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Silaethene in Pyrolysis of Spiro[silacyclobutane-1,9′-[9*H*-9]silafluorene]

Daiyo Terunuma,* Makoto Nakamura, Eiji Miyazawa, and Hiroyuki Nohira
Department of Applied Chemistry, Faculty of Engineering, Saitama University, Urawa, Saitama 338

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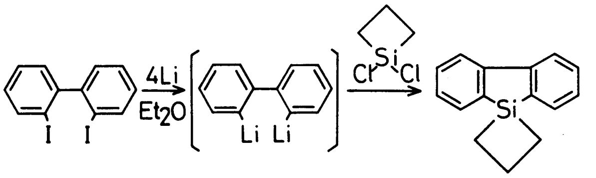
Synopsis. A new silaspiro compound, i.e., spiro[silacyclobutane-1,9′-[9H-9]silafluorene](**1**) was synthesized in 75% yield. It was found that the pyrolysis of **1** at 650 °C under a reduced pressure gave a head-to-tail silaethene dimer in 15% yield. Copyrolysis of **1** in the presence of benzophenone gave 1,1-diphenylethene and a siloxane oligomer in 50 and 30% yield, respectively.

Current attention has been concentrated to the preparation and characterization of a silicon-carbon double bond.1) It is suggested that 1-silafulvene systems have strong π stability and high reactivity, on the contrary 2-silafluvene systems have weak π stability and low reactivity.2) In this connection, the generation of 1-silafluvene was already investigated.3)

In the course of our studies on the synthesis of silicon-containing cyclic compounds,4) we have interested in spiro[silacyclobutane-1,9′-[9H-9]silafluorene] (**1**). Because the generation of 2-silafluvene type intermediate would be expected with extrusion of ethene in the pyrolysis of **1**.

Results and Discussion

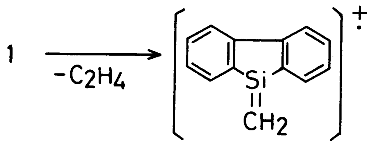
Compound **1** was obtained by treating 1,1-dichlorosilacyclobutane with biphenyl-2,2′-diyldilithium in 75% yield (Scheme 1).



1 (75%)

Scheme 1.

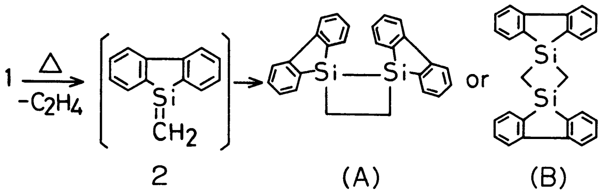
The mass spectrum of **1** shows relatively simple fragmentation including the base peak (*m*/*z* 194) corresponded to the silaethene fragment (Scheme 2).



m/*z* 194

Scheme 2.

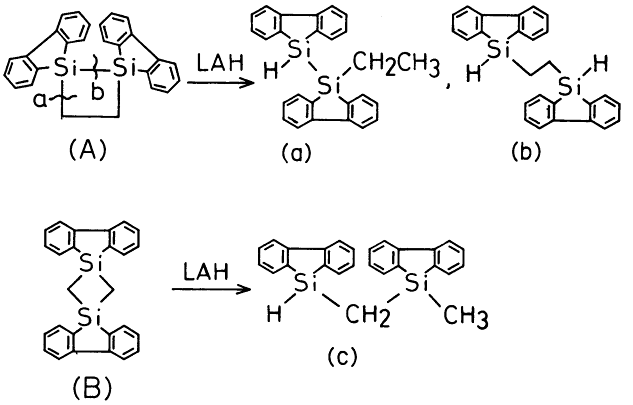
Then the pyrolysis of **1** was carried out at 650 °C under a reduced pressure (ca. 10^{-3} Torr[†]). A white crystalline product was obtained. The parent peak of the mass spectrum of the product was consistent with the molecular weight of a dimer of 2-silafluvene derivative (**2**) (*m*/*z* 388). Thus it is clear that **2** is generated under these reaction conditions and successive reaction of **2** occurs to give the dimer (Scheme 3).



