Photolysis of Organopolysilanes. Photochemical Behavior of Phenylethynyldisilanes

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Abstract: The photolysis of phenylethynylpentamethyldisilane (1) afforded 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (8) and 1,1-dimethyl-3-phenyl-3-trimethylsilyl-1-silapropadiene. The absorption and emission spectra of 1 were measured at 300 and 77 K. The total emission spectrum at 77 K showed the normal fluorescence from (π,π^*) at 303 nm, the intramolecular CT fluorescence at 395 nm, and the phosphorescence from ${}^{3}(\pi,\pi^{*})$ at 410.5 nm. 1.1-Dimethyl-2phenyl-3-phenyldimethylsilyl-1-silacyclopropene (12), 1-methyl-1,2-diphenyl-3-trimethylsilyl-1-silacyclopropene (14), and 1,1,2-triphenyl-3-trimethylsilyl-1-silacyclopropene (15) have been prepared by photolysis of 1-phenylethynyl-2-phenyltetramethyl-, 1-phenylethynyl-1-phenyltetramethyl-, and 1-phenylethynyl-1,1-diphenyltrimethyldisilane, respectively. The molecular orbital calculations of ethynyl- and phenylethynyldisilane, 1-silacyclopropene, 2-silyl-1-silacyclopropene, and related compounds have been carried out. A mechanism for the formation of the silacyclopropenes is discussed on the basis of the MO calculations, emission spectra, and results of photochemical experiments.

Introduction

In 1961 Vol'pin et al. reported the synthesis of a compound which they supposed to have the silacyclopropene structure.^{2,3} However, the proposed structure was soon shown to be incorrect, with the actual product being the 1,4-disilacyclohexa-2,5-diene.4-6 Since that time many attempts have been made to prepare silacyclopropene,⁷ but all reactions designed to produce this ring system were unsuccessful until recently. In 1976 Conlin and Gaspar reported that dimethylsilylene generated by thermolysis of 1,2-dimethoxytetramethyldisilane reacts with 2-butyne to give tetramethyl-1-silacyclopropene.⁸ Subsequently, Seyferth and his co-workers,⁹ we,¹⁰ and Sakurai et al.¹¹ have reported independently isolation of the 1-silacyclopropene derivatives. Recently we have found that photolysis of alkynyl-substituted disilane derivatives affords a convenient route to the silacyclopropenes.¹²⁻¹⁵ In this paper, we describe a detailed photochemical study of phenylethynyldisilanes and the results of molecular orbital calculations of ethynyl- and phenylethynyldisilane, silacyclopropenes, and related compounds.

Results and Discussion

The starting phenylethynyldisilanes-phenylethynylpentamethyldisilane (1), 1-phenylethynyl-2-phenyltetramethyldisilane

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Scheme I



(2), 1-phenylethynyl-1-phenyltetramethyldisilane (3), and 1phenylethynyl-1,1-diphenyltrimethyldisilane (4)-were prepared by the reaction of phenylethynyllithium with the corresponding chlorodisilanes.

Photolysis of Phenylethynyldisilanes. First we examined the photolysis of phenylethynylpentamethyldisilane (1) in the presence of a quenching agent. When a benzene solution of 1 in the presence of acetone was irradiated at room temperature with a low-pressure mercury lamp with a Vycor filter under a purified nitrogen atmosphere, four products, 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclopent-3-ene (5), 2,2,5,5tetramethyl-3-phenyl-4-trimethylsilyl-1-oxa-2-silacyclopent-3-ene (6), phenyltrimethylsilylacetylene, and 1-phenyl-1-trimethylsilyl-3-methyl-1,2-butadiene (7), were obtained in 51, 2, 10, and 5% yield,¹⁰ respectively (Scheme I). The formation of products 5 and 6 can be explained by the two-atom insertion^{9b,10,11,16} of acetone into 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (8), while 7 can be rationalized in terms of cycloaddition of acetone to 1-silapropadiene A to afford silaoxetane intermediate B, followed by loss of the Me₂SiO moiety. Structures 5-7 were identified by mass and proton NMR spectrometric analysis (see

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Figure 1. Absorption (in cyclohexane) and emission spectra of a 2×10^{-5} M MP solution of 1 at 300 and 77 K.

