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# Preparation and Some Reactions of Dibenzo-7-silanorbornadiene Derivatives[1]

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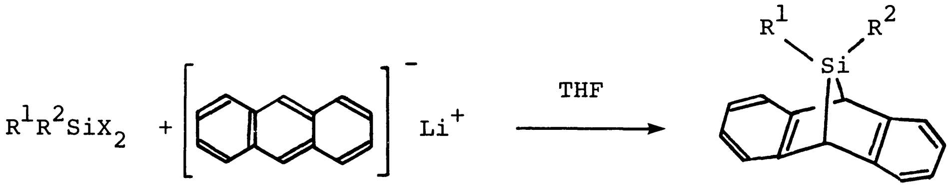
On irradiation, dibenzo-7-silanorbornadienes with bulky substituents on silicon generated the corresponding crowded silylenes that dimerized to kinetically stable disilenes in the absence of trapping agents. Dibenzo-7-silanorbornadienes also underwent a new type of photochemical isomerization competitively.

Polycyclic compounds with a divalent silicon unit as a bridge are generally good precursors of the corresponding silylenes. We have reported recently 1,4-diphenyl-benzo-7-silanorbornadiene derivatives as an excellent source of silylenes.[2] On the other hand, the corresponding dibenzo-7-silanorbornadienes are relatively unknown. Mayer and Neumann[3a] have reported 7-methyl- and 7,7-dimethyl-derivatives and very recently, Weidenbruch et al.[3b] have prepared the 7-t-butyl-derivative, but nothing is reported on the reaction of these compounds. We report herein preparation of new dibenzo-7-silanorbornadiene derivatives with very bulky substituent(s) on the silicon atom. Some of them disclosed quite interesting reactions.

The reaction of anthracene dianions with dichloro- or difluorosilanes (1)[4] in THF afforded dibenzo-7-silanorbornadiene (2) in moderate to low yield.[5]



1 2

1a: $R^1 = R^2 = Ar^1$, X = Cl
1b: $R^1$ = t-Bu, $R^2 = Ar^2$, X = F
1c: $R^1$ = t-Bu, $R^2 = Ar^1$, X = Cl
1d: $R^1$ = Me, $R^2 = Ar^3$, X = F
1e: $R^1$ = Et, $R^2 = Ar^3$, X = F

2a: $R^1 = R^2 = Ar^1$ (58%)
2b: $R^1$ = t-Bu, $R^2 = Ar^2$ (45%)
2c: $R^1$ = t-Bu, $R^2 = Ar^1$ (55%)
2d: $R^1$ = Me, $R^2 = Ar^3$ (4.2%)
2e: $R^1$ = Et, $R^2 = Ar^3$ (1.3%)

$Ar^1$ = mesityl(= 2,4,6-trimethylphenyl), $Ar^2$ = 2,4,6-triisopropylphenyl
$Ar^3$ = 2,4,6-tri-t-butylphenyl

Dibenzo-7-silanorbornadienes display a $^{29}$Si resonance at very low field similarly to 7-silabicyclo[2.2.1]heptadienes reported previously.[6] $^{29}$Si NMR data are