Scheme 3.

On the other hand, the silaethene can be dimerized in the two manners,5) head-to-head (A) and head-to-tail (B).

NMR spectrum (^{29}Si) of the dimer (δ +2.1 based on TMS) suggests 1,3-disilacyclobutane structure (B).6) The disilacyclobutane derivative has been known to undergo ring-openning reaction in the presence of lithium aluminum hydride (LAH).7) The dimer was treated with LAH. The expected product from A and B are shown in Scheme 4.

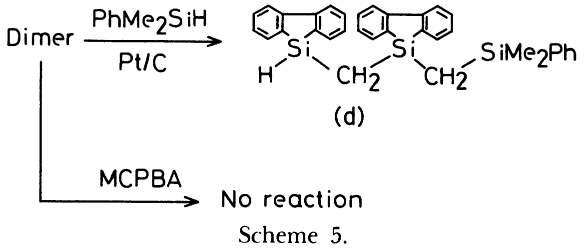


Scheme 4.

NMR spectra data of the product [^{13}C NMR ($CDCl_3$) δ −5.20 (t, CH_2), −2.27 (q, CH_3)] shows (c) in Scheme 4 which indicates the dimer structure of (**B**).

Furthermore, the reaction of the dimer with dimethylphenylsilane in the presence of platinum/carbon8) afforded corresponding ring-opened product (d) (Scheme 5), but no reaction occurred with *m*-chloroperbenzoic acid (MCPBA).

These results show that the dimer has the structure of type B.



Scheme 5.

Then copyrolysis of **1** with benzophenone was investigated. The reaction was carried out at 540 °C under a

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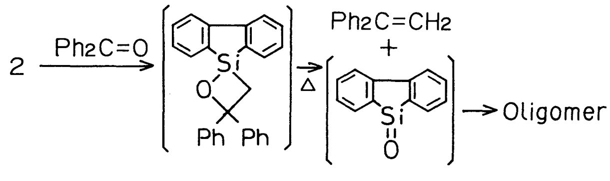
[†] 1 Torr=133.322Pa.

reduced pressure (ca. 10^{-3} Torr). 1,1-Diphenylethene and a siloxane oligomer were obtained in a 50 and 30% yield, respectively. Although we could not find out the direct evidence for the existence of the intermediates, it seems to be reasonable to consider that the reaction proceeds via a manner similar to that described in the copyrolysis of the silacyclobutane derivatives with benzophenone[9] (Scheme 6).



Scheme 6.

Experimental

The melting points and boiling points are uncorrected. The IR spectra were determined with a JASCO IR-A 302 spectrometer. The NMR spectra were determined at 90 MHz with a JEOL FX90Q and at 200 MHz with a JEOL FX200 spectrometers in $CDCl_3$ using TMS as an internal standard. The mass spectra were recorded on a JEOL-01SG instrument. Biphenyl-2,2′-diyldilithum was prepared in a manner similar to that described in the literature.[10]

Spiro[silacyclobutane-1,9′-[9H-9]silafluorene] (1). In a flask lithium (2.0 g, 0.29 gram-atoms) and dry ether (30 ml) were placed. A solution of 2,2′-diiodobiphenyl (12.0 g, 29.6 mmol) in dry ether (50 ml) was added to the mixture at reflux temperature with stirring under a dry nitrogen atmosphere. The mixture was refluxed for 1 h after the addition was complete. In another flask, a solution of 1,1-dichlorosilacyclobutane (4.0 g, 28.4 mmol) in dry ether (40 ml) was placed. The etheral solution of biphenyl-2,2′-diyldilithium was added to the solution of the chlorosilane by means of a syringe at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, allowed to stand at room temperature for 1 h. The reaction mixture was hydrolyzed and the organic layer was separated and dried (Na_2SO_4). Evaporation and distilation gave **1** in 4.4 g (75%) yield. Bp 131 °C/0.25 Torr. n_D^{25} 1.6511. IR (neat) 2900, 1600, 1430, 1350, 1260, 1130, 1060, 850, 740, 720, 680, 540 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.56 (t, 4, Si-CH_2), 2.38 (quintet, CH_2), 7.1—7.8 (m, 8, Ar). ^{13}C NMR ($CDCl_3$) δ=15.0 (Si-CH_2), 19.29 (CH_2), 120.55, 127.48, 130.68, 133.11, 135.61, 147.58 (Ar). ^{29}Si NMR ($CDCl_3$) δ=12.9. UV (cyclohexane) ε_{max}(nm) 237 (4.51×10^4), 244 (3.84×10^4), 281 (1.40×10^4), 293 (1.21×10^4). Found: C, 81.00; H, 6.51%. Calcd for $C_{15}H_{14}Si$: C, 81.02; H, 6.34%.

