Reactions of Silicon Atoms with Benzene: A Matrix-Spectroscopic Study[‡]

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Keywords: Matrix isolation / Photochemistry / Isomerizations / Silicon / Density functional calculations

The reaction of silicon atoms with benzene in argon at 10 K has been studied. The addition to the aromatic π-system of benzene occurs in a [1,4]-fashion. Upon irradiation the π-adduct 7-silabicyclo[2.2.1]heptadien-7-ylidene (**2**) rearranges to the formal C–C insertion product 1-silacycloheptatrienylidene (**3**). The structural elucidation of the new species is based on comparison of the experimental observations with density functional calculations.
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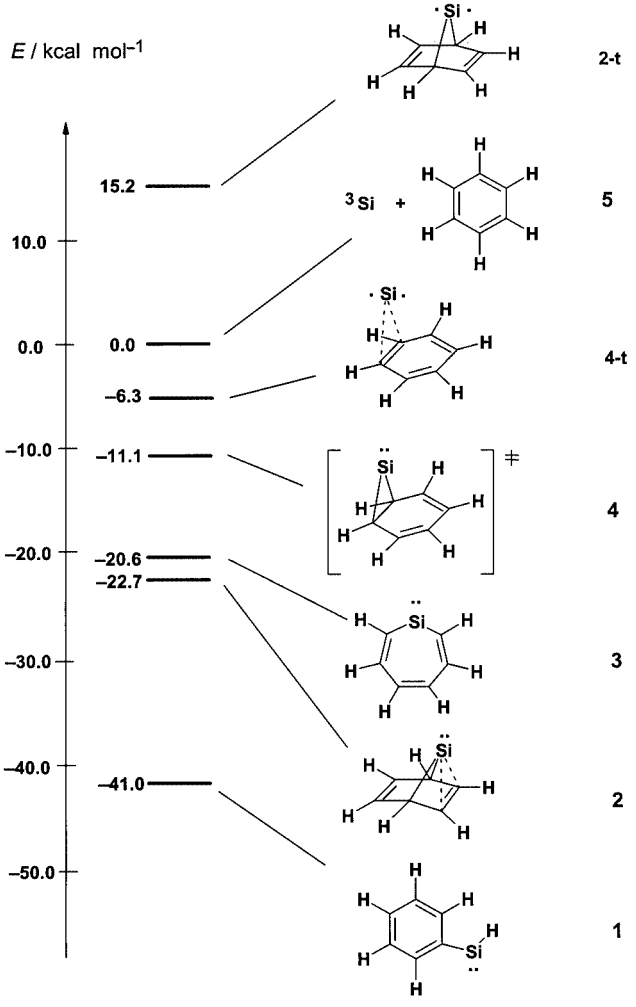
Introduction

Thermally generated silicon atoms react with compounds containing isolated[1] or conjugated[2] double bonds in an argon matrix at 10 K with formation of π-adducts, which can subsequently be isomerized to the corresponding insertion products by irradiation.[1,2] It was tempting to test whether the same type of reaction also occurs with substrate molecules possessing an aromatic π-system, the simplest example being benzene. The results with this model compound are presented below.

Calculations

In order to have a guideline for our experimental work several stationary points on the C_6H_6Si potential energy surface, together with the corresponding vibrational spectra, were calculated with the 6-311+G** basis set and the B3LYP functional. Scheme 1 gives the calculated relative energies.

The global minimum is phenylsilylene (**1**), the formal product of the insertion of a silicon atom into the C−H bond of benzene (**5**). The stabilization energy compared with the two components − triplet silicon atom and benzene (**5**) − is 41.0 kcal·mol^{-1}. Besides **1** two other isomers **2** and **3** are predicted to be formed in exothermic reactions from ^{3}Si atoms and **5** and can be expected as reaction products. In addition to the thermodynamic situation one has also to take into account which isomer is formed by the most suited pathway. In this respect the C−H and C−C insertion products **1** and **3** should be disfavored. A better



Scheme 1. Calculated relative energies of some C_6H_6Si isomers (B3LYP/6-311+G**)