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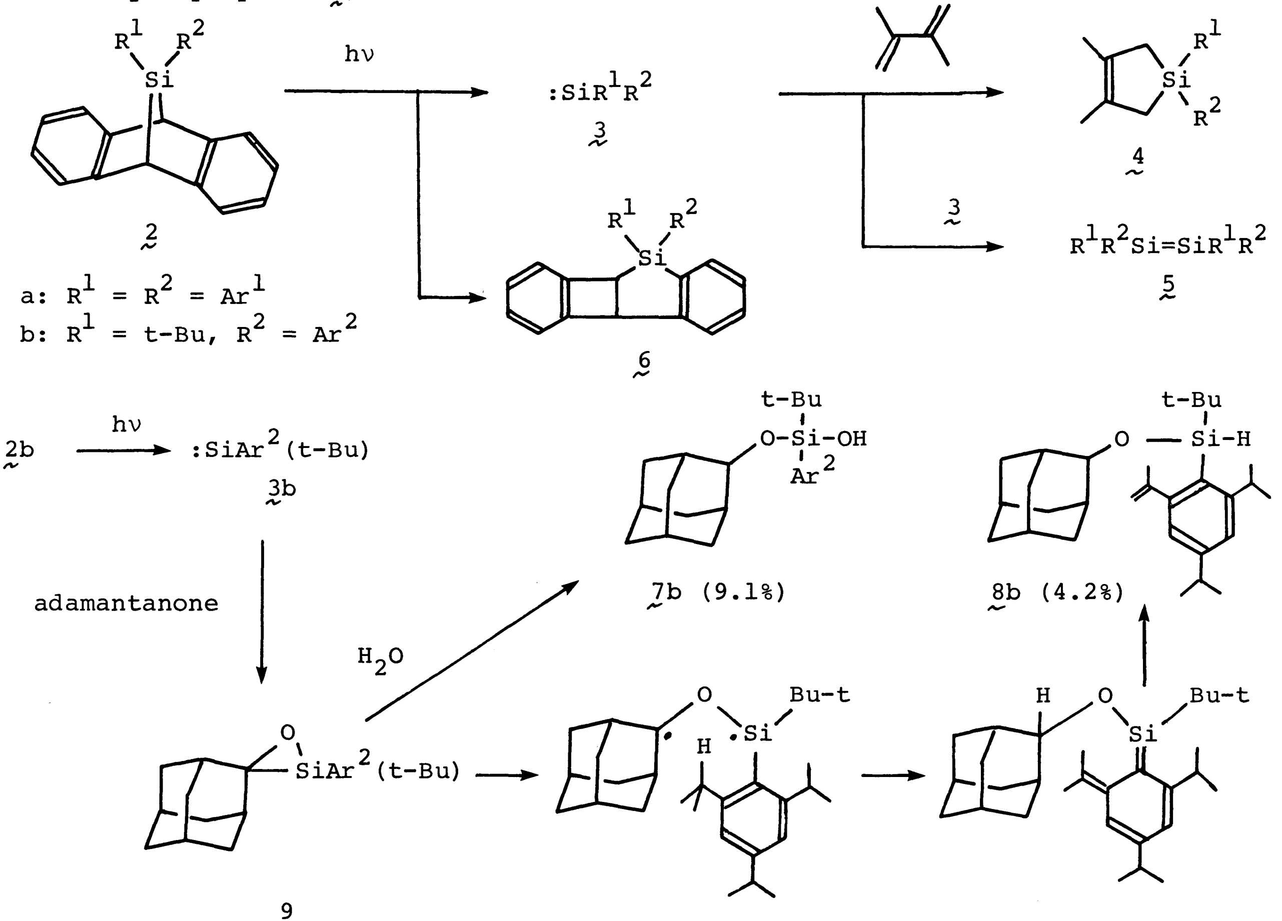
in δ ppm: 2a; 45.4, 2b; 69.0, 2c; 70.1, and 2d; 51.0. These resonances appear at almost the same low field to those of $sp^2$-hybridized silicon atoms of disilene and silene derivatives.[7)] We have explained the origin of such an anomalous deshielding for the 7-silicon atoms in terms of an enhanced polarization at the ground state of the molecules associated to σ-π conjugation.[6)]

Photolysis of benzene solutions of 2a and 2b with a 450 W high pressure Hg lamp in the presence of 10 molar excess 2,3-dimethyl-1,3-butadiene gave the corresponding silacyclopentenes, 4a and 4b, in 34 and 24% yield, respectively.[8)] The formation of 4 can be explained by intermediate silylenes (3). In the absence of the trapping reagent, silylenes generated from 2a and 2b in benzene in quartz NMR tubes dimerized to form kinetically stable disilene 5a and 5b, respectively.[9)]

While a typical bulky silylene, dimesitylsilylene (3a) has been reported to react with adamantanone to give a (1 : 2) adduct,[10a)] t-butyl(triisopropylphenyl)-silylene (3b), photochemically generated from 2b in the presence of adamantanone, gave a silanol (7b) and a (1 : 1) adduct (8b) in 9 and 4% yield, respectively.[11)] The formation of these two products can be rationalized by intermediacy of an oxasilacyclopropane (9)[10b)] shown in Scheme 1.

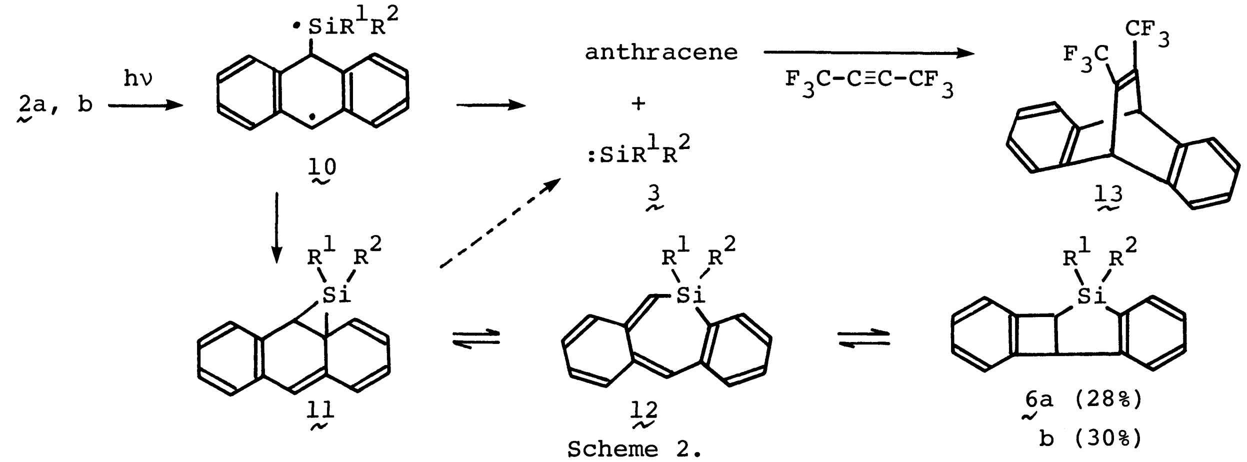


Scheme 1.

