Thermal Rearrangement of (1-Silaethen-1-yl)benzenes into 3,4-Benzo-1-Hydro-1-Silacyclobutenes. Novel Sigmatropic 1,3-Hydrogen Shift from Aryl Carbon to sp2 Silicon of the Silicon-Carbon Double Bond

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Thermal Rearrangement of (1-Silaethen-1-yl)benzenes into 3,4-Benzo-1-hydro-1-silacylclobutenes. Novel Sigmatropic 1,3-Hydrogen Shift from Aryl Carbon to sp^2 Silicon of the Silicon−Carbon Double Bond†

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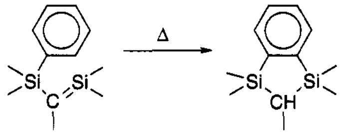
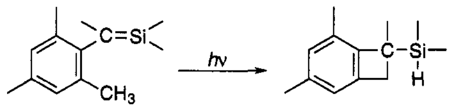
*Summary: A sigmatropic 1,3-hydrogen shift from an aryl carbon to an sp^2 silicon of the silicon−carbon double bond of silenes $CH_2{=}Si(CH_3){-}C_6H_4{-}Si(CH_3){=}CH_2$ and $CH_2{=}Si(CH_3)Ph$ was observed for the first time when studying very low pressure pyrolysis of 1,4-bis(1-silacyclobut-1-yl)benzene and 1-methyl-1-phenyl-1-silacyclobutane. Ring closure of the resultant 1,4-diradical produces 3,4-benzo-1-methyl-1-sila-3-cyclobutene (**9**), in the case of the latter. This finding opens a new approach to the formation of condensed aromatic silacycles via a monosilacyclobutane [4 → 2 + 2] cyclodecomposition−transient silene rearrangement sequence.*

Silenes, compounds containing a silicon−carbon p_π−p_π double bond, have attracted great interest since 1967.[1,2] Stable, sterically protected silenes have been reported.[3] Most transient silenes are highly reactive molecules which spontaneously dimerize in the absence of trapping reagents. Some silenes undergo rearrangements;[4] e.g., arylsilenes undergo sigmatropic hydrogen shifts resulting in ring closure products, such as (i) a 1,4-hydrogen shift from an aryl carbon to an sp^2 carbon of the silicon−carbon double bond[5,6a]

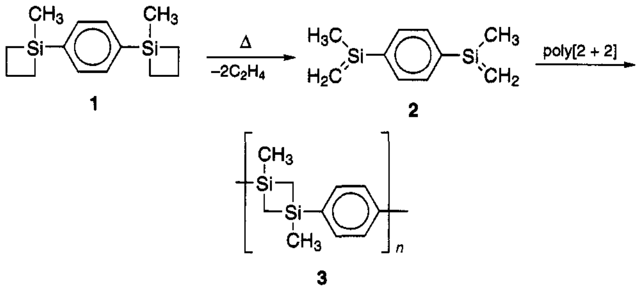


and (ii) a 1,5-hydrogen shift from an *o*-methyl group to the sp^2 silicon of the silicon−carbon double bond[6b,c]



No rearrangement, but only cyclodimerization or addition products, were observed for both Si- and C-phenyl substituted silenes.[7]

Scheme 1



With the aim of obtaining organosilicon polymer coatings by poly[2 + 2] cycloaddition of transient silenes containing two Si=C double bonds (Scheme 1) under conditions of chemical vapor deposition (CVD) we have been studying the very low pressure pyrolysis (VLPP) of 1,4-bis(1-methyl-1-silacyclobut-1-yl)benzene (**1**).[8] All experiments were performed within a temperature range of 670−730 °C and pressure 10^{-3}−10^{-2} Torr in a vertical quartz tube reactor connected at the top to a large-volume vessel to facilate CVD polymerization. The polymer deposit is formed on the walls and on objects inside the vessel. Vapors of the starting compound were passed from the bottom to the top of the reactor. Volatile products were collected in a trap cooled with liquid nitrogen. Some experiments were carried out in

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1994.

[1] (a) Gusel'nikov, L. E.; Flowers, M. C. *Chem. Commun.* **1967**, 864. (b) Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419.