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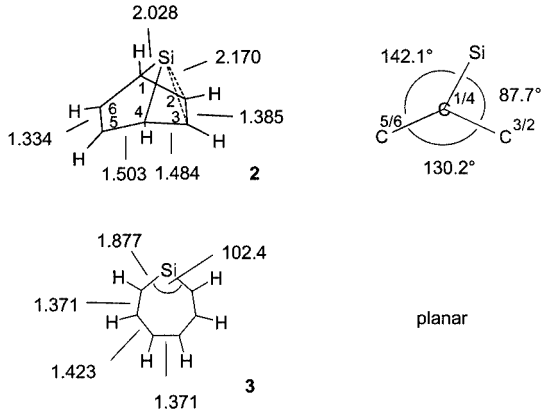
candidate is the [1,4]-π-adduct **2**. According to the calculations the [1,2]-π-adduct **4** with a norcaradiene-type structure does not represent a minimum, but only a transition state. It is noteworthy that in case of the carbon analog the norcaradiene-type carbene is calculated to be a minimum with a singlet ground state.[3] On the other hand the triplet [1,2]-π-adduct **4-t** with a nearly intact benzene ring represents a minimum. The corresponding triplet [1,4]-π-adduct **2-t** is higher in energy than the starting materials and should therefore not be formed in the reaction of these components.



Scheme 2. Some calculated structural features of the C_6H_6Si isomers **2** and **3** (B3LYP/6-311+G**; bond lengths in Å, angles in °)

As is shown below, the only detectable thermal reaction product is the singlet [1,4]-π-adduct **2**. The mechanism for the formation of **2** from ^{3}Si atoms and benzene **5** seems to be relatively complex. It has to be assumed that in the first step a 1,2-addition occurs. Along the pathway to the final product **2** two additional events have to take place, namely intersystem crossing and a formal 1,3-shift of the Si−C bond.

The calculated structural features of **2** and **3** are given in Scheme 2. A typical phenomenon is, once more (see the preceding paper), the tendency of the silylene bridge to undergo additional coordination to one of the two double bonds. As a result the bridge does not bisect the molecule but is strongly bent toward the centres of coordination.

1-Silacycloheptatrienylidene (**3**) is a planar molecule with a delocalized electron sextet. The bond alternation is diminished compared to standard bond lengths, as for instance in isomer **2**. The parallelism between **3** and 1-silacyclopropenylidene is obvious. This compound, identified by us before,[4] contains a delocalized 2π-electron system and its best Lewis structure has to be described by a three-center π-bond orbital.

Table 1. Calculated energies and vibrational spectra of some C_6H_6Si isomers (B3LYP/6-311+G**)