Scheme II



radical coupling products

Experimental Section). The location of the trimethylsilyl group on the five-membered ring in compound **5** was confirmed by protodesilylation. Thus, treatment of **5** with dry hydrogen chloride in diethyl ether at room temperature for 7 h gave 2,2,5,5-tetramethyl-4-phenyl-1-oxa-2-silacyclopent-3-ene (**9**) in 77% yield. Prolonged reaction with hydrogen chloride under otherwise the same conditions afforded **9** and 2-methyl-3-phenyl-1,3-butadiene¹⁷ (**10**) in 31 and 33% yield, respectively. The formation of **10** clearly



indicates that both the Me_3Si and Me_2Si groups are attached to the same carbon atom.

Irradiation of 1 in the absence of acetone under similar photolysis conditions followed by distillation of the photolysis mixture under reduced pressure gave a 49% yield of silacyclopropene (8), which is extremely air-sensitive, in addition to a 10% yield of phenyltrimethylsilylacetylene. In this case, a volatile product which might be formed from the silapropadiene intermediate could not be detected either by VPC or spectroscopic analysis. The photolysis of 1 in the presence of diethylmethylsilane afforded 8 and 1,1-diethyl-1,2,2-trimethyldisilane¹⁸ arising from insertion of dimethylsilylene into the silicon-hydrogen bond in diethylmethylsilane in 52 and 13% yield, respectively, along with 25% yield of phenyltrimethylsilylacetylene. In this photolysis, neither 1-trimethylsilyl-1-dimethylsilylphenylethene (11) nor radical coupling products such as 1,1,2,2-tetraethyldimethyldisilane were detected by spectroscopic and VPC analyses, indicating that no triplet diradical intermediate (C) was formed (Scheme II).

Irradiation of 1-phenylethynyl-2-phenyltetramethyldisilane (2) with a low-pressure mercury lamp in the absence of a trapping



agent afforded 1,1-dimethyl-2-phenyl-3-phenyldimethylsilyl-1silacyclopropene (12) and 1,1,2,2-tetramethyl-3-phenyl-4-



phenyldimethylsilyl-1,2-disilacyclobutene (13) in 54 and 2% yield, respectively, in addition to phenyl(phenyldimethylsilyl)acetylene (14%) and the starting disilane 2 (2%).

The photolysis of 1-phenylethynyl-1-phenyltetramethyldisilane (3) in a hexane solution produced 1-methyl-1,2-diphenyl-3-trimethylsilyl-1-silacyclopropene (14), along with a 10% yield of phenyltrimethylsilylacetylene and 2% of the starting phenylethynyldisilane 3. Unfortunately, silacyclopropene 14 could not be detected by VPC techniques, although 14 could be distilled under reduced pressure without decomposition. Therefore, we treated the distillate with methanol and determined the yield of 14 as methoxysilanes. Thus, treatment of the distillate with dry methanol under a nitrogen atmosphere afforded two methoxysilanes, 1-trimethylsilyl-1-methoxymethylphenylsilyl-2-phenylethene (16) and 1-methoxymethylphenylsilyl-1-phenyl-2-trimethylsilylethene (17), in 46 and 20% yields, respectively, indicating that silacyclopropene 14 was produced in 66% yield. Similar photolysis of 1-phenylethynyl-1,1-diphenyltrimethyldisilane (4) gave 1,1,2-triphenyl-3-trimethylsilyl-1-silacyclopropene (15) which could be isolated by distillation under reduced pressure. Again, silacyclopropene 15 could not be detected by VPC. After methanolysis of the distillate, two methoxysilanes 18 and 19 were obtained in 43 and 18% yield, respectively, in addition to 11% yield of phenyltrimethylsilylacetylene and 2% of unchanged 4 (Scheme III).

Compounds 8, 12, 14, and 15 are as extremely air-sensitive as silacyclopropenes reported previously; on exposure to air they

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immediately decomposed to give nonvolatile substances.

