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Silicon–Carbon Unsaturated Compounds. 29. Photochemical Behavior of 2,6- and 2,7-Bis(pentamethyldisilanyl)naphthalene

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The photolyses of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene (**1a** and **1b**) in the presence of methanol, acetone, and isobutene have been investigated. Irradiation of **1a** and **1b** with a low-pressure mercury lamp in the presence of methanol gave 7,8-dihydro-6-(methoxydimethylsilyl)-2-(pentamethyldisilanyl)-7-(trimethylsilyl)naphthalene and 5,6-dihydro-7-(methoxydimethylsilyl)-2-(pentamethyldisilanyl)-6-(trimethylsilyl)naphthalene. The photolysis of **1a** in the presence of acetone afforded 6-(isopropoxydimethylsilyl)-2-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene and 2-(pentamethyldisilanyl)-5,6-(1,1,3,3-tetramethyl-2-oxa-3-sila-1,3-propanediyl)-6-(trimethylsilyl)naphthalene. Similarly, the photolysis of **1b** in the presence of acetone gave 7-(isopropoxydimethylsilyl)-2-(pentamethyldisilanyl)-8-(trimethylsilyl)naphthalene and 2-(pentamethyldisilanyl)-7,8-(1,1,3,3-tetramethyl-2-oxa-1-sila-1,3-propanediyl)-7-(trimethylsilyl)naphthalene (**5b**). Similar photolysis of **1a** in the presence of isobutene yielded 6-(isobutyldimethylsilyl)-2-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene and 5-(pentamethyldisilanyl)benzo[1,2]-1,1,8,8-tetramethyl-1-sila-2-(trimethylsilyl)cyclonona-2,3-diene, while **1b** gave 7-(isobutyldimethylsilyl)-2-(pentamethyldisilanyl)-8-(trimethylsilyl)naphthalene, 4-(pentamethyldisilanyl)-benzo[1,2]-1,1,8,8-tetramethyl-1-sila-2-(trimethylsilyl)cyclonona-2,3-diene, and 7,8-(1,1,3,3-tetramethyl-1-sila-1,3-propanediyl)-2-(pentamethyldisilanyl)-7-(trimethylsilyl)naphthalene. Compound **5b** has been characterized by an X-ray diffraction study. Compound **5b** crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions a = 25.598 (7) Å, b = 12.846 (3) Å, c = 8.732 (2) Å, V = Å^3, and D_{calcd} = 1.039 g/cm^3 (Z = 4). The results of ab initio MO calculations for 2,6- and 2,7-bis(disilanyl)naphthalene are also described.

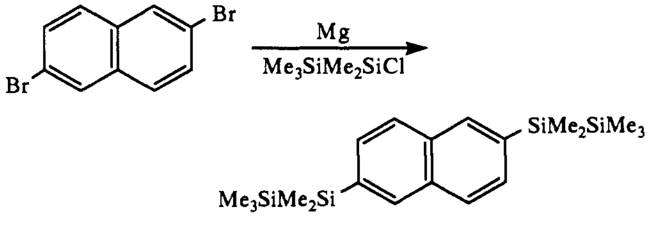
Introduction

Recently, we have found that the photolysis of 1,2-, 1,3-, and 1,4-bis(pentamethyldisilanyl)benzenes in the presence of isobutene produces reactive silenes arising from a 1,3-trimethylsilyl shift to the phenyl ring, and the resulting silenes react with isobutene to give products formed from the ene reaction.[2] In the absence of a trapping agent, these silenes are transformed into nonvolatile substances. In marked contrast to the photolysis of 1,4-bis(pentamethyldisilanyl)benzene, 1,4-bis(pentamethyldisilanyl)naphthalene affords a photoisomer, 4-(hydrodimethylsilyl)-1-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene in the absence of a trapping agent.[3] Similar photolysis of 1,4-bis(disilanyl)naphthalene in the presence of methanol, however, gives two products, the photoisomer and the methanol adduct derived from the reaction of the silene arising from a 1,3-trimethylsilyl shift to the C_2 position of the naphthyl ring with methanol. On the other hand, irradiation of 1,5-bis(pentamethyldisilanyl)naphthalene under the some conditions gives 5-(hydrodimethylsilyl)-1-(pentamethyldisilanyl)-4-(trimethylsilyl)naphthalene as the sole product in the presence or absence of methanol.[3]

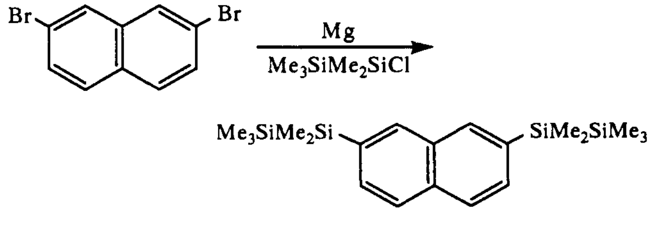
In this paper, we report the photochemical behavior of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene, which is different in many aspects from that of the 1,4- and 1,5-isomers, and X-ray crystallographic analysis of a compound obtained from the photolysis of 2,7-bis(pentamethyldisilanyl)naphthalene in the presence of acetone. We also report the results of ab initio molecular orbital calculations of 2,6- and 2,7-bis(perhydrodisilanyl)naphthalene.

Results and Discussion

The starting 2,6-bis(pentamethyldisilanyl)naphthalene (**1a**) and 2,7-bis(pentamethyldisilanyl)naphthalene (**1b**) were prepared by the reaction of di-Grignard reagents from 2,6- and 2,7-dibromonaphthalene with chloropentamethyldisilane in THF in 71 and 57% yields, respectively.



1a



1b

Photolysis of 1a and 1b in the Presence of Methanol. When compound 1a was photolyzed with a low-pressure immersion mercury lamp bearing a Vycor filter

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[1] (a) Hiroshima University. (b) Kyoto University. (c) Tottori University. (d) Mitsui Petrochemical Industries, Ltd.

[2] Ishikawa, M.; Sakamoto, H.; Kanetani, F.; Minato, A. *Organometallics* **1989**, *8*, 2767.

[3] Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Minato, A. *Organometallics* **1991**, *10*, 880.

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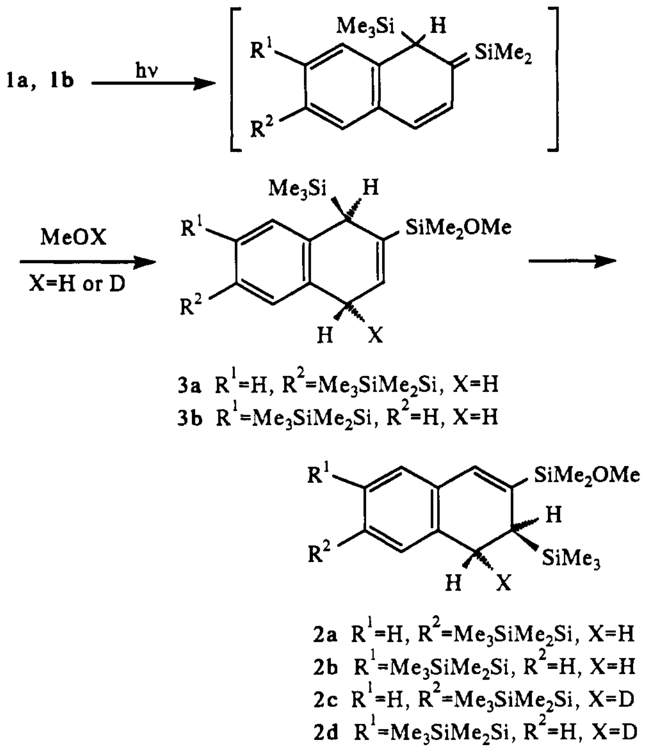
Scheme I



3a R^1=H, R^2=Me_3SiMe_2Si, X=H
3b R^1=Me_3SiMe_2Si, R^2=H, X=H

2a R^1=H, R^2=Me_3SiMe_2Si, X=H
2b R^1=Me_3SiMe_2Si, R^2=H, X=H
2c R^1=H, R^2=Me_3SiMe_2Si, X=D
2d R^1=Me_3SiMe_2Si, R^2=H, X=D

(254 nm) in the presence of methanol in hexane, a product identified as 7,8-dihydro-6-(methoxydimethylsilyl)-2-(pentamethyldisilanyl)-7-(trimethylsilyl)naphthalene (**2a**) was obtained in 48% yield. In this photolysis, methanol used as a trapping agent was separated from the solvent hexane, due to poor solubility. We thought that such poor solubility of methanol must be responsible for the low yield of the adduct **2a**. Therefore, benzene was used as the solvent for the photolysis using methanol as a trapping agent. In fact, irradiation of **1a** in the presence of a 5-fold excess of methanol in benzene afforded the methanol adduct **2a** in 75% yield. Similar photolysis of compound **1b** in the presence of methanol gave 5,6-dihydro-7-(methoxydimethylsilyl)-2-(pentamethyldisilanyl)-6-(trimethylsilyl)naphthalene (**2b**) in 54% yield (Scheme I). The products **2a** and **2b** were readily isolated by preparative GLC.

The structures of **2a** and **2b** were verified by mass, IR, and ^1H and ^{13}C NMR spectrometric analysis, as well as by elemental analysis. The 500-MHz ^1H NMR spectra for **2a** and **2b** show the presence of three kinds of proton resonances at 2.15 (C_7–H, br d, J_{cis} = 6.6 Hz), 2.80 (C_8–H, br d, J_{gem} = 14.7 Hz), and 3.18 ppm (C_8–H, dd, J_{cis} = 6.6 Hz, J_{gem} = 14.7 Hz) for **2a** and at 2.17 (C_6–H, dd, J_{trans} = 1.4 Hz, J_{cis} = 6.7 Hz), 2.78 (C_5–H, dd, J_{trans} = 1.4 Hz, J_{gem} = 15.0 Hz), and 3.19 ppm (C_5–H, dd, J_{cis} = 6.7, J_{gem} = 15.0 Hz) for **2b**. These results are consistent with the proposed structures. Furthermore, saturation of the resonance of the trimethylsilyl protons on the C_6 position of **2b** performed in an NOE-FID difference experiment at 500 MHz produced a positive NOE effect for the protons at 2.78 and 3.19 ppm, as well as the dimethylsilyl protons of a methoxydimethylsilyl group.

The photolysis of **1a** and **1b** in the presence of methanol-d_1 gives adducts **2c** and **2d** whose mass spectra show a parent peak at m/e 421, respectively, indicating that **2c** and **2d** contain deuterium in the molecule. The ^1H NMR spectra of **2c** and **2d** reveal two resonances at 2.15 and 2.77 ppm for **2c** and at 2.17 and 2.76 ppm for **2d**, indicating that the proton at 3.18 ppm for **2a** and 3.19 ppm for **2b** is replaced by deuterium. In both cases, no isomers were detected by spectroscopic analysis. The coupling constants of the protons on sp^3 carbons in the dihydronaphthyl ring and the results of the NOE-FID difference experiment clearly indicate that the deuterium atom of **2c** and **2d** is located trans to the trimethylsilyl group on the dihydronaphthyl ring.