Species (point group, state)[a] Energy, ZPE included [hartrees][a]	Vibrational spectrum: wavenumber (IR intensity) symmetry
1 (C_s, ^{1}A′) −521.670667	127.8 (0) a″, 232.2 (0) a′, 259.6 (0) a″, 385.9 (30) a′, 419.3 (0) a″, 438.3 (1) a″, 629.10 (0) a′, 703.1 (11) a′, 708.6 (52) a″, 754.7 (37) a″, 824.2 (81) a′, 867.10 (0) a″, 950.7 (1) a″, 999.2 (0) a″, 1012.8 (5) a′, 1020.9 (0) a″, 1044.5 (1) a′, 1096.6 (1) a′, 1105.4 (104) a′, 1184.5 (1) a′, 1208.8 (8) a′, 1305.6 (6) a′, 1348.8 (10) a′, 1456.3 (22) a′, 1502.1 (3) a′, 1597.4 (1) a′, 1619.2 (44) a′, 2007.4 (275) a′, 3147.7 (3) a′, 3159.10 (0) a′, 3169.9 (4) a′, 3178.5 (24) a′, 3187.3 (21) a′
2 (C_s, ^{1}A′) −521.641505	293.7 (3) a′, 349.3 (0) a″, 409.1 (0) a′, 458.3 (1) a″, 492.9 (30) a′, 581.2 (0) a″, 614.2 (0) a′, 699.4 (3) a″, 727.10 (32) a′, 846.8 (20) a″, 862.9 (64) a′, 878.9 (2) a″, 921.7 (0) a″, 931.7 (8) a′, 969.7 (0) a″, 972.6 (45) a′, 1022.6 (2) a′, 1031.3 (0) a″, 1053.9 (1) a″, 1109.6 (0) a′, 1130.1 (1) a′, 1289.9 (26) a′, 1307.3 (0) a″, 1347.2 (8) a″, 1367.9 (11) a″, 1492.9 (9) a′, 1649.1 (22) a′, 3148.4 (18) a″, 3150.0 (1) a′, 3169.1 (4) a″, 3173.2 (11) a″, 3187.5 (14) a′, 3193.8 (21) a′
3 (C_{2v}, ^{1}A$_1$) −521.638152	83.2 (1) b_1,169.5 (0) a_2, 331.3 (4) a_1,358.1 (0) b_2, 370.5 (0) b_1, 540.10 (0) a_2, 591.9 (56) a_1, 628.8 (4) b_2, 629.0 (55) b_1, 721.3 (14) a_1, 822.7 (0) a_2, 874.1 (1) b_1, 880.1 (4) b_2, 895.7 (1) a_1, 1023.3 (0) a_2, 1040.5 (0) b_1, 1058.8 (0) a_2, 1060.9 (1) b_2, 1251.1 (1) a_1, 1283.7 (3) b_2, 1317.3 (4) a_1, 1410.8 (0) b_2, 1428.2 (95) a_1, 1498.4 (10) b_2, 1508.9 (94) a_1, 1593.1 (2) b_2,1634.9 (3) a_1, 3064.7 (12) a_1, 3065.10 (1) b_2, 3094.4 (77) b_2, 3095.9 (4) a_1, 3130.8 (15) b_2, 3151.7 (33) a_1
4 (C_s, ^{1}A′) −521.622973	−182.7 (1) a″, 155.4 (0) a′, 384.6 (3) a′, 477.9 (9) a″, 495.3 (25) a″, 501.4 (10) a′, 596.3 (1) a′, 611.6 (4) a″, 728.4 (94) a′, 775.2 (0) a″, 826.8 (4) a′, 888.3 (0) a′, 889.9 (1) a″, 950.9 (3) a′, 952.9 (1) a″, 970.2 (3) a′, 976.0 (0) a″, 1032.7 (2) a″, 1099.6 (30) a′, 1176.4 (1) a′, 1197.7 (1) a″, 1295.5 (31) a′, 1318.3 (3) a″, 1393.3 (7) a″, 1441.5 (4) a′, 1593.3 (5) a′, 1660.6 (0) a″, 3077.5 (2) a″, 3095.6 (14) a′, 3155.5 (3) a″, 3160.3 (2) a′, 3175.7 (34) a″, 3187.0 (18) a′
4-t (C_s, ^{3}A″) −521.615275	80.4 (2) a′, 123.7 (0) a″, 151.0 (1) a′, 393.5 (2) a″, 397.10 (1) a′, 602.7 (0) a″, 611.8 (2) a′, 659.1 (1) a″, 705.5 (71) a′, 833.0 (11) a′, 837.10 (0) a″, 906.6 (1) a″, 961.8 (8) a′, 985.5 (3) a′, 992.6 (0) a″, 1016.2 (0) a″, 1031.4 (5) a′, 1047.3 (1) a″, 1172.10 (3) a′, 1185.4 (1) a′, 1192.5 (1) a″, 1353.3 (0) a′, 1373.4 (0) a″, 1486.1 (15) a″, 1488.10 (10) a′, 1572.6 (12) a′, 1602.6 (0) a″, 3170.1 (0) a″, 3178.1 (3) a′, 3183.4 (9) a″, 3194.3 (8) a″, 3194.7 (10) a′, 3204.2 (0) a′
2-t (C_{2v}, ^{3}B$_1$) −521.581091	176.7 (1) b_2, 254.9 (15) a_1, 268.4 (1) b_1, 383.6 (0) a_1, 426.3 (0) a_2, 519.5 (0) b_2, 606.8 (0) a_1, 618.6 (0) a_2, 729.6 (3) b_1, 743.5 (77) a_1, 855.8 (2) b_2, 923.6 (9) b_2, 933.7 (10) a_1, 933.8 (0) a_2, 959.6 (9) b_2, 980.9 (0) a_1, 1020.2 (1) b_2, 1028.3 (1) b_1, 1102.6 (0) a_2, 1138.8 (0) b_1, 1159.6 (0) a_1, 1300.1 (2) b_1, 1332.6 (0) a_2, 1403.9 (14) b_2, 1406.5 (0) a_2, 1527.7 (10) b_1, 1602.7 (5) a_1, 3162.7 (9) b_2, 3165.5 (0) a_1, 3179.1 (0) a_2, 3184.1 (11) b_2, 3198.6 (14) b_1, 3202.5 (5) a_1

[a] ^{3}Si (^{3}P) −289.3941676. C_6H_6 **5** (D_{6h}, ^{1}A$_{1g}$) −232.211107.

