880 *Organometallics* **1991**, *10*, 880–887

Silicon–Carbon Unsaturated Compounds. 26. Photochemical Behavior of 1,4- and 1,5-Bis(pentamethyldisilanyl)naphthalene

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Received May 11, 1990

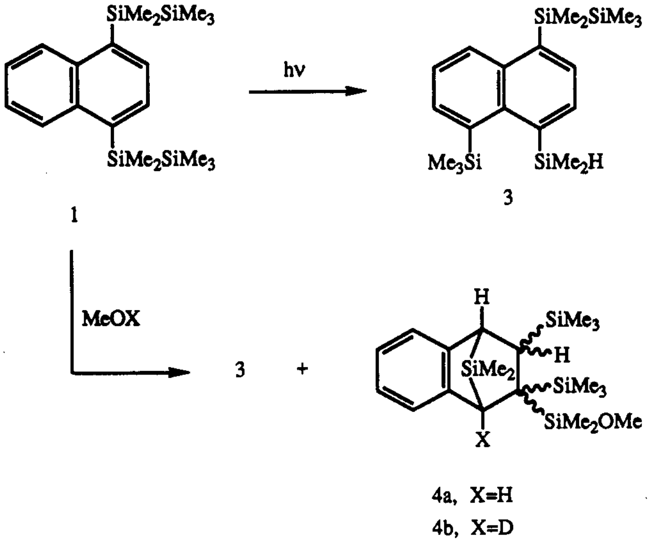
The photolysis of 1,4-bis(pentamethyldisilanyl)naphthalene (1) in the absence of a trapping agent gave 4-(dimethylsilyl)-1-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene (3). Irradiation of 1 in the presence of methanol afforded 3 and 6-(methoxydimethylsilyl)-6,7-bis(trimethylsilyl)-5,8-(dimethylsilano)-5,6,7,8-tetrahydronaphthalene. Similar photolysis of 1,5-bis(pentamethyldisilanyl)naphthalene (2) in the presence or absence of methanol produced 5-(dimethylsilyl)-1-(pentamethyldisilanyl)-4-(trimethylsilyl)naphthalene as the sole product. Irradiation of 1 in a mixed solvent consisting of methanol and benzene in a ratio of 1:1.5 by volume produced 1,4-bis(dimethylsilyl)naphthalene and a trace amount of 4-(dimethylsilyl)-1-(pentamethyldisilanyl)naphthalene, while 2 afforded 5-(dimethylsilyl)-1-(pentamethyldisilanyl)naphthalene and 1,5-bis(dimethylsilyl)naphthalene. The ab initio MO calculations have been carried out on 1,4- and 1,5-bis(disilanyl)naphthalene and also 1- and 2-(disilanyl)naphthalene. We have reinvestigated the photolysis of 1- and 2-(pentamethyldisilanyl)naphthalene (11 and 12) and found that the photolysis of 11 in the presence or absence of a trapping agent gave 8-(dimethylsilyl)-1-(trimethylsilyl)naphthalene, while 12 in the presence of isobutene produced 2-(isobutyldimethylsilyl)-1-(trimethylsilyl)naphthalene.

Introduction

The photolysis of organopolysilanes affords a convenient method for the synthesis of various reactive species such as silylenes or silenes.[1,2] In 1975, we found that irradiation of a benzene solution of pentamethylphenyldisilane gives a silene arising from a 1,3-shift of a trimethylsilyl group to an ortho carbon atom in the phenyl ring.[3] Work following this original discovery showed that the photochemical formation of this type of silene is a remarkably general one for various benzenoid aromatic disilanes.[2] All silenes thus formed react with a trapping agent, such as alkenes, alkynes, and carbonyl compounds to give ene products.[2] In the absence of the trapping agent, these silenes are transformed into nonvolatile substances.

The chemical behavior of the silenes generated photochemically from 1-(disilanyl)naphthalenes, however, is different in many aspects from that of the silenes produced from the benzenoid disilanes. For instance, irradiation of 1-(pentamethyldisilanyl)naphthalene produces an isomer of the starting disilanylnaphthalene as the sole product, even in the presence of a trapping agent. No adduct arising from the reaction of the silene with the trapping agent is detected in the photolysis mixture. In a previous paper, we reported this isomer to be 1-(dimethylsilyl)–2–(trimethylsilyl)naphthalene on the basis of the chemical reaction.[4] However, this has turned out to be an erroneous structural assignment. Careful studies of the 500-MHz ^{1}H NMR data and also an independent synthesis of this compound indicated that this must be 8-(dimethylsilyl)-1-(trimethylsilyl)naphthalene.

Scheme I



In order to learn much more about the photochemical behavior of the disilanyl-substituted naphthalenes, we have now initiated systematic investigations of these compounds. In this paper, we report the anomalous photochemical behavior of 1,4- and 1,5-bis(pentamethyldisilanyl)naphthalene and the results of a reinvestigation on the photolysis of 1- and 2-(pentamethyldisilanyl)naphthalene. We also report ab initio molecular orbital calculations of 1,4- and 1,5-bis(disilanyl)naphthalene and 1- and 2-(disilanyl)naphthalene.

Results

The starting 1,4-bis(pentamethyldisilanyl)naphthalene (1) and 1,5-bis(pentamethyldisilanyl)naphthalene (2) were

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(1) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(2) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

(3) (a) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923. (b) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139.

(4) Ishikawa, M.; Oda, M.; Miyoshi, N.; Fabry, L.; Kumada, M.; Yamabe, T.; Akagi, K.; Fukui, K. *J. Am. Chem. Soc.* **1979**, *101*, 4612.

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synthesized by the reaction of di-Grignard reagents prepared from 1,4- and 1,5-dibromonaphthalene[5] and magnesium with chloropentamethyldisilane in a mixed solvent consisting of ether, THF, and benzene.

Photolysis of 1 and 2. When compound 1 was irradiated internally with a low-pressure mercury lamp bearing a Vycor filter (254 nm) in a hexane solution at room temperature, a product identified as 4-(dimethylsilyl)-1-(pentamethyldisilanyl)-5-(trimethylsilyl)naphthalene (3) was obtained in 32% yield as the sole volatile product. The distillation of the resulting photolysis mixture showed that nonvolatile products, which remained as a residue in the flask, were produced in this photolysis. Similar irradiation of 1 in benzene afforded 3 in 34% yield (Scheme I). No other volatile products were detected in the photolysis mixture by either spectrometric analysis or GLC analysis. The photolysis of 1 in deuteriobenzene under the same conditions again gave 3 in 33% yield. The ^{1}H NMR spectrum of this compound shows a septet resonance at δ 5.18 ppm, due to an Si–H proton. Its mass spectrum also shows a parent ion at m/e 388, indicating that the product contains no deuterium atom in the molecule. These results indicate that the hydrogen on a silicon atom must come from the naphthyl ring, but not from the solvent used.

Next, we carried out the photolysis of 1 in the presence of a trapping agent, in order to learn the origin of the nonvolatile substances produced in the photolysis of 1. The photolysis of 1 in the presence of a 40-fold excess of acetone and also in the presence of a 100-fold excess of isobutene afforded compound 3 in 33% and 34% yields, respectively, as the sole volatile product. No product containing acetone or isobutene was detected in the resulting photolysis mixture. Again, nonvolatile products were produced in these photolyses. The photolysis of 1 in the presence of a 50-fold excess of methanol, a compound that seems to be an efficient trapping agent for reactive intermediates such as silenes in benzene, however, gave an adduct, 6-(methoxydimethylsilyl)-6,7-bis(trimethylsilyl)-5,8-(dimethylsilano)-5,6,7,8-tetrahydronaphthalene (4a) in 48% yield, in addition to a 30% yield of compound 3. Irradiation of 1 in the presence of methanol-d_1 under the same photolysis conditions afforded a methanol-d_1 adduct, 5-deuterio-6-(methoxydimethylsilyl)-6,7-bis(trimethylsilyl)-5,8-(dimethylsilano)-5,6,7,8-tetrahydronaphthalene (4b) in 47% yield, in addition to a 39% yield of compound 3 which contains no deuterium atom in the molecule.

