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Preliminary communication

Intramolecular rearrangements of silenes II ☆. Synthesis of 1-methyl-1-hydro-1-silaacenaphthene from 1-methyl-1-naphthyl-1-silacyclobutane via [4 → 2 + 2]thermocyclodecomposition – transient silene rearrangement sequence. Novel 1,4-hydrogen shift from aryl carbon to sp^2 silicon of the silicon–carbon double bond

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Abstract

A clean rearrangement of 1-naphthyl-1-methylsilene generated by 1-naphthyl-1-methyl-1-silacyclobutane gas-phase [4 → 2 + 2]-thermocyclodecomposition results in 1-methyl-1-silacenaphthene. It involves a novel 1,4-hydrogen shift from carbon of an aromatic nucleus to an sp^2 silicon of the silicon–carbon double bond.

Keywords: Aryl; Silenes; Silaacenaphthene; Rearrangement; Silacyclobutane; 1,4-H shift

Silene intramolecular rearrangements are the subject of specific interest because of both mechanistic pecularities and synthetic utility [1]. Recently we have achieved transient silene rearrangement sequences in the synthesis of 3,4-benzo-1-methyl-1-hydro-1-silacyclobutene via [4 → 2 + 2]thermocyclodecomposition [2]. The rearrangement (Scheme 1) occurs as a sigmatropic 1,3-hydrogen shift from an aryl carbon to an sp^2 silicon of the silicon–carbon double bond followed by ring closure (RC) of the resulting 1,4-diradical.

Here we report a clean rearrangement of 1-naphthyl-1-methylsilene (**1**) involving a novel 1,4-hydrogen shift from a carbon of an aromatic nucleus to an sp^2 silicon of the silicon–carbon double bond which results in 1-methyl-1-silaacenaphthene (**2**) (Scheme 2), 1-naphthyl-1-methyl-1-silacyclobutane (**3**) [4 → 2 + 2]thermocyclodecomposition [3] being used to generate **1**.

All experiments were performed within a temperature range of 720–760°C and pressure 3×10^{-2} Torr in

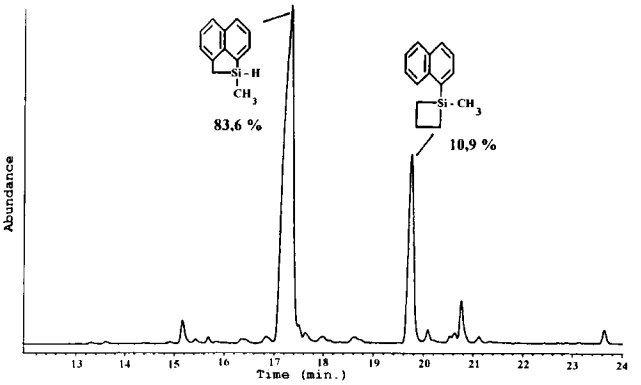

Fig. 1. A chromatogram (HP-5 25 m × 0.32 mm capillary column with 5% of crosslinked phenyl methyl silicone) of the reaction mixture resulting from pyrolysis of **3** (740°C, 3×10^{-2} Torr).

☆ For part I, see Ref. [2]

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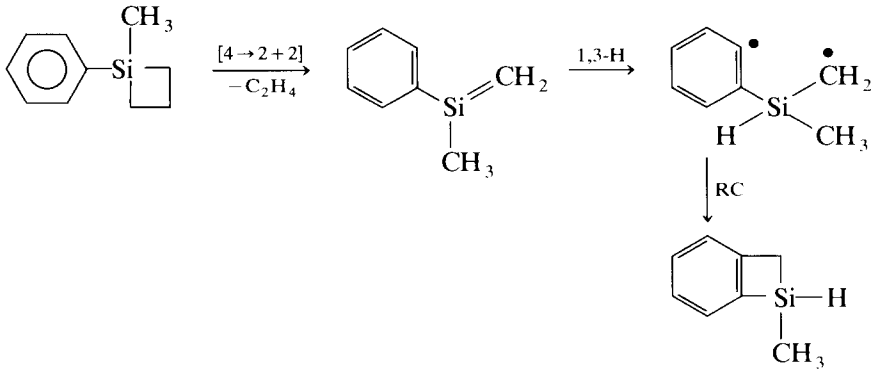
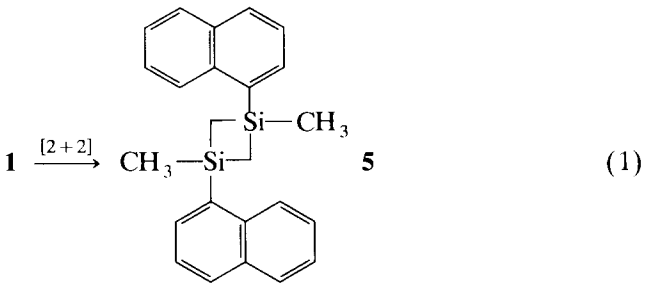


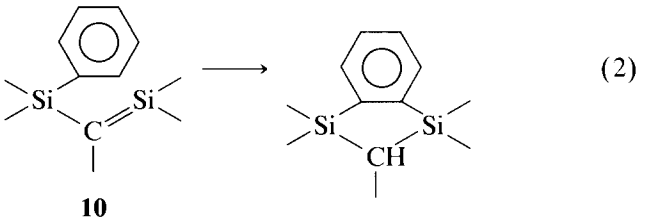
Scheme 1.

a flow hollow vertical quartz tube reactor. Vapors of a starting compound were passed from top to bottom of the reactor. Products were collected in a trap cooled with liquid nitrogen. Silene precursor **3** was prepared by reaction of 1-naphthylmagnesium bromide with 1-methyl-1-chloro-1-silacyclobutane according to the procedure [4].