Since the photolysis of 2-(pentamethyldisilanyl)naphthalene gives the silene arising from a 1,3-trimethylsilyl shift to the C_1 position in the naphthyl ring,[3] the present photolyses can also be expected to produce the silenes formed from a 1,3-trimethylsilyl shift to the C_1 position of the naphthyl ring. However, all spectral data obtained for **2a** and **2b** are consistent with those of the products derived from a 1,3-trimethylsilyl shift to the C_3 position, but not to the C_1 position. In order to check whether or not the trimethylsilyl group migrates to the C_1 position in the naphthyl ring, as in the case of 2-(pentamethyldisilanyl)naphthalene, we investigated the photolysis of **1b** in detail and found that in the early stages of the photolysis, 5,8-dihydro-7-(methoxydimethylsilyl)-2-(pentamethyldisilanyl)-8-(trimethylsilyl)naphthalene (**3b**) is produced as a primary product. Thus, when compound **1b** was irradiated for 75 min, 72% of **1b** was photolyzed and the product **3b** was produced in 28% yield, in addition to 16% of **2b**. No other regio- and stereoisomers were detected by either GLC or spectroscopic analysis. Compound **3b** could readily be separated from **2b** by MPLC through a silica gel column, eluting with hexane, and was identified on the basis of 2D COSY and NOESY experiments recorded in $CDCl_3$ at 500 MHz (see Figures 1 and 2).

As expected, irradiation of a benzene solution of **3b** with a low-pressure mercury lamp under the same conditions led to complete rearrangement to compound **2b**. The results indicate that the photolysis of **1b** produces the silene arising from a 1,3-trimethylsilyl shift to the C_1 position in the naphthyl ring, and the silene thus formed reacts with methanol to give the primary product, 5,8-dihydronaphthyl derivative **3b**, which rearranges to give a thermodynamically more stable isomer that has conjugation of the double bond with the aromatic ring, 7,8-dihydronaphthyl derivative **2b**, as shown in Scheme I. In the photolysis of **1a**, the rate of isomerization from **3a** to **2a** is rapid, and therefore, **3a** could not be isolated, even in the early stages of the photolysis.

The fact that the photolysis of **1a** and **1b** in the presence of methanol-d_1 produces no regio- and stereoisomers indicates that the addition of methanol to the silenes and photochemical isomerization of the primary methanol adducts proceed with high stereospecificity. Presumably, methanol adds across the silicon–carbon double bond from the side opposite the trimethylsilyl group attached to the ring carbon atom[4] and the photochemical 1,3-trimethylsilyl shift in the methanol–adduct proceeds with a suprafacial fashion[5] to give the final product **2**.

Photolysis of 1a and 1b in the Presence of Acetone. We have recently reported that the silene produced from the photolysis of 1,4-bis(pentamethyldisilanyl)naphthalene reacts with methanol, but it does not react with other trapping agents such as acetone and isobutene. The silenes produced from **1a** and **1b**, however, react readily with acetone and isobutene.[3] Thus, irradiation of **1a** with a

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(4) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *162*, 223.

(5) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie and Academic Press: New York, 1970. A 1,3-silyl shift to the sp^2 carbon has been reported; see for example: Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

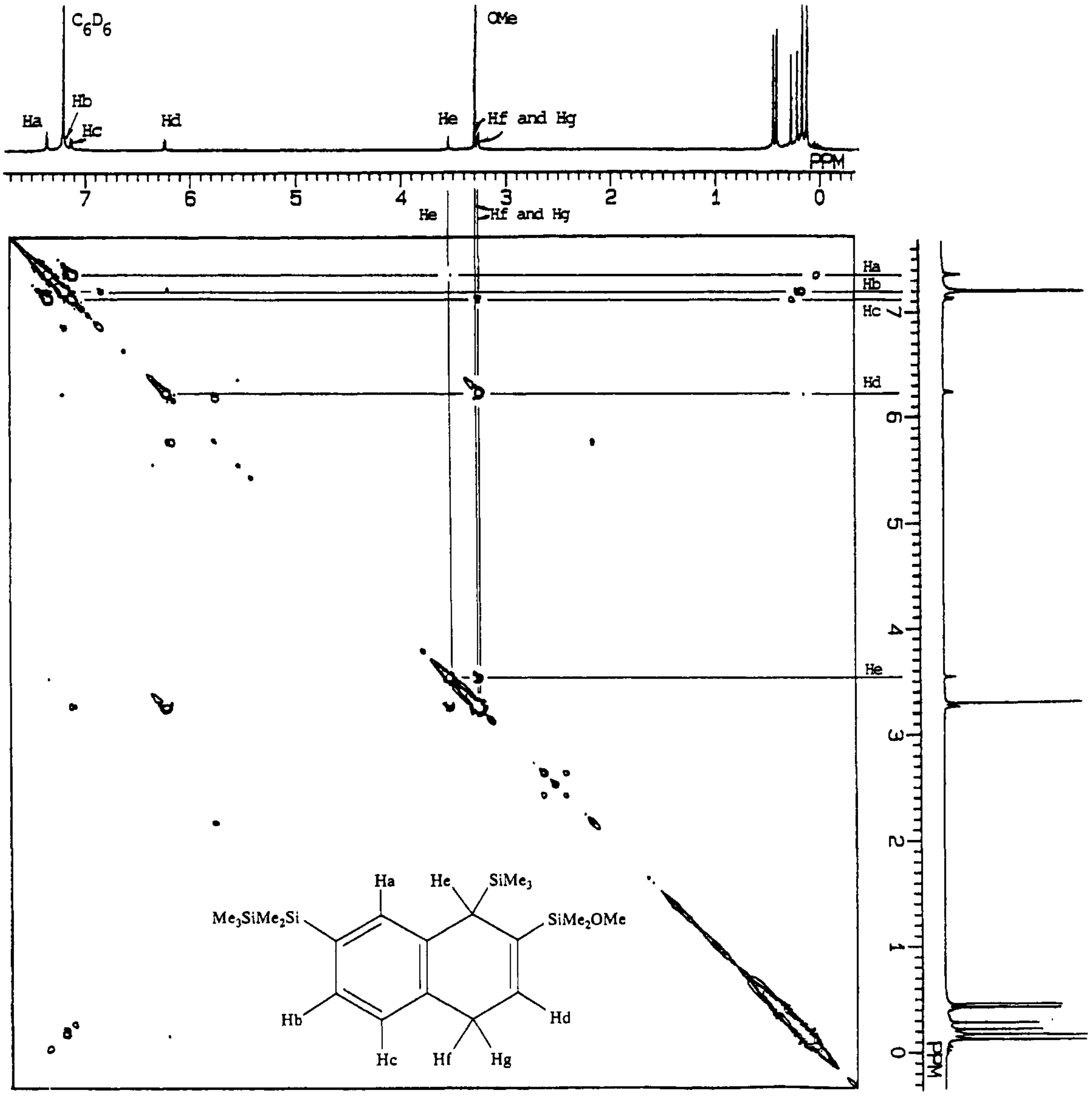


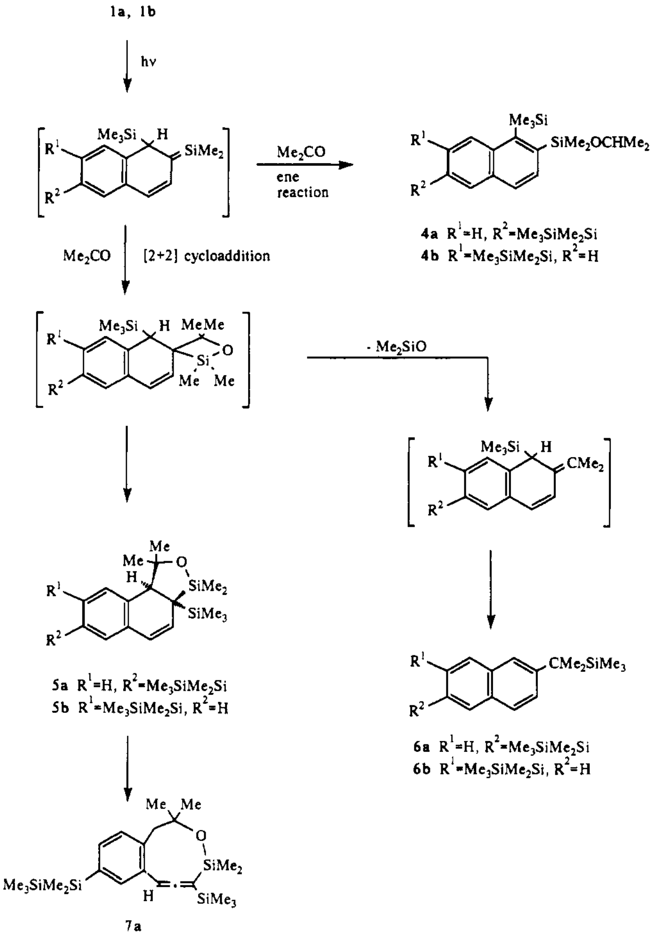
Figure 1. Two-dimensional COSY experiment for **2b** in C_6D_6 at 500 MHz.

low-pressure mercury lamp in the presence of a 3-fold excess of acetone in a hexane solution gave 6-(isopropoxydimethylsilyl)-2-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene (**4a**) and 2-(pentamethyldisilanyl)-5,6-(1,1,3,3-tetramethyl-2-oxa-3-sila-1,3-propanediyl)-6-(trimethylsilyl)naphthalene (**5a**) in 36 and 25% yields, in addition to a small amount of two products, **6a** (3% yield) and **7a** (2% yield) (Scheme II). Pure **4a** was separated from the others by preparative GLC, while products **5a**, **6a**, and **7a** were isolated by MPLC. For compound **5a**, the syn and anti conformation with respect to the hydrogen atom and the trimethylsilyl group on the two juncture carbon atoms in two fused rings might be possible; however, only one isomer, probably the syn isomer was obtained (see below). No other stereoisomers were detected by spectroscopic study.

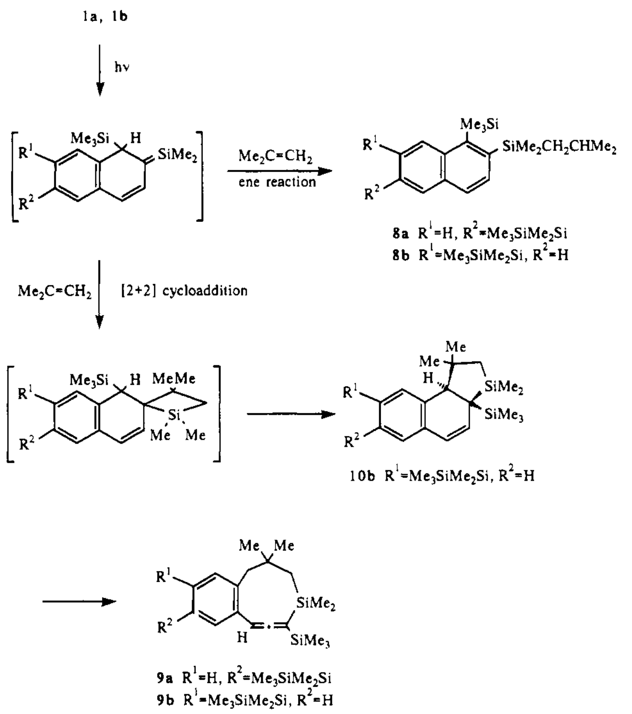
Similar photolysis of **1b** in the presence of acetone afforded 7-(isopropoxydimethylsilyl)-2-(pentamethyldisilanyl)-8-(trimethylsilyl)naphthalene (**4b**) and 2-(pentamethyldisilanyl)-7,8-(1,1,3,3-tetramethyl-2-oxa-1-sila-1,3-propanediyl)-7-(trimethylsilyl)naphthalene (**5b**), which were isolated by MPLC as a pure form in 35 and 34% yields. Again, no stereoisomers were detected for **5b**. A small amount of two products, **6b** (6% yield) and an unidentified product which was shown by its IR spectrum to have an allenic structure (4% yield), were produced in this photolysis.