The structures of 3 and 4a were confirmed by mass, IR, and ^{1}H and ^{13}C NMR spectroscopic analysis. All spectral data obtained for 3 and 4a were consistent with the proposed structures. The location of the silyl groups on the naphthyl ring for the product 3 was determined by NOE-FID difference experiments. Thus, irradiation of the dimethylsilyl protons of a pentamethyldisilanyl group results in the strong enhancement of two protons at the C_2 and C_8 positions of the naphthyl ring, while saturation of the dimethylsilyl protons of a hydrodimethylsilyl group shows enhancement of a proton at the C_3 position, as well as an Si–H proton. As expected, saturation of trimethylsilyl protons on the C_5 atom led to a positive NOE of a proton at the C_6 position and an Si–H proton. ^{1}H NMR chemical shifts and coupling constants and ^{13}C NMR chemical shifts that were the basis of the identification for 4a are shown in Figure 1. The ^{13}C–^{1}H COSY spectrum of 4a shows that Ha, Hb, and Hc couple with C_5, C_8, and C_7, respectively, indicating that each of these three protons attaches to different sp^3 ring carbons (Figure 2a). In the long-range ^{13}C–^{1}H COSY spectrum of 4a, Ha couples with C_5, C_{8a} C_{4a}, and C_6 carbons, respectively, while Hb couples with C_5 and C_{8a} carbons (Figure 2b). These results are wholy consistent with the proposed structure. Furthermore, the fact that saturation of the methoxy protons of a methoxydimethylsilyl group leads to a positive NOE of two trimethylsilyl protons as well as one methyl proton of Me^{a}Me^{b}SiOMe also supports the structure of 4a. Although 4a could be isolated as a single isomer, configuration of the silyl groups on C_6 and C_7 has not yet been confirmed.

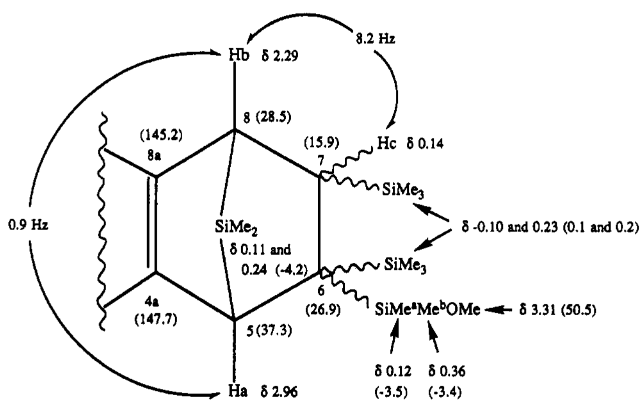

Figure 1. Selected ^{1}H (^{13}C) NMR data for compound **4a**.

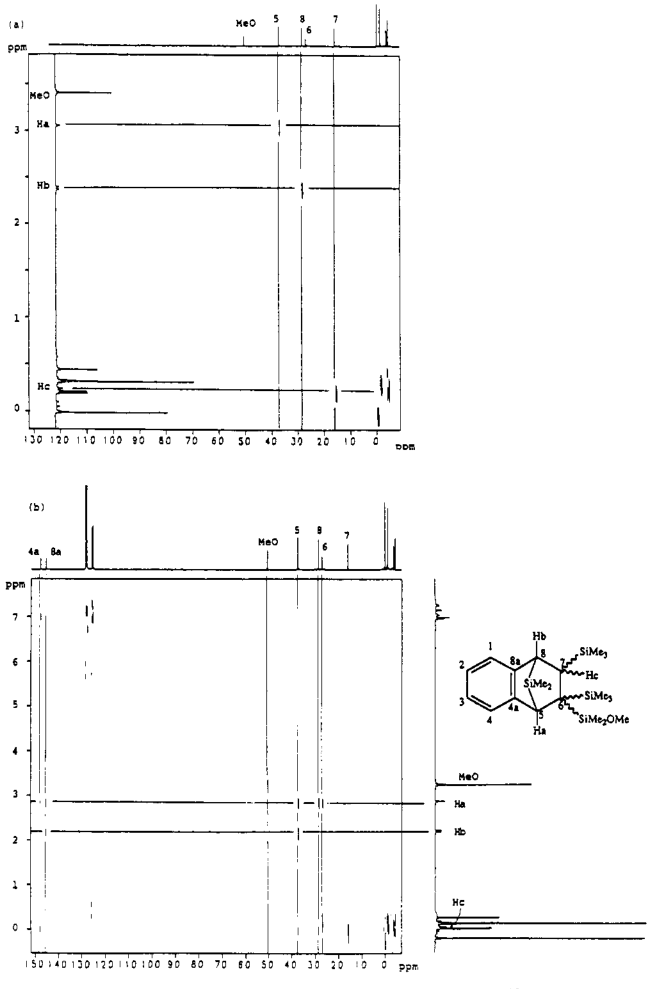

Figure 2. C–H shift correlated spectrum of **4a**: (a) ^{13}C–^{1}H COSY and (b) long-range ^{13}C–^{1}H COSY.

To our surprise, the photolysis of 1 in a mixed solvent consisting of methanol and benzene in a ratio of 1:1.5 by volume, which produces a homogeneous solution, yielded

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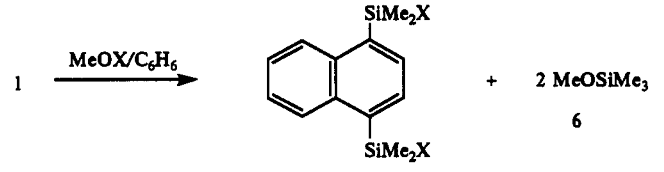
(5) Pawliczek, J. B.; Guenther, H. *Tetrahedron* **1970**, *26*, 1755.



5a, X=H
5b, X=D

1,4-bis(dimethylsilyl)naphthalene (**5a**) and methoxytrimethylsilane (**6**) in 50% and 165% yields, respectively. Neither **3** nor **4a** was detected by either GLC or spectroscopic analysis. In this photolysis, a trace amount of 4-(dimethylsilyl)-1-(pentamethyldisilanyl)naphthalene (less than 5% yield), arising from cleavage of one of two silicon–silicon bonds in the starting compound **1** by methanol, was detected by GC–mass spectrometric analysis of the resulting photolysis mixture.

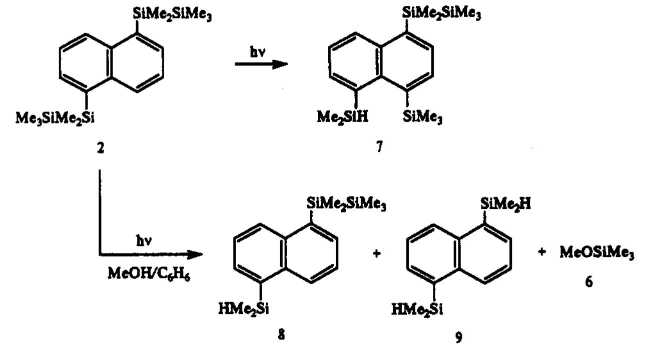
All spectral data obtained for **5a** were identical with those of an authentic sample prepared by the reaction of the di-Grignard reagent of 1,4-dibromonaphthalene with chlorodimethylsilane. Similar irradiation of **1** in a methanol-d_1–benzene solution gave 1,4-bis(deuteriodimethylsilyl)naphthalene (**5b**).

