Photochemically Generated Silicon–Carbon Double-Bonded Intermediates. 10. Photochemical Behavior of 1-Disilanyl- and 2-Disilanylnaphthalenes

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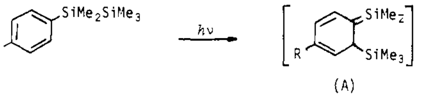
Abstract: The photolysis of 1-pentamethyldisilanyl-, 1-(1′-phenyltetramethyldisilanyl)-, and 1-(2′-phenyltetramethyldisilanyl)naphthalene and 2-pentamethyldisilanyl- and 2-(2′-phenyltetramethyldisilanyl)naphthalene has been investigated. Irradiation of 1-disilanylnaphthalenes in the presence or absence of a trapping agent afforded isomers, 1-hydrosilyl-2-silylnaphthalenes, via photochemical formation of the silicon–carbon double-bonded intermediate, followed by an intramolecular 1,3-hydrogen shift. From photolysis of 2-disilanylnaphthalenes in the presence of a trapping agent, however, addition products, which could be formed from the reaction of the unsaturated silicon species with the trapping agent, were obtained. The CNDO/2 calculations have been carried out on 1-perhydrodisilanyl- and 2-perhydrodisilanylnaphthalene and also on the silicon–carbon double-bonded intermediates produced from the disilane derivatives.

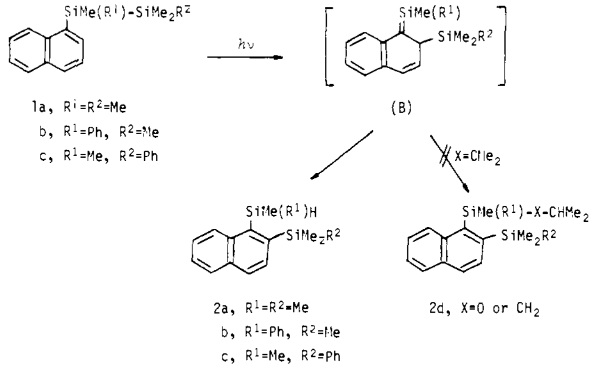
Introduction

Although the chemistry of thermally generated silicon–carbon double-bonded intermediates has been extensively investigated,[2] much less interest has been shown in the chemistry of photochemically generated ones.[3] Recently, we have found that the silicon–carbon double-bonded intermediates can readily be generated by photolysis of aryl-,[4] ethenyl-,[5,6] and ethynyldisilane,[7,8] and described some of their chemical nature in a series of papers.[3,9,10] In the photolysis of benzenoid aryldisilanes, the unsaturated silicon intermediates (A) may be produced from a 1,3 shift of the silyl group to an ortho carbon atom in the benzene ring. These studies have now been extended to the disilanyl-substituted naphthalene system to examine the possibility of the formation of similar reactive intermediates via photorearrangement of the silyl group to the naphthalene ring. We have found that, although both 1-disilanyl- and 2-disilanylnaphthalenes undergo photolysis upon irradiation with a low-pressure mercury lamp, yielding the respective silicon–carbon double-bonded intermediates, chemical behavior of the two types of the intermediates is different in many respects.



Results and Discussion

Scheme I



Photolysis of 1-Disilanyl-Substituted Naphthalene. 1-Pentamethyldisilanylnaphthalene (**1a**) was photolyzed under a variety of conditions. In marked contrast to the photolysis of benzenoid aryldisilanes, which produced reactive intermediates A readily adding to substrates such as olefins,[3,4a,b] alcohols,[4c] and carbonyl compounds,[10] the reactive intermediate from the 1-naphthyl system never added to these substrates. An isomer, 1-dimethylsilyl-2-trimethylsilylnaphthalene (**2a**), was obtained in all experiments attempted. Thus, when a solution of **1a** in dry benzene containing isobutene was irradiated at room temperature with a low-pressure mercury lamp bearing a Vycor filter under a purified nitrogen atmosphere, 40% yield of **2a** was obtained as the sole volatile product, besides 20% of unchanged **1a** (Scheme I). No 1-isobutyldimethylsilyl-2-trimethylsilylnaphthalene (**2d**) which might be expected to arise from addition of silicon–carbon double-bonded intermediate B to isobutene was detected. Similar photolysis of **1a** in the presence of acetone and of methanol in benzene again afforded isomer **2a** in 62 and 66% yield, respectively. In both cases, however, a small amount of 1-trimethylsilylnaphthalene (less than 3% yield) was also obtained. The formation of this compound can be explained in terms of a photochemical 1,2 migration of the naphthyl ring from one silicon atom to the other, with concurrent extrusion of dimethylsilylene. Such a photochemical 1,2-aryl shift has already been demonstrated for the photolysis of aryldisilanes.[4c,11]

Interestingly, irradiation of **1a** in the absence of the trapping agent again afforded **2a** in 64% yield. No other volatile products were observed by either VPC or spectroscopic analysis of the reaction mixture. The production of **2a** which can be explained by an intramolecular hydrogen shift in intermediate B was of considerable interest to us, because, to our knowledge, photochemically generated silicon–carbon double-bonded intermediates from benzenoid aryldisilanes do not afford any volatile products in the absence of a trapping agent.[4b] We have found that such isomerization involving a rapid 1,3-hydrogen shift in intermediate B is a remarkably general reaction for 1-disilanyl-substituted naphthalenes. Thus, irradiation of 1-(1′-phenyltetramethyldisilanyl)naphthalene (**1b**) in the presence of acetone afforded 1-methylphenylsilyl-2-trimethylsilylnaphthalene (**2b**) in 61% yield. In this case, the migration of the trimethylsilyl group occurs exclusively to the naphthalene ring, but not to the benzene ring (see **2e** in Scheme II). From this photolysis, 1-trimethylsilylnaphthalene arising from extrusion of methylphenylsilylene was also obtained in 7% yield, whereas trimethylphenylsilane which can be expected from loss of methylnaphthylsilylene was observed only in a

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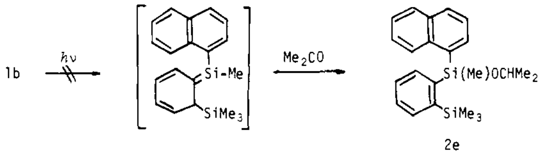
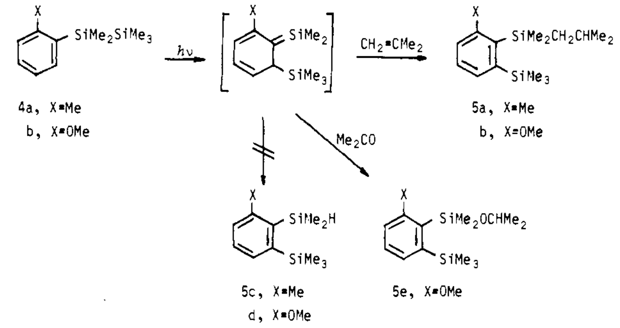
Table I. Spectroscopic Data for Photolysis Products