The structures of **4a,b** and **5a,b** were verified by mass, IR, and ^1H and ^{13}C NMR spectrometric analysis. The position of the trimethylsilyl group on the naphthyl ring of **4a** was confirmed by the NOE-FID difference experiment. Thus, irradiation of trimethylsilyl protons (0.57 ppm) at the C_5 position led to a positive NOE for the dimethylsilyl protons of an isopropoxydimethylsilyl group and for the proton attached to C_4 in the naphthyl ring. Similarly, saturation of the trimethylsilyl protons (0.80 ppm) at the C_8 position of compound **4b** produced a positive NOE for the dimethylsilyl protons of an isobutyldimethylsilyl group and a proton on C_1 of the naphthyl ring. These results are consistent with the proposed structure for **4a** and **4b**. The structure of **5b** was confirmed to be the syn conformation with respect to the hydrogen and the trimethylsilyl group on the two juncture carbons in the fused ring by X-ray crystallographic analysis, as well as by spectroscopic analysis. ^1H and ^{13}C chemical shifts for **5a** are similar to those of **5b**, and we assigned **5a** as the syn isomer. Unfortunately, all attempt to isolate minor products, **6a** and **6b**, in a pure form were unsuccessful. However, mass spectra of **6a** and **6b** show a parent peak at m/e 372, corresponding to $C_{21}H_{36}Si_3$. The

Scheme II



Scheme III



^{1}H NMR spectrum of **6a** reveals four singlets at δ -0.09, 0.06, 0.37, and 1.42 ppm with relative intensity 3:3:2:2, due to Me_3Si, Me_3Si, Me_2Si, and Me_2C, and multiple resonances at 7.29–7.69 ppm, attributed to naphthyl ring protons. Compound **6b** also shows four singlets at δ -0.01, 0.19, 0.52, and 1.45 ppm and at 7.56 (d, 2 H, J = 8.0 Hz), 7.81 (d, 2 H, J = 8.0 Hz), and 8.18 ppm (s, 2 H) due to naphthyl ring protons. Therefore, we tentatively assigned **6a** and **6b** to 6-[1-(trimethylsilyl)ethyl]- and 7-[1-(trimethylsilyl)ethyl]-2-(pentamethyldisilanyl)naphthalene, respectively. The mass spectrum of **7a** shows a parent ion peak at m/e 446. We have made assignment for this compound on the basis of IR and ^{1}H NMR spectra. Its IR spectrum reveals a strong absorption band at 1906 cm^{-1}, due to $\nu_{C=C=C}$. The ^{1}H NMR spectrum shows two singlets for Me_2Si and two singlets for Me_2C, and also three singlets due to pentamethyldisilanyl and trimethylsilyl protons, indicating the presence of the [(pentamethyldisilanyl)benzo]oxasilacyclononadiene structure. Therefore, we assigned **7a** as 5-(pentamethyldisilanyl)benzo[1,2-*e*]-1,1,8,8-tetramethyl-9-oxa-1-sila-2-(trimethylsilyl)cyclonona-2,3-diene.

Scheme II illustrates a possible mechanistic interpretation of the observed reaction course. The mechanism involves the addition of acetone to the silene. Compounds **4a** and **4b** may be explained by the ene reaction of the silene with acetone,[6] while **5a** and **5b** can be understood by [2 + 2] cycloaddition giving a silaoxetane intermediate,[7] followed by the ring expansion to a oxasilacyclopentane ring accompanying a 1,2-trimethylsilyl shift. Unfortunately, in these reactions, no evidence could be found that the silaoxetanes were formed initially. However, the ring enlargement of the silaoxetanes in the dark, leading to a six-membered system has been reported by Brook and his co-workers.[8] If the formation of the silaoxetane is true, the present reactions involve the first example of the [2 + 2] cycloaddition of the silene formed from the photolysis of aryldisilanes.[9] All reactions of the silenes produced photochemically from aryldisilanes reported to date proceed to give ene adducts, analogous to **4a** and **4b**.[6] Products **6a** and **6b** are probably formed by the disruption of the silaoxetane to give dimethylsilanone and dimethylmethylene compounds, which would be transformed into a more stable naphthyl derivative **6** via a 1,3-trimethylsilyl shift. The formation of the silanone and olefin from the silaoxetane is well-known.[7] Compound **7a** is presumably formed by enlargement of the five-membered ring to the nine-membered system with the carbon–carbon bond scission and a 1,5-hydrogen shift.[10] That compound **7a** was produced photochemically from **5a** was confirmed by the observation that the photolysis of **5a** in deuterio-

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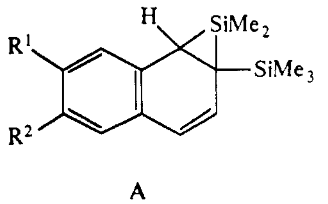
[6] Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

[7] Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Part 2, Chapter 17.

[8] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

[9] One might consider the possibility that the production of **5** involves a silacyclopropane derivative (A), arising from a 1,2-silyl shift, followed



A

by two-atom insertion of acetone to the silacyclopropane ring. However, this is not true, because the photolysis of **1a** and **1b** in the presence of methanol gives no products such as ring-opened products, derived from the reaction of the silacyclopropane with methanol.

[10] Kira, M.; Taki, T.; Sakurai, H. *J. Org. Chem.* **1989**, *54*, 5647 and references are cited herein.

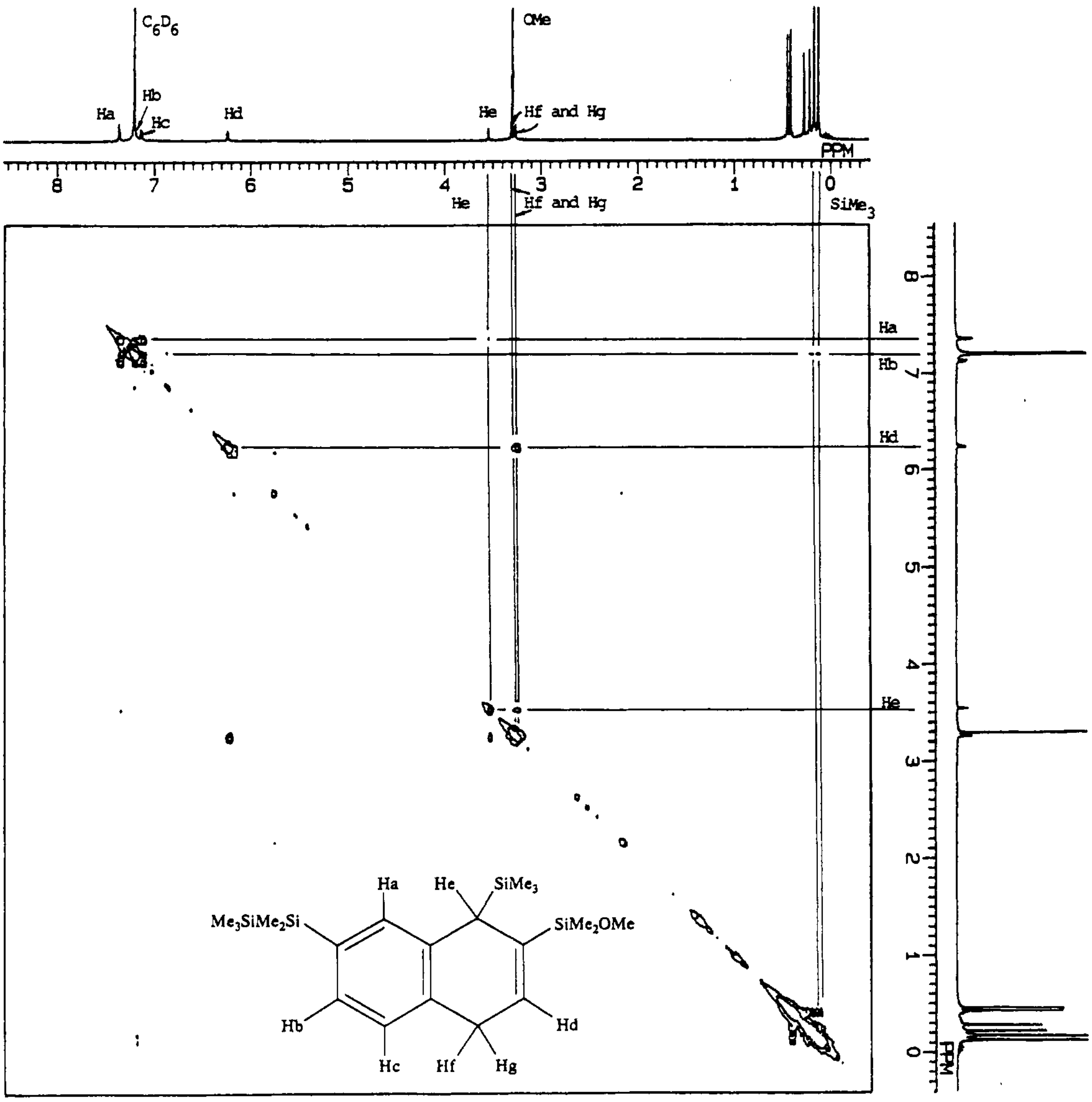


Figure 2. Two-dimensional NOESY experiment for **2b** in C_6D_6 at 500 MHz.

benzene afforded **7a** in 85% yield.

Photolysis of 1a and 1b in the Presence of Isobutene. Irradiation of **1a** in the presence of isobutene under the same conditions gave 6-(isobutyldimethylsilyl)-2-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene (**8a**) and 5-(pentamethyldisilanyl)benzo[1,2]-1,1,8,8-tetramethyl-1-sila-2-(trimethylsilyl)cyclonona-2,3-diene (**9a**) in 32 and 48% yields, respectively. Similar irradiation of **1b** in the presence of isobutene afforded 7-(isobutyldimethylsilyl)-2-(pentamethyldisilanyl)-8-(trimethylsilyl)naphthalene (**8b**) and 4-(pentamethyldisilanyl)benzo[1,2-*e*]-1,1,8,8-tetramethyl-1-sila-2-(trimethylsilyl)cyclonona-2,3-diene (**9b**) in 43 and 22% yields. In this photolysis, a product, 7,8-(1,1,3,3-tetramethyl-1-sila-1,3-propanediyl)-2-(pentamethyldisilanyl)-7-(trimethylsilyl)naphthalene (**10b**) was isolated in 28% yield (Scheme III). The products, **8a** and **9a**, and **8b**–**10b** were isolated respectively by MPLC, eluting with a hexane solution.

The structures of all products obtained in both photolyses were confirmed by mass, IR, and ^{1}H and ^{13}C NMR spectrometric analysis. The position of silyl groups on the naphthyl ring for **8a** and **8b** were established by NOE-FID difference experiments at 500 MHz. Thus, saturation of the trimethylsilyl protons (0.53 ppm) on the naphthyl ring of **8a** produced a positive NOE for the proton at the C_4 position (8.13 ppm) and for the isobutyl protons, while irradiation of the trimethylsilyl protons (0.07 ppm) of a pentamethyldisilanyl group caused the strong enhancement of the proton at the C_1 (7.85 ppm) and C_3 positions (7.46 ppm) of the ring.

For **8b**, irradiation of the trimethylsilyl protons at the C_8 position (0.70 ppm) led to enhancement of the proton at the C_1 position (8.64 ppm) and the isobutyl protons. Similar irradiation of the trimethylsilyl protons (0.20 ppm) of a pentamethyldisilanyl group markedly enhanced the signals from the protons at the C_1 (8.64 ppm) and C_3 positions (7.63 ppm). These results are wholly consistent with the proposed structures for **8a** and **8b**.