The photolysis of 1,5-bis(pentamethyldisilanyl)naphthalene **2** in hexane under the same conditions gave 5-(dimethylsilyl)-1-(pentamethyldisilanyl)-4-(trimethylsilyl)naphthalene (**7**) in 74% yield, as the sole product (Scheme II). The structure of **7** was verified by mass, IR, and ^{1}H and ^{13}C NMR spectroscopic methods, and also by NOE-FID difference experiments. Saturation of trimethylsilyl protons on the C$_4$ atom in the naphthyl ring produced a positive NOE of a proton at the C$_3$ position and an Si–H proton. Irradiation of dimethylsilyl proton on the C$_5$ position resulted in the enhancement of trimethylsilyl protons on C$_4$ and a proton on C$_6$. These results are consistent with the proposed structure.

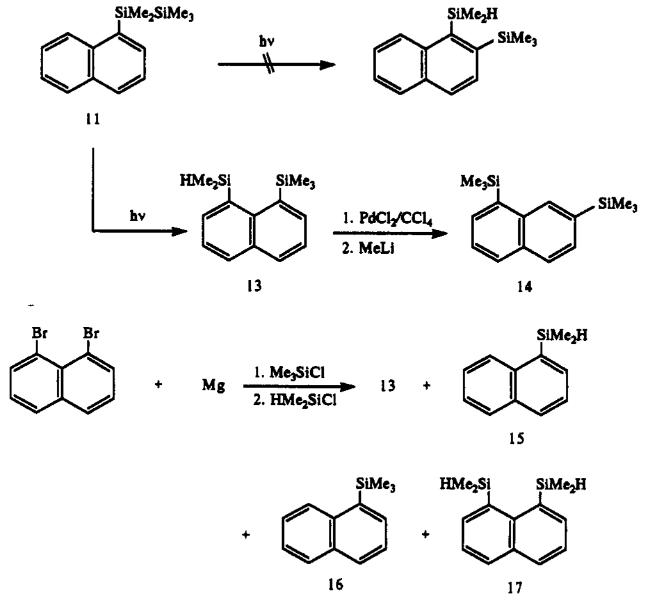
In sharp contrast to the photochemical behavior of **1**, compound **2** affords no adduct with methanol. Thus, irradiation of **2** in the presence of a 50-fold excess of methanol in benzene produced compound **7** in 37% yield. No other volatile products were detected by either GLC or spectroscopic analysis. Irradiation of **2** in a mixed solvent consisting of methanol and benzene with a ratio of 1:1.5 by volume gave 5-(dimethylsilyl)-1-(pentamethyldisilanyl)naphthalene (**8**), 1,5-bis(dimethylsilyl)naphthalene (**9**), and methoxytrimethylsilane (**6**) in 18%, 36%, and 110% yields, respectively. Similar irradiation of **2** in the mixed solvent containing a higher concentration of methanol (methanol:benzene = 4:1) afforded **8** and **9** in 3% and 36% yields, respectively. In this photolysis, compound **7** could not be detected in the reaction mixture. All spectral data obtained for compounds **8** and **9** were wholly consistent with the proposed structures (see Experimental Section).

Reinvestigation of the Photolysis of 1- and 2-(Pentamethyldisilanyl)naphthalene. Since the photolysis of **1** and **2** in the absence of methanol gave only the product arising from migration of the trimethylsilyl group to the C$_8$ position of the naphthyl ring, but not to the C$_2$ position, we suspected that erroneous structure assignments had been made for the products obtained from the photolysis of 1- and 2-(disilanyl)naphthalenes reported previously.[4] Therefore, we have reinvestigated the photolysis of 1- and 2-(pentamethyldisilanyl)naphthalene (**11** and **12**).

Scheme II



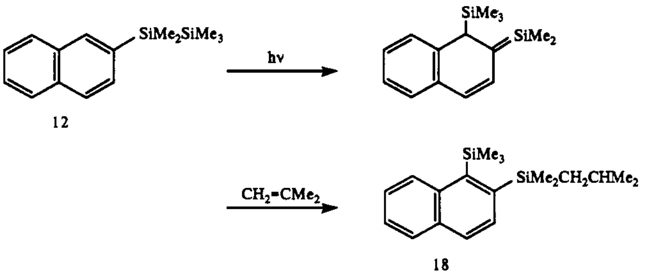
Scheme III



Irradiation of **11** in the presence or absence of isobutene in a hexane solution afforded (dimethylsilyl)(trimethylsilyl)naphthalene (**13**), whose spectral data were identical with those reported previously.[4] In the photolysis of **11**, if the trimethylsilyl group migrates to the C$_8$ position of the naphthyl ring, 8-(dimethylsilyl)-1-(trimethylsilyl)naphthalene will be produced. As expected, saturation of the resonance of trimethylsilyl protons of **13** performed in NOE-FID difference experiments at 500 MHz produced a positive NOE of a proton on the C$_7$ position, while irradiation of the dimethylsilyl protons of the hydrodimethylsilyl group led to enhancement of a proton on the C$_2$ position. These results are wholly consistent with the 1,8-disubstituted structure. In order to obtain more information on the structure of **13**, we attempted to transform it to bis(trimethylsilyl)naphthalene, which might be readily identified by spectroscopic method. Treatment of **13** with a catalytic amount of palladium dichloride in carbon tetrachloride, followed by methylation using methyllithium, however, gave 1,7-bis(trimethylsilyl)naphthalene (**14**) as the sole product. We therefore decided to synthesize **13** by an independent route. When a di-Grignard reagent prepared from 1,8-dibromonaphthalene was treated with chlorotrimethylsilane and then chlorodimethylsilane, a mixture consisting of 1-(dimethylsilyl)naphthalene (**15**), 1-(trimethylsilyl)naphthalene (**16**), 1,8-bis(hydrodimethylsilyl)naphthalene (**17**), and 8-(dimethylsilyl)-1-(trimethylsilyl)naphthalene were obtained 10%, 17%, 21%, and 16% yields, respectively (Scheme III).

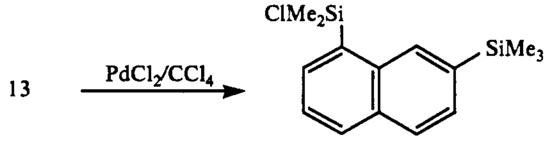
The product, 8-(dimethylsilyl)-1-(trimethylsilyl)naphthalene could be isolated from the reaction mixture by preparative GLC. All spectral data obtained for this product were identical with those of **13**, indicating that the

Scheme IV



photochemical migration of the trimethylsilyl group in compound **11** occurred on the C_8 position in the naphthyl ring, but not to the C_2 position as reported previously.[4]

For the formation of 1,7-bis(trimethylsilyl)naphthalene (**14**) observed in the reaction of **13** with a palladium catalyst in carbon tetrachloride, followed by methylation, the intramolecular migration of a silyl group should be involved. In order to confirm this, a mixture of **13** and a palladium catalyst in carbon tetrachloride was allowed to stand at room temperature, and the resulting product was isolated by preparative GLC. The chloro compound thus obtained was identified as 1-(chlorodimethylsilyl)-7-(trimethylsilyl)naphthalene on the basis of NOE-FID experiments, indicating that the trimethylsilyl group on the C_8 position of compound **13** migrates to the C_7 position, during the hydrogen–chlorine exchange.