IR Spectroscopic Observations

The FT-IR spectrum of the reaction products after cocondensation of silicon atoms and benzene (**5**) in argon (ratio 1:100) is represented in Figure 1. It is evident that only the [1,4]-π-adduct **2** is formed. Table 1 summarizes the calculated IR spectra of some relevant isomers of the elemental composition C_6H_6Si.

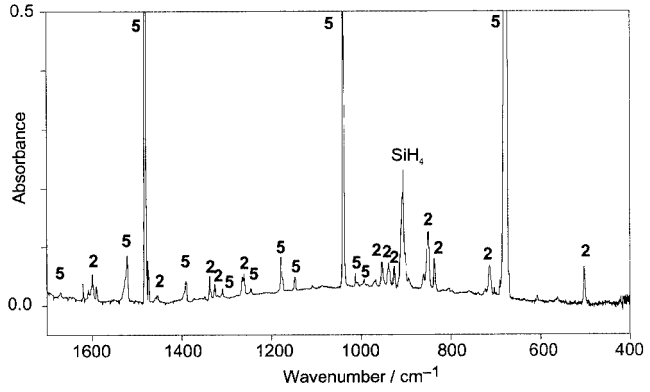


Figure 1. IR spectrum of the reaction product of Si atoms with benzene (**5**) in an argon matrix at 10 K

Upon irradiation with light of wavelength 313 nm the bands of **2** diminish and a set of new absorptions can be detected. By comparison with the calculated spectra the photoproduct can be identified as 1-silacycloheptatrienylidene (**3**). It was not possible to convert **2** completely into **3**. Longer irradiation did not lead to a higher amount of **3**. In addition this photoreaction turned out not to be reversible. The photoinduced interconversion of **2** into **3** is best demonstrated by the difference spectrum shown in Figure 2.

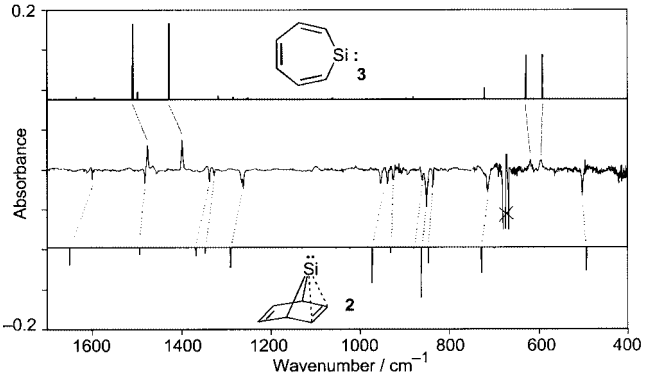


Figure 2. Top: calculated (B3LYP/6-311+G**) IR spectrum of 1-silacycloheptatrienylidene **3**; center: difference FT-IR spectrum of the photoreaction **2** → **3** (obtained by subtraction of the spectra taken after and before irradiation with 313 nm for 3 h); bottom: calculated IR spectrum (B3LYP/6-311+G**) of [1,4]-π-adduct **2**

Table 2. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C_6H_6Si isomers (a) **[H$_6$]2** and (b) **[D$_6$]2**

(a) isomer **[H$_6$]2** Sym.	Approx. description	Calculation	Experiment
a′	SiC str.	293.7 (2.8)	
a′′	SiC str.	349.3 (0.0)	
a′	ring def.	409.1 (0.2)	
a′′	ring def.	458.3 (0.6)	
a′	SiC str.	492.9 (30.2)	502.8 (s)
a′′	ring def.	581.2 (0.3)	
a′	ring def.	614.2 (0.1)	
a′′	ring def.	699.4 (2.6)	
a′	CH def.	728.0 (31.8)	713.9 (s)
a′′	CH def.	846.8 (20.0)	836.8 (m)
a′	CH def.	862.9 (64.0)	851.0 (s)
a′′	CH def.	878.9 (2.2)	860.2 (w)
a′′	CH def.	921.7 (0.0)	
a′	ring breath.	931.7 (8.0)	924.6 (w)
a′′	CH def.	969.7 (0.3)	938.2 (m)
a′	CH def.	972.6 (44.9)	953.5 (m)
a′	CC str.	1022.6 (2.0)	
a′′	CC str.+ CH def.	1031.3 (0.5)	
a′′	CC str.+ CH def.	1053.9 (1.5)	
a′	CC str.+ CH def.	1109.6 (0.4)	
a′	CC str.+ CH def.	1130.1 (1.3)	
a′	CC str.+ CH def.	1289.9 (25.8)	1261.1 (m)
a′′	CH def.	1307.3 (0.0)	
a′′	CH def. + CC str.	1347.2 (7.9)	1362.8 (w)
a′′	CH def.	1367.9 (11.3)	1338.3 (w)
a′	CC str.	1492.9 (9.1)	1465.5 (w)
a′	CC str.	1649.1 (21.5)	1599.3 (w)
a′′	CH str.	3148.4 (17.9)	
a′	CH str.	3150.0 (0.8)	
a′′	CH str.	3169.1 (4.0)	
a′′	CH str.	3173.2 (10.9)	
a′	CH str.	3187.5 (14.4)	
a′	CH str.	3193.8 (21.0)	