compd	^{1}H NMR chemical shifts, δ ppm	significant infrared frequencies (neat), cm^{-1}	M$^+$, *m/e*
2a	0.23 (Me_2SiH, d, 6 H, *J* = 3.5 Hz), 0.48 (Me_3Si, s, 9 H), 5.2 (HSiMe, sept, 1 H, *J* = 3.5 Hz), 7.3–8.0 (ring protons, m, 6 H)	2200, 1255, 910, 890	258
2b	0.46 (Me_3Si, s, 9 H), 0.55 (MeSiH, d, 3 H, *J* = 3.9 Hz), 5.69 (HSi, q, 1 H, *J* = 3.9 Hz), 7.2–7.9 (ring protons, m, 11 H)	2200, 1430, 1250, 1110	320
2c	−0.18 (Me_2SiH, d, 6 H, *J* = 3.8 Hz), 0.57 (Me_2Si, s, 6 H), 4.91 (HSi, sept, 1 H, *J* = 3.8 Hz), 7.1–7.9 (ring protons, m, 11 H)	2200, 1425, 1250, 1100	320
5a	0.40 (Me_3Si, s, 9 H), 0.48 (Me_2Si, s, 6 H), 0.92 (CH_2Si, d, 2 H, *J* = 6.4 Hz), 0.96 (Me_2C, d, 6 H, *J* = 6.0 Hz), 1.80 (HC, m, 1 H), 2.50 (MeC_6H_5, s, 3 H), 7.1–7.5 (ring protons, m, 3 H)	2960, 1370, 1360, 1250, 1140	278
5b	0.35 (Me_3Si and Me_2Si, s, 15 H), 0.80 (CH_2Si, d, 2 H), 0.88 (Me_2C, d, 6 H, *J* = 6.0 Hz), 1.74 (HC, m, 1 H), 3.79 (MeO, s, 3 H), 6.7–7.2 (ring protons, m, 3 H)	2940, 1550, 1450, 1390, 1250, 1150	294
5e	0.35 (Me_3Si and Me_2Si, s, 15 H), 1.28 (Me_2C, d, 6 H, *J* = 6.4 Hz), 3.80 (MeO, s, 3 H), 4.18 (HC, sept, 1 H, *J* = 6.4 Hz), 6.7–7.2 (ring protons, m, 3 H)	2980, 1550, 1450, 1380, 1370, 1250, 1050	296
8a	0.47 (Me_2Si, s, 6 H), 0.57 (Me_3Si, s, 9 H), 1.00 (Me_2C, d, 6 H, *J* = 6.5 Hz), 1.01 (CH_2Si, d, 2 H, *J* = 6.6 Hz), 1.92 (CH, m, 1 H), 7.3–8.2 (ring protons, m, 6 H)	1380, 1365, 1255	314
8b	0.33 (Me_2Si, s, 6 H), 0.70 (Me_2Si, s, 6 H), 0.88 (Me_2C and CH_2Si, d, 8 H, *J* = 6.0 Hz), 1.80 (CHSi, m, 1 H), 7.1–8.0 (ring protons, m, 11 H)	1660, 1435, 1270, 1260, 1110	376

Scheme II



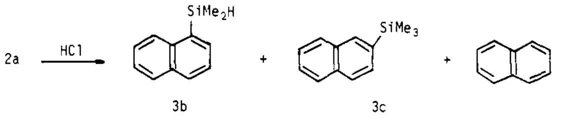
Scheme III



trace amount (less than 0.5%). This result indicates that the rate of shift of the naphthyl group is faster than that of the phenyl group.

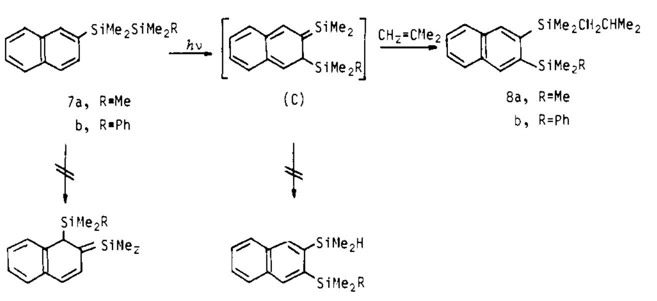
Irradiation of 1-(2′-phenyltetramethyldisilanyl)naphthalene (**1c**) in the absence of a quencher under similar photolysis conditions gave 1-dimethylsilyl-2-dimethylphenylsilylnaphthalene (**2c**) in 29% yield. In this case, however, 1-phenyldimethylsilylnaphthalene (**3a**), arising from an intramolecular 1,2-naphthyl shift from one silicon atom to the other, was also obtained in 22% yield. Similar irradiation of **1c** in the presence of acetone again gave **2c** in 25% yield, in addition to 22% yield of **3a**. Again, no adduct which can be expected from the reaction of intermediate B with acetone was obtained.

The structures of the photoproducts, **2a–c**, were identified by mass, IR, and ^{1}H NMR spectroscopic analysis as shown in Table I. Further support for the structure of the products comes from protodesilylation of **2a** by dry hydrogen chloride. Thus, treatment of **2a** in a 1:1 mixture of diethyl ether and benzene with bubbling dry hydrogen chloride at room temperature for 4 h yielded 1-dimethylsilylnaphthalene (**3b**), 2-trimethylsilylnaphthalene (**3c**), and naphthalene in 14, 45, and 20% yield, respectively. The IR and ^{1}H NMR spectra of **3b** and **3c** were identical with those of the authentic samples. In this reaction, neither 1-trimethylsilylnaphthalene nor 2-dimethylsilylnaphthalene was detected. These results clearly indicate that the R^2Me_2Si– group migrates from a naphthyl silicon atom to a C_2 atom in the naphthalene ring, and then hydrogen on this carbon migrates to the silicon atom. Such anomalous chemical behavior of intermediate B might be attributed to the presence of a peri hydrogen atom which would sterically prevent access of the attacking molecule such as an olefin to the silicon-carbon double bond in the intermediate B. However, this is not true, because irradiation of aryldisilanes bearing a bulky substituent on an ortho carbon of the phenyl ring, for example, *o*-tolylpentamethyldisilane (**4a**) and *o*-methoxyphenylpentamethyldisilane (**4b**), in the presence of isobutene under similar photolysis conditions yielded the respective adducts, **5a** and **5b**, in moderate yields (Scheme III). Compound **4b** also reacts with acetone under the same conditions to give adduct **5e** in 22% yield. In all photolyses, however, the hydrosilane derivatives such as **5c** and **5d** could not be detected by mass and ^{1}H NMR spectrometric analysis as well as by VPC analysis. A compound having a bulkier substituent, *o*-*tert*-butoxyphenylpentamethyldisilane (**6**), is photochemically stable under the conditions used; the starting disilane **6** was recovered almost quantitatively. No production of isomers analogous to **2a–c** in the photolysis of **4a**, **4b**, and **6** requires consideration of factors which govern the reaction pathway, other than the steric requirement of the peri hydrogen. As will be discussed in the following section, intermediate B (see Figure 2) is expected to be in the excited state, in contrast to intermediate C or the silicon-carbon double-bonded intermediates from benzenoid disilanes which are thought to be in the ground state. This may account for the anomalous chemical behavior of intermediate B.