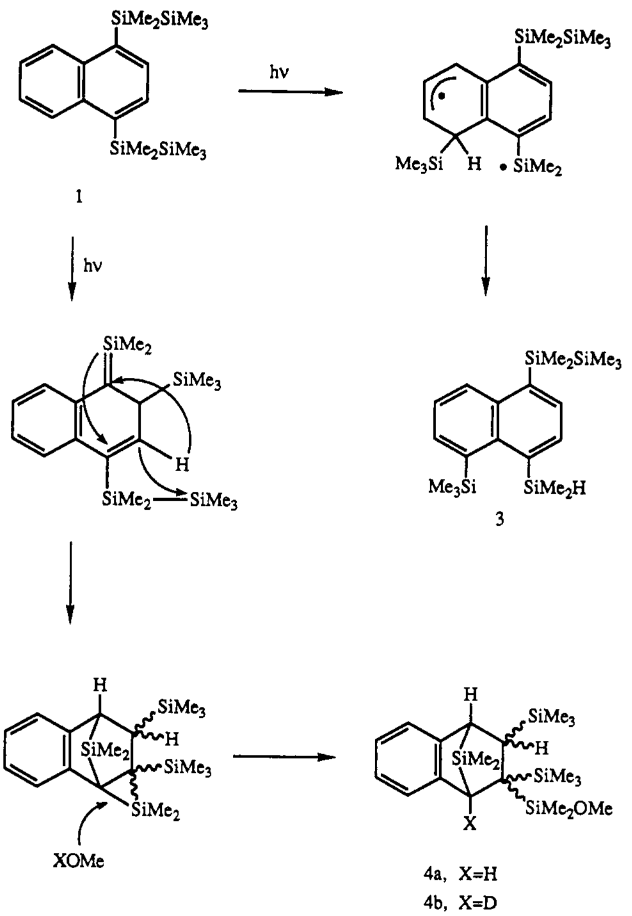


We have reported previously that the photolysis of **12** in the presence of isobutene produced 2-(isobutyldimethylsilyl)-3-(trimethylsilyl)naphthalene derived from the ene reaction of the silene arising from migration of the trimethylsilyl group to the C_3 position with isobutene. Recently, however, Sakurai reported that the product formed in this experiment was 2-(isobutyldimethylsilyl)-1-(trimethylsilyl)naphthalene (**18**).[6] We also have reinvestigated this photochemical reaction. The 500-MHz ^1H NMR spectra of the product and NOE-FID experiments clearly show that the structure of the product must be 2-(isobutyldimethylsilyl)-1-(trimethylsilyl)naphthalene, indicating that the trimethylsilyl group migrates to the C_1 position, but not to the C_3 position (Scheme IV). Furthermore, saturation of the trimethylsilyl protons resulted in enhancement of a proton at the C_8 position, while irradiation of the dimethylsilyl protons of the isobutyldimethylsilyl group produced a positive NOE of a proton at the C_3 position.

Discussion

Mechanism for the Photolysis of 1 and 2. The photolysis of **1** in the presence of methanol gives **3** in an amount almost equal to that in the absence of methanol. The product **4**, however, is produced only in the presence of methanol. Presumably, products **3** and **4** are formed by a different mechanism. For the formation of compound **3**, considering the fact that photolysis in deuteriobenzene produced **3** without any incorporation of a deuterium atom, it seems likely that radical scission of a silicon–silicon bond of the photoexcited molecule takes place in the solvent cage and homolytic aromatic substitution of the resulting trimethylsilyl radical occurs on the C_8 position of the naphthyl ring. Then the ipso hydrogen migrates to the silyl center to give the product **3**.

Scheme V



A possible mechanism for the formation of **4** would involve a series of reactions involving a silene intermediate that would be formed from a 1,3-trimethylsilyl shift to the C_2 atom. The silene would undergo rearrangement to a tricyclic compound containing a silacyclopropane ring, and the reaction of the resulting silacyclopropane with methanol would afford the product **4**, as shown in Scheme V. The fact that the photolysis with methanol-d_1 produced adduct **4b** containing a deuterium atom at the C_5 position strongly supports this mechanism. The product **6** arising from the photolysis of **1** in the presence of a large excess of methanol must be produced by the direct reaction of photoexcited **1** with methanol, before migration of a trimethylsilyl group to the naphthyl ring. The direct reaction of photoexcited disilanes[7,8] with alcohol has been reported in the photolysis of 1-(disilanyl)dibenzosiloles.[9] The formation of **7–9** in the photolysis of **2** can also be understood in a similar manner to that of **3** and **5**.

Ab Initio MO Calculations. In the photochemical reactions of both **1** and **2**, the terminal silyl group of the disilanyl moiety attached to the C_1 atom migrates to the C_8 position of the naphthyl ring. We have performed ab

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(6) Sakurai, H. *Silicon Chemistry*, Proceedings of the Eighth International Symposium on Organosilicon Chemistry, St. Louis, Missouri, 1987; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1987; Chapter 16, p 163.

(7) Shizuka, H.; Sata, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341.

(8) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837.

(9) Ishikawa, M.; Tobohashi, T.; Kumada, M. *J. Organomet. Chem.* **1984**, *264*, 79.

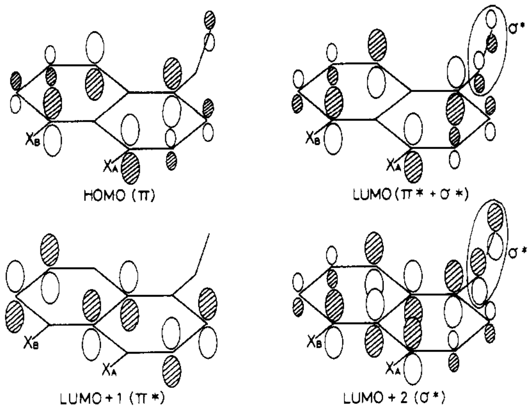


Figure 3. Orbital patterns for A and B. $X_{A,B}$ = H_3SiSiH_2 for A and B, respectively.

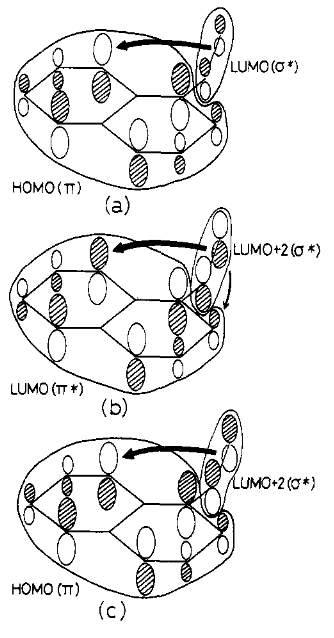


Figure 4. Orbital interaction between (a) HOMO and LUMO, (b) LUMO and LUMO+2, and (c) HOMO and LUMO+2. Substituents X_A and X_B shown in Figure 2 are omitted.

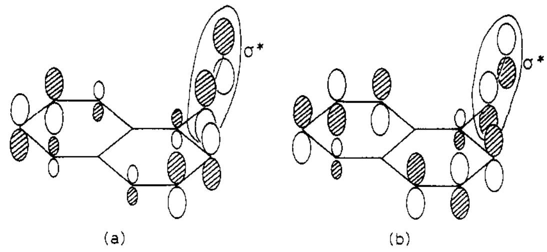


Figure 5. LUMO+3 pattern for (a) compound A and (b) compound B. Substituents X_A and X_B shown in Figure 2 are omitted.

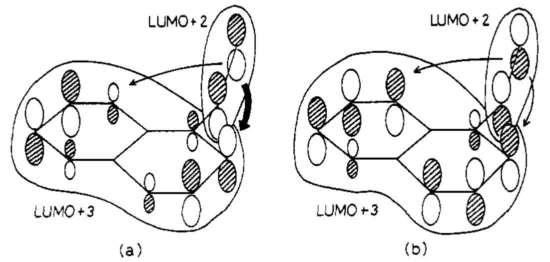
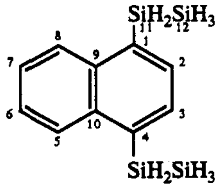
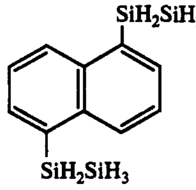


Figure 6. Orbital interaction between LUMO+2 and LUMO+3 for (a) compound A and (b) compound B. Substituents X_A and X_B shown in Figure 2 are omitted.

initio SCF MO calculations for 1,4- and 1,5-bis(disilanyl)naphthalene (A and B) using the Gaussian-82 program[10] in order to elucidate this phenomenon in terms of orbital interactions. The STO-3G basis set was employed for the calculations. For compounds A and B, we employed geometries such that the plane spanned by C–Si and Si–Si bonds is perpendicular to the plane of the naphthyl ring because of the advantage of σ–π conjugation.[11,12] All the Si atoms take sp^3 hybridization in staggered conformation with the following bond lengths:[4,13] 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; all bonds are equal for the naphthyl ring. The symmetry of compound A is C_2 and that of compound B is C_i.