[2] For reviews see: (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (b) Gusel'nikov, L. E.; Nametkin, N. S. In *Advances in Organosilicon Chemistry*; Voronkov, M. G., Ed.; Mir Publishers: Moscow, 1985; p 69. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (d) Gusel'nikov, L. E.; Avakyan, V. G. *Sov. Sci. Rev., Sect. B* **1989**, *13*, 39. (e) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds* Patai, S., Rappoport, Z. Eds.; Wiley: Chichester, U. K., 1989; Chapter 17, p 1015.

[3] (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) For a review see: Brook, A. G.; Baines, K. A. *Adv. Organomet. Chem.* **1986**, *25*, 1.

[4] For rearrangements of silenes, see ref 2e.

[5] The authors' explanation of this reaction is the addition of a C−H bond in the ortho position of an aromatic ring across the Si=C bond.

[6] (a) Eaborn, C.; Happer, D. A. R.; Hitchcock, P. B.; Hopper, S. P.; Safa, K. D.; Washburne, S. S.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *186*, 309. (b) Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487. (c) Baines, K. M.; Brook, A. G.; Ford, R. R.; Lickiss, P. D.; Saxena, A. K.; Chaterton, W. J.; Sawyer, J. F.; Behnam, B. A. *Organometallics* **1989**, *8*, 693.

[7] (a) Auner, N.; Grobe, J. *J. Organomet. Chem.* **1980**, *188*, 151. (b) Boudjouk, P.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 54. (c) Valkovich, P. B.; Ito, T. I.; Weber, W. P. *J. Org. Chem.* **1974**, *39*, 3543. (d) Bertrand, G.; Dubac, J.; Mazerolles, P.; Ancelle, J. *Nouv. J. Chim.* **1982**, *6*, 381.

[8] **1** was prepared from *p*-$BrMgC_6H_4MgBr$ and 1-chloro-1-methyl-1-silacyclobutane in 65% yield. IR (CsI, Ar, 10 K): 3090 (vw), 3050 (w), 3010 (w), 2990 (s), 2940 (s), 2920 (s, sh), 2870 (m), 1520 (w), 1480 (w, br), 1440 (m), 1420 (m), 1400 (s), 1370 (w, sh), 1360 (w), 1330 (vw), 1265 (w, sh), 1251 (m, br), 1215 (vw, br), 1190 (w), 1179 (vw), 1146 (w, sh), 1140 (vs), 1133 (m), 1125 (s), 1115 (w, sh), 1100 (vw), 1070 (w), 1015 (vw), 953 (vw), 928 (w), 908 (s), 882 (m, sh), 873 (vs, br), 830 (m), 813 (w, sh), 797 (s), 786 (vs, br), 747 (w), 730 (m, br), 720 (m, sh), 688 (w, br), 670 (w, sh), 663 (m), 658 (m), 638 (w), 554 (s), 541 (s), 520 (vw), 506 (w), 501 (w) cm^{-1}. MS (70 eV): *m/z* 246 (5%, $M^{\bullet+}$), 218 (100, $[M - 28]^{\bullet+}$), 190 (37, $[M - (2 \times 28)]^{\bullet+}$), 175 (11), 161 (6), 148 (13), 145 (9), 133 (6), 119 (6), 105 (8), 95 (12), 81 (5), 67 (6), 53 (9), 43 (25).

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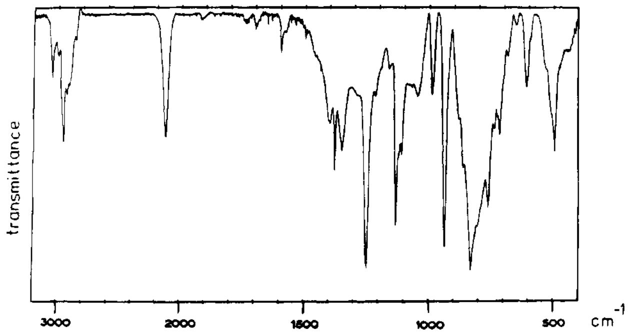
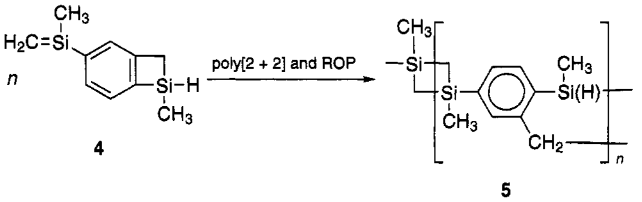