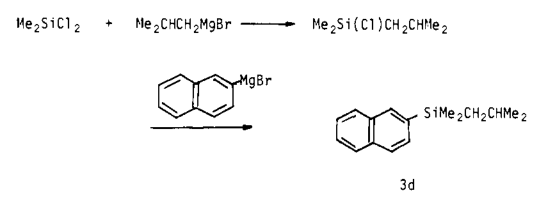


Photolysis of 2-Disilanyl-Substituted Naphthalene. In marked contrast to the 1-disilanyl-substituted naphthalenes, photolysis of 2-pentamethyldisilanylnaphthalene (**7a**) gives intermediate C, which readily adds to the substrate present (Scheme IV). Thus, irradiation of **7a** in the presence of isobutene in benzene afforded 2-isobutyldimethylsilyl-3-trimethylsilylnaphthalene (**8a**) in 37% yield, as the sole volatile product, in addition to 13% of unchanged **7a**. Interestingly, photolysis of **7a** in the absence of quenchers did not produce

Scheme IV



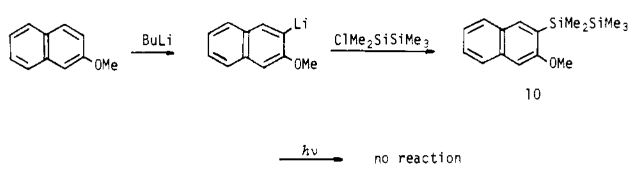
any volatile products such as 2-dimethylsilyl-3-trimethylsilylnaphthalene (**9**), but afforded polymeric substances. The location of two silyl groups in the naphthalene ring of compound **8a** was confirmed by the protodesilylation reaction. Thus, the reaction of **8a** with dry hydrogen chloride in ether for 20 min gave **3c**, 2-isobutyldimethylsilylnaphthalene (**3d**), and naphthalene in 12, 70, and 6% yield, respectively. In this reaction, none of the 1-silyl-substituted naphthalene was observed by either VPC technique or spectroscopic analysis. In every respect, compound **3d** was identical with an authentic



sample prepared from the reaction of 1 equiv of isobutylmagnesium bromide with dimethyldichlorosilane, followed by treating the resulting mixture with 2-naphthylmagnesium bromide.

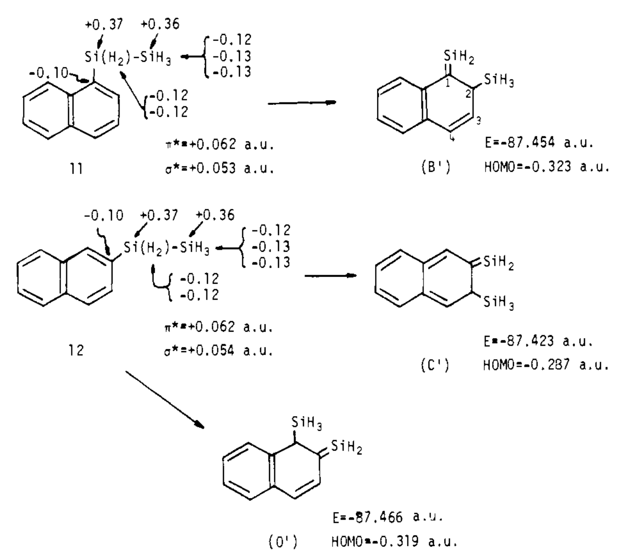
The photolysis of 2-(2′-phenyltetramethyldisilanyl)naphthalene (**7b**) in the presence of isobutene under the same conditions produced again the 2,3-bis(silyl)-substituted naphthalene (**8b**) as the sole volatile product, in addition to 6% of unchanged **7b**. Neither the 1,2 isomer which might be expected from the reaction of intermediate D with isobutene nor the 1,2-bis(silyl)-substituted benzene whose structure is analogous to that of **2e** was detected. The mass, IR, and ^{1}H NMR data for products **8a** and **8b** are listed in Table I.

All attempts to produce the intermediate D (R = Me) which might be expected to arise from rearrangement of the trimethylsilyl group from silicon to an α position in the naphthalene ring were unsuccessful. Thus, irradiation of 2-pentamethyldisilanyl-3-methoxynaphthalene (**10**), obtained from 2-methoxynaphthyllithium[12] and chloropentamethyldisilane in hexane, in the presence of a trapping agent such as isobutene, acetone, methanol, or water afforded no addition products. The starting disilane **10** was recovered quantitatively.



CNDO/2 Calculations. As mentioned above, the following important questions remain to be answered for the present photochemical reactions. First, why does the silyl group migrate only to the C_3 atom (but not to the C_1 atom) of the naphthalene ring in the photolysis of 2-disilanylnaphthalenes? Second, why does the intramolecular 1,3-hydrogen shift always occur in preference to the addition reaction in the photolysis of 1-disilanylnaphthalenes? In order to answer these questions we have carried out the molecular orbital calculations of disilanylnaphthalenes **11** and **12**, and of three types of intermediate, B′, C′, and D′, using a CNDO/2 approximation (Scheme V).

Scheme V



The calculations of total energy for intermediates C′ and D′ indicate that C′ is less stable by 25.8 kcal/mol than D′, as can readily be understood from the degree of conjugation in the intermediates. This situation is more clearly shown in the orbital energy of the highest occupied molecular orbital: HOMO (C′) = −0.287 au, whereas HOMO (D′) = 0.319 au. Nevertheless, the less stable intermediate C′ is always produced in the photolysis of the 2-disilanylnaphthalenes. This suggests that the photochemical pathway in the present system is strongly controlled by other factors such as the symmetry nature of the frontier orbitals of the disilanylnaphthalenes. Therefore, it is interesting to consider the reaction pathway by using the concept of orbital interaction.

In both cases of 1-disilanyl- and 2-disilanylnaphthalenes, the HOMO is predominantly a π orbital of the naphthyl ring. This has been confirmed by the observation of the ionization potentials of substituted polysilanylnaphthalenes.[13] The lowest unoccupied molecular orbital (LUMO) and next LUMO (NLUMO) of these compounds correspond to the antibonding orbital (σ^*) of a silicon-silicon σ bond and the π^* of the naphthyl ring, respectively. Each energy of π^* and σ^* of compounds **11** and **12,** and total energy of intermediates (B′, C′, and D′) and their energy of HOMO are given in Scheme V, together with net charges of some atoms in **11** and **12.** It should be noted here that the net charges of both Si atoms are largely positive [$Si_{1'}$(+0.37)-$Si_{2'}$(+0.36)] and therefore the Si-Si σ bond is quite favorable to accept the electron, e.g., from HOMO. The $\pi \rightarrow \sigma^*$ transition which is an intramolecular charge transfer rather than excitation is, therefore, of greater advantage than the $\pi \rightarrow \pi^*$ excitation. Because of the antibonding character of σ^*, the $Si_{1'}$-$Si_{2'}$ σ bond is weakened directly by the charge transfer to facilitate a 1,3-silyl shift and the formation of the C-$Si_{1'}$ π bond. Once $\pi \rightarrow \sigma^*$ transition is brought about by the photoabsorption, the subsequent orbital interaction leading to such bond formation can be expected to occur between the HOMO of the naphthyl group and a terminal silyl part of σ^*. For the photochemical reaction leading to the formation of the intermediate C′ from compound **12,** the phase of the $2p_z$ atomic orbital of C_2 of the HOMO is required to be the same as that of the $3p_z$ atomic orbital of $Si_{1'}$ of the LUMO for the effective C_2-$Si_{1'}$ π bond formation. At the same time, the phase relationship between the $2p_z$ atomic orbital at C_3 atom of the HOMO and the $3p_z$ atomic orbital at $Si_{2'}$ of the LUMO is necessary to be favorable for forming a new C_3-$Si_{2'}$ single bond. As can be seen from the π and σ^* orbital interactions of **12** (see Figure 1a), such a relationship is completely