Pyrorysis of 1. Pyrolysis was carried out using a vacuum flow system. Compound **1** (527 mg, 2.4 mmol) was added into a quartz tube (l=40 cm, d=0.8 cm) maintained at 640 °C through preheated tube (ca. 300 °C) under a reduced pressure (4×10^{-3} Torr). The products were collected in a liq. N_2 trap, and washed out with benzene. Evaporation and filtration gave crystalline product. It was purified by recrystallization from benzene. Yield 70 mg (15%). Mp 323—326 °C. MS M^+ 388. IR (KBr) 3050, 1600, 1435, 1340, 1260, 1130, 1080, 940, 770, 730, 710, 630 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.17 (s, 4H, Si-CH_2), 7.2—8.0 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$) δ=1.10 (Si-CH_2), 121.1, 128.0, 131.0, 132.8, 137.5, 147.5 (Ar). ^{29}Si NMR ($CDCl_3$) δ=+2.1. UV (cyclohexane) ε_{max} (nm) 238 (9.65×10^4), 245 (1.02×10^5), 283 (3.44×10^4).

Copyrorysis of **1** (500 mg, 2.25 mmol) in the presence of benzophenone (410 mg, 2.25 mmol) was carried out at 540 °C in a manner similar to that described above. 1,1-Diphenylethene and the siloxane oligomer were separated from the reaction mixture by TLC (benzene-hexane 4 : 1) in 50% (200 mg) and 30% (130 mg) yield, respectively. 1,1-Diphenylethene; ^1H NMR (CCl_4) δ=5.35 (s, 2H, =CH_2), 7.20 (s, 10H, Ph). Oligomer IR (KBr) 3000, 1590, 1420, 1260, 1120, 1060, 740, 500 cm^{-1}. ^1H NMR (CCl_4) δ=7.0—8.2 (Ar).

Reaction of the Dimer with LAH. LAH (50 mg, 1.3 mmol) was added to a solution of the dimer (200 mg, 0.5 mmol) in dry ether (30 ml). The mixture was refluxed for 1 h with stirring. Usual work-up and purification by TLC (benzene) gave ring-opened product in 120 mg (60%) yield. ^1H NMR ($CDCl_3$) δ=0.40 (s, H, Si-CH_3), 0.61 (d, 2H, Si-CH_2-Si), 4.87 (t, 1H, Si-H), 7.1—7.8 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$) δ=−5.20 (t, CH_2), −2.27 (q, Si-CH_3), 120.77, 127.33, 130.20, 130.33, 132.99, 133.64, 135.46, 138.19, 147.69, 148.34 (Ar).

Reaction of the Dimer with Dimethylphenylsilane in the Presence of Pt/C Catalyst. A mixture of the dimer (39.8 mg, 0.10 mmol), dimethylphenylsilane (1.00 g, 7.4 mmol), and 5% Pt/C (10 mg) was placed in a test tube. The tube was sealed under a dry nitrogen atmosphere, and it was kept at 100 °C for 55 h. After evaporation of excess dimethylphenylsilane, the product was separated by TLC (hexane-benzene 3 : 1) and recrystallized from pentane. Yield 16.1 mg (30%). ^1H NMR ($CDCl_3$) δ=−0.06 (s, 6H, Si-CH_3), 0.44 (s, 2H, Si-CH_2-Si), 0.58 (d, 2H, Si-CH_2), 4.82 (t, 1H, Si-H), 7.1—7.8 (m, 21H, Ar).

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