A



B

Orbital patterns for the naphthyl ring of both A and B are about the same as shown in Figure 3. The HOMO corresponds to the π orbital of the naphthyl ring. The LUMO and LUMO+1 correspond to the π^* orbital of the naphthyl ring, where the LUMO also contributes to the antibonding orbital (σ^*) of a silicon–silicon σ bond. The LUMO+2 corresponds to σ^* of a silicon–silicon σ bond.

For the migration of the SiH_3 group to the C_8 atom, we consider the orbital interactions of HOMO(π)–LUMO(σ^*), LUMO(π^*)–LUMO+2(σ^*), and HOMO(π)–LUMO+2(σ^*), as shown in Figure 4. As can be seen from the orbital pattern shown in Figure 4, the Si_{11}–Si_{12} σ bond is weakened by the excitation due to the antibonding character of σ^*. In the orbital interaction between HOMO(π) and LUMO(σ^*) or LUMO(π^*) and LUMO+2(σ^*) the 2p$_z$ atomic orbital of the C_1 atom and the 3p$_z$ atomic orbital of the Si_{11} atom have the same phase, and therefore a π bond of C_1–Si_{11} would be formed effectively. The upper part of the 2p$_z$ atomic orbital of the C_8 atom and the lower part of the 3p$_z$ atomic orbital of the Si_{12} atom have the same phase, and this may be favorable to the formation of a new C_8–Si_{12} bond. In the case of the LUMO–LUMO+2 interaction, the upper part of the 2p$_z$ atomic orbital of the C_2 atom and the lower part of the 3p$_z$ atomic orbital of the Si_{12} atom also show the same phase, which is favorable for the formation of a C_2–Si_{12} bond. However, the contribution of the 2p$_z$ atomic orbital of the C_8 atom to the LUMO is larger than that of the 2p$_z$ atomic orbital of the C_8 atom for A and B. Hence, the terminal silyl group migrates to the C_8 atom in both cases of the HOMO–LUMO and LUMO–LUMO+2 interactions. The orbital interaction between HOMO and LUMO+2 is also favorable for the formation of the C_8–Si_{12} bond.

The photochemical behavior of compound 1 is different from that of 2, that is, the terminal silyl group in compound 1 can migrate to the C_2 position as well as to the C_8 position, whereas in the case of 2 it does not. In order

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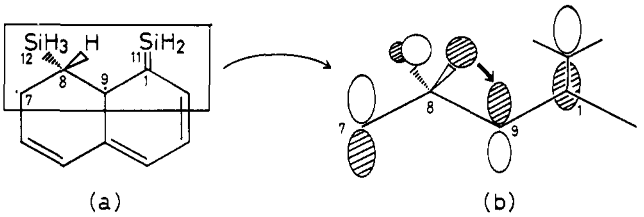

Figure 7. (a) Biradical structure of the silene. (b) HOMO of $\cdot CH_2CH(SiH_3)CHCH{=}SiH_2\cdot$.

to explain these phenomena, we have to consider the influence of orbitals above the LUMO+2 upon the orbital interactions. The LUMO+3, LUMO+4, and LUMO+5 correspond to s* of a silicon–silicon s bond in both cases of compound A and B. In these three orbitals only the LUMO+3 moderately contributes to the $2p_z$ atomic orbitals of the carbon atoms in the naphthyl ring, as shown in Figure 5. The contribution of the $2p_z$ atomic orbital of the C_2 atom is larger than that of the $2p_z$ atomic orbital of the C_8 atom in compound A, whereas in B contributions of the two atomic orbitals are about the same. Figure 6a shows the orbital interaction between the LUMO+2 and LUMO+3 in compound A, which is favorable for the formation of a C_2–Si_{12} bond. In compound B, however, no difference between the C_2 and C_8 positions for the ease of migration of the silyl group can be observed, as shown in Figure 6b. The orbital energies of the HOMO, LUMO, LUMO+1, LUMO+2, and LUMO+3 for both compounds A and B are calculated to be −0.203 56, 0.196 99, 0.261 68, 0.323 02, and 0.405 07 for A and −0.240 15, 0.197 21, 0.261 85, 0.321 90, and 0.412 45 for B, respectively. Comparison of the energies of the LUMO+2 and LUMO+3 of A with those of B shows that the LUMO+2 of B is more stabilized than that of A but the LUMO+3 is destabilized. Therefore, the energy gap between the LUMO+2 and LUMO+3 for B is larger than that for A, and consequently, contribution of the interaction between the LUMO+2 and LUMO+3 for B would be smaller than that for A. We can hence conclude that the difference of the reactivity between 1 and 2 can be explained by taking the LUMO+3 into account.

When a silyl radical from the disilanyl moiety migrates to the C_8 position, the hydrogen on this carbon should move to the Si_{11} radical center. However, if we consider that the hydrogen attached to the C_8 atom remains intact in the migration of the terminal silyl group, the biradical species would be formed, as shown in Figure 7a. We have taken out a fragment $CH_2CH(SiH_3)CHCH{=}SiH_2$ from the biradical intermediate and carried out ab initio SCF MO calculations for the fragment using the STO-3G basis set. We employed a geometry such that all atoms but the Si_{12} and H atoms attached to the C_8 position are coplanar and that the C_1, C_7, C_9, and Si_{11} atoms take sp^3 hybridization and the C_8 and Si_{12} atoms take sp^3 hybridization in staggered conformation with the following bond lengths:[4,13] C–Si_{11} = 1.60 Å, and the others are the same as those listed above. Figure 7b shows the orbital pattern for the HOMO of the fragment. The phase of the 1s atomic orbital of hydrogen attached to the C_8 atom is the same as that of the upper part of the $2p_z$ atomic orbital of the C_9 atom. Consequently, the phase relationship between these atomic orbitals is favorable for the formation of a new C_9–H σ bond. Additionally, the newly formed C_9–H bond results in a highly strained ring system, and the subsequent 1,3-hydrogen shift from C_9 to the Si_{11} atom should readily occur.

The reinvestigation of the photolysis of 1-(pentamethyldisilanyl)naphthalene showed that the terminal trimethylsilyl group migrates only to the C_8 atom but not to the C_2 atom (see below). The regioselectivity can be explained in the same way as for compound A and B mentioned above. The orbital patterns for the naphthyl ring of 1-(disilanyl)naphthalene are almost identical with those in Figure 3. For 1-(disilanyl)naphthalene, the HOMO, LUMO, LUMO+1, and LUMO+2 correspond to the π, π^*, and π^* orbitals of the naphthyl ring and the σ^* orbital of a silicon–silicon σ bond, respectively. LUMO has also the σ^* character. We can thus consider the orbital interactions between the LUMO and LUMO+2 and between the HOMO and LUMO+2. These interactions are favorable for the scission of the Si_{11}–Si_{12} σ bond because of the antibonding character of σ^* and for the formation of a C_8–Si_{12} σ bond. The HOMO–LUMO interaction also favors the C_8–Si_{12} bond formation.

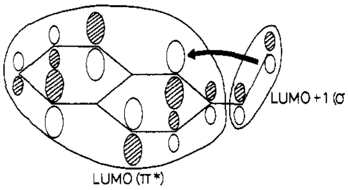

Figure 8. Orbital interaction between LUMO (π^*) and LUMO+1 (σ^*) in the photochemical reaction of 2-(disilanyl)naphthalene.