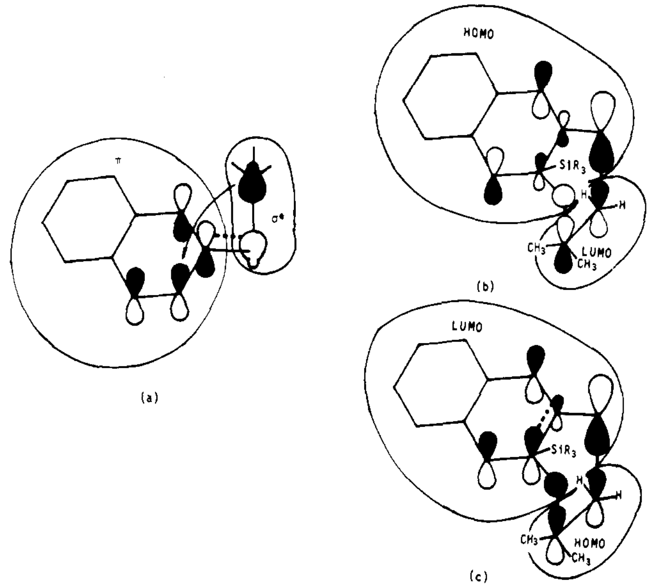


Figure 1. A schematic representation of the orbital interactions: (a) π-σ* interaction; (b) interaction between HOMO of C′ and LUMO of isobutene; (c) interaction between LUMO of C′ and HOMO of isobutene.

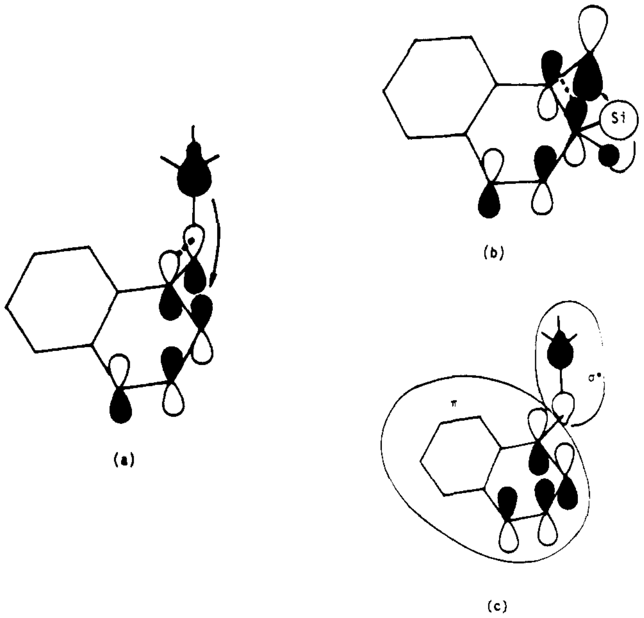
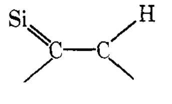


Figure 2. A schematic representation of the molecular orbitals: (a) NLUMO (π*) of 11; (b) LUMO (π*) of B′; (c) π-σ* interaction.

satisfied for the production of the intermediate C′. In the formation of the intermediate D′, however, the phase relationship between C$_1$ and Si$_{2'}$, is antibonding and hence the photochemical pathway leading to the intermediate D′ may not be allowed. Furthermore, in the intermediate C′ both phase relationships between the 2p$_z$ atomic orbital of C$_2$ and that of C$_3$ and between the lower part of 3p$_z$ of Si$_{1'}$ and 1s of hydrogen atom connected to C$_3$ of the HOMO are antibonding as shown in Figure 1b. This means that the intramolecular 1,3-hydrogen shift from the C$_3$ atom to the Si$_{1'}$ atom followed by π-bond formation between C$_2$ and C$_3$ is unfavorable. The intermediate C′ thus formed may then react with the substrate having a double bond, to give an addition product. In the addition step, the intermediate C′ acts as an electron acceptor toward the substrate and therefore the orbitals of the LUMO of C′ would interact with the HOMO of the double bond in the substrate. As shown in Figure 1c, such orbital patterns of the interactions are quite favorable for the formation of a p σ single bond between Si$_{1'}$ and an olefinic carbon atom of the substrate and a π bond between C$_2$ and C$_3$ atom, and for the migration of hydrogen from the C$_3$ atom in the naphthyl ring onto a carbon atom of the substrate, as observed in the photolysis experiments. The inverse HOMO-LUMO interaction is also favorable, even though the contribution is small.

According to the orbital mixing rule, the phase pattern of the



of LUMO in the intermediate A arising from photolysis of the phenyldisilanes is almost the same as that of C′, and hence intermediate A reacts with substrates to give the adducts as observed, but not-isomerization products arising from a 1,3-hydrogen shift. The addition of intermediates A and B to the substrates can be considered as an ene-type reaction.

On the other hand, if one applies similar considerations to **11**, the symmetry correlation between C$_2$ in the HOMO and Si$_{2'}$ in the LUMO is found not to be favorable for the formation of intermediate B′, even if the Si-Si bond is weakened (Figure 2c). In this case, the next LUMO (π*) induced by the π→π* transition may then dominantly contribute to the reaction leading to intermediate B′. In the π* orbital, the carbon-silicon π bond is bonding, the silicon-silicon bond is antibonding, and particularly the phase between Si$_{2'}$ and C$_2$ is bonding which is favorable for the formation of intermediate B′, as shown in Figure 2a. Moreover, in this case, both phase relationships between 2p$_z$ of C$_1$ and that of C$_2$ and the lower part of 3p$_z$ at Si$_{1'}$ and the hydrogen atom connected to the C$_2$ atom in π* of intermediate B′ are bonding as shown in Figure 2b. This means that the subsequent through-space migration of hydrogen on the C$_2$ atom easily occurs to reproduce the naphthyl ring as was observed in the experiment.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry nitrogen. Photolysis was carried out using a 10-W immersion low-pressure mercury lamp bearing a Vycor filter. All photolyses were followed by VPC analysis using a 2 m × 0.5 cm stainless column with 20% Silicone DC oil. Yields were determined by VPC using an internal standard on the basis of the disilanes used (unless otherwise noted, conversion of the starting compounds is approximately 100%). Identification of the products by VPC method was done using two different columns (30% Apiezon Grease on Celite 545 and 20% Silicone DC on Chromosorb W).