IR spectra for **9a** and **9b** reveal a strong absorption band at 1904 and 1903 cm^{-1} attributed to $\nu_{C=C=C}$, respectively. ^{1}H NMR spectra show a singlet at 5.68 ppm for **9a** and at 5.69 ppm for **9b**, due to allene hydrogen, and ^{13}C NMR spectra of both compounds show a resonance attributable to allene carbon at 212.4 ppm. In the H-H NOESY correlation spectrum of **9a**, one of two methyl protons of the C_8 position in the nine-membered ring couples with hydrogens on the C_7 position in the same ring and also with hydrogen on the C_4 position (6.99 ppm) of the benzene ring, consistent with the proposed structure. Compound **10b** could readily be identified by spectroscopic methods (see Experimental Section).

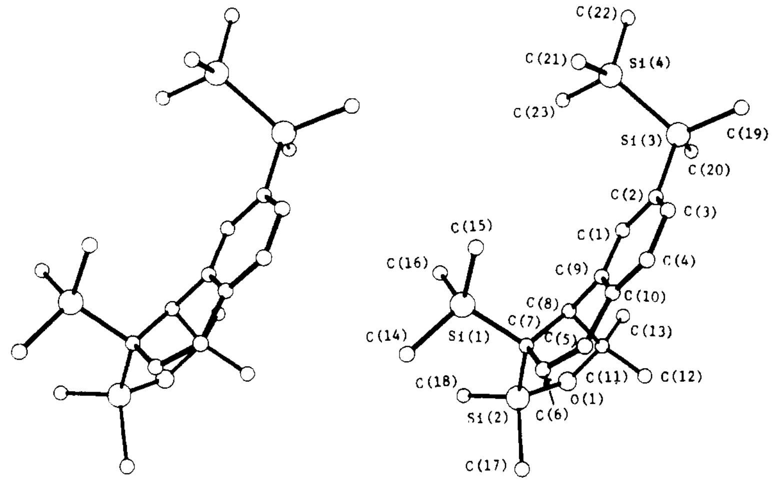
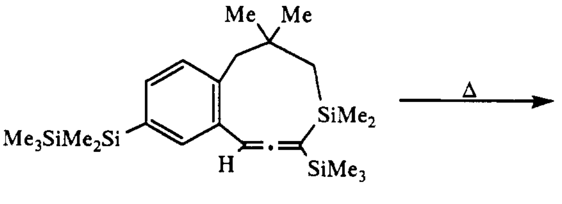


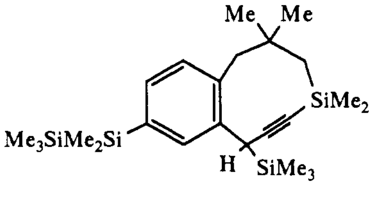
Figure 3. Stereoscopic view of **5b** with the atomic numbering.

As illustrated in Scheme III, the formation of **8a** and **8b** may be explained by the ene reaction of the silenes generated photochemically from **1a** and **1b** with isobutene, while **9a** and **9b** can be understood in terms of [2 + 2] cycloaddition, giving spiro intermediates, followed by two successive ring enlargements, the initial ring enlargement involves the formation of the fused five-membered ring, and then the benzocyclononadiene system.

Although compound **9a** can be isolated by MPLC on the silica gel column, we also have attempted to isolate this compound by using GLC; however, **9a** could not be isolated, but a rearranged product identified as 5-(pentamethyldisilanyl)benzo[1,2-*e*]-1,1,8,8-tetramethyl-1-sila-4-(trimethylsilyl)cyclonona-2-yne (**11a**) was obtained. No **9a** was detected by spectrometric analysis. Presumably, thermal rearrangement of **9a** to **11a** occurred in the GLC column. The IR spectrum of **11a** exhibits an absorption band at 2163 cm^{-1} due to $\nu_{C\equiv C}$. The ^{13}C NMR spectrum of **11a** reveals two signals at 89.5 and 106.8 ppm, attributed to the carbon–carbon triple bond. The H–H NOESY correlation spectrum indicates that methyl protons of the C_8 position couple with two hydrogens on C_9 and one of two hydrogens on C_7, while the hydrogen on the C_4 position couples with the hydrogen of C_1 in the benzene ring. All spectral data obtained from **11a** are consistent with the proposed structure.



9a



11a

X-ray analysis of 5b. Compound **5b** was crystallized from ethanol into the space group $P2_12_12_12_1$ with cell dimensions of a = 25.598 (7), b = 12.846 (3), and c = 8.732 (2) Å, which were determined from 17 sets of setting angles in the range $40 < 2\theta < 60°$. Graphite-monochromatized Cu Kα radiation was used to collect intensity data of the crystal with dimensions 0.2 × 0.1 × 0.1 mm for all the reflections in the range $2 < 2\theta < 124°$ in (hkl). All the intensity data were measured on a Rigaku AFC-5 rotating-anode four-circle diffractometer. The θ–2θ scan method was employed, with θ-scanning width $(1.2 + 0.15 \tan \theta)°$. Three standard reflections monitored every 100 reflections showed no significant variation in intensity. Out of 2408 unique reflections measured, 2055 intensities are $F > 3\sigma(F_o)$. The intensities were corrected only for Lorentz and polarization factors. The structure was solved by MULTAN.[11] Positional parameters and anisotropic thermal parameters for Si and C atoms were refined by block-diagonal least-squares refinement.[12] Atomic parameters of H atoms located in the difference Fourier map were not refined in the least-squares refinement but were included in the structure factor calculation of the refinement. Hydrogen atoms of three methyl groups, C21, C22, and C23, with high temperature factors were not included in the refinement. $w\sum|F_o - F_c|^2$ was minimized with weight $w = 1.0$ for $0 < F_o < 19$ and $w = [1.0 + 0.400(F_o - 19)]^{-1}$ for $F_o > 19$. Finally, R, R_w, and S values were converged to 0.066, 0.081, and 1.007, respectively. Atomic scattering factors were from ref 13.

A stereoview of the molecule with the atomic numbering system drawn by DCM-3 is represented in Figure 3.[14] The Si–C single bonds are in the range from 1.828 (21) to 1.913 (5) Å, and an Si–Si single bond is 2.331 (3) Å in length. The final atomic coordinates and equivalent isotropic temperature factors for all the non-hydrogen atoms are given in Table I. Bond distances and angles are listed in Table II. There is no close intramolecular contact. All computations were performed on the HITAC 280D computer at the Tottori University Computing Center or on the FACOM M780/30 computer at Data Processing Center of Kyoto University.

Ab Initio MO Calculations. We have also studied the mechanism of the photochemical reactions of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene, **1a** and **1b**, by ab initio quantum chemical calculations based on the Hartree–Fock method with the STO-3G basis set by using the GAUSSIAN-82 program.[15] In the present calculation all

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(12) Ashida, T. *HBLS-V. The Universal Crystallographic Computing System-Osaka*; The Computing Center: Osaka University, 1973; Vol. 55.

(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (present distributor: Kluwer Academic Publishers, Dordrecht).

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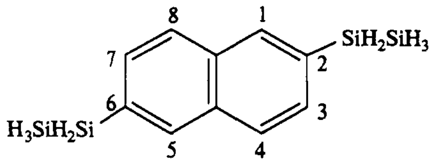
Table I. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Their Esd's in Parentheses for All the Non-Hydrogen Atoms

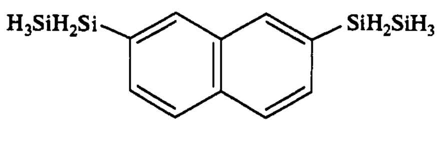
atom	*x*	*y*	*z*	B_{eq}[a]
Si1	0.3861 (1)	0.2946 (1)	0.5629 (2)	3.02 (3)
Si2	0.4835 (1)	0.1692 (1)	0.4179 (2)	2.93 (3)
Si3	0.2132 (1)	0.2192 (2)	−0.0440 (2)	3.68 (3)
Si4	0.1547 (1)	0.2285 (1)	0.1600 (3)	4.03 (3)
O1	0.4710 (2)	0.0880 (3)	0.2774 (5)	3.8 (1)
C1	0.3102 (2)	0.2186 (4)	0.1158 (6)	2.8 (1)
C2	0.2771 (2)	0.2756 (5)	0.0205 (6)	3.2 (1)
C3	0.2913 (3)	0.3785 (5)	−0.0116 (7)	3.7 (1)
C4	0.3372 (3)	0.4197 (5)	0.0437 (7)	3.8 (1)
C5	0.4174 (2)	0.4073 (4)	0.2041 (8)	3.5 (1)
C6	0.4422 (2)	0.3619 (4)	0.3196 (7)	3.1 (1)
C7	0.4259 (2)	0.2595 (4)	0.3842 (6)	2.6 (1)
C8	0.3937 (2)	0.1940 (4)	0.2664 (5)	2.4 (1)
C9	0.3572 (2)	0.2592 (4)	0.1711 (6)	2.7 (1)
C10	0.3704 (2)	0.3617 (4)	0.1357 (6)	2.9 (1)
C11	0.4312 (2)	0.1234 (4)	0.1716 (7)	3.3 (1)
C12	0.4579 (3)	0.1776 (6)	0.0402 (6)	4.4 (1)
C13	0.4032 (3)	0.0259 (5)	0.1143 (9)	4.7 (2)
C14	0.4300 (3)	0.3666 (6)	0.6963 (7)	4.3 (1)
C15	0.3298 (3)	0.3815 (7)	0.5099 (9)	5.1 (2)
C16	0.3584 (3)	0.1778 (6)	0.6599 (8)	4.9 (2)
C17	0.5478 (3)	0.2353 (6)	0.3900 (11)	5.4 (2)
C18	0.4876 (3)	0.0913 (6)	0.5961 (8)	4.8 (2)
C19	0.1895 (3)	0.2942 (10)	−0.2158 (10)	7.3 (3)
C20	0.2241 (3)	0.0818 (7)	−0.0996 (14)	7.1 (2)
C21	0.1509 (8)	0.3609 (8)	0.2387 (22)	16.5 (7)
C22	0.0895 (4)	0.1804 (17)	0.1054 (20)	13.9 (6)
C23	0.1782 (5)	0.1410 (11)	0.3165 (16)	10.5 (4)

[a] $B_{eq} = (4/3)(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma + B_{13}ac\cos\beta + B_{23}bc\cos\alpha$.

the methyl groups in the pentamethyldisilanyl groups of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene have been replaced with hydrogen atoms for the simplicity of calculation. We have thus created 2,6- and 2,7-bis(perhydrodisilanyl)naphthalene (A and B).



A



B

The geometries employed for A and B are the same as those employed in our previous paper;[3] i.e., the plane spanned by the C–Si and Si–Si bonds is perpendicular to the naphthyl ring, and all the Si atoms take sp^3 hybridization in staggered conformation. The following bond lengths are used in our calculation: C–Si = 1.84 Å, Si–Si = 2.30 Å, Si–H = 1.457 Å, C–C = 1.39 Å, and C–H = 1.10 Å. Both of the symmetries of A and B are C_2.

The results of MO calculation have shown that the orbital patterns for the naphthyl rings of A and B are almost the same. Also, the orbital patterns are almost the same as those of 2-(disilanyl)naphthalene, which was treated in our previous paper.[3] Hence, discussion described therein can also be used here in order to explain the mechanism of the trimethylsilyl migration to the C_1 position. The HOMO, LUMO, and LUMO + 1 for A and B have shown to corresponding to the π and π^* orbitals of the naphthyl ring and the σ^* orbital of the silicon–silicon σ bond, respectively. LUMO has also the σ^* character. Considering the orbital interaction between LUMO and LUMO + 1, the plane relationship in this interaction is favorable for the trimethylsilyl migration to the C_1 position, as shown in Figure 4. In the HOMO–LUMO and HOMO–LUMO + 1 interactions, the migration of the silyl group to the C_3 position is allowed, but the coefficient of the C_3 position of the HOMO is small. Consequently, the migration to this position may not occur. We have thus explained the mechanism of the trimethylsilyl migration to the C_1 position in the photochemical reactions of **1a** and **1b** in terms of the orbital interaction between the LUMO and LUMO + 1.