In the photolysis of 2-(pentamethyldisilanyl)naphthalene, a trimethylsilyl group migrates only to the C_1 atom, but not to the C_3 atom. We have also performed ab initio SCF MO calculations for 2-(disilanyl)naphthalene using the STO-3G basis set. The geometrical parameters are the same as those listed above.[4,13] The orbital patterns for the naphthyl ring are almost the same as those obtained for compound A and B shown in Figure 3. The HOMO, LUMO, and LUMO+1 for 2-(disilanyl)naphthalene correspond to the π and π^* orbital of the naphthyl ring and the σ^* orbital of the silicon–silicon σ bond, respectively. The LUMO also has σ^* character. In this case we should consider the orbital interaction between the LUMO and LUMO+1, and then the phase relationship in this interaction would be favorable for the formation of a new C_1–Si_{12} bond, as shown in Figure 8. In the HOMO–LUMO interaction or the HOMO–LUMO+1 interaction, the migration of the silyl group to the C_3 atom is allowed, but the coefficient of the HOMO at the C_3 atom is small. Hence the migration to this carbon may not occur so easily.

In conclusion, the photochemical migration of the trimethylsilyl group in 1,5-bis(pentamethyldisilanyl)naphthalene and, 1- and 2-(pentamethyldisilanyl)naphthalene occurs exclusively at the α-carbon of the naphthyl ring, while in the photolysis of 1,4-bis(pentamethyldisilanyl)naphthalene, the trimethylsilyl group migrates to both the α- and β-carbons.

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, a JNM-GX-400 spectrometer, a Varian Model XL-300 spectrometer, a JEOL Model JNM-FX-90A spectrometer, and a JEOL Model JNM-PMX-60 spectrometer, using deuteriochloroform or carbon tetrachloride containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimazu Model GCMS-QP 1000.

Materials. 1,4- and 1,5-dibromonaphthalene were prepared as reported in the literature.[5] Ether, benzene, THF, and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use.

Preparation of 1,4-Bis(pentamethyldisilanyl)naphthalene (1). Into a 100-mL three-necked flask were placed 2 g (0.087 mol) of magnesium and 14 g (0.08 mol) of chloropentamethyldisilane in 20 mL of a mixed solvent consisting of ether, benzene, and THF in a ratio of 1:1:2. To this mixture was added 12 g (0.0420 mol) of 1,4-dibromonaphthalene dissolved in 10 mL of the same solvent over a period of 10 min with stirring at room temperature. The mixture was stirred for 4 h at room temperature and hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water and then dried over potassium carbonate. The solvent was evaporated, and the residue was distilled under reduced pressure to give 4 g (26% yield) of 1: bp 160 °C (0.5 Torr); mp 38 °C; MS [*m/e* (ion)] 388 (M^+); 400-MHz ^1H NMR (δ, in $CDCl_3$) 0.07 (s, 18 H, Me_3Si), 0.50 (s, 12 H, Me_2Si), 7.46 (dd, 2 H, J = 6.3, 3.3 Hz, H on C_6 and C_7), 7.59 (s, 2 H, H on C_2 and C_3), 7.99 (dd, 2 H, J = 6.3, 3.3 Hz, H on C_5 and C_8); 100-MHz ^{13}C NMR (δ, in $CDCl_3$) -2.3, -1.5, 124.7, 129.5, 132.7, 137.1, 139.1. Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.95; H, 9.20.

Preparation of 1,5-Bis(pentamethyldisilanyl)naphthalene (2). Into a 100-mL three-necked flask were placed 1.6 g (0.070 mol) of magnesium and 11.0 g (0.066 mol) of chloropentamethyldisilane in a mixed solvent consisting of ether, benzene, and THF in a ratio of 1:1:2. To this was added 9.4 g (0.033 mmol) of 1,5-dibromonaphthalene in 10 mL of the mixed solvent at room temperature. The mixture was stirred for 4 h at room temperature and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated from the aqueous layer, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and then washed with water. After evaporation of the solvent, the residue was distilled under reduced pressure to give 2.0 g (16% yield) of 2: bp 170 °C (0.4 Torr); mp 82.0 °C (after recrystallization from ethanol); MS [*m/e* (ion)] 388 (M^+); 400-MHz ^1H NMR (δ, in $CDCl_3$) 0.08 (s, 18 H, Me_3Si), 0.51 (s, 12 H, Me_2Si), 7.44 (dd, 2 H, J = 7.8, 6.7 Hz, H on C_3 and C_7), 7.64 (dd, 2 H, J = 6.7, 1.0 Hz, H on C_2 and C_6), 7.99 (dd, 2 H, J = 7.8, 1.0 Hz, H on C_4 and C_8); 100-MHz ^{13}C NMR (δ, in $CDCl_3$) -2.2, -1.5, 124.5, 129.8, 132.8, 137.1, 138.9. Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.58; H, 9.38.

Photolysis of 1 in Hexane. Into a 25-mL reaction vessel fitted internally with a 6-W low-pressure mercury lamp was placed a solution of 324 mg (0.833 mmol) of 1 in 25 mL of hexane. The solution was irradiated for 6 h with a slow stream of argon bubbling through the mixture at room temperature. At this stage, ca. 100% of 1 was photolyzed. After addition of pentadecane (15.4 mg, 0.0748 mmol) as an internal standard to the photolysis mixture, the resulting solution was analyzed by GLC as being compound 3 (32% yield). Pure 3 was isolated by preparative GLC: MS [*m/e* (ion)] 388 (M^+); IR ν_{Si-H} 2110 cm^{-1}; 400-MHz ^1H NMR (δ, in $CDCl_3$) 0.08 (s, 9 H, Me_3Si), 0.25 (d, 6 H, J = 3.3 Hz, $Me_2Si(H)$), 0.43 (s, 9 H, Me_3Si), 0.50 (s, 6 H, Me_2Si), 5.18 (sept, 1 H, J = 3.3 Hz, HSi), 7.40 (dd, 1 H, J = 6.9, 8.2 Hz, H on C_7), 7.56 (d, 1 H, J = 6.7 Hz, H on C_2), 7.69 (d, 1 H, J = 6.7 Hz, H on C_3), 7.86 (dd, 1 H, J = 6.9, 1.3 Hz, H on C_6), 7.94 (dd, 1 H, J = 8.2, 1.3 Hz, H on C_8); 100-MHz ^{13}C NMR (δ, in C_6D_6) -3.1 -2.2, -1.4, -1.0, 129.2, 129.3, 133.4, 133.7, 135.3, 136.9, 137.3, 137.5, 137.8, 140.3. Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.51; H, 9.19.

Photolysis of 1 in Benzene. A mixture of 238 mg (0.613 mmol) of 1 and 15.4 mg (0.0546 mmol) of eicosane as an internal standard in 25 mL of benzene was irradiated for 3 h. The mixture was analyzed by GLC as being 3 (34% yield). The product 3 was isolated by preparative GLC. All spectral data obtained for this product were identical with those of 3.

Photolysis of 1 in Deuteriobenzene. A solution of 48 mg (0.124 mmol) of 1 and 7.3 mg (0.0323 mmol) of hexadecane as an internal standard in 2 mL of deuteriobenzene was irradiated externally for 7 h at room temperature with a low-pressure mercury lamp in a sealed quartz tube. The resulting photolysis mixture was analyzed by GLC as being 3 (33% yield). The mass spectrum and ^1H NMR spectrum for this product were identical with those of 3.