^{1}H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solution containing methylene chloride as an internal standard. Mass spectra were measured on a Hitachi Model RMU-6D fitted with an all-glass direct inlet accessory. Ionizing voltage was 70 eV for all compounds. Infrared spectra of thin liquid films were determined using a Hitachi Model EPI-G3 grating infrared spectrophotometer. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the photolysis products. Most of the products were easily separated by using a 3/8 in. × 20 ft column containing SE-30 (30%) on Chromosorb W.

MO Calculations. MO calculations were carried out by the CNDO/2 approximation where the d orbitals were not included in the present basis set because the CNDO/2 version often gives overestimation of d-orbital contribution, contrary to the small contribution of nonempirical method,[14] and in particular the contribution of the d orbital seems to be small in the course of reaction.

For compounds **11** and **12**, 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,[15,16] and both Si atoms take sp^3 hybridization in gauche conformation with the following bond lengths:[14] C-Si = 1.84 Å, Si-Si = 2.30 Å, Si-H = 1.475 Å, C-C 1.39 Å, and C-H = 1.10 Å, all equally for the naphthalene ring. For intermediates (B′, C′, and D′) we employed identical lengths of the bonds except for 1.60 Å of the Si═C.

1-Pentamethyldisilanylnaphthalene (1a). To a solution of 1-naphthylmagnesium bromide prepared from 12.4 g (0.06 mol) of 1-bromonaphthalene and 1.7 g (0.075 g-atom) of magnesium in a mixed solvent consisting of tetrahydrofuran (THF), ether, and benzene (8:15:23 mL), according to the method of Sommer et al.,[17] was added 10 g (0.06 mol) of chloropentamethyldisilane in 30 mL of THF with stirring. The reaction mixture was refluxed for 3 h, and then hydrolyzed with water. The organic layer was washed with water and dried over anhydrous potassium carbonate. The solvents were evaporated and the residue was distilled through a short column under reduced pressure to give 4.3 g (28% yield) of **1a**:[13] bp 135-137 °C (3 Torr); $n^{20}{}_D$ 1.5732; NMR δ 0.08 (Me_3Si, s, 9 H), 0.51 (Me_2Si, s, 6 H), and 7.3-8.1 (ring protons, m, 7 H); mass spectrum *m/e* 258 (M^+). Anal. Calcd for $C_{15}H_{22}Si_2$: C, 69.69; H, 8.58. Found: C, 69.59; H, 8.74.

1-(1′-Phenyltetramethyldisilanyl)naphthalene (1b). A solution of 1-naphthylmagnesium bromide prepared from 5.2 g (0.025 mol) of 1-bromonaphthalene and 0.6 g (0.025 g-atom) of magnesium in a mixed solvent as above was added to 4.3 g (0.025 mol) of 1,1-difluorotetramethyldisilane[18] in 30 mL of dry benzene. The mixture was refluxed for 3 h. To this mixture was added a solution of phenylmagnesium chloride prepared from 5.7 g (0.050 mol) of chlorobenzene and 1.2 g (0.050 g-atom) of magnesium in 40 mL of THF. The mixture was refluxed for 24 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over anhydrous potassium carbonate. The solvent was evaporated and the residue was distilled through a short column to give 3.0 g (38% yield) of **2b**: bp 188-190 °C (2 Torr); $n^{20}{}_D$ 1.6008; IR 1430, 1250, 850 cm^{-1}; mass spectrum *m/e* 320 (M^+); NMR δ 0.25 (Me_3Si, s, 9 H), 0.81 (MeSi, s, 3 H), and 7.2-8.0 (ring protons, m, 12 H). Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.54. Found: C, 75.11; H, 7.68.

1-(2′-Phenyltetramethyldisilanyl)naphthalene (1c). A solution of 1-naphthylmagnesium bromide prepared from 14.5 g (0.070 mol) of 1-bromonaphthalene and 1.7 g (0.070 g-atom) of magnesium in a mixed solvent (THF-ether-benzene, 8:15:23 mL) was added to 13 g (0.066 mol) of 1,2-dichlorotetramethyldisilane in 50 mL of THF at room temperature. The mixture was then refluxed for 3 h. To this mixture was added 50 mL of 1.2 M phenylmagnesium chloride-THF solution at room temperature and then the mixture was refluxed for 3 h. The mixture was hydrolyzed with dilute hydrochloric acid. After workup in the usual manner, fractional distillation gave 12 g (55% yield) of **1c**: bp 181-183 °C (3 Torr); $n^{20}{}_D$ 1.6110; IR 1425, 1240, 1100, 830 cm^{-1}; mass spectrum *m/e* 320 (M^+); NMR δ 0.29 (Me_2Si, s, 6 H), 0.45 (Me_2Si, s, 6 H), 7.2-7.6 (ring protons, m, 12 H). Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.54. Found: C, 74.42; H, 7.66.

1-Phenyldimethylsilylnaphthalene (3a). A solution of 1-naphthylmagnesium bromide prepared from 2.29 g (11 mmol) of 1-bromonaphthalene and 0.07 g (25 mg-atoms) of magnesium in a THF-ether-benzene mixture was added to 1.71 g (10 mmol) of phenyldimethylchlorosilane in 2 mL of THF at room temperature. The mixture was refluxed for 4 h and hydrolyzed with water. After distillation of the mixture, **3a** (70% yield) was isolated by preparative VPC: $n^{20}{}_D$ 1.6132; IR 1429, 1250, 1100 cm^{-1}; mass spectrum *m/e* 262 (M^+); NMR δ 0.65 (Me_2Si, s, 6 H) and 7.1-7.9 (ring protons, m, 12 H). Anal. Calcd for $C_{18}H_{18}Si$: C, 82.39; H, 6.91. Found: C, 82.48; H, 7.10.

1-Dimethylsilylnaphthalene (3b). A solution of 1-naphthylmagnesium bromide prepared from 17 g (0.082 mol) of 1-bromonaphthalene and 2 g (0.083 g-atom) of magnesium in a mixed solvent was slowly added to 15 g (0.13 mol) of methyldichlorosilane in 30 mL of THF at room temperature. The mixture was refluxed for 2 h. To convert any chlorosilanes to methyl derivatives, 60 mL of 3.0 M methylmagnesium bromide in ether was then added. The mixture was again refluxed for 5 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. Distillation under reduced pressure afforded 11.4 g (74% yield) of **3b** as a colorless liquid: bp 112-115 °C (2 Torr); $n^{20}{}_D$ 1.5930; mass spectrum *m/e* 186 (M^+); NMR δ 0.47 (Me_2Si, d, 6 H, J = 3.8 Hz), 4.86 (HSi, septet, 1 H, J = 3.8 Hz), and 7.2-8.1 (ring protons, m, 7 H). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 77.90; H, 7.82.