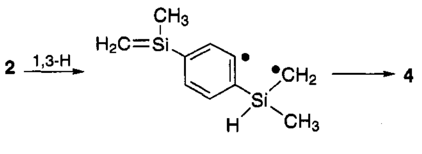
Figure 1. VLPP of **1** (640 °C, 6×10^{-2} Torr): infrared spectrum of a CVD polymer obtained on the stainless steel plate.

a VLPP system connected to an optical cryostat so that volatile products could be either condensed on the CsI target at 77 K in order to measure their low-temperature infrared spectra (LTIR) or cocondensed with a matrix gas (Ar or N_2 in 500–700-fold excess) on the target at 10–15 K to record their matrix isolation infrared spectra (MI/IR).[9]

Under CVD conditions pyrolysis of **1** results in formation of ethylene[10] and an insoluble polymer deposit whose IR spectrum (Figure 1) exhibits absorptions at 1350, 937, and 608 cm^{-1} characteristic of the 1,3-disilacyclobutane ring[11a] expected for the structure **3**. Surprisingly, a prominent Si–H absorption at 2122 cm^{-1} was observed. Together with bands at 1045 and 988 cm^{-1} and an absorption profile at 900–700 cm^{-1} characteristic of 1,2,4-trisubstituted benzenes,[11b] as well as absorptions at 1379, 1213, 1161, and 1110 cm^{-1},[11c] a structure resulting from ring-opening polymerization (ROP) of the benzo-1-silacyclobutene moiety of **4** is indicated. A deposit thus is built up by both fragments **3** and **5**:



We deduced that formation of the benzosilacyclobutene moiety might be due to an unknown rearrangement of **2** into **4** occurring via a 1,3-hydrogen shift from an aryl carbon to an sp^2 silicon of the silicon–carbon double bond:[12]



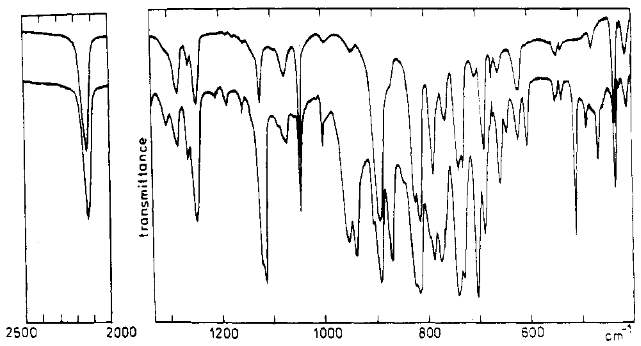
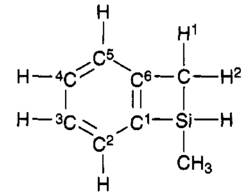


Figure 2. LTIR spectra (77 K) of (lower spectrum) VLPP products of **6** (670 °C, 6×10^{-2} Torr) and (upper spectrum) **9**, isolated from the VLPP products of **6**.

To verify this arylsilene–benzosilacyclobutene rearrangement, we have studied the VLPP of a model compound, i.e., 1-methyl-1-phenyl-1-silacyclobutane (**6**).[13] In the LTIR spectrum of the VLPP products of **6** (Figure 2), besides absorptions of the starting compound (1110, 910, 508 cm^{-1}), ethylene (960 cm^{-1}),[10] and the *E* and *Z* isomers of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (**10**; 1113, 940, 734, 702, 605 cm^{-1}),[14] the expected cyclodimerization products of silene **7**, a number of absorptions (2130, 1595, 1455, 1440, 1390, 1282, 1262, 1246, 1123, 1044, 895, 827, 815, 788, 740, 730, 688, 435, 412 cm^{-1}) could be assigned to 3,4-benzo-1-methyl-1-sila-3-cyclobutene (**9**), a product of intramolecular rearrangement of silene **7**.



9

A liquid sample of the pyrolyzate was obtained by trap-to-trap distillation on warming of the CsI target. Its study by GC/MS/FTIR revealed the presence of **9**[15] and **10**[16,17] as the main reaction products, in the molar ratio 1.3:1. In addition, **9** was isolated from the pyrolyzate and characterized by its NMR spectra.[18] Its LTIR spectrum is also given in Figure 2.

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(9) For details of the experiment see: Gusel'nikov, L. E.; Volkova, V. V.; Avakyan, V. G.; Nametkin, N. S. *J. Organomet. Chem.* **1980**, *201*, 137.