Absorption and Emission Spectra of 1. Figure 1 shows the absorption ($\epsilon = 2.2_5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 258 nm in cyclohexane) and emission spectra of 1 in MP (methylcyclohexane:isopentane, 3:1 v/v) at 300 and 77 K. The fluorescence spectrum at 300 K has a peak at 310 nm with a vibrational structure and also a long tail at longer wavelengths. The emission at 310 nm may originate from the (π,π^*) state, considering its vibrational structure. The tail emission at longer wavelengths corresponds to that from the intramolecular CT state of 1 as will be discussed later. At 300 K, the fluorescence quantum yields for the former and the latter were very small $(7.3 \times 10^{-3} \text{ and } 6.5 \times 10^{-4}, \text{ respectively})$. The longer wavelength fluorescence increased with decreasing temperature. The total emission spectrum at 77 K consists of three parts: the normal fluorescence from (π,π^*) (λ_{max} 303 nm, Φ_F = 0.015), the intramolecular CT fluorescence (λ_{max} 395 nm, Φ_{CT} = 0.26), and the phosphorescence from $^{3}(\pi,\pi^{*})$ (λ_{max} 410.5 nm, $\Phi_{\rm P} = 0.24$). The excitation spectra at these emission maxima were close to the absorption spectrum. Very recently, it has been demonstrated that broad and structureless fluorescence spectra of phenyl and naphthyldisilanes with large Stokes shifts are assigned to the emissions from the intramolecular CT states produced by charge transfer from the excited aromatic moiety to the disilanyl group [i.e., the $2p\pi^* \rightarrow 3d\pi$ (or $2p\pi^* \rightarrow \sigma^*$)].¹⁹ The broad and structureless band at 395 nm in the present work is similar to the bands of the intramolecular CT fluorescence spectra of the aryldisilanes. The theoretical MO calculations in the next section support the presence of the CT state of 1. Therefore, the fluorescence band at 395 nm is attributed to that from the intramolecular CT state of 1. The MO calculations show that the CT state corresponds to the (π, σ^*) state resulting from the charge transfer $2p\pi^* \rightarrow \sigma^*$ (Si-Si). However, the MO calculations were carried out without 3d atomic orbitals. An alternative interpretation is that the CT state is caused by the charge transfer $2p\pi^*$ \rightarrow 3d π [i.e., the CT state is $(\pi, 3d\pi)$]. The disilarly group provides a vacant $3d\pi$ orbital, which may be formed by the linear combination of 3d atomic orbitals, having a relatively low-energy level compared with that of a single 3d atomic orbital. The energy separation between $2p\pi$ and $3d\pi$ orbitals becomes small upon excitation, and the $2p\pi^* \rightarrow 3d\pi$ CT state $[1(\pi, 3d\pi)]$ leading to the longer wavelength emission may be produced. It is unknown at the present time whether the CT state is (π, σ^*) or $(\pi, 3d\pi)$. Anyway, intramolecular charge transfer from the phenylethynyl moiety to the Si-Si group occurs in the excited singlet state. The phosphorescence spectrum of 1 (λ_{max} 410.5 nm, $\Phi_P = 0.24$, and $\tau_{\rm P} \sim 1$ s) overlaps with the broad CT band. Considering the value of lifetime $\tau_{\rm P}$ and its vibrational structure, the phosphorescence is emitted from ${}^{3}(\pi,\pi^{*})$. The energy levels for the fluorescent states of ${}^{1}(\pi,\pi^{*})$ and ${}^{1}CT$ and the phosphorescent state of ${}^{3}(\pi,\pi^{*})$ were determined to be 94.3, 72.3, and 69.6 kcal/mol, respectively, from the total emission spectrum in Figure 1. It is noteworthy that the energy gap between ¹CT and ³ (π,π^*) is very small (2.7 kcal/mol). At higher temperatures the CT emission may be quenched by fast intersystem crossing ${}^{1}CT \rightarrow {}^{3}(\pi,\pi^{*})$ and also the photochemical process. In fact, the fluorescence intensity at 300 K is very low as described above. The photochemical reactions of 1 sensitized by triplet acetophenone $(E_{\rm T} = 73.7 \text{ kcal/mol})^{20}$ and acetone $(E_T = 79-82 \text{ kcal/mol})^{20}$ at room temperature were carried out using a high-pressure mercury lamp with a Pyrex filter (>300 nm). No photoproducts such as those obtained by the direct excitation at 254 nm could be detected. Thus, the reactive state of 1 should be the excited singlet state, probably ¹CT, but not the triplet excited state. The MO calculations in the next section support the ${}^{1}CT$ mechanism for the photochemical reaction of 1. For naphthyldisilanes, it is found recently that the photochemical reaction originates from the ¹CT state.²¹ The ¹CT state of the



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Figure 2. HOMO-(LU + 4)MO of phenylethynyldisilane (20).

aryldisilanes including 1 seems to be significantly reactive at higher temperatures.