2-Trimethylsilylnaphthalene (3c). This compound was prepared in 77% yield, according to the method reported by Benkeser et al.:[19] bp 115-117 °C (2 Torr); $n^{20}{}_D$ 1.5740 (lit.[19] bp 93-95 °C (0.5 Torr)); NMR δ 0.41 (Me_3Si, s, 9 H) and 7.2-8.0 (ring protons, m, 7 H).

2-Isobutyldimethylsilylnaphthalene (3d). To a Grignard reagent prepared from 3.3 g (0.024 mol) of isobutyl bromide and 0.8 g (0.033 g-atom) of magnesium in 30 mL of dry ether was added 3.1 g (0.024 mol) of dichlorodimethylsilane with ice cooling. The reaction mixture was heated to reflux for 8 h. To the mixture was then added 2-naphthylmagnesium bromide prepared from 5.0 g (0.024 mol) of 2-bromonaphthalene and 0.8 g (0.033 g-atom) of magnesium in a mixed solvent consisting of benzene, ether, and THF (3:2:1). The mixture was again refluxed for 5 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. Distillation gave 1.5 g (26% yield) of crude 2-isobutyldimethylsilylnaphthalene, bp 135-138 °C (3 torr). Pure **3d** was isolated by preparative VPC: $n^{20}{}_D$ 1.5543; mass spectrum *m/e* 242 (M^+); NMR δ 0.43 (Me_2Si, s, 6 H), 0.92 (CH_2C, d, 2 H, J = 7.0 Hz), 1.00 (MeC, d, 6 H, J = 6.5 Hz), 1.71 (HCC, m, 1 H), 7.4-8.0 (ring protons, m, 7 H). Anal. Calcd for $C_{16}H_{22}Si$: C, 79.27; H, 9.12. Found: C, 79.01; H, 9.41.

***o*-Tolylpentamethyldisilane (4a).** A solution of *o*-tolyllithium prepared from 1.7 g (0.24 g-atom) of finely cut lithium and 10.3 g (0.06 mol) of *o*-bromotoluene in 80 mL of THF was added to 10 g (0.06 mol) of chloropentamethyldisilane in 10 mL of THF at room temperature. The mixture was stirred for 4 h at room temperature and then hydrolyzed with water. The organic layer was dried over potassium carbonate. Fractional distillation under reduced pressure gave 5.4 g (57% yield) of a colorless liquid, **4a**: bp 88 °C (4 Torr); $n^{20}{}_D$ 1.5202; mass spectrum *m/e* 222 (M^+); NMR δ 0.06 (Me_3Si, s, 9 H), 0.36 (Me_2Si, s, 6 H), 2.40 (MeC_6H_4, s, 3 H), and 7.1-7.5 (ring protons, m, 4 H). Anal. Calcd for $C_{12}H_{22}Si_2$: C, 64.78; H, 9.97. Found: C, 64.50; H, 9.95.

***o*-Anisylpentamethyldisilane (4b).** To a solution of *o*-anisyllithium[20] prepared from 6.5 g (0.06 mol) of anisole and 46 mL of 1.3 M butyllithium-hexane solution was added 8 g (0.048 mol) of chloropentamethyldisilane in 10 mL of hexane. The mixture was refluxed for 5 h and then hydrolyzed with water. The organic layer was washed with water and dried over potassium carbonate. Distillation of the mixture under reduced pressure gave 5.9 g (42% yield) of **4b**: bp 69 °C (2 Torr); mass spectrum *m/e* 238 (M^+); NMR δ 0.02 (Me_3Si, s, 9 H), 0.28 (Me_2Si, s, 6 H), 3.78 (MeO, s, 3 H), and 6.6-7.3 (ring protons, m, 4 H). Anal. Calcd for $C_{12}H_{22}OSi_2$: C, 60.44; H, 9.30. Found: C, 60.67; H, 9.30.

***o-tert*-Butoxyphenylpentamethyldisilane (6).** To a solution of *o-tert*-butoxyphenyllithium prepared from 4.8 g (0.033 mol) of *tert*-butyl phenyl ether and 39 mL of 1.3 M butyllithium-hexane solution in 80 mL of cyclohexane was added 8.4 g (0.05 mol) of chloropentamethyldisilane in 10 mL of cyclohexane. The mixture was refluxed for 24 h and then hydrolyzed with water. The organic layer was washed with water and dried over potassium carbonate. Distillation of the product under reduced pressure using a short column afforded 5 g (13% yield) of **6**: bp 88-91 °C (2 Torr); $n^{20}{}_D$ 1.5071; mass spectrum *m/e* 280 (M^+); NMR δ 0.06 (Me_3Si, s, 9 H), 0.33 (Me_2Si, s, 6 H), 1.55 (Me_3C, s, 9 H), and 6.7-7.3 (ring protons, m, 4 H). Anal. Calcd for $C_{14}H_{28}OSi_2$: C, 64.22; H, 10.06. Found: C, 64.52; H, 10.06.

2-Pentamethyldisilanylnaphthalene (7a). To a solution of 2-naphthylmagnesium bromide prepared from 11.5 g (0.056 mol) of 2-bromonaphthalene and 2.0 g (0.083 g-atom) of magnesium in 50 mL of a mixed solvent consisting of benzene, ether, and THF (3:2:1) was added 5.0 g (0.030 mol) of chloropentamethyldisilane in 10 mL of THF. The mixture was refluxed for 6 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. Distillation of the products using a short column under reduced pressure gave 3.0 g (40% yield) of **7a**:[21] bp 119 °C (2 Torr); $n^{20}{}_D$ 1.5712; mass spectrum *m/e* 258 (M^+); NMR δ 0.05 (Me_3Si, s, 9 H), 0.39 (Me_2Si, s, 6 H), and 7.3-7.9 (ring protons, m, 7 H). Anal. Calcd for $C_{15}H_{22}Si_2$: C, 69.69; H, 8.58. Found: C, 69.70; H, 8.54.

2-(2′-Phenyltetramethyldisilanyl)naphthalene (7b). To a solution of 2-naphthylmagnesium bromide prepared from 12.5 g (0.060 mol) of 2-bromonaphthalene and 1.5 g (0.063 g-atom) of magnesium in 30 mL of a mixed solvent was added 10.5 g (0.046 mol) of 1-chloro-2-phenyltetramethyldisilane in 10 mL of THF. The mixture was refluxed for 6 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. Distillation of the mixture under reduced pressure gave 9.4 g (64% yield) of **7b**: bp 182-183 °C (3 Torr); mp 28 °C; IR 1425, 1260, 1100, 1075, 845 cm^{-1}; mass spectrum *m/e* 322 (M^+); NMR δ 0.35 (Me_2Si, s, 6 H), 0.39 (Me_2Si, s, 6 H), and 7.2-7.7 (ring protons, m, 12 H).

Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.55. Found: C, 74.68; H, 7.74.