Photolysis of 1 in the Presence of Methanol. A mixture of 198 mg (0.508 mmol) of 1, 1 mL (50 molar equiv) of methanol, and 25.3 mg (0.112 mmol) of hexadecane as an internal standard in 25 mL of benzene was irradiated for 3 h at room temperature. At this stage, ca. 100% of 1 was photolyzed. GLC analysis of the resulting mixture showed the formation of 3 and 4a in 30% and 48% yields. Products 3 and 4a were isolated by preparative GLC. For product 3, all spectral data were identical with those of the authentic sample. For 4a: MS [*m/e* (relative intensity)] 420 (5), 405 (3), 347 (94), 289 (49), 243 (65), 201 (28), 185 (100), 147 (16), 131 (40), 116 (5), 89 (13), 73 (3); IR ν_{Si-O} 1090 cm^{-1}; 400-MHz ^1H NMR (δ, in C_6D_6) -0.10 (s, 9 H, Me_3Si), 0.10 (s, 3 H, MeSi), 0.12 (s, 3 H, MeSi), 0.14 (d, 1 H, J = 8.2 Hz, H on C_8), 0.23 (s, 9 H, Me_3Si), 0.26 (s, 3 H, MeSi), 0.36 (s, 3 H, MeSi), 2.29 (dd, 1 H, J = 8.2, 0.9 Hz, H on C_8), 2.96 (br s, 1 H, H on C_5), 3.31 (s, 3 H, MeO), 7.02–7.34 (m, 4 H, aromatic ring protons); 75-MHz ^{13}C NMR (δ, in C_6D_6) -4.2 (2 C), -3.6, -3.4, -1.0, 0.2, 15.9, 26.9, 28.5, 37.3, 50.5, 125.0, 125.2, 125.6, 125.8, 145.2, 147.7. Exact MS calcd for $C_{21}H_{40}OSi_4$: 420.2156. Found: 420.2175.

Photolysis of 1 in the Presence of Methanol-d_1. A mixture of 261 mg (0.673 mmol) of 1, 1 mL of methanol-d_1, and 19.7 mg (0.116 mmol) of dodecane as an internal standard in 25 mL of benzene was photolyzed for 2 h at room temperature. The photolysis mixture was analyzed by GLC as being 3 (39%) and 4b (48% yield). Products 3 and 4b were isolated by preparative GLC. For 4b: MS [*m/e* (relative intensity)] 421 (3), 406 (1), 348 (36), 290 (19), 244 (49), 202 (31), 186 (77), 146 (24), 131 (100), 106 (10), 89 (26), 73 (6); IR ν_{Si-O} 1090 cm^{-1}; 60-MHz ^1H NMR (δ, in C_6D_6) -0.10 (s, 9 H, Me_3Si), 0.11 (s, 3 H, MeSi), 0.12 (s, 3 H, MeSi), 0.14 (d, 1 H, J = 8 Hz, H on C_8), 0.23 (s, 9 H, Me_3Si), 0.24 (s, 3 H, MeSi), 0.36 (s, 3 H, MeSi), 2.29 (d, 1 H, J = 8 Hz, H on C_8), 3.31 (s, 3 H, MeO), 7.02–7.34 (m, 4 H, aromatic ring protons). Exact MS Calcd for $C_{21}H_{39}DOSi_4$: 421.2209. Found: 421.2224.

Photolysis of 1 in a Mixed Solvent Consisting of Methanol and Benzene. A 5-mL quartz tube was carefully dried, and dry argon was passed through the tube to remove the trace of oxygen and moisture from the inside. It was then capped with a rubber septum. Into this was placed 29.9 mg (0.071 12 mmol) of 1 dissolved in a mixed solvent consisting of 2 mL of methanol and 3 mL of benzene. The mixture was irradiated externally with a low-pressure mercury lamp for 20 h. To the resulting photolysis mixture were added 0.169 mmol of heptane and 0.0619 mmol of heptadecane as internal standards. The mixture was analyzed by a GC–mass spectrometer as being 5a (50% yield), 6 (165% yield), and 4-(dimethylsilyl)-1-(pentamethyldisilanyl)naphthalene (less than 5% yield, MS [*m/e* (ion)] 316 (M^+)). The mass spectral data and retention time on GLC for 5a and 6 were identical with those of the authentic samples.

Isolation of 5a. A mixture of 289 mg (0.743 mmol) of 1 and 19.7 mg (0.0872 mmol) of hexadecane as an internal standard in a mixed solvent consisting of 10 mL of methanol and 15 mL of benzene was photolyzed for 5 h at room temperature. At this stage, ca. 100% of 1 was photolyzed. The resulting mixture was analyzed by GLC as being 5a (36% yield) and a trace of 4-(dimethylsilyl)-1-(pentamethyldisilanyl)naphthalene. Pure 5a was isolated by preparative GLC: MS [*m/e* (ion)] 244 (M^+); IR ν_{Si-H} 2120 cm^{-1}; 60-MHz ^1H NMR (δ, in $CDCl_3$) 0.51 (d, 12 H, J = 4 Hz, Me_2Si), 4.85 (sept, 2 H, J = 4 Hz, HSi), 7.46 (dd, 2 H, J = 6, 3 Hz, H on C_6 and C_7), 7.64 (s, 2 H, H on C_2 and C_3), 8.10 (dd, 2 H, J = 6, 3 Hz, H on C_5 and C_8); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -3.2, 125.7, 128.7, 133.0, 136.7, 137.9. Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.73; H, 8.16.

Photolysis of 1 in a Mixed Solvent Consisting of Methanol-d_1 and Benzene. A mixture of 75 mg (0.192 mmol) of 1 and 10.7 mg (0.0686 mmol) of undecane as an internal standard in a mixed solvent consisting of 2 mL of methanol-d_1 and 3 mL of benzene in a sealed quartz tube was irradiated externally for 32 h at room temperature. The resulting mixture was analyzed by GLC as being 3 (4%), 4b (8%), and 5b (9% yield). Pure 5b was isolated by preparative GLC: MS [*m/e* (ion)] 246 (M^+); 60-MHz ^1H NMR (δ, in $CDCl_3$) 0.51 (s, 12 H, Me_2Si), 7.46 (dd, 2 H, J = 6, 3 Hz, H on C_6 and C_7), 7.64 (s, 2 H, H on C_2 and C_3), 8.10 (dd, 2 H, J = 6, 3 Hz, H on C_5 and C_8).

Photolysis of 2 in Hexane. Into a 25-mL reaction vessel was placed a solution of 146 mg (0.376 mmol) of 2 and 26.6 mg (0.0943 mmol) of eicosane as an internal standard in 25 mL of hexane. The solution was irradiated with a low-pressure mercury lamp for 2 h at room temperature. The resulting mixture was analyzed by GLC as being 7 (74% yield). Pure 7 was isolated by preparative GLC: MS [*m/e* (ion)] 388 (M^+); IR ν_{Si-H} 2200 cm^{-1}; 400-MHz ^1H NMR (δ, in $CDCl_3$) 0.01 (s, 9 H, Me_3Si), 0.18 (d, 6 H, J = 3.4 Hz,

$Me_2Si(H)$), 0.37 (s, 9 H, Me_3Si), 0.45 (s, 6 H, Me_2Si), 5.13 (sept, 1 H, J = 3.4 Hz, HSi), 7.34 (dd, 1 H, J = 8.2, 6.8 Hz, H on C_7), 7.50 (d, 1 H, J = 6.8 Hz, H on C_2), 7.68 (br d, 1 H, J = 6.8 Hz, H on C_8), 7.75 (d, 1 H, J = 6.8 Hz, H on C_3), 7.92 (dd, 1 H, J = 8.2, 1.3 Hz, H on C_6); 100-MHz ^{13}C NMR (δ, in $CDCl_3$) -2.2, -1.8, -1.5, 3.2, 123.2, 131.4 (2 C), 133.5, 135.8, 137.4, 138.8, 140.3, 140.6, 140.8. Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.66; H, 9.22.

Photolysis of 2 in the Presence of Methanol. A mixture of 198 mg (0.510 mmol) of **2** and 1 mL of methanol in 25 mL of benzene was irradiated with a low-pressure mercury lamp for 3.5 h. The mixture was analyzed by GLC using pentadecane as an internal standard as being **7** (37% yield). All spectral data for **7** were identical with those of an authentic sample.