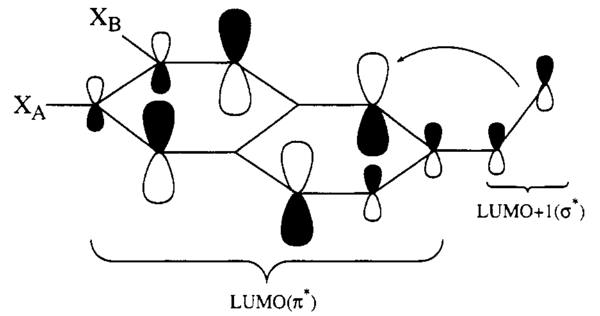


Figure 4. Orbital interaction between LUMO and LUMO + 1 of A (X_A = SiH_2SiH_3 and X_B = H) and B (X_A = H and X_B = SiH_2SiH_3).

Experimental Section

General Considerations. All photolyses were carried out under an atmosphere of purified argon. ^1H and ^{13}C NMR spectra were determined with a JEOL Model JNM-GX-500 spectrometer, Varian Models XL-300 and XL-200 spectrometers, a JEOL Model JMN-FX-90A spectrometer, and a JEOL Model JMN-PMX-60A spectrometer, using deuteriochloroform, deuteriobenzene, and carbon tetrachloride solutions containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 and a JEOL Model JMS-D300 spectrometer equipped with a JMA-2000 data processing system.

Materials. 2,6- and 2,7-dibromonaphthalene were prepared as reported in the literature.[16] Benzene, THF, and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use.

Preparation of 2,6-Bis(pentamethyldisilanyl)naphthalene (1a). Into a 300-mL three-necked flask equipped with a reflux condenser and a 200-mL dropping funnel were placed 1.7 g (70.0 mmol) of magnesium and 20 mL of THF. To this were added 9.0 g (31.5 mmol) of 2,6-dibromonaphthalene and 15.6 g (93.5 mmol) of chloropentamethyldisilane dissolved in 140 mL of THF through a dropping funnel over a period of 50 min at room temperature. After the resulting mixture was heated to reflux for 12 h, the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give crude **1a** (140–170 °C/0.5 mmHg). Recrystallization of the crude product from ethanol gave 8.5 g (71% yield) of pure **1a**: mp 142 °C; MS *m/e* 388 (M^+); 60-MHz ^1H NMR (δ, in CCl_4) 0.05 (s, 18 H, Me_3Si), 0.38 (s, 12 H, Me_2Si), 7.42 (d, 2 H, J = 8 Hz, H on C_3 and C_7), 7.73 (d, 2 H, J = 8 Hz,

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Table II. Bond Distances (Å) and Angles (deg) and Their Esd's in Parentheses

Si1–C7	1.917 (6)	Si1–C14	1.864 (8)	Si1–C15	1.881 (9)
Si1–C16	1.862 (9)	Si2–O1	1.641 (5)	Si2–C7	1.900 (6)
Si2–C17	1.868 (10)	Si2–C18	1.853 (9)	Si3–Si4	2.331 (3)
Si3–C2	1.876 (7)	Si3–C19	1.885 (15)	Si3–C20	1.852 (12)
Si4–C21	1.836 (22)	Si4–C22	1.841 (24)	Si4–C23	1.867 (18)
O1–C11	1.447 (8)	C1–C2	1.394 (9)	C1–C9	1.396 (8)
C1–H1	0.993 (82)	C2–C3	1.402 (9)	C3–C4	1.374 (10)
C3–H3	0.984 (87)	C4–C10	1.387 (9)	C4–H4	1.027 (81)
C5–C6	1.327 (10)	C5–C10	1.466 (9)	C5–H5	0.975 (86)
C6–C7	1.491 (9)	C6–H6	0.980 (84)	C7–C8	1.564 (8)
C8–C9	1.507 (8)	C8–C11	1.560 (8)	C8–H8	0.873 (86)
C9–C10	1.393 (8)	C11–C12	1.506 (11)	C11–C13	1.526 (11)
C12–H121	1.051 (8)	C12–H122	0.845 (85)	C12–H123	0.976 (79)
C13–H131	0.979 (81)	C13–H132	0.951 (84)	C13–H133	1.078 (86)
C14–H141	0.948 (85)	C14–H142	0.891 (85)	C14–H143	1.037 (91)
C15–H151	0.859 (83)	C15–H152	1.120 (83)	C15–H153	1.101 (81)
C16–H161	1.066 (89)	C16–H162	0.914 (82)	C16–H163	1.016 (85)
C17–H171	0.951 (87)	C17–H172	0.938 (83)	C17–H173	0.890 (88)
C18–H181	1.054 (86)	C18–H182	1.044 (89)	C18–H183	1.015 (84)
C19–H191	1.658 (81)	C19–H192	1.031 (86)	C19–H193	0.932 (84)
C20–H201	1.011 (85)	C20–H202	1.021 (87)	C20–H203	0.905 (85)

C7–Si1–C14	107.74 (0.30)	C7–Si1–C15	110.28 (0.33)
C7–Si1–C16	112.53 (0.33)	C14–Si1–C15	108.71 (0.37)
C14–Si1–C16	110.18 (0.37)	C15–Si1–C16	107.36 (0.39)
O1–Si2–C7	96.89 (0.25)	O1–Si2–C17	111.34 (0.35)
O1–Si2–C18	107.21 (0.32)	C7–Si2–C17	112.73 (0.35)
C7–Si2–C18	120.23 (0.32)	C17–Si2–C18	107.78 (0.40)
Si4–Si3–C2	108.14 (0.21)	Si4–Si3–C19	112.03 (0.44)
Si4–Si3–C20	108.29 (0.40)	C2–Si3–C19	108.89 (0.49)
C2–Si3–C20	108.30 (0.43)	C19–Si3–C20	109.14 (0.58)
Si3–Si4–C21	111.59 (0.66)	Si3–Si4–C22	111.53 (0.75)
Si3–Si4–C23	108.61 (0.56)	C21–Si4–C22	111.07 (1.00)
C21–Si4–C23	107.59 (0.87)	C22–Si4–C23	106.17 (0.92)
Si2–O1–C11	114.57 (0.39)	C2–C1–C9	122.22 (0.55)
C2–C1–H1	125.02 (4.75)	C9–C1–H1	112.66 (4.75)
Si3–C2–C1	120.48 (0.47)	Si3–C2–C3	122.04 (0.49)
C1–C2–C3	117.20 (0.58)	C2–C3–C4	120.92 (0.64)
C2–C3–H3	122.67 (5.08)	C4–C3–H3	115.83 (5.08)
C3–C4–C10	121.41 (0.64)	C3–C4–H4	118.36 (4.57)
C10–C4–H4	120.22 (4.56)	C6–C5–C10	121.75 (0.62)
C6–C5–H5	117.23 (5.11)	C6–C5–H6	26.64 (2.46)
C10–C5–H5	121.00 (5.10)	C10–C5–H6	148.12 (2.49)
H5–C5–H6	90.68 (5.64)	C5–C6–C7	122.75 (0.60)
C5–C6–H5	26.04 (2.52)	C5–C6–H6	115.99 (4.94)
C7–C6–H5	148.78 (2.54)	C7–C6–H6	121.16 (4.93)
H5–C6–H6	90.02 (5.51)	Si1–C7–Si2	115.48 (0.29)
Si1–C7–C6	104.46 (0.40)	Si1–C7–C8	112.41 (0.36)
Si1–C7–H8	98.49 (2.81)	Si2–C7–C6	112.26 (0.41)
Si2–C7–C8	100.55 (0.35)	Si2–C7–H8	83.71 (2.81)
C6–C7–C8	111.97 (0.47)	C6–C7–H8	141.75 (2.83)
C8–C7–H8	29.87 (2.81)	C7–C8–C9	113.05 (0.43)
C7–C8–C11	109.70 (0.44)	C7–C8–H8	87.03 (5.63)
C9–C8–C11	114.34 (0.45)	C9–C8–H8	141.27 (5.64)
C11–C8–H8	86.59 (5.63)	C1–C9–C8	121.14 (0.50)
C1–C9–C10	119.07 (0.52)	C8–C9–C10	119.79 (0.49)
C4–C10–C5	121.66 (0.57)	C4–C10–C9	119.07 (0.55)
C5–C10–C9	119.17 (0.53)	O1–C11–C8	106.04 (0.47)
O1–C11–C12	108.28 (0.56)	O1–C11–C13	106.41 (0.55)
O1–C11–H8	85.20 (2.84)	C8–C11–C12	114.48 (0.56)
C8–C11–C13	111.23 (0.55)	C8–C11–H8	30.03 (2.82)
C12–C11–C13	109.97 (0.62)	C12–C11–H8	143.40 (2.87)
C13–C11–H8	97.73 (2.85)	C11–C12–H121	107.23 (4.40)
C11–C12–H122	121.45 (5.77)	C11–C12–H123	108.76 (4.68)
H121–C12–H122	101.57 (7.22)	H121–C12–H123	115.64 (6.40)
H122–C12–H123	102.54 (7.40)	C11–C13–H131	112.80 (4.79)
C11–C13–H132	107.60 (5.09)	C11–C13–H133	107.47 (4.62)
H131–C13–H132	92.58 (6.95)	H131–C13–H133	103.33 (6.62)
H132–C13–H133	131.62 (6.86)	Si1–C14–H141	104.36 (5.14)
Si1–C14–H142	110.26 (5.45)	Si1–C14–H143	103.50 (5.05)
H141–C14–H142	112.90 (7.49)	H141–C14–H143	118.38 (7.20)
H142–C14–H143	106.87 (7.42)	Si1–C15–H151	96.42 (5.56)
Si1–C15–H152	85.02 (4.27)	Si1–C15–H153	109.02 (4.26)
H151–C15–H152	136.32 (7.02)	H151–C15–H153	125.40 (7.00)
H152–C15–H153	94.38 (6.02)	Si1–C16–H161	124.39 (4.80)
Si1–C16–H162	103.61 (5.18)	Si1–C16–H163	108.08 (4.82)
H161–C16–H162	117.98 (7.05)	H161–C16–H163	108.02 (6.78)
H162–C16–H163	88.77 (7.05)	Si2–C17–H171	108.49 (5.28)

Table II (Continued)

Si2–C17–H172	115.68 (5.12)	Si2–C17–H173	116.92 (5.67)
H171–C17–H172	101.57 (7.33)	H171–C17–H173	108.11 (7.73)
H172–C17–H173	104.80 (7.62)	Si2–C18–H181	109.34 (4.69)
Si2–C18–H182	110.86 (4.91)	Si2–C18–H183	108.92 (4.74)
H181–C18–H182	105.07 (6.78)	H181–C18–H183	111.77 (6.66)
H182–C18–H183	110.84 (6.82)	Si3–C19–H191	124.75 (2.89)
Si3–C19–H192	117.69 (4.84)	Si3–C19–H193	113.70 (5.22)
H191–C19–H192	90.50 (5.55)	H191–C19–H193	71.22 (5.86)
H192–C19–H193	126.62 (7.11)	Si3–C20–H201	110.04 (4.85)
Si3–C20–H202	103.79 (4.91)	Si3–C20–H203	127.48 (5.45)
H201–C20–H202	107.62 (6.88)	H201–C20–H203	96.85 (7.25)
H202–C20–H203	109.87 (7.31)	C5–H5–C6	36.72 (3.43)
C5–H6–C6	37.38 (3.33)	C7–H8–C8	63.09 (5.02)
C7–H8–C11	93.97 (4.11)	C8–H8–C11	63.38 (5.04)

H on C_4 and C_8), 7.81 (s, 2 H, H on C_1 and C_5); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) −3.9, −2.2 (MeSi), 126.8, 130.5, 133.0, 133.8, 137.6 (naphthyl ring carbons). Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.65; H, 9.26.