(b) isomer **[D$_6$]2** Sym.	Approx. description	Calculation	Experiment
a′	SiC str.	279.0 (2.8)	
a′′	SiC str.	338.3 (0.0)	
a′	ring def.	351.8 (2.5)	
a′′	ring def.	406.0 (0.5)	
a′	SiC str.	457.8 (19.0)	467.5 (w)
a′′	CD def.	499.1 (0.1)	
a′	CD def.	565.1 (8.9)	557.4 (w)
a′	CD def.	606.2 (5.7)	597.8 (m)
a′′	ring def.	657.7 (1.6)	
a′′	CD def.	675.0 (7.7)	663.3 (w)
a′	SiC str.	699.1 (60.5)	689.5 (s)
a′′	CD def.	718.9 (9.5)	
a′	CD def.	723.6 (15.7)	705.6 (m)
a′′	CD def.	745.6 (1.5)	
a′	CD def.	789.0 (0.2)	
a′	CD def.	815.0 (5.9)	776.1 (w)
a′′	CD def.	819.6 (0.9)	
a′′	ring def.	821.6 (0.3)	
a′	CD def.	829.3 (2.5)	
a′	ring breath.	932.0 (1.1)	
a′′	ring def.	933.3 (1.2)	
a′′	CD def.	1016.9 (0.1)	
a′	CC str.	1163.3 (17.3)	1141.7 (m)
a′′	CC str.	1169.3 (3.3)	1150.1 (w)
a′	CC str.	1240.0 (0.8)	
a′	CC str.	1422.5 (15.8)	1395.2 (w)
a′	CC str.	1599.9 (25.5)	1558.2 (m)
a′′	CD str.	2320.6 (9.5)	
a′	CD str.	2322.7 (0.2)	
a′′	CD str.	2333.4 (4.8)	
a′′	CD str.	2339.9 (2.4)	
a′	CD str.	2366.6 (6.9)	
a′	CD str.	2380.7 (7.4)	

Table 3. Calculated (B3LYP/6-311+G**) and experimental IR spectrum of C_6H_6Si isomers (a) **[H$_6$]3** and (b) **[D$_6$]3**

(a) isomer **[H$_6$]3** Sym.	Approx. description	Calculation	Experiment
b_1	ring def. oop	83.2 (0.7)	
a_2	ring def. oop	169.5 (0.0)	
a_1	ring def. ip	331.3 (4.0)	
b_2	ring def. ip	358.1 (0.4)	
b_1	ring def. oop	370.5 (0.4)	
a_2	ring def. oop	541.0 (0.0)	
a_1	SiC str.	591.9 (55.7)	596.4 (m)
b_2	SiC str.	628.8 (4.0)	
b_1	CH def. oop	629.0 (55.1)	618.5 (m)
a_1	ring def. ip	721.3 (13.9)	
a_2	CH def. oop	822.7 (0.0)	
b_1	CH def. oop	874.1 (0.9)	
b_2	ring def. ip	880.1 (3.5)	
a_1	ring breath.	895.7 (1.2)	
a_2	CH def. oop	1023.3 (0.0)	
b_1	CH def. oop	1040.5 (0.3)	
a_2	CH def. oop	1058.8 (0.0)	
b_2	CC str.	1060.9 (1.3)	
a_1	CH def. ip + CC str.	1251.1 (1.4)	
b_2	CH def. ip + CC str.	1283.7 (2.7)	
a_1	CH def. ip + CC str.	1317.3 (4.3)	
b_2	CH def. ip + CC str.	1410.8 (0.1)	
a_1	CH def. ip + CC str.	1428.2 (95.0)	1389.3 (s)
b_2	CC str. + CH def. ip	1498.4 (9.5)	
a_1	CC str. + CH def. ip	1508.9 (94.0)	1475.9 (s)
b_2	CC str.	1593.1 (2.4)	
a_1	CC str.	1634.9 (3.5)	
a_1	CH str.	3064.7 (12.2)	
b_2	CH str.	3066.0 (0.6)	
b_2	CH str.	3094.4 (76.8)	
a_1	CH str.	3095.9 (3.8)	
b_2	CH str.	3130.8 (15.0)	
a_1	CH str.	3151.7 (33.5)	