A typical chromatogram is shown in Fig. 1. It indicates **2** to be the main reaction product. 1,3-disilacyclobutane **5**, a product of silene **1** cyclodimerisation, was not observed after trap-to-trap distilation of the reaction mixture. NMR, MS and FTIR data for **2** are given in Table 1.



(1)



(2)

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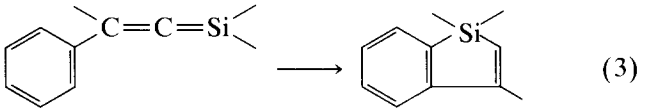

(3)

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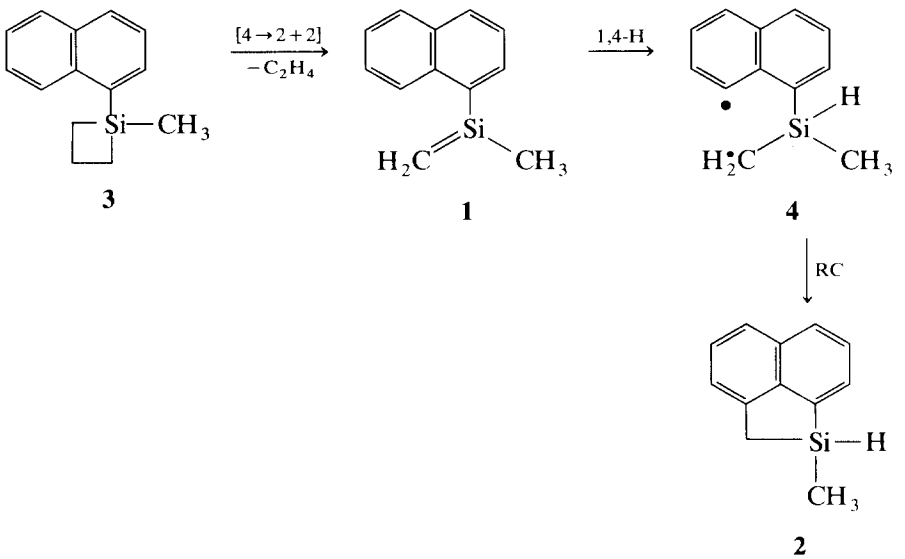
Any other rearrangement products, i.e. **7** and **9**, to be expected from 1,3-H and 1,5-H migrations (Scheme 3) were not observed.

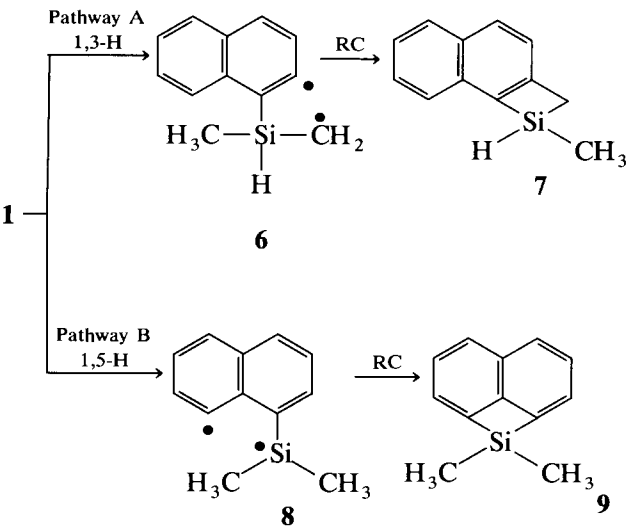
Indeed, 1,4-H migration (Scheme 2) looks preferable to 1,3-H and 1,5-H migrations (Scheme 3) because of



Scheme 2.

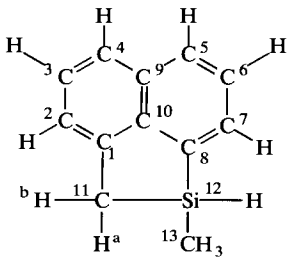
greater thermodynamic stability of the resulting rearrangement product. The only 1,4-H migrations known to the authors are those from the sp^2 carbon of the phenyl group to the sp^2 carbon of the silicon–carbon double bond which appear to occur under thermal rearrangements of silene **10** (under reflux or in the gas phase [7a]) and 1-silaallene **11** in the liquid phase [7b].