Preparation of 2,7-Bis(pentamethyldisilanyl)naphthalene (1b). Into a 300-mL three-necked flask equipped with a reflux condenser and a 200-mL dropping funnel were placed 4.1 g (169.0 mmol) of magnesium and 20 mL of THF. To this were added 15.8 g (55.2 mmol) of 2,7-dibromonaphthalene and 24.5 g (146.3 mmol) of chloropentamethyldisilane dissolved in 140 mL of THF through a dropping funnel over a period of 50 min at room temperature. After the mixture was heated to reflux for 12 h, the mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extract were combined, washed with water, and dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give crude **1b**. Recrystallization of the crude product from ethanol gave 12.3 g (57% yield) of pure **1b**: bp 147 °C/0.3 mmHg; mp 55 °C; MS *m/e* 388 (M^+); 60-MHz ^{1}H NMR (δ, in CCl_4) 0.09 (s, 18 H, Me_3Si), 0.41 (s, 12 H, Me_2Si), 7.37 (d, 2 H, *J* = 8 Hz, H on C_3 and C_6), 7.65 (d, 2 H, *J* = 8 Hz, H on C_4 and C_5), 7.77 (s, 2 H, H on C_1 and C_8); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) −3.8, −2.1, 126.7, 130.7, 132.8, 133.5, 134.0, 137.2. Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.71; H, 9.30.

Photolysis of 1a in the Presence of Methanol in Hexane. Into a 25-mL reaction vessel fitted internally with a 6-W low-pressure mercury lamp was placed a solution of 201.8 mg (0.520 mmol) of **1a**, 1.0 mL of methanol, and 51.9 mg (0.282 mmol) of tridecane as an internal standard in 25 mL of hexane. The mixture was irradiated for 5 h with a slow stream of argon bubbling through the mixture at room temperature. At this stage, ca. 100% of **1a** was consumed. The resulting mixture was analyzed by GLC as being compound **2a** (48% yield). Product **2a** was isolated by preparative GLC: mp 34.5–35.5 °C; MS *m/e* 420 (M^+); IR ν_{Si-O} 1094 cm^{-1}; 500-MHz ^{1}H NMR (δ, in C_6D_6) 0.00 (s, 9 H, Me_3Si–C), 0.15 (s, 9 H, Me_3Si–Si), 0.323 (s, 3 H, MeSi), 0.325 (s, 3 H, MeSi), 0.40 (s, 3 H, MeSi), 0.41 (s, 3 H, MeSi), 2.15 (br d, 1 H, *J* = 6.6 Hz, H on C_7), 2.80 (br d, 1 H, *J* = 14.7 Hz, H on C_8), 3.18 (dd, 1 H, *J* = 14.7, 6.6 Hz, H on C_8), 3.36 (s, 3 H, MeO), 6.94 (s, 1 H, H on C_5), 7.03 (d, 1 H, *J* = 7.3 Hz, H on C_4), 7.34 (s, 1 H, H on C_1), 7.37 (d, 1 H, *J* = 7.3 Hz, H on C_3); 75-MHz ^{13}C NMR (δ, in C_6D_6) −4.2, −3.8, −2.3, −2.2, −1.6, −1.0, 28.0, 31.1, 50.1, 125.3, 132.6, 132.9, 135.4, 135.9, 136.0, 139.0, 144.2. Anal. Calcd for $C_{21}H_{40}OSi_4$: C, 59.93; H, 9.58. Found: C, 59.80; H, 9.53.

Photolysis of 1a in the Presence of Methanol in Benzene. A solution of 195.3 mg (0.502 mmol) of **1a**, 0.1 mL (2.5 mmol) of methanol, and 17.9 mg (0.097 mmol) of tridecane in 25 mL of benzene was photolyzed for 2 h. At this point, ca. 100% of **1a** was photolyzed. The resulting mixture was analyzed by GLC as being **2a** (75% yield). Pure **2a** was isolated by preparative GLC. All spectral data obtained for **2a** were identical with the authentic sample.

Photolysis of 1a in the Presence of Methanol-*d*$_1$. A solution of 196.1 mg (0.504 mmol) of **1a**, 0.1 mL (2.4 mmol) of methanol-*d*$_1$, and 12.7 mg (0.065 mmol) of tridecane as an internal standard in 25 mL of benzene was irradiated for 2 h. The reaction mixture was analyzed by GLC as being **2c** (56% yield). Product **2c** was isolated by preparative GLC: MS *m/e* 421 (M^+); IR ν_{Si-O} 1090 cm^{-1}; 90-MHz ^{1}H NMR (δ, in C_6D_6) 0.00 (s, 9 H, Me_3Si–C), 0.16 (s, 9 H, Me_3Si–Si), 0.33 (2s, 6 H, 2 MeSi), 0.40 (s, 3 H, MeSi), 0.41 (s, 3 H, MeSi), 2.15 (br s, 1 H, H on C_7), 2.77 (br s, 1 H, H on C_8), 3.36 (s, 3 H, MeO), 6.94 (s, 1 H, H on C_5), 7.03 (d, 1 H, *J* = 7.7 Hz, H on C_4), 7.34 (s, 1 H, H on C_1), 7.38 (d, 1 H, *J* = 7.7 Hz, H on C_3). Exact MS Calcd for $C_{21}H_{39}DOSi_4$: 421.2219. Found: 421.2247.

Photolysis of 1b in the Presence of Methanol. A solution of 194.1 mg (0.500 mmol) of **1b**, 0.1 mL (2.4 mmol) of methanol, and 18.4 mg (0.093 mmol) of tetradecane as an internal standard in 25 mL of benzene was photolyzed for 2 h. The photolysis mixture was analyzed by GLC as being **2b** (54% yield). Pure **2b** was isolated by preparative GLC: MS *m/e* 420 (M^+); IR ν_{Si-O} 1094 cm^{-1}; 200-MHz ^{1}H NMR (δ, in C_6D_6) 0.02 (s, 9 H, Me_3Si–C), 0.17 (s, 9 H, Me_3Si–Si), 0.36 (s, 6 H, Me_2Si–O), 0.44 (s, 6 H, Me_2Si–Si), 2.17 (dd, 1 H, *J* = 6.7, 1.4 Hz, H on C_6), 2.78 (dd, 1 H, *J* = 15.0, 1.4 Hz, H on C_5), 3.19 (dd, 1 H, *J* = 15.0, 6.7 Hz, H on C_5), 3.39 (s, 3 H, MeO), 7.06 (s, 1 H, H on C_8), 7.10 (d, 1 H, *J* = 7.8 Hz, H on C_4), 7.37 (s, 1 H, H on C_1), 7.38 (d, 1 H, *J* = 7.8 Hz, H on C_3); 50-MHz ^{13}C NMR (δ, in C_6D_6) −3.5, −3.4, −1.8, −1.7, −1.1, −0.6, 28.2, 31.5, 50.6, 127.7, 131.6, 133.9, 135.9, 136.5, 137.2, 138.0, 144.2. Anal. Calcd for $C_{21}H_{40}OSi_4$: C, 59.93; H, 9.58. Found: C, 59.73; H, 9.57.

Photolysis of 1b in the Presence of Methanol-*d*$_1$. A solution of 232.8 mg (0.599 mmol) of **1b**, 0.1 mL of methanol-*d*$_1$, and 15.2 mg (0.077 mmol) of tetradecane as an internal standard in 25 mL of benzene was photolyzed for 2 h. The photolysis mixture was analyzed by GLC as being **2b** (52% yield). Pure **2b** was isolated by preparative GLC: MS *m/e* 421 (M^+); IR ν_{Si-O} 1093 cm^{-1}; 90-MHz ^{1}H NMR (δ, in C_6D_6) 0.03 (s, 9 H, Me_3Si–C), 0.17 (s, 9 H, Me_3Si–Si), 0.37 (s, 6 H, Me_2Si–O), 0.44 (s, 6 H, Me_2Si–Si), 2.17 (br s, 1 H, H on C_6), 2.76 (br s, 1 H, H on C_5), 3.39 (s, 3 H, MeO), 7.08 (s, 1 H, H on C_8), 7.11 (d, 1 H, *J* = 8 Hz, H on C_4), 7.24 (s, 1 H, H on C_1), 7.40 (d, 1 H, *J* = 8 Hz, H on C_3). Exact MS Calcd for $C_{21}H_{39}DOSi_4$: 421.2219. Found: 421.2200.

Isolation of 3b. A solution of 395.3 mg (1.02 mmol) of **1b**, 0.1 mL (2.4 mmol) of methanol, and 86.6 mg (0.44 mmol) of tetradecane as an internal standard in 25 mL of benzene was irradiated for 75 min. At this stage 72% of **1b** was photolyzed. The resulting mixture was analyzed by GLC as being **2b** (16% yield) and **3b** (28% yield). Products **2b** and **3b** were isolated from the mixture by preparative GLC. All spectral data obtained for **2b** were identical with those of an authentic sample. For **3b**: MS *m/e* 420 (M^+); IR ν_{Si-O} 1090 cm^{-1}; 500-MHz ^{1}H NMR (δ, in C_6D_6) 0.12 (s, 9 H, Me_3Si), 0.17 (s, 9 H, Me_3Si), 0.21 (s, 3 H, MeSi), 0.27 (s, 3 H, MeSi), 0.41 (s, 3 H, MeSi), 0.44 (s, 3 H, MeSi), 3.26 (m, 2 H, H on C_5), 3.30 (s, 3 H, MeO), 3.54 (br s, 1 H, H on C_8), 6.24 (dd, 1 H, *J* = 4.8, 3.3 Hz, H on C_6), 7.13 (d, 1 H, *J* = 7.7 Hz, H on C_4), 7.355 (d, 1 H, *J* = 7.7 Hz, H on C_3), 7.357 (br s, 1 H, H on C_1); 22.5-MHz ^{13}C NMR (δ, in C_6D_6) −3.8, −3.6, −2.0, −1.7, −0.8, 33.3, 39.8, 49.9, 127.3, 130.7, 132.7, 134.2, 134.8, 135.9, 139.3, 140.8. Exact MS Calcd for $C_{21}H_{40}OSi_4$: 420.2153. Found: 420.2143.

Photolysis of 3b. A solution of 20.0 mg (0.048 mmol) of **3b** in 0.6 mL of deuteriobenzene was irradiated externally for 4 h at room temperature with a 6-W low-pressure mercury lamp in a quartz NMR tube (5 mm o.d.). The GLC analysis and NMR spectrum of the resulting solution showed that all **3b** was converted to **2b**.