In addition to silacyclopentene 4a (34%) derived by 3a, a new type of tetracyclic compounds, 2,3,6,7-dibenzo-4-silabicyclo[3.2.0]heptadiene (6a), was obtained in 28% yield by irradiation of a cyclohexane solution of 2a containing 2,3-dimethylbutadiene in a quartz tube under argon. The structure of 6a is fully compatible with its spectroscopic properties.12) In addition to the signals due to two types of mesityl groups on silicon, two doublets, appeared at $\delta$ 3.61 (d, J = 1.5 Hz, 1H), and 4.45 ppm (d, J = 1.5 Hz, 1H) in $CD_2Cl_2$, are assignable to those of H(5) and H(1), respectively. Furthermore, the reaction of 6a with hexafluoro-2-butyne in a sealed tube at 300 °C for 38 h gave dibenzobicyclo[2.2.2]octatriene (13)13) in 43% yield. Under these conditions, 2a remained unchanged.

Taking these facts into consideration, we rationalize the mechanism of the reaction as shown in Scheme 2. At first, 2 undergoes photo-induced 1,3-silyl migration to yield 11 possibly through a diradical (10). Similar 1,3-silyl migration has been observed in the photolysis of a 5,6-disilacyclohexa-1,3-diene.14) In a similar manner to a vinyl-silacyclopropane,15) formed by addition of dimethylsilylene to 1,4-diphenylbutadiene, 11 undergoes isomerization to an isobenzosilepin (12) through fission of a carbon-carbon instead of a carbon-silicon bond. Compound 12 contains an o-xylylene unit and undergoes ring closure to 6 quite readily. Formation of 13 from 6 indicates that anthracene should be produced through cycloreversion of 6 followed by a few steps as depicted in Scheme. Recently, analogous photo-isomerization of N-aryl-1,4-dihydro-1,4-iminonaphthalene has been reported.16) The fact that 6 was obtained from 2 in the presence of 2,3-dimethylbutadiene, a triplet quencher, implies that the silylene extrusion as well as the photochemical isomerization occurs from the singlet excited state of 2.17)

Photochemical behaviors of 2 can now be explained by the intermediacy of 10, which either generates 3 or is transformed to 11, competitively. Silylenes could also be extruded from 11 in a thermochemical process similar to silacycloheptatriene that generates silylene through intermediate silanorcaradiene.18)



Scheme 2.

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References

1) Chemistry of Organosilicon Compounds 225.
2) H. Sakurai, H. Sakaba, and Y. Nakadaira, J. Am. Chem. Soc., 104, 6156 (1982); H. Sakurai, Y. Nakadaira, and H. Sakaba, Organometallics, 2, 1484 (1983).
3) a) B. Mayer and W. P. Neumann, Tetrahedron Lett., 21, 4887 (1980); b) A. Schäfer, W. Weidenbruch, K. Peters, and H. -G. Schnering, Angew. Chem., Int. Ed. Engl., 23, 302 (1984).

4) Y. Nakadaira, K. Oharu, and H. Sakurai, J. Organomet. Chem., 309, 247 (1986).

5) $^1$H, $^{13}$C, and $^{29}$Si NMR spectra are in accord with the structure given. Spectral data are exemplified by those of **2a** as follows: **2a**; mp 195 - 196 °C; MS m/e (%) M$^+$ 444 (48), 147 (100); $^1$H-NMR (CDCl$_3$) $\delta$ 1.98 (s, 6H), 2.33 (s, 12H), 4.08 (s, 2H), 6.44 (s, 4H), 6.6 - 7.2 (m, 8H); $^{29}$Si-NMR (CDCl$_3$) $\delta$ 45.4. **2b**: mp 154 -155 °C, **2c**: mp 160 -161. Mp's were not recorded for **2d** and **2e**.

6) H. Sakurai, Y. Nakadaira, T. Koyama, and H. Sakaba, Chem. Lett., 1983, 213.

7) G. Raabe and J. Michl, Chem. Rev., 85, 419 (1985).