(10) The only gaseous reaction product revealed by GC.

(11) (a) Oppengeim, V. D. Ph.D. Thesis, Topchiev Institute of Petrochemical Synthesis, Academy of Sciences, Moscow, 1970 (in Russian). (b) Kusakov, M. M.; Pokrovskaya, E. S.; Shishkina, M. V.; Shimanko, N. A.; Prokofeva, E. A. *Izv. Akad. Nauk, Ser. Fiz.* **1962**, *26*, 1257. (c) Compare with absorptions at 1390, 1196, 1154, and 1106 cm^{-1}, which we observed upon ring-opening polymerization of **9**.

(12) In the MI/IR spectrum of VLPP products of **1**, apart from absorptions of the starting compound[8] and ethylene (945 cm^{-1}), absorptions at 2152, 1445, 1252, 1225, 1135, 1107, 1077, 1048, 1039, 920, 901, 898, 883, 841, 822, 810, 748, 713, 674, and 480 cm^{-1} were preliminaryily assigned to intermediates **2** and **4**.

(13) For synthesis of **6** see: Vdovin, V. M.; Nametkin, N. S.; Grinberg, P. L. *Dokl. Akad. Nauk SSSR* **1963**, *150*, 799.

(14) These absorptions were distinguished upon annealing the sample.

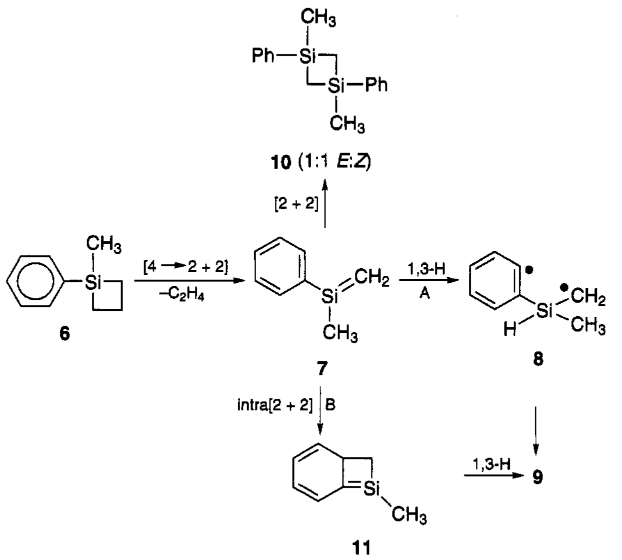
(15) **9**: MS (70 eV): *m/z* 134 (80%, $M^{\bullet+}$), 133 (18 $[M - 1]^+$), 119 (100, $[M - 15]^+$), 117 (11), 105 (10), 93 (20), 97 (5), 67 (9), 53 (16). FTIR (gas phase): 3061, 2925, 2133, 1581, 1440, 1261, 1122, 1043, 895, 818, 729, 696 cm^{-1}.

(16) (*E*)-**10**: MS (70 eV) *m/z* 268 (18%, $M^{\bullet+}$), 253 (100, $[M - 15]^+$), 190 (79, $[M - 78]^{\bullet+}$), 177 (71, $[M - 91]^+$); FTIR (gas phase) 3063 (m), 2967 (w), 2908 (vw), 1425 (vw), 1353 (vw), 1255 (w), 1110 (m), 940 (vs), 824 (s), 777 (s), 710 (s) cm^{-1}.

(17) (*Z*)-**10**: MS (70 eV): *m/z* 268 (18%, $M^{\bullet+}$), 253 (100, $[M - 15]^+$), 190 (80, $[M - 78]^{\bullet+}$), 177 (72, $[M - 91]^+$); FTIR (gas phase) 3063 (m), 2967 (w), 2908 (vw), 1426 (vw), 1352 (vw), 1255 (w), 1193 (vw), 1109 (m), 941 (vs), 809 (s), 725 (m) cm^{-1}.