3-Methoxy-2-pentamethyldisilanylnaphthalene (10). In a 300-mL three-necked flask was placed 7.9 g (0.05 mol) of 2-methoxynaphthalene dissolved in 80 mL of dry cyclohexane. To this was added 40 mL of 1.3 M butyllithium–hexane solution at room temperature. The mixture was refluxed for 14 h and then 30 mL of ether was added to the mixture. The reaction mixture was again refluxed for 6 h. Then 8.3 g (0.05 mol) of chloropentamethyldisilane was added and heated to reflux for 4 h. The mixture was hydrolyzed with water and dried over sodium sulfate. Distillation gave 6.4 g (45% yield) of white crystals: bp 138 °C (2 Torr); mp 49.5 °C (after recrystallization from 95% methanol); IR 1630, 1590, 1450, 1430, 1245, 1220, 1170, 1060, 1000 cm^{-1}; mass spectrum *m/e* 288 (M^+); NMR δ 0.05 (Me_2Si, s, 9 H), 0.40 (Me_2Si, s, 6 H), 3.82 (MeO, s, 3 H), and 6.9–7.7 (ring protons, m, 6 H). Anal. Calcd for $C_{16}H_{24}OSi_2$: C, 66.60; H, 8.38. Found: C, 66.64; H, 8.55.

Photolysis of 1-Pentamethyldisilanylnaphthalene (1a). A. In the Presence of Isobutene. A mixture of 1.0154 g (3.93 mmol) of **1a,** 0.2339 g (0.83 mmol) of eicosane, and 20 mL of isobutene in 80 mL of dry benzene was placed in a 100-mL reaction vessel, fitted with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated at room temperature for 7 h with a slow stream of nitrogen bubbling through the mixture. After the solvent and isobutene were evaporated off, the residue was analyzed by VPC as being 1-dimethylsilyl-2-trimethylsilylnaphthalene (**2a**, 40% yield) and 20% of the starting **1a**. The residue was distilled under reduced pressure to give volatile products. Pure **2a** was isolated by preparative VPC. Anal. Calcd for $C_{15}H_{22}Si_2$: C, 69.69; H, 8.52. Found: C, 69.39; H, 8.72.

B. In the Presence of Acetone. A mixture of 1.0311 g (3.99 mmol) of **1a,** 0.2160 g (1.09 mmol) of tetradecane as an internal standard, and 200 μL of acetone in 80 mL of benzene was irradiated for 8 h at room temperature. After workup in a similar way to A, 62% yield of **2a** was obtained.

C. In the Presence of Methanol. A mixture composed of 0.7070 g (2.74 mmol) of **1a,** 0.0830 g (0.42 mmol) of tetradecane, and 1 mL of dry methanol in 100 mL of benzene was irradiated for 5 h. After the usual workup, 66% yield of **2a** was obtained.

D. In the Absence of a Trapping Agent. A solution of 1.0147 g (3.95 mmol) of **1a** in 100 mL of dry benzene was irradiated for 7 h at room temperature. VPC analysis of the reaction mixture showed that **2a** was formed in 64% yield. The ^{1}H NMR, IR, and mass spectral data of **2a** isolated by preparative VPC were identical with those of the sample obtained from experiment A.

Photolysis of 1-(1′-Phenyltetramethyldisilanyl)naphthalene (1b). A solution of 0.7128 g (2.22 mmol) of **1b,** 0.0862 g (0.31 mmol) of eicosane as an internal standard, and 200 μL of dry acetone as a quenching agent in 100 mL of benzene was photolyzed for 18 h at room temperature. After evaporation of the solvent, the residue was distilled under reduced pressure. VPC analysis of the distillate showed that 1-methylphenylsilyl-2-trimethylsilylnaphthalene was formed in 61% yield, in addition to 7% yield of 1-trimethylsilylnaphthalene and 9% of unchanged **1b.** Product **2b** was isolated by preparative VPC. Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.54. Found: C, 74.69; H, 7.73.

Photolysis of 1-(2′-Phenyltetramethyldisilanyl)naphthalene (1c). A. In the Presence of Acetone. A solution of 0.6930 g (2.17 mmol) of **1c,** 250 μL of acetone, and 0.1801 g (0.64 mmol) of eicosane in 100 mL of benzene was irradiated for 5 h at room temperature. VPC analysis of the reaction mixture showed that 1-dimethylsilyl-2-phenyldimethylsilylnaphthalene (**2c**) and 1-phenyldimethylsilylnaphthalene (**3a**) were produced in 29 and 22% yield, respectively. Both **2c** and **3a** were isolated by preparative VPC. The IR, mass, and ^{1}H NMR spectra of **3a** were identical with those of the authentic sample. Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.55. Found: C, 74.92; H. 7.85.

B. In the Absence of a Trapping Agent. A solution of 0.6902 g (2.16 mmol) of **1c** and 0.1304 g (0.46 mmol) of eicosane was irradiated at room temperature for 5 h. The solvent was distilled off and the residue was then analyzed by VPC as being **3a** (22% yield) and **2c** (25% yield).

Photolysis of *o*-Tolylpentamethyldisilane (4a). A solution of 0.8269 g (3.72 mmol) of **4a,** 0.0462 g (0.20 mmol) of cetane, and 15 mL of isobutene in 85 mL of benzene was irradiated for 4 h with ice cooling. The solvent was distilled off and the residue was then analyzed by VPC as being adduct **5a** (26% yield) and the starting **4a** (21%). Product **5a** was isolated by preparative VPC. Anal. Calcd for $C_{16}H_{30}Si_2$: C, 68.98; H, 11.15. Found: C, 69.22; H, 10.85.

Photolysis of *o*-Anisylpentamethyldisilane (4b). A. In the Presence of Isobutene. A mixture of 1.0065 g (4.22 mmol) of **4b,** 0.1541 g (0.68 mmol) of cetane, and 10 mL of isobutene was photolyzed for 36 h at room temperature. Similar workup of the mixture afforded adduct **5b** in 23% yield, in addition to 20% of **4b.** Anal. Calcd for $C_{16}H_{30}OSi_2$: C, 65.24; H, 10.27. Found: C, 65.51; H, 10.45.

B. In the Presence of Acetone. Irradiation of 0.8113 g (3.41 mmol) of **4b** and 0.1038 g (0.46 mmol) of cetane in the presence of 250 μL of acetone in benzene for 9 h afforded **5e** in 22% yield, along with 13% of unchanged **4b.** Anal. Calcd for $C_{15}H_{28}O_2Si_2$: C, 60.75; H, 9.52. Found: C, 61.04; H, 9.59.

Photolysis of 2-Pentamethyldisilanylnaphthalene (7a). A. In the Presence of Isobutene. A mixture of 0.9123 g (3.53 mmol) of **7a,** 10 mL of isobutene, and 0.1103 g (0.39 mmol) of eicosane in 80 mL of benzene was irradiated for 6 h at room temperature. After benzene and unchanged isobutene were evaporated, the residue was analyzed by VPC as being **8a** (37% yield) and 13% of the starting **7a.** Pure **8a** was isolated by preparative VPC. Anal. Calcd for $C_{19}H_{33}Si_2$: C, 72.54; H, 9.61. Found: C, 72.24; H, 9.65.