Obviously, the rearrangement described in this communication involves a novel type of 1,4-H migration, i.e. that from the sp^2 carbon of the naphthyl group to the sp^2 silicon of the silicon–carbon double bond of silene **2**. It opens a new approach to the synthesis of 1-hydro-1-silaacenaphthenes which conventional preparation involves reduction of the Si–Cl bond of 1,1-dichloro-1-silaacenaphtene produced by high temperature synthesis from trichlorosilane and α-methylnaphthalene [8].



Scheme 3.

Table 1
NMR parameters [a], Mass and FTIR spectra [b] of 1-methyl-1-silaacenaphthene



^{1}N NMR (C_6D_6): δ (ppm) 0.21 [d, 3H, $^3J(H^{13}H^{12})$ = 3.6 Hz, $SiCH_3$]; 2.02 [ddt, 1H, $^2J(H^{11\,a}H^{11\,b})$ = −18.2 Hz, $^3J(H^{11\,a}H^{12\,b})$ = 3.4 Hz, $^4J(H^{11\,a}H^2)$ = 1.0 Hz, $^6J(H^{11\,a}H^4)$ = −1.0 Hz, $H^{11\,a}$]; 2.38 [ddt, 1H, $^2J(H^{11\,b}H^{11\,a})$ = −18.2 Hz, $^3J(H^{11\,b}H^{12})$ = 3.4 Hz, $^4J(H^{11\,b}H^2)$ = 1.0 Hz, $^6J(H^{11\,b}H^4)$ = −1.0 Hz, $H^{11\,b}$]; 4.97 [broadened sextet, 1H, $^3J(H^{12}H^{13})$ = 3.6 Hz, $^3J(H^{12}H^{11})$ = 3.4 Hz, $^4J(H^{12}H^7)$ = 0.5 Hz, $^6J(H^{12}H^5)$ = 0.3 Hz, H^{11}]; 7.29 [m, 1H, $^3J(H^2H^3)$ = 6.8, $^4J(H^2H^4)$ = 1.0 Hz, $^4J(H^2H^{11})$ = 1.0 Hz, H^2]; 7.33 [t, 1H, $^3J(H^3H^2)$ = 6.8 Hz, $^3J(H^3H^4)$ = 6.8 Hz, H^3]; 7.35 [dd, 1H, $^3J(H^6H^5)$ = 7.8 Hz, $^3J(H^6H^7)$ = 6.2 Hz, H^6]; 7.52 [m, 1H, $^3J(H^4H^3)$ = 6.8 Hz, $^4J(H^4H^2)$ = 1.0 Hz, $^6J(H^4H^{11})$ = −1.0 Hz, H^4]; 7.61 [ddd, 1H, $^3J(H^7H^6)$ = 6.2 Hz, $^4J(H^7H^5)$ = 1.0 Hz, $^4J(H^7H^{12})$ = 0.5 Hz, H^7]; 7.68 [ddd, 1H, $^3J(H^5H^6)$ = 7.8 Hz, $^4J(H^5H^7)$ = 1.0 Hz, $^6J(H^5H^{12})$ = 0.3 Hz, H^5]
^{13}C NMR ($CDCl_3$): δ (ppm) −3.40 (1C, C^{13}); 15.57 (1C, C^{11}); 124.84, 125.63, 127.13, 127.23 (4C, C^2, C^3, C^4, C^6); 128.7 (1C, C^5); 131.20 (1C, C^7); 132.98 (1C, C^9); 138.60 (1C, C^{10}); 142.95 (1C, C^8); 144.25 (1C, C^1).
^{29}Si NMR ($CDCl_3$): δ (ppm) −9.80.

MS (70 eV): m/z 186 (5%), 185 (19%), 184 (M^+, 100%), 183 (50%), 182 (12%), 181 (13%), 170 (10%), 169 (61%), 168 (18%), 167 (60%), 155 (12%), 153 (7%), 152 (8%), 142 (6%), 141 (13%), 139 (7%), 115 (12%), 77 (5%), 53 (10%).

FTIR (gas-phase) 3055 m, 2970 w, 2912 w, 2184 vw, sh, 2136 vs, 1578 vw, 1490 w, 1453 w, 1329 vw, 1256 w, 1128 w, 1073 w, 1011 vw, 936 m, sh, 893 s, 827 s, 776 s, 722 w cm^{-1}.

[a] Bruker WP-200SY; spectrometer frequencies: ^{1}H 200.13 MHz, ^{13}C 50.31 MHz, ^{29}Si 39.768 MHz. Different double resonance techniques were used to assign signals in ^{1}H NMR spectra. Protons possessing long range spin–spin interactions with Si–H and CH_2 were assigned to H^5, H^7 and H^2, H^4, correspondingly. In addition increments of the substituents effect [5] were used to assign H^1 and H^3 as additivities to the chemical shifts of naphtalene. As H^1, H^2, H^3 and CH_2 signals represent a strongly coupling spin system their NMR parameters were found by computer simulating spectrum with standard PANIC program. Assignments in ^{13}C NMR spectrum were made using both DEPT technique and increments of the substituents effect to δ ^{13}C of naphthalene [6]. [b] Hewlett-Packard GC/MS/FTIR System.

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