Photolysis of 1a in the Presence of Acetone. A solution of 194.7 mg (0.501 mmol) of **1a**, 0.1 mL (1.4 mmol) of acetone, and 10.4 mg (0.057 mmol) of tridecane as an internal standard in 25 mL of hexane was irradiated for 4 h at room temperature. GLC analysis of the resulting mixture showed the formation of **4a** (36% yield), together with other products whose peaks could not be separated from each other. Crude **4a**, pure **5a** (55.9 mg, 25% yield) and **7a** (4.5 mg, 3% yield), and a 1:1.4 mixture of **1a** and **6a** (14.6 mg, 2% yield for **6a**) were separated from the reaction mixture by treatment with MPLC (silica gel, eluent hexane). Further purification of **4a** was carried out by preparative GLC. Product **6a** could not be isolated and was identified by using a mixture. For **4a**: MS *m/e* 446 (M^+); IR ν_{Si-O} 1081 cm^{-1}; 200-MHz ^1H NMR (δ, in $CDCl_3$) 0.08 (s, 9 H, Me_3Si-Si), 0.42 (s, 6 H, Me_2Si-Si), 0.49 (s, 6 H, Me_2Si-O), 0.57 (s, 9 H, Me_3Si-C), 1.21 (d, 6 H, J = 6.1 Hz, Me_2C), 4.14 (sept, 1 H, J = 6.1 Hz, $HCMe_2$), 7.49 (dd, 1 H, J = 8.6, 1.3 Hz, H on C_3), 7.69 (d, 1 H, J = 8.3 Hz, H on C_7), 7.76 (d, 1 H, J = 8.3 Hz, H on C_8), 7.87 (br s, 1 H, H on C_1), 8.19 (d, 1 H, J = 8.6 Hz, H on C_4); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -4.0, -2.2, 2.1, 4.2, 25.8, 65.7, 127.2, 128.2, 129.1, 130.9, 132.5, 134.7, 137.0, 137.6, 145.4, 147.3. Anal. Calcd for $C_{23}H_{42}OSi_4$: C, 61.81; H, 9.47. Found: C, 61.75; H, 9.40. For **5a**: MS *m/e* 446 (M^+); 90-MHz ^1H NMR (δ, in C_6D_6) -0.06 (s, 9 H, Me_3Si), 0.14 (s, 9 H, Me_3Si), 0.35 (s, 6 H, Me_2Si), 0.41 (s, 6 H, Me_2Si), 1.15 (s, 3 H, MeC), 1.49 (s, 3 H, MeC), 3.17 (br s, 1 H, H on C_5), 5.89 (dd, 1 H, J = 9.6, 1.1 Hz, H on C_7), 6.43 (d, 1 H, J = 9.6 Hz, H on C_8), 7.05 (d, 1 H, J = 7.3 Hz, H on C_4), 7.31 (br s, 1 H, H on C_1), 7.32 (dd, 1 H, J = 7.3, 1.2 Hz, H on C_3); 22.5-MHz ^{13}C NMR (δ, in C_6D_6) -4.0, -2.3, -2.2, -1.2, 1.7, 2.1, 26.0, 29.9, 31.1, 53.8, 84.6, 125.2, 131.6, 132.0, 132.7, 134.7, 137.9. Anal. Calcd for $C_{23}H_{42}OSi_4$: C, 61.81; H, 9.47. Found: C, 62.02, H, 9.62. For **6a**: MS *m/e* 372 (M^+); 60-MHz ^1H NMR (δ, in CCl_4) -0.09 (s, 9 H, Me_3Si), 0.06 (s, 9 H, Me_3Si), 0.37 (s, 6 H, Me_2Si), 1.42 (s, 6 H, Me_2C), 7.29-7.69 (m, 6 H, ring protons). For **7a**: MS *m/e* 446 (M^+); IR $\nu_{C=C=C}$ 1906 cm^{-1}; 90-MHz ^1H NMR (δ, in C_6D_6) 0.14 (s, 9 H, Me_3Si), 0.22 (s, 9 H, Me_3Si), 0.39 (2s, 9 H, Me_2Si and Me on ring silicon), 0.44 (s, 3 H, Me on ring silicon), 1.21 (s, 3 H, MeC), 1.38 (s, 3 H, MeC), 2.43 (d, 1 H, J = 14.9 Hz, H on C_7), 4.17 (d, 1 H, J = 14.9 Hz, H on C_7), 5.88 (s, 1 H, allene proton), 6.94 (d, 1 H, J = 7.7 Hz, H on $C_{4'}$), 7.21 (dd, 1 H, J = 7.7, 1.3 Hz, H on $C_{3'}$), 7.35 (br s, 1 H, H on $C_{1'}$); 22.5-MHz ^{13}C NMR (δ, in C_6D_6), -3.8, -2.0, -0.2, 1.9, 3.7, 30.6, 34.4, 46.6, 76.9, 83.3, 92.6, 128.2, 131.0, 134.3, 134.7, 137.7, 138.5, 213.0. Exact MS Calcd for $C_{23}H_{42}OSi_4$: 446.2313. Found: 446.2314.

Photolysis of 5a. A 0.6-mL deuteriobenzene solution of 5.3 mg of **5a** was placed in a quartz NMR tube and irradiated externally at room temperature. After 3 h of irradiation, the ^1H NMR spectrum of the resulting solution showed that almost all of **5a** was photolyzed and **7a** was formed in 85% yield.

Photolysis of 1b in the Presence of Acetone. A solution of 195.2 mg (0.502 mmol) of **1b**, 0.1 mL (1.4 mmol) of acetone, and 15.9 mg (0.080 mmol) of tetradecane as an internal standard in 25 mL of hexane was irradiated for 4 h. The resulting mixture was analyzed by GLC as being **4b** (34% yield), **5b** (43% yield), **6b**, and an unidentified product (4% yield). The reaction mixture was separated by MPLC (silica gel, eluent hexane). Pure **4b** (59 mg) and **5b** (75.8 mg) and a mixture of **6b** and **1b** (17 mg, 6% yield for **6b**) in the ratio of 2:1 were obtained. For **4b**: MS *m/e* 446 (M^+); IR ν_{Si-O} 1020 cm^{-1}; 200-MHz ^1H NMR (δ, in $CDCl_3$) 0.19 (s, 9 H, Me_3Si-Si), 0.54 (s, 6 H, Me_2Si-O), 0.57 (s, 6 H, Me_2Si-Si), 0.80 (s, 9 H, Me_3Si-C), 1.21 (d, 6 H, J = 6.0 Hz, Me_2C), 4.01 (sept, 1 H, J = 6.0 Hz, HCO), 7.64 (dd, 1 H, J = 8.1, 1.0 Hz, H on C_3), 7.74 (d, 1 H, J = 8.3 Hz, H on C_5), 7.79 (d, 1 H, J = 8.3 Hz, H on C_6), 7.80 (d, 1 H, J = 8.1 Hz, H on C_4), 8.71 (d, 1 H, J = 1.0 Hz, H on C_1); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -3.9, -2.1, 2.2, 4.3, 25.8, 65.7, 127.2, 127.4, 130.2, 131.1, 133.1, 135.4, 135.6, 137.4, 145.3, 147.6. Anal. Calcd for $C_{23}H_{42}OSi_4$: C, 61.81; H, 9.47. Found: C, 61.72; H, 9.38. For **5b**: mp 88-91.5 °C; MS *m/e* 446 (M^+); IR ν_{Si-O} 1095 cm^{-1}; 200-MHz ^1H NMR (δ, in C_6D_6) -0.01 (s, 9 H, Me_3Si-C), 0.18 (s, 9 H, Me_3Si-Si), 0.42 (s, 6 H, Me_2Si-O), 0.44 (s, 3 H, MeSi-Si), 0.45 (s, 3 H, MeSi-Si), 1.22 (s, 3 H, MeC), 1.63 (s, 3 H, MeC), 3.30 (br s, 1 H, H on C_8), 5.94 (dd, 1 H, J = 9.5, 2.0 Hz, H on C_6), 6.41 (d, 1 H, J = 9.5 Hz, H on C_5), 7.08 (d, 1 H, J = 7.7 Hz, H on C_4), 7.41 (s, 1 H, H on C_1), 7.43 (d, 1 H, J = 7.7 Hz, H on C_3); 22.5-MHz ^{13}C NMR (δ, in C_6D_6) -4.2, -3.9, -2.2, 1.7, 2.1, 26.0, 30.4, 31.1, 53.9, 84.6, 125.2, 125.9, 132.4, 132.8, 133.3, 133.9, 135.3, 138.1. Anal. Calcd for $C_{23}H_{42}OSi_4$: C, 61.81; H, 9.47. Found: C, 61.79; H, 9.40. For **6b**: MS *m/e* 372 (M^+); 60-MHz ^1H NMR (δ, in C_6D_6) -0.01 (s, 9 H, Me_3Si), 0.19 (s, 9 H, Me_3Si), 0.52 (s, 6 H, Me_2Si), 1.45 (s, 6 H, Me_2C), 7.56 (2d, 2 H, J = 8 Hz, H on C_3 and C_6), 7.81 (2d, 2 H, J = 8 Hz, H on C_4 and C_5), 8.18 (2s, 2 H, H on C_1 and C_8).

Photolysis of 1a in the Presence of Isobutene. A mixture of 195.8 mg (0.504 mmol) of **1a**, 5 g (89.3 mmol) of isobutene, and 20.3 mg (0.084 mmol) of heptadecane as an internal standard in 25 mL of hexane was irradiated for 6 h. The resulting mixture was analyzed by GLC as being **8a** (32% yield) and **9a** (48% yield). Products **8a** and **9a** were isolated by MPLC (silica gel, eluent hexane). For **8a**: MS *m/e* 444 (M^+); 200-MHz ^1H NMR (δ, in $CDCl_3$) 0.07 (s, 9 H, Me_3Si-Si), 0.40 (s, 6 H, Me_2Si-Si), 0.42 (s, 6 H, Me_2Si-C), 0.53 (s, 9 H, Me_3Si-C), 0.93 (d, 6 H, J = 6.6 Hz, Me_2C), 0.96 (d, 2 H, J = 6.6 Hz, H_2C-$CHMe_2$), 1.86 (m, 1 H, $HCMe_2$), 7.46 (dd, 1 H, J = 8.6, 1.4 Hz, H on C_3), 7.67 (d, 1 H, J = 9.0 Hz, H on C_7), 7.72 (d, 1 H, J = 9.0 Hz, H on C_8), 7.85 (br s, 1 H, H on C_1), 8.13 (d, 1 H, J = 8.6 Hz, H on C_4); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -4.0, -2.2, 2.1, 4.4, 25.3, 26.3, 28.6, 127.1, 128.0, 129.0, 131.9, 132.2, 134.6, 136.8, 137.7, 146.7, 147.2. Anal. Calcd for $C_{24}H_{44}Si_4$: C, 64.79; H, 9.97. Found: C, 64.62; H, 9.81. For **9a**: MS *m/e* 444 (M^+); IR $\nu_{C=C=C}$ 1904 cm^{-1}; 500-MHz ^1H NMR (δ, in C_6D_6) 0.06 (s, 9 H, Me_3Si-Si), 0.08 (s, 3 H, Me on ring silicon), 0.16 (s, 9 H, Me_3Si-C), 0.30 (s, 3 H, Me on ring silicon), 0.31 (s, 6 H, Me_2Si-Si), 0.51 (s, 2 H, H on C_9), 0.92 (s, 3 H, MeC), 1.04 (s, 3 H, MeC), 2.07 (d, 1 H, J = 13.8 Hz, H on C_7), 4.01 (d, 1 H, J = 13.8 Hz, H on C_7), 5.68 (s, 1 H, allene proton), 6.99 (d, 1 H, J = 8.3 Hz, H on $C_{4'}$), 7.21 (s, 1 H, H on $C_{1'}$), 7.22 (d, 1 H, J = 8.3 Hz, H on $C_{3'}$). 22.5-MHz ^{13}C NMR (δ, in C_6D_6) -3.7, -2.0, -0.2, 0.7, 1.1, 29.2, 33.5, 34.0, 37.2, 45.2, 83.4, 90.7, 128.0, 130.8, 134.3, 134.7, 137.2, 139.3, 212.4. Exact MS Calcd for $C_{24}H_{44}Si_4$: 444.2520. Found: 444.2550.