Photolysis of 2 in a Mixed Solvent Consisting of Methanol and Benzene. Into a 5-mL quartz tube was placed 39.7 mg (0.102 mmol) of **2** in a mixed solvent consisting of 2 mL of methanol and 3 mL of benzene. The mixture was irradiated externally with a low-pressure mercury lamp for 28 h. To this were added 0.104 mmol of decane and 0.0874 mmol of hexadecane as internal standards, and then the mixture was analyzed by a GC-mass spectrometer as being **8** (18% yield), **9** (36% yield), and **6** (110% yield). The mass spectral data and retention time on GLC for **8**, **9**, and **6** were identical with those of the authentic samples.

Isolation of 8 and 9. A mixture of 134 mg (0.345 mmol) of **2** and 20.3 mg (0.0898 mmol) of hexadecane as an internal standard in a mixed solvent consisting of 10 mL of methanol and 15 mL of benzene was irradiated for 2 h at room temperature. The resulting photolysis mixture was analyzed by GLC as being **7** (7% yield), **8** (14% yield), and **9** (30% yield). Products **7**-**9** were isolated by preparative GLC. All spectral data for **7** were identical with those of an authentic sample. For **8**: MS [*m/e* (ion)] 316 (M^+); IR ν_{Si-H} 2120 cm^{-1}; 60-MHz ^1H NMR (δ, in CCl_4) -0.06 (s, 9 H, Me_3Si), 0.47 (d, 6 H, J = 3 Hz, $Me_2Si(H)$), 0.49 (s, 6 H, Me_2Si), 4.84 (sept, 1 H, J = 3 Hz, HSi), 7.17-8.21 (m, 6 H, ring protons); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -6.9, -4.9, -3.3, 124.5, 125.2, 128.9, 129.6, 130.6, 133.0, 133.2, 133.4, 136.9, 137.0. Anal. Calcd for $C_{17}H_{28}Si_3$: C, 64.48; H, 8.91. Found: C, 64.38; H, 8.91. For **9**: white crystal; mp 46.8 °C; MS [*m/e* (ion)] 258 (M^+); IR ν_{Si-H} 2120 cm^{-1}; 60-MHz ^1H NMR (δ, in CCl_4) 0.49 (d, 12 H, J = 4 Hz, Me_2Si), 5.44 (sept, 1 H, J = 4 Hz, HSi), 7.22-9.10 (m, 6 H, ring protons); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -3.0, 125.2, 129.7, 133.4, 136.8, 137.0. Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.78; H, 8.25.

Preparation of 13. Into a 50-mL flask were placed 100 mg (4.1 mmol) of magnesium and 10 mL of THF. To this was added a mixture of 500 mg (1.8 mmol) of 1,8-dibromonaphthalene and 0.5 mL (4.0 mmol) of chlorotrimethylsilane in 10 mL of THF at room temperature. The reaction mixture was stirred for 3 h at room temperature, and then 0.5 mL (4.5 mmol) of chlorohydrodimethylsilane in 10 mL of THF was added to the mixture. The mixture was stirred for 12 h and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over potassium carbonate. The solvents were evaporated off, and the residue was chromatographed, eluting with hexane. GLC analysis of this resulting mixture showed the formation of **13** and **15**-**17** in 16%, 10%, 17%, and 21% yields, respectively. Products **13** and **15**-**17** were isolated by preparative GLC. All spectral data for **13** were identical with those of the compound obtained from the photolysis of **11**. For **15**: MS [*m/e* (ion)] 186 (M^+); IR ν_{Si-H} 2120 cm^{-1}; 60-MHz ^1H NMR (δ, in CCl_4) 0.50 (d, 6 H, J = 3 Hz, Me_2Si), 4.78 (sept, 1 H, J = 3 Hz, HSi), 7.05-8.00 (m, 7 H, ring protons). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 77.09; H, 7.49. For **16**: MS [*m/e* (ion)] 200 (M^+); 60-MHz ^1H NMR (δ, in CCl_4) 0.51 (s, 9 H, Me_3Si), 7.11-8.04 (m, 7 H, ring protons). Anal. Calcd for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 77.87; H, 7.93. For **17**: MS [*m/e* (ion)] 244 (M^+); IR ν_{Si-H} 2170 cm^{-1}; 90-MHz ^1H NMR (δ, in C_6D_6) 0.42 (d, 12 H, J = 3.5 Hz, Me_2Si), 5.29 (sept, 2 H, J = 3.5 Hz, HSi), 7.28-7.77 (m, 6 H, ring protons); 22.5-MHz ^{13}C NMR (δ, in C_6D_6) -0.7, 124.6, 131.5, 133.7, 134.2, 136.0, 138.3. Anal. Calcd for $C_{14}H_{20}Si_2$: C, 68.78; H, 8.25. Found: C, 68.62; H, 8.23.

Reaction of 13 with a Catalytic Amount of Palladium Dichloride in Carbon Tetrachloride. A solution of 376.8 mg (0.971 mmol) of **13** in the presence of ca. 5 mg (2.8 × 10^{-2} mmol) of palladium dichloride in 10 mL of carbon tetrachloride was stirred for 3 days at room temperature. The reaction mixture was filtered to remove the catalyst, and the solvent carbon tetrachloride was distilled off. The residue was evaporated under reduced pressure (0.5 Torr) to give 169.9 mg of the chloro compound. To this compound was added 0.5 mL of a 1.5 M MeLi-ether solution under an argon atmosphere. The mixture was stirred for 2 h, and then it was filtered. The filtrate was concentrated, and the residue was separated by medium-pressure LPC to give 82 mg (31% yield) of **14**: MS [*m/e* (ion)] 272 (M^+); 90-MHz ^1H NMR (δ, in $CDCl_3$) 0.37 (s, 9 H, Me_3Si), 0.49 (s, 9 H, Me_3Si), 7.51-8.31 (m, 6 H, ring protons); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -1.1 (Me_3Si), 0.3 (Me_3Si), 125.5, 128.1, 129.2, 129.5, 133.2, 133.6, 134.2, 136.3, 137.5, 138.3. Anal. Calcd for $C_{16}H_{24}Si_2$: C, 70.51; H, 8.88. Found: C, 70.42; H, 8.82.

Isolation of 1-(Chlorodimethylsilyl)-7-(trimethylsilyl)-naphthalene. A mixture of 376.8 mg (0.971 mmol) of **13** and ca. 5 mg (2.8 × 10^{-3} mmol) of palladium dichloride in 8 mL of carbon tetrachloride was stirred for 3 days at room temperature. The mixture was filtered, and the filtrate was concentrated. The residue was distilled under reduced pressure (0.5 Torr) to give 284.5 mg (69% yield) of a crude product. The pure compound was isolated by preparative GLC: MS [*m/e* (ion)] 292 (M^+); 500-MHz ^1H NMR (δ, in $CDCl_3$) 0.43 (s, 9 H, Me_3Si), 0.94 (s, 6 H, Me_2ClSi), 7.52 (dd, 1 H, J = 8.4, 7.0 Hz, H on C_3), 7.69 (dd, 1 H, J = 8.1, 1.1 Hz, H on C_6), 7.89 (dd, 1 H, J = 7.0, 1.1 Hz, H on C_2), 7.91 (br d, 1 H, J = 8.1, H on C_5), 7.95 (br d, 1 H, J = 8.0 Hz, H on C_4), 8.51 (br d, 1 H, J = 0.7 Hz, H on C_8); 22.5-MHz ^{13}C NMR (δ, in $CDCl_3$) -1.1 (Me_3Si), 3.7 (Me_2ClSi), 125.3, 125.9, 126.9, 127.7, 128.0, 128.2, 129.7, 129.8, 131.2, 133.8. Anal. Calcd for $C_{15}H_{21}ClSi_2$: C, 61.50; H, 7.23. Found: C, 61.44; H, 7.20.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research by the Ministry of Education, Science, and Culture to which the authors' thanks are due. We also express our appreciation to Shin-etsu Chemical Co., Ltd., Nitto Electric Industrial Co., Ltd., and Dow Corning Japan Ltd., for financial support.