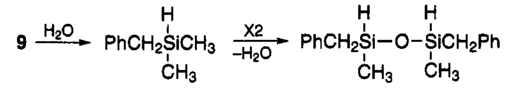
(18) **9**: ^{1}H NMR (neat) δ 0.26 (3H, d, $^3J_{CH_3SiH} = 4.0$ Hz, $SiCH_3$), 1,-93 (1H, dd, $^2J_{H^1CH^2} = 16.5$Hz, $^3J_{H^1CSiH} = 1.0$ Hz, CH^1), 2.17 (1H, dd, $^2J_{H^2CH^1} = 16.5$, $^3J_{H^2CSiH} = 1.0$ Hz, CH^2), 5.16 (1H, qt, $^3J_{HSiCH_3} = 4.0$ Hz, $^3J_{HSiCH_2} = 1.0$, SiH), 6.85–7.15 (4H, m, phenylene); $^{13}C\{^1H\}$ (neat) δ −2.82 (1C, $SiCH_3$), 17.77 (1C, CH_2), [127.01 (1C), 127.07 (1C), 131.25 (2C), C^2, C^3, C^4, C^5], [142.77 (1C), 151,82 (1C), C^1, C^6]; ^{29}Si NMR (neat) δ −10.925.

Scheme 2



One can imagine two pathways for the rearrangement of **7** to **9** (Scheme 2). Pathway A consists of a thermally "forbidden" sigmatropic 1,3-hydrogen shift from the carbon of the aromatic nucleus to the sp^2 silicon of the silicon−carbon double bond followed by ring closure of the resulting 1,4-diradical.[19] Another obviously less attractive pathway, B, involves intramolecular [2 + 2] cycloaddition of the silicon−carbon double bond to the phenyl group followed by a 1,3-hydrogen shift in the resulting silene **11**.

Actually, the observation of **2** and **4**[12] (but not absorptions due to the cyclohexadiene moiety expected for pathway B intermediates, e.g., **11**) and our recent results[20] on similar arylsilene rearrangements involving 1,4- and 1,5-H shifts followed by cyclization of diradicals (e.g., rearrangement of both 1-methyl-1-benzylsilene and 1-methyl-1-*o*-tolylsilene to 1,1-dimethyl-3,4-benzo-1-silacyclobutene and silaindanes, as well as the rearrangement of 1-methyl-1-naphthylsilene to 1-methyl-1-hydro-1-silaacenaphthene) may be considered as supporting evidence for pathway A. Thus, the above experimental data are more consistent with pathway A. This rearrangement opens a new approach to the synthesis of 3,4-benzo-1-silacyclobutenes.[21] By varying the pressure one can change the **9** to **10** ratio: the lower the pressure, the higher the contribution of the 1,3-hydrogen shift. At higher pyrolysis temperatures (above 730 °C) the yield of **9** decreases because of formation of secondary products, e.g., styrene, benzene, dimethylphenylsilane. Traces of water cleave the Si−C$_{\mathrm{aryl}}$ bond of **9**, resulting in disiloxane **12**.[22]



$$\mathbf{9} \xrightarrow{\mathrm{H_2O}} \mathrm{PhCH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{Si}}}\mathrm{CH_3} \xrightarrow[-\mathrm{H_2O}]{\mathrm{X2}} \mathrm{PhCH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{Si}}}\mathrm{-O-}\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{Si}}}\mathrm{CH_2Ph}$$

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(19) (a) A somewhat similar rearrangement of CH$_2$=Si(Me)CH$_2$SiMe$_3$ was envisioned as arising from 1,5-hydrogen atom transfer to produce the 1,4-diradical, which closes to give the product. See: Barton, T. J.; Burns, G. T.; Gscheidner, D. *Organometallics* **1983**, *3*, 8. (b) To the best of our knowledge, only one 1,3-hydrogen shift from sp^2 carbon to sp^2 silicon of the silicon−carbon double bond has been proved for a rearrangement of the intermediate 4-(trimethylsilyl)-silabuta-1,3-diene into silylallene: Barton, T. J.; Zhang, X. Unpublished results.

(20) Volkova, V. V.; Gusel'nikov, L. E.; Volnina, E. A.; Buravtseva, E. N. *First Organosilicon Microsymposium*; May 17, 1994, Moscow; Nesmeyanov Institute on Organoelement Chemistry; Abstracts, p 3 (in Russian).

(21) For the synthesis of 3,4-benzo-1-silacyclobutenes see: (a) Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 5589. (b) Eaborn, C.; Walton, D. R. M.; Chan, M. *J. Organomet. Chem.* **1967**, *9*, 251.

(22) **12**: MS (70 eV) *m/z* 271 (5%, [M − 15]$^+$), 195 (100, [M − 91]$^+$); FTIR (gas phase) 2135 (ν_{SiH}), 1064 (ν_{SiOSi}) cm^{-1}.