(b) isomer **[D$_6$]3** Sym.	Approx. description	Calculation	Experiment
b_1	ring def. oop	75.9 (0.8)	
a_2	ring def. oop	52.5 (0.0)	
a_1	ring def. ip	324.6 (3.6)	
b_1	ring def. oop	328.2 (0.2)	
b_2	ring def. ip	346.8 (0.4)	
a_2	CD def. oop	460.8 (0.0)	
b_1	CD def. oop	466.2 (28.2)	
a_1	SiC str.	566.8 (44.8)	567.6 (m)
b_2	SiC str.	600.2 (3.8)	
a_2	CD def. oop	640.2 (0.0)	
a_1	ring def. ip	683.3 (19.1	
b_1	CD def. oop	688.2 (0.2)	
a_1	ring breath.	789.3 (0.2)	
b_2	ring def. ip	800.5 (1.0)	
a_2	CD def. oop	815.1 (0.0)	
b_1	CD def. oop	841.8 (0.2)	
b_2	CD def. ip	854.9 (0.1)	
a_2	CD def. oop	858.4 (0.0)	
a_1	CD def. ip	907.4 (0.2)	
a_1	CD def. ip	949.5 (4.0)	
b_2	CC str.	956.7 (3.5)	
b_2	CD def. ip	1112.4 (0.0)	
a_1	CC str. + CD def. ip	1180.8 (36.8)	1160.7 (m)
b_2	CC str. + CD def. ip	1315.4 (7.1)	1289.8 (w)
a_1	CC str. + CD def. ip	1485.5 (156.4)	1455.2 (s)
b_2	CC str. + CD def. ip	1564.9 (1.3)	
a_1	CC str. + CD def. ip	1576.6 (0.4)	
a_1	CD str.	2252.5 (2.7)	
b_2	CD str.	2252.9 (0.0)	
$_2$	CD str.	2282.7 (43.6)	
a_1	CD str.	2285.2 (3.6)	
b_2	CD str.	2306.9 (11.0)	
a_1	CD str.	2327.9 (19.9)	

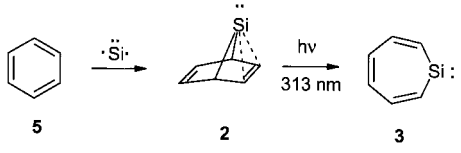
From the comparison with the calculated spectra it follows that the π-adduct **2** indeed gives the C−C insertion product **3** upon irradiation.

As far as the mechanism of this photoreaction is concerned it is tempting to assume that upon irradiation **2** is transferred into a norcaradiene species (**4** or **4-t**) followed by ring opening to the cycloheptatriene-type isomer.

The elucidation of structures **2** and **3** also follows from the data given in Tables 2 and 3. A typical band of **2** is the Si−C stretching vibration at 502 cm^{-1} which shifts in the deuterated compound only to 467.5 cm^{-1}. Isomer **3** is characterized by two strong C−C stretching vibrations at 1389.3 and 1475.9 cm^{-1} (protonated form) or 1160.7 and 1455.2 cm^{-1} (deuterated molecule). The high intensities reflect the dipolar property of **3**.

Conclusion

Two facts are remarkable. First, addition of a silicon atom to benzene occurs exclusively in a [1,4]-fashion. Second, photoexcitation of the [1,4]-adduct **2** opens a surprisingly easy entry to 1-silacycloheptatrienylidene (**3**).



5 2 3

Experimental Section

General: Equipment used for vaporization of silicon, cocondensation of silicon atoms with a substrate molecule, and subsequent irradiation of the reaction products has been described before (preceding paper in this journal[2]).

Acknowledgments

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