Molecular Orbital Calculations. In order to clarify the mechanism of the photochemical reactions described above, we have carried out the molecular orbital (MO) calculations for some simplified model compounds. First we considered the reaction of phenylethynyldisilane (20) shown in the following equation as



the model for the photochemical reaction of 1. The preliminary calculations using 20 showed essentially the same orbital patterns as those obtained from more simplified compound, ethynyldisilane (23). Therefore, we used 2-silyl-1-silacyclopropene (24), 3-silyl-1-silapropadiene (25), and a singlet diradical intermediate (26) as model compounds to discuss the mechanism of the photochemical reactions. The geometries of these model compounds are partially optimized as indicated below. The STO-3G basis set²² is employed for the ab initio SCF calculations. The partial "orthogonality constrained basis set expansion (OCBSE) method" by Davidson²³ is used for the open-shell structures. The calculations were carried out with the use of GAUSSIAN-70²⁴ and GAUSSIAN-76 programs.

Several MOs of 20 calculated by use of the same geometry as 23, except for the phenyl ring, are schematically described in Figure 2. In this figure, the lowest unoccupied molecular orbital (LUMO) and the next LUMO ((LU + 1)MO) correspond to the π^* of the phenylethynyl and phenyl moieties, respectively, while the second MO above the LUMO ((LU + 2)MO) corresponds to the π^* of the silulethynyl moiety. Apparently, all of these orbitals make no contribution to the photochemical cleavage of the Si-Si bond. The (LU + 3)MO, on the other hand, is strongly

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Photochemical Behavior of Phenylethynyldisilanes



Figure 3. (a) HOMO, LUMO, and (LU + 2)MO of ethynyldisilane (23). (b) Contour maps of HOMO, LUMO, and (LU + 2)MO of ethynyldisilane (23). The lines are contours of 0.003, 0.01, 0.03, and 0.1 from the outside. The broken lines indicate negative signs.



Figure 4. Atomic net charges of ethynyldisilane (23).

antibonding for the two silicon atoms. As can be seen from the orbital pattern of the (LU + 3)MO, the phase relationship between the $3p\pi$ atomic orbital at Si² and the $2p\pi$ atomic orbital at C² and also the relationship between the $3p\pi$ atomic orbital at Si¹ and the $2p\pi$ atomic orbital at C¹ are quite favorable for the formation of 3-phenyl-3-silyl-1-silapropadiene (21). Therefore, if the HOMO \rightarrow (LU + 3)MO transition is brought about by photoabsorption, the $\sigma(Si^1-Si^2)$ bond is weakened to facilitate a 1,3-silyl shift and the formation of the $\pi(Si^2-C^1)$ bond. Likewise, the HOMO \rightarrow (LU + 4)MO transition suggests that it induces a 1,2-silyl shift to afford 2-phenyl-3-silyl-1-silacyclopropene (22). These transitions may be attributed to charge transfer from the π orbital of the phenylethynyl group to the $\sigma^*(Si^1-Si^2)$ orbital. Indeed, observation of the charge-transfer band in the emission spectrum of 1 as discussed above strongly suggests this kind of transition.

Some important MOs of ethynyldisilane (23) and the atomic net charges are shown in Figures 3a and 4. The HOMO, LUMO, and (LU + 2)MO for compound 23 are quite similar to the HOMO, (LU + 3)MO, and (LU + 4)MO of 20, respectively. This means that such simplified compounds as 23-26 can be used to consider the mechanism of the photoinduced intramolecular rearrangement. The geometries for 23-26 are determined after optimizations with respect to some bond lengths and angles (see Figure 5). The maps of the HOMO, LUMO, and (LU + 2)MO of 23 are presented in Figure 3b. The HOMO is bonding for π (C¹-C²) and σ (Si¹-Si²), but antibonding for π (C¹-Si¹), whereas



Figure 5. Geometries of ethynyldisilane (23), 2-silyl-1-silacyclopropene (24), 3-silyl-1-silapropadiene (25), and diradical 26. The bond lengths are in Å. Values with underline are optimized. Values in parentheses with the exception of angles for sp^2 (120°) and sp^3 (109° 47′) are taken from ref 25, and other values are those which are optimized for compounds 27, 29b(S), 30, and 31 in Figure 7.