B. In the Absence of a Trapping Agent. A mixture of 0.19 mmol of **7a** and 0.031 mmol of cetane in 10 mL of benzene was placed in a quartz tube. The solution was deoxygenated by bubbling dry nitrogen for 3 min and the tube was sealed with a serum cap. It was then irradiated externally with a low-pressure mercury lamp for 3.5 h at room temperature. VPC analysis of the mixture showed that 83% of **7a** was photolyzed at this stage. However, no volatile product was detected.

Photolysis of 2-(2′-Phenyltetramethyldisilanyl)naphthalene (7b) in the Presence of Isobutene. A benzene solution containing 0.5128 g (1.60 mmol) of **7b,** 0.1551 g (0.55 mmol) of eicosane, and 10 mL of isobutene was irradiated for 2 h at room temperature. Similar workup of the mixture afforded 36% yield of adduct **8b** and 6% of the starting **7b.** Photoproduct **8b** was isolated by VPC. Anal. Calcd for $C_{24}H_{32}Si_2$: C, 76.53; H, 8.56. Found: C, 76.26; H, 8.27.

Photolysis of 2-Pentamethyldisilanyl-3-methoxynaphthalene (10). A solution of 0.4577 g (1.59 mmol) of **10,** 0.0490 g (0.46 mmol) of octadecane, and 20 mL of isobutene in 80 mL of benzene was irradiated for 24 h at room temperature. VPC analysis of the mixture showed that 96% of **10** was recovered. At this stage, no volatile products were detected by VPC analysis. In similar photolysis of **10** in the presence of acetone, methanol, and water for 24 h, 99, 96, and 96% of the starting **10** were recovered, respectively.[22] The IR and ^{1}H NMR spectra of the recovered compound were identical with those of the starting **10.**

Protodesilylation of 2a. A solution of 1.0142 g (3.92 mmol) of **1a** in 100 mL of benzene was irradiated for 7 h at room temperature. After the solvent was evaporated, the residue was distilled under reduced pressure up to ca. 200 °C (3 Torr), to give crude **2a.** In a 250-mL two-necked flask, fitted with a condenser and an inlet tube for hydrogen chloride, were placed a solution of the crude **2a** and 0.1962 g (0.694 mmol) of eicosane as an internal standard dissolved in 100 mL of a 1:1 mixture of dry ether and benzene. Dry hydrogen chloride was passed into the solution for 4 h with ice cooling. At this stage 51% of the starting **2a** was cleaved by HCl. The mixture was washed with water to neutral and dried over potassium carbonate. Then the product was analyzed by VPC as being naphthalene (20% yield), **3b** (14% yield), and **3c** (45% yield). Products **3b** and **3c** were isolated by preparative VPC. The IR and ^{1}H NMR spectra of both **3b** and **3c** were identical with those of the authentic samples.

Protodesilylation of 8a. In a 100-mL two-necked flask were placed a mixture of crude **8a** obtained from the photolysis of 0.9123 g (3.53 mmol) of **7a** and 20 mL of isobutene in 80 mL of benzene and 0.1103 g (0.39 mmol) of eicosane in 50 mL of dry ether. Into this was introduced dry hydrogen chloride for 20 min with ice cooling. After the reaction mixture was washed with water the organic layer was analyzed by VPC as being naphthalene (6% yield), **3c** (12% yield), and **3d** (70% yield), in addition to a trace of **8a.** Product **3d** was isolated by preparative VPC. The IR, mass, and ^{1}H NMR spectra of **3d** were identical with those of the authentic sample.

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Hydroxyphosphoranes and Phosphoranoxide Anions—Synthesis, Reactivity, and Acidity of Pentacoordinate Phosphorus Acids

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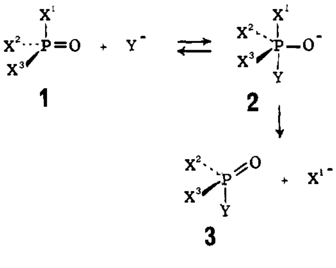
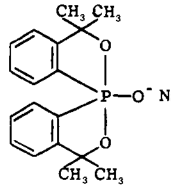
Abstract: The reaction between phosphorus oxychloride and bifunctional alkoxy Grignard reagents gives stable pentacoordinate magnesium phosphoranoxides, such as **9**. The less basic of these, the fluoro-substituted anion of **9**, is not protonated by aqueous ammonium chloride and is isolated as a crystalline salt. Protonation of the phosphoranoxide anions of **4** and **9** gives hydroxyphosphoranes **6** and **10**. While **6** equilibrates in solution with its open-chain tautomer **7**, only the hydroxyphosphorane structure is detected for **10**. Sodium phosphoranoxide **4** reacts with methyl iodide, giving the methoxyphosphorane **20**. Trifluoromethanesulfonic acid reacts with **6** or with olefin **12** to give the stable spirocyclic dioxyphosphonium salt **17**. The analogous reaction between **10** and this acid yields a complex mixture of products. Phosphonium salt **17** and Grignard reagents give dioxyphosphoranes **18** and **19**. The pK_a of **6** is estimated to be in the range 10–11, while the more acidic **10** has a pK_a of 5.3 ± 0.2.

Hydroxyphosphoranes and their conjugate bases, phosphoranoxide anions **2**, are commonly accepted as intermediates or transition states in nucleophilic displacements at the tetracoordinate phosphorus of compounds containing P=O bonds.[2] Recently, acid-catalyzed[3] or thermal[4] conversions of tetrahedral phosphine oxides into exceptionally stable pentacoordinate trigonal bipyramidal (TBP) oxyphosphoranes have been observed. This has paved the way for the synthesis of a thermally stable hydroxyphosphorane.[5] Trapping unstable hydroxyphosphoranes[6] and spectroscopic evidence[7] for equilibrium between a hydroxy phosphate and a hydroxyphosphorane in solution have also been reported. None of these hydroxyphosphoranes, all containing five-membered ring alkoxy or carboxy ligands, gave stable metal phosphoranoxides. In every case, deprotonation of the pentacoordinate phosphorus species led to tetra- or hexacoordinate species.[5,7]

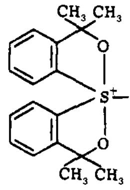


Treatments of some hydroxyphosphoranes with amines have been reported[8,9] to yield crystalline complexes. The spectral data[8,9] are not, however, consistent with deprotonation of the hydroxyphosphoranes to form salts, as we shall establish in this paper.

Earlier studies in this laboratory, centered on tetracoordinate TBP sulfuranes[10,11] and pentacoordinate sulfurane oxides, suggested to us that the phosphoranoxide anion of **4**, isoelectronic with stable sulfurane oxide **5**, might be isolable. This proved possible.[12] We now report further studies, including the preparation and some properties of a new, very stable hydroxyphosphorane, **10**. Acidities and reactivities of two compounds containing this new functional group, pentacoordinate phosphorus hydroxy acids, are discussed.



4, $\delta_{^{31}P}$ -26.9



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Results and Discussion

Synthesis and Structure. In a recent communication[12] we