8) **4a**: MS m/e (%) M$^+$ 348 (3), 228 (100); $^1$H-NMR (CDCl$_3$) $\delta$ 1.70 (s, 6H), 2.00 (s, 4H), 2.21 (s, 6H), 2.28 (s, 12H), 6.83 (s, 4H); **4b**: MS m/e (%) M$^+$ 370 (9), 313 (100); $^1$H-NMR (CDCl$_3$) $\delta$ 0.97 (s, 9H), 1.23 (d, J = 17 Hz, 2H), 1.29 (d, J = 7.0 Hz, 18H), 1.62 (d, J = 17 Hz, 2H), 1.73 (s, 6H), 2.88 (sep, J = 7.0 Hz, 1H), 2.98 (sep, J = 7.0 Hz, 2H), 7.00 (s, 2H).

9) The formation of **5a** and **5b** is supported by existence of characteristic $^{29}$Si-NMR signals at $\delta$ 63.6 and 96.5 (presumably an E isomer), respectively.$^{7)}$

10) a) W. Ando, Y. Hamada, and A. Sekiguchi, J. Chem. Soc. Chem., Commun., 1983, 952; b) W. Ando, Y. Hamada, and A. Sekiguchi, Tetrahedron Lett., 1982, 23, 5323.

11) **7b**: MS m/e (%) M$^+$ 456 (0.1), 399 (63), 135 (100); $^1$H-NMR (C$_6$D$_6$) $\delta$ 1.27 (d, J = 6.5 Hz, 6H), 1.29 (s, 9H), 1.42 (d, J = 6.5 Hz, 6H), 1.45 (d, J = 6.5 Hz, 6H), 1.44 - 2.60 (m, 15H), 1.83 (s, 1H), 2.74 (sep, J = 6.5 Hz, 1H), 3.60 (sep, J = 6.5 Hz, 1H), 4.30 (sep, J = 6.5 Hz, 1H), 7.17 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H); **8b**: MS m/e (%) M$^+$ 438 (4), 381 (80), 247 (100); $^1$H-NMR (C$_6$C$_6$) $\delta$ 1.15 (d, J = 6.8 Hz, 6H), 1.18 (s, 9H), 1.40 (d, J = 6.6 Hz, 3H), 1.41 (d, J = 6.6 Hz, 3H), 1.20 - 2.45 (m, 14H), 2.13 (t, J = 1.0 Hz, 3H), 2.73 (sep, J = 6.8 Hz, 1H), 3.60 (sep, J = 6.6 Hz, 1H), 3.98 (t, J = 3.4 Hz, 1H), 4.98 (dq, J = 2.8, 1.0 Hz, 1H), 5.15 (dq, J = 2.8, 1.0 Hz, 1H), 5.21 (s, 1H), 6.98 (d, J = 2.0 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H).

12) **6a**: MS m/e (%) M$^+$ 444 (27), 429 (100); $^1$H-NMR (CD$_2$Cl$_2$) $\delta$ 2.05 (s, 6H), 2.15 (s, 3H), 2.35 (s, 3H), 2.49 (s, 6H), 3.61 (d, J = 1.5 Hz, 1H), 4.45 (d, J = 1.5 Hz, 1H), 6.9 - 7.6 (m, 12H); $^{13}$C-NMR (CDCl$_3$) $\delta$ 20.6 (q), 21.3 (q), 22.8 (q), 23.2 (q), 59.0 (d), 67.0 (d), 122.3 (d), 124.7 (d), 125.0 (d), 125.3 (d), 125.7 (d), 127.6 (d), 128.0 (d), 128.6$_0$ (d), 128.6$_4$ (d), 129.6 (d), 132.1 (d), 134.7 (d), 136.0 (s), 137.7 (s), 140.8 (s), 141.9 (d), 143.0 (s), 143.6 (s), 145.5 (s), 153.1 (s), 156.3 (s); $^{29}$Si-NMR (CDCl$_3$) $\delta$ -9.9.

13) C. G. Krespan, B. C. McKusick, and T. L. Cairns, J. Am. Chem. Soc., 83, 3428 (1961).

14) Y. Nakadaira, S. Kanouchi, and H. Sakurai, J. Am. Chem. Soc., 96, 5623 (1974).

15) H. Sakurai, Y. Kobayashi, R. Sato, and Y. Nakadaira, Chem. Lett., 1983, 1197.

16) S. Yamada, S. Sato, and M. Ohashi, J. Chem. Soc., Chem. Commun., 1984, 1643; L. A. Motyka, Tetrahedron Lett., 26, 2827 (1985).

17) Recently, photochemical extrusion of dimethylsilylene from 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene has been claimed to occur from a triplet state. J. A. Hawari and D. Griller, Organometallics, 3, 1123 (1984).

18) Y. Nakadaira, "Organosilicon and Bioorganosilicon Chemistry," ed by H. Sakurai, Ellis Horwood (1985), Chap. 14.

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