Figure 6. Relative energies of ethynyldisilane (23), 2-silyl-1-silacyclopropene (24), 3-silyl-1-silapropadiene (25), and diradical 26.

the LUMO is antibonding for $\pi(C^1-C^2)$ and $\sigma(Si^1-Si^2)$, but bonding for $\pi(C^1-Si^1)$. Therefore, the HOMO \rightarrow LUMO transition gives rise to cleavage of the Si-Si bond and simultaneously breaks one of the $\pi(C^1-C^2)$ bonds, producing a new $\pi(C^1-Si^1)$ bond. Thus, 3-silvl-1-silapropadiene (25) is formed from rearrangement of photoexcited 23 via a 1,3-silyl shift. Moreover, Figure 3b clearly suggests that the HOMO \rightarrow (LU + 2)MO transition in 23 leads to a 1,2-silyl shift, giving singlet diradical species 26, which may be proposed as the most proper intermediate as will be discussed below. This singlet diradical intermediate can readily be stabilized to form 2-silyl-1-silacyclopropene (24). The diagram of the relative total energies (kcal/mol) for 23-26 is presented in Figure 6. The energy of 26 is higher by ca. 85 kcal/mol than that of 23. However, photoexcited 23 with sufficiently high energy to give 26 would be formed by the absorption of light (254 nm). On the other hand, the energy of silacyclopropene 24 is lower by 30 kcal/mol than that of 25. This is consistent with the experimental results in which the silacyclopropenes are obtained as the major products.

We propose the singlet 1,3-diradical **26** as a key intermediate for the formation of 2-silyl-1-silacyclopropene (**24**). However,



Figure 7. Geometries of 27-31 (see Figure 5). For compounds 28a, 28b, and 28c, the same values for 29b are used.



Figure 8. Possible reaction paths of ethynylsilane (27). Broken lines indicate an unfavorable path.

one must take account of some other intermediates such as carbene species, and of an alternative pathway leading to the products. For this purpose, we carried out the calculations of the simplest monosilanes 27–31, with partially optimized structures as shown in Figure 7, and examined the possibility of the reaction pathways shown in Figure 8. The relative total energy of each species is shown in Figure 9. The reaction path $27 \rightarrow 28a \rightarrow 30$ keeps the closed-shell structure; however, the activation energy is calculated to be ca. 133 kcal/mol, indicating that this process seems very unlikely. Such a high activation energy may be due to the strongly polarized structure of 28a in the transition state. In the reaction path involving a singlet diradical, $27 \rightarrow 28b(S)$ (excited singlet



Reaction coordinate

Figure 9. Reaction profile for isomerization of ethynylsilane (27).

state) \rightarrow 30, however, the energy barrier (81 kcal/mol) is lower than the excitation energy of the initial reactant 27.

It is of interest to consider the pathway leading to the singlet carbene (29a(S)) in more detail. As mentioned above, the path $27 \rightarrow 28a \rightarrow 29a(S)$ seems unlikely because of the high-energy barrier. An alternative pathway involves the reaction of $28b(S) \rightarrow 29b(S) \rightarrow 29a(S)$. In this case, 29b(S) is more stable than 29a(S), and the reconversion of 29a(S) to 28b(S) has very small barriers (see Figures 9 and 10), so that the ensuing step follows instantaneously to form the final product, 1-silacyclopropene (30). These situations resemble the vinylmethylene system.²⁶ In our calculations using the minimal basis set (without d-type functions), the total energy of the singlet carbene 29a(S). This energy difference

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Figure 10. State correlation diagram between diradicals and carbene species.

may be improved to some extent by carrying out more sophisticated calculations containing many CIs with an extended basis set, but the conclusion mentioned above will not be altered. The direct path 29a(S) to 30 would also have a high-energy barrier. Ultimately, the singlet carbene may not dominantly appear throughout photochemical isomerizations.

Although triplet intermediates have no contributions in the present reactions as indicated by the trapping experiments, it is still interesting to consider the stability of triplet carbene 29c(T) (triplet state). In contrast to the same stability in the singlet intermediates 28b(S) and 29b(S), triplet 1,3-diradical 28c(T) is 6 kcal/mol less stable than 29d(T). Unlike the case of vinyl-methylene,²⁶ the energy difference between 29c(T) and 29d(T) is only 5 kcal/mol (see Figure 10), although 29d(T) is more stable. Therefore, if the intermediate were the triplet species, 1,3-diradical 29d(T) would be found dominantly as an intermediate.

