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Preliminary communication

Silicon–carbon unsaturated compounds

XXX. Thermal isomerization of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene and 2-mesityl-2-(phenylethynyl)hexamethyltrisilane

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Abstract

The thermolysis of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene at 280 °C afforded 1-mesityl-3,3-dimethyl-4-phenyl-5-(trimethylsilyl)-1,3-disilacyclo-4-pentene and 1-mesityl-1,3-bis(trimethylsilyl)-1-silaindene. Similar thermolysis of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane produced the same products.

Recently, we have found that the reaction of 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene (**1**) with tetrakis(triethylphosphine)nickel(0) gives a nickelasilacyclobutene which readily isomerizes to a silapropadiene-nickel complex. We have also demonstrated that the silapropadiene-nickel complex can be produced by the nickel-catalyzed reaction of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane (**2**) [1–3]. In this paper we report that the thermolysis of **1** and **2** affords isomerization products which can be best explained by assuming the formation of the 1-silapropadiene intermediate.

When 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopropene **1** was heated in a sealed glass tube at 280 °C for 6 h, two products, 1-mesityl-3,3-dimethyl-4-phenyl-5-(trimethylsilyl)-1,3-disilacyclo-4-pentene [4*] (**3**) and 1-mesityl-1,3-bis(trimethylsilyl)-1-silaindene [5*] (**4**) were obtained in 49 and 28% yields, respectively (Scheme 1).

The structures of **3** and **4** were verified by spectrometric analysis, as well as by elemental analysis. The ^{1}H NMR spectrum of **3** shows resonances at δ −0.34, 0.08,

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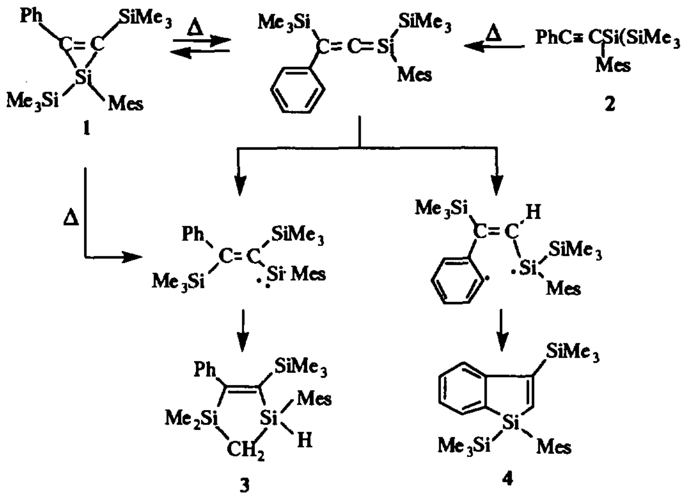
* Reference number with asterisk indicates a note in the list of references.



Scheme 1

and 0.22_3 ppm in the ratio of 3 : 1 : 1, attributed to trimethylsilyl protons and two non-equivalent methylsilyl protons on the silicon atom, and two double-doublets at δ −0.03 ($J = 14.8$, 4.0 Hz) and 0.22_4 ppm ($J = 14.8$, 4.6 Hz), due to two non-equivalent protons at the C_2 position of the 1,3-disilacyclo-4-pentene ring, as well as a double-doublet at δ 5.34 ppm ($J = 4.6$, 4.0 Hz) attributed to the proton on the silicon atom. The position of the trimethylsilyl group on the silaindene ring of compound **4** was confirmed by the NOE-FID difference experiment at 500 MHz. Thus, saturation of trimethylsilyl protons on the sp^2 carbon caused a positive NOE of the vinylic proton, while irradiation of trimethylsilyl protons on the ring silicon atom led to enhancement of the vinylic proton. Irradiation of this vinylic proton resulted in the enhancement of the *ortho*-methyl protons of a mesityl group as well as two trimethylsilyl protons. These results are wholly consistent with the proposed structures for **3** and **4**.

Interestingly, the thermolysis of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane **2** in a sealed tube at 280 °C for 30 h gave products **3** and **4** in 25 and 18% yields, respectively, in addition to nonvolatile substances. No other volatile products, except a small amount of the starting compound **2** (less than 5%) which was recovered unchanged, were detected by GLC analysis.

Scheme 1 illustrates a possible route leading to the observed products **3** and **4**. Compound **3** is probably formed by intramolecular insertion of a silylene which would be formed from isomerization of either silacyclopropene or 1-silapropadiene into a C–H bond of a trimethylsilyl group. Such intramolecular insertion of the silylene into a C–H bond has been observed in the pyrolysis of allylpentamethyldisilane [6] and other system [7]. The exsistence of the equilibrium between silacyclopropene and 1-silapropadiene has been confirmed in the photolysis of compound **1** [3]. Compound **4** may be explained by hydrogen shift from the *ortho* position of a phenyl group to an internal carbon of the silapropadiene, followed by coupling of the resulting diradical. Similar ring closure of the silene has been reported by Eaborn et al. [8]. We are continuing to explore this and related system.

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4 For compound **3**: ^{1}H NMR δ ($CDCl_3$) -0.34 (9H, s, Me_3Si), -0.03 (1H, dd, $J = 14.8$, 4.0 Hz, H_aCH_b), 0.08 (3H, s, MeSi), 0.22_3 (3H, s, MeSi), 0.22_4 (1H, dd, $J = 14.8$, 4.6 Hz, H_bCH_a), 2.27 (3H, s, *p*-Me), 2.46 (6H, s, *o*-Me), 5.34 (1H, dd, $J = 4.6$, 4.0 Hz, HSi), 6.81–7.31 (7H, m, phenyl and mesityl ring protons); ^{13}C NMR δ ($CDCl_3$) -7.2 (CH_2), -0.9 (MeSi), -0.5 (MeSi), 0.6 (Me_3Si), 21.2 (*p*-Me), 26.9 (*o*-Me), 125.5, 125.8, 126.3, 127.7, 128.8, 131.0, 139.3, 146.8 (aromatic carbons), 163.1, 182.5 (olefinic carbons); MS, *m/e* 394 (M^+). Anal. Found: C, 69.84; H, 8.68. $C_{23}H_{34}Si_3$ calc.: C, 69.98; H, 8.68%.

5 For compound **4**: ^{1}H NMR δ ($CDCl_3$) 0.02 (9H, s, Me_3Si), 0.32 (9H, s, Me_3Si), 2.25 (3H, s, *p*-Me), 2.55 (6H, s, *o*-Me), 6.83 (2H, s, mesityl ring protons), 7.11 (1H, s, olefinic proton), 7.23–7.83 (4H, m, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) -0.8 (Me_3Si), -0.5 (Me_3Si), 20.9 (*p*-Me), 25.9 (*o*-Me), 125.4, 125.5, 127.5, 127.8, 128.5, 134.1, 138.7, 139.6, 144.6, 146.2 (mesityl and phenyl ring carbons), 152.4, 162.9 (olefinic carbons); MS, *m/e* 394 (M^+). Anal. Found: C, 69.97; H, 8.63. $C_{23}H_{34}Si_3$ calc.: C, 69.98; H, 8.68%.

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