Isomerization of 8a to 11a. Compound **8a** was injected on the column of preparative GLC (silicone SE-30, column temperature 280 °C), and the resulting peak was collected. For **11a**: MS *m/e* 444 (M^+); IR $\nu_{C\equiv C}$ 2163 cm^{-1}; 500-MHz ^1H NMR (δ, in C_6D_6) 0.01 (s, 3 H, Me on ring silicon), 0.21 (s, 9 H, Me_3Si-C), 0.25 (s, 3 H, Me on ring silicon), 0.38 (s, 9 H, Me_3Si-Si), 0.42 (s, 2 H, H on C_9), 0.48 (s, 6 H, Me_2Si-Si), 0.85 (s, 3 H, Me-C), 0.99 (s, 3 H, Me-C), 2.36 (d, 1 H, J = 13.2 Hz, H on C_7), 2.53 (d, 1 H, J = 13.2 Hz, H on C_7), 3.59 (s, 1 H, H on C_4), 7.03 (d, 1 H, J = 7.3 Hz, H on $C_{4'}$), 7.36 (d, 1 H, J = 7.3 Hz, H on $C_{3'}$), 8.07 (s, 1 H, H on $C_{1'}$); 100-MHz ^{13}C NMR (δ, in C_6D_6) -4.4, -3.9, -3.7 (MeSi), -2.0 (Me_3Si-C), -1.6 (MeSi), 0.6 (Me_3Si-Si), 28.0 (C_4), 30.2 (C_9), 31.6 (Me-C), 33.2 (C_8), 34.4 (Me-C), 47.0 (C_7), 89.5 ($C\equiv C$), 106.8 ($C\equiv C$), 127.6 ($C_{2'}$), 130.7 ($C_{4'}$), 131.1 ($C_{3'}$), 132.4 ($C_{1'}$), 136.7, 137.4 (C_5 and C_6). Exact MS Calcd for $C_{24}H_{44}Si_4$: 444.2520. Found: 444.2534.

Photolysis of 1b in the Presence of Isobutene. A solution of 413.7 mg (1.06 mmol) in **1b**, 5 g (89.3 mmol) of isobutene, and 55.8 mg (0.281 mmol) of tetradecane as an internal standard in 25 mL of hexane was irradiated for 6 h. The resulting mixture was analyzed by GLC as being **8b** (43%), **9b** (22%), and **10b** (28%). Products **8b**, **9b**, and **10b** were isolated by MPLC (silica gel, eluent hexane). For **8b**: MS *m/e* 444 (M^+); 200-MHz ^1H NMR (δ, in $CDCl_3$) 0.20 (s, 9 H, Me_3Si-Si), 0.54 (s, 6 H, Me_2Si), 0.57 (s, 6 H, Me_2Si), 0.70 (s, 9 H, Me_3Si-C), 1.05 (d, 6 H, J = 6.7 Hz, Me_2C), 1.07 (d, 2 H, J = 6.7 Hz, H_2C), 1.94 (m, 1 H, $HCMe_2$), 7.63 (dd, 1 H, J = 8.0, 0.8 Hz, H on C_3), 7.72 (d, 1 H, J = 8.4 Hz, H on C_5), 7.79 (d, 1 H, J = 8.0 Hz, H on C_4), 7.82 (d, 1 H, J = 8.4 Hz, H on C_6), 8.64 (br s, 1 H, H on C_1); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -3.9, -2.1, 2.1, 3.3, 25.3, 26.4, 28.6, 127.0, 127.4, 130.0, 132.1, 132.7, 135.3, 137.5, 147.0. Anal. Calcd for $C_{24}H_{44}Si_4$: C, 64.79; H, 9.97. Found: C, 64.69; H, 9.76. For **9b**: MS *m/e* 444 (M^+); IR $\nu_{C=C=C}$ 1903 cm^{-1}; 90-MHz ^1H NMR (δ, in C_6D_6) 0.16 (s, 3 H, Me on ring silicon), 0.18 (s, 9 H, Me_3Si-Si), 0.28 (s, 9 H, Me_3Si-C), 0.38 (s, 3 H, Me on ring silicon), 0.42 (s, 3 H, MeSi-Si), 0.43 (s, 3 H, MeSi-Si), 0.48 (d, 1 H, J = 6.9 Hz, H on C_9), 0.61 (d, 1 H, J = 6.9 Hz, H on C_9), 1.06 (s, 3 H, MeC), 1.12 (s, 3 H, MeC), 2.20 (d, 1 H, J = 14.1 Hz, H on C_7), 4.11 (d, 1 H, J = 14.1 Hz, H on C_7), 5.69 (s, 1 H, allene proton), 6.99 (d, 1 H, J = 7.9 Hz, H on $C_{2'}$), 7.32 (s, 1 H, H on $C_{4'}$), 7.33 (d, 1 H, J = 7.9 Hz, H on $C_{1'}$); 22.5-MHz ^{13}C NMR (δ, in C_6D_6) -3.9, -3.7, -2.1, -0.2, 0.7, 1.1, 29.1, 33.4, 34.0, 37.3, 45.4, 83.4, 90.9, 128.4, 132.3, 134.8, 135.2, 138.0, 140.7, 212.4. Anal. Calcd for $C_{24}H_{44}Si_4$: C, 64.79; H, 9.97. Found: C, 64.78; H, 9.97. For **10b**: mp 83.0-84.0 °C; MS *m/e* 444 (M^+); 90-MHz ^1H NMR (δ, in C_6D_6) -0.04 (s, 9 H, Me_3Si), 0.17 (s, 9 H, Me_3Si), 0.28 (s, 3 H, Me-Si), 0.31 (s, 3 H,

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MeSi), 0.42 (s, 3 H, MeSi), 0.44 (s, 3 H, MeSi), 0.88 (s, 3 H, MeC), 1.23 (s, 3 H, MeC), 2.83 (br s, 1 H, H on C_8), 5.93 (dd, 1 H, J = 9.5, 1.1 Hz, H on C_5), 6.35 (d, 1 H, J = 9.5 Hz, H on C_6), 7.03 (d, 1 H, J = 7.3 Hz, H on C_3), 7.31 (br s, 1 H, H on C_1), 7.40 (dd, 1 H, J = 7.3, 1.1 Hz, H on C_4); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) −4.1, −3.7, −2.1, −1.9, 0.3, 0.5, 25.2, 29.2, (2 C), 32.1, 45.7, 54.9, 124.4, 125.2, 132.4, 133.6, 134.3, 135.0, 136.0, 136.9. Anal. Calcd for $C_{24}H_{44}Si_4$: C, 64.79; H, 9.97. Found: C, 64.76; H, 9.94.

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Registry No. **1a**, 134388-71-9; **1b**, 134388-72-0; **2a**, 134388-73-1; **2b**, 134388-75-3; **2c**, 134388-74-2; **3b**, 134418-54-5; **4a**, 134388-76-4; **4b**, 134388-79-7; **5a**, 134388-77-5; **5b**, 134418-56-7; **6a**, 134388-78-6; **6b**, 134388-80-0; **7a**, 134418-55-6; **8a**, 134388-81-1; **8b**, 134388-83-3; **9a**, 134418-57-8; **9b**, 134418-58-9; **10b**, 134388-84-4; **11a**, 134388-82-2; 2,6-dibromonaphthalene, 13720-06-4; chloropentamethyldisilane, 1560-28-7; 2,7-dibromonaphthalene, 58556-75-5; isobutene, 115-11-7.

Supplementary Material Available: Tables of positional parameters and equivalent isotropic thermal parameters of non-hydrogen atoms, anisotropic thermal parameters, and distances and angles for **5b** (2 pages); a listing of observed structure factors, their standard deviations, and calculated structure factors for **5b** (6 pages). Ordering information is given on any current masthead page.

Silicon–Carbon Unsaturated Compounds. 31. Photochemical Behavior of 1,1- and 1,2-Dinaphthyltetramethyldisilanes

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The photolysis of 1,1-bis(1-naphthyl)tetramethyldisilane in the presence or absence of a trapping agent gave 1-[methyl(1-naphthyl)silyl]-8-(trimethylsilyl)naphthalene, while 1,2-bis(1-naphthyl)tetramethyldisilane afforded 2,3-dihydro-1,1,3,3-tetramethyl-1,3-disilaphenalene-2-spiro-1′,2′-dihydronaphthalene as a main product, along with dimethylbis(1-naphthyl)silane. Irradiation of 1,1-bis(2-naphthyl)tetramethyldisilane in the presence of isobutene produced two types of adducts arising from the reaction of a silene with isobutene, 2-[isobutylmethyl(2-naphthyl)silyl]-1-(trimethylsilyl)naphthalene and 1,2-dihydro-1,2-[1,1,3-trimethyl-3-(2-naphthyl)-3-silapropano]-2-(trimethylsilyl)naphthalene. Similar irradiation of 1,2-bis(2-naphthyl)tetramethyldisilane afforded silene adducts 2-(isobutyldimethylsilyl)naphthalene, 2-(isobutyldimethylsilyl)-1-[dimethyl(2-naphthyl)silyl]naphthalene, and 1,2-dihydro-1,2-(1,1,3,3-tetramethyl-3-silapropano)-2-[dimethyl(2-naphthyl)silyl]naphthalene.

Introduction

Recently, we have found that the photolysis of 1-(pentamethyldisilanyl)naphthalene and 1,5-bis(pentamethyldisilanyl)naphthalene affords the respective photoisomers arising from radical scission of a silicon–silicon bond, followed by migration of the resulting trimethylsilyl radical to the C_8 position of the naphthyl ring and then a 1,4 shift of the ipso hydrogen to the radical center as the sole product.[1] 1,4-Bis(pentamethyldisilanyl)naphthalene, however, undergoes photolysis to give two products; one involves the photochemical isomerization analogous to that observed in the photolysis of the 1,5-isomer and the other comprises the formation of a silene derived from a 1,3-trimethylsilyl shift to the C_2 position of the naphthyl ring. The silene thus formed reacts with only methanol to give 6-(methoxydimethylsilyl)-6,7-bis(trimethylsilyl)-5,8-(dimethylsilano)-5,6,7,8-tetrahydronaphthalene but does not react with other trapping agents such as acetone and isobutene.[1]

The photolysis of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene afforded the products derived from the silenes that are produced from a 1,3-trimethylsilyl shift to the C_1 position of the naphthyl ring.[2] No isomers arising from radical scission of the silicon–silicon bond, followed by migration of the resulting trimethylsilyl radical to the C_1 position and then a 1,3 shift of the ipso hydrogen to the silyl radical center, are detected in the photolysis products. In contrast to the silene generated from the 1,4-isomer, the silenes from the 2,6- and 2,7-isomers react readily with methanol, acetone, and isobutene to give addition products.

In an effort to learn much more about the photochemical behavior of the naphthyl-substituted disilanes, we investigated the photolysis of 1,1- and 1,2-bis(1-naphthyl)tetramethyldisilane and 1,1- and 1,2-bis(2-naphthyl)tetramethyldisilane.

Results and Discussion

1,1-Bis(1-naphthyl)tetramethyldisilane (**1**) and 1,1-bis(2-naphthyl)tetramethyldisilane (**3**) were synthesized by the reaction of 1,1-dichlorotetramethyldisilane with 2 molar equiv of the corresponding naphthyllithium in 44

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