CH₃), 55.98 (OMe), 113.89, 127.61, 128.34, 128.54 (aromatic ring carbons), 140.31, 143.06 (C=), 202.78 (=C=); IR 1903 cm⁻¹; Exact MS Calcd for C₂₃H₄₄O₄Si₄ (M⁺): 448.2469; Found: 448.2462.

**Thermal Isomerization of Z-1b.** A solution of 0.0854g (0.191 mmol) of **Z-1b** in 1 mL of toluene was heated in a sealed degassed glass tube at 100 °C 1 h. After evaporation of the solvent, the residue was subjected to recycling preparative GPC eluting with benzene to give **2b** in 71% isolated yield as a colorless viscous oil: MS 448 (M⁺); ¹H NMR (δ, C₆D₆) 0.21, 0.27, 0.40 (s, 9H, SiMe₃), 1.13 (s, 9H, t-Bu), 1.90 (s, 1H, Me), 7.01-7.05, 7.19-7.28 (m, 5H, Ph); ¹³C NMR (δ, C₆D₆) 1.35, 2.00, 3.87 (SiMe₃), 17.40 (Me), 29.01 (CH₃-C), 28.35 (CH₃-C), 34.91 (C-CH₃), 55.98 (OMe), 113.89, 127.61, 128.34, 128.54 (aromatic ring carbons), 140.31, 143.06 (C=), 202.78 (=C=); IR 1903 cm⁻¹; Exact MS Calcd for C₂₃H₄₄O₄Si₄ (M⁺): 448.2469; Found: 448.2462.
Photolysis of E-1a. A solution of 0.1374 g (0.32 mmol) of E-1a in 60 mL of hexane was irradiated internally with a 6W low-pressure mercury lamp bearing a Vycor filter at ambient temperature for 100 min. After evaporation of the solvent, the residue was analyzed by NMR, as being 3a in 24% yield. A trace of Z-1a was also found to be formed in the spectra. Subjecting the residue to recycling preparative HPLC gave 3a as a colorless viscous oil. Data for 3a: MS m/z 434 (M+), 419 (M+-Me), 361 (M+-SiMe3); 1H NMR (δ, CDCl3) −0.28, −0.07, 0.36 (s, 9H, SiMe3), 1.12 (s, 9H, t-Bu), 5.20 (s, 1H, CH), 6.89-7.28 (m, 5H, Ph); 13C NMR (δ, CDCl3) −2.33, 0.16, 0.29 (SiMe3), 28.17 (CH3-C), 34.74 (C-CH3), 98.01 (C-O), 123.71, 126.17, 127.99, 128.14 (aromatic ring carbons), 144.79, 165.69 (C=C); 29Si NMR (δ, CDCl3) −93.91, −39.87, 6.28. The 1H and 13C NMR signals for the ring CH were in the same region as those of the compounds having a similar oxasilacylcopentene ring, reported previously (Clark, T. B.; Woerpel, K. A. J. Am. Chem. Soc. 2004, 126, 9522). Data for Z-1a: 1H NMR (δ, CDCl3) 0.052 (s, 27H, SiMe3), 1.13 (s, 9H, t-Bu), 6.88 (s, 1H, olefin), 6.93-7.28 (m, 5H, Ph); 13C NMR (δ, CDCl3) 2.54 (SiMe3), 26.22 (CH3-C), 42.84 (C-CH3), 123.71, 126.14, 128.09, 134.06 (aromatic ring carbons), 148.94, 167.86 (C=C), 203.31 (C=O).

Photolysis of Z-1b. Photolysis of Z-1b was carried out in a fashion similar to that above. Data for 3b: MS m/z 448 (M+), 433 (M+-Me), 375 (M+-SiMe3); 1H NMR (δ, CDCl3) −0.086, 0.20, 0.37 (s, 9H, SiMe3), 1.32 (s, 9H, t-Bu), 1.90 (s, 1H, Me), 6.95-6.97, 7.15-7.17 (m, 5H, Ph); 13C NMR (δ, CDCl3) 0.19, 0.81, 1.49 (SiMe3), 16.55 (Me), 29.74 (CH3-C), 36.52
(C-CH₃), 107.41 (C-O), 124.13, 128.29, 128.72, 128.85 (aromatic ring carbons), 146.24, 159.94 (C=C). Exact MS Calcd for C₂₃H₄₄OSi₄ (M⁺): 448.2469; Found: 448.2455.

Data for E-1b: H NMR (δ, C₆D₆) 0.30 (s, 27H, SiMe₃), 1.26 (s, 9H, t-Bu), 1.90 (s, 1H, Me), 6.95-6.97, 7.15-7.17 (m, 5H, Ph); C NMR (δ, C₆D₆) 2.06 (SiMe₃), 16.39 (Me), 28.37 (CH₃-C), 46.17 (CQCH), 126.29, 127.61, 128.72, 140.30 (aromatic ring carbons), 143.55, 156.93 (C=C), 201.31 (C=O).

Figure S1. Optimized geometries of the models, derived from DFT calculations.
Figure S1. Optimized geometries of the models, derived from DFT calculations. Some of hydrogen atoms are omitted for clarity (continued).
Figure S2. Optimized geometries of the models ORTEP Drawing of E-1a and Z-1b. Protons are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.