In conclusion, the photochemical transformation of phenylethynyldisilanes into silacyclopropenes and silapropadienes may be initiated from different excited states. The formation of the silacyclopropenes involves two steps, via a singlet diradical intermediate analogous to 26, while the silapropadienes are produced by a concerted pathway.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were determined on thin liquid films using a Hitachi Model EPI-G3 grating infrared spectrometer. Gas chromatographic separations were carried out using columns packed with 30% SE-30 Silicone on Celite 545. NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer. Solutions in deuteriobenzene containing cyclohexane as an internal standard were used in determination of chemical shifts for silacyclopropenes. All of the other compounds were determined in carbon tetrachloride using cyclohexane as an internal standard. Mass spectra were measured on a JEOL Model JMS-D 300 equipped with a JMA-2000 data-processing system. The yields of the silacyclopropenes were determined by VPC using an internal standard on the basis of unrecovered phenylethynyldisilanes.

Phenylethynylpentamethyldisilane (1). In a 200-mL flask was placed a solution of 8.81 g (0.086 mol) of phenylacetylene in 10 mL of dry ethyl ether. To this was added 50 mL of 1.73 M butyllithium-hexane solution at -78 °C for 1 h. After the addition the mixture was stirred for 30 min at room temperature. To it was added 15.6 g (0.094 mol) of chloropentamethyldisilane in 50 mL of dry ether in the course of 15 min with ice-cooling. The mixture was then heated to reflux for 2 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over calcium chloride. After evaporation of the solvent, the residue was distilled under reduced pressure to give 15.3 g (77% yield) of a colorless liquid: bp 87 °C (3 mm); n^{20}_D 1.5266; IR 2160 cm⁻¹; ¹H NMR δ (ppm) 0.18 (9 H, s, Me₃Si), 0.28 (6 H, s, Me₂Si), 7.2-7.5 (5 H, m, ring protons). Anal. Calcd for C₁₃H₂₀Si₂: C, 67.17; H, 8.67. Found: C, 67.37; H, 8.69.

1-Phenylethynyl-2-phenyltetramethyldisilane (2). To 4.3 g (0.042 mol) of phenylacetylene in 50 mL of hexane was added 24 mL of 1.5 M butyllithium-hexane solution at -78 °C for 10 min. The mixture was stirred for 30 min at room temperature, and then 7.3 g (0.032 mol) of 1-chloro-2-phenyltetramethyldisilane in 20 mL of hexane was added to

the mixture at room temperature. After the mixture was refluxed for 30 min, it was hydrolyzed with water. The organic layer was washed with water and dried over potassium carbonate. Fractional distillation through a short column gave 8.3 g (88% yield) of **2**: bp 135 °C (2 mm); $n^{20}_{\rm D}$ 1.5802; IR 2150 cm⁻¹; ¹H NMR δ (ppm) 0.26 (6 H, s, Me₂Si), 0.45 (6 H, s, Me₂Si), 7.1–7.6 (10 H, m, ring protons). Anal. Calcd for C₁₈H₂₂Si₂: C, 73.40; H, 7.53. Found: C, 73.68; H, 7.65.

1-Phenylethynyl-1-phenyltetramethyldisilane (3). To a solution of phenylethynyllithium, prepared from 4.0 g (0.039 mol) of phenylacetylene dissolved in 50 mL of hexane and 22 mL of 1.6 M butyllithium-hexane, was added 7.4 g (0.032 mol) of 1-chloro-1-phenyltetramethyldisilane in 20 mL of hexane at room temperature. Similar workup of the mixture afforded 8.0 g (85% yield) of 3: bp 126 °C (1 mm); $n^{20}_{\rm D}$ 1.5771; IR 2155 cm⁻¹; ¹H NMR δ (ppm) 0.17 (9 H, s, Me₃Si), 0.52 (3 H, s, MeSi), 7.2–7.6 (10 H, m, ring protons). Anal. Calcd for C₁₈H₂₂Si₂: C, 73.40; H, 7.53. Found: C, 73.23; H, 7.68.

1-Phenylethynyl-1,1-diphenyltrimethyldisilane (4). To a solution of phenylethynyllithium prepared from 4.0 g (0.039 mol) of phenylacetylene dissolved in 50 mL of hexane and 22 mL of 1.6 M butyllithium-hexane was added 8.0 g (0.028 mol) of 1-chloro-1,1-diphenyltrimethyldisilane at room temperature. Similar workup afforded 8.5 g (87% yield) of 4: bp 196 °C (1.5 mm); mp 47-48 °C; IR 2155 cm⁻¹; ¹H NMR δ (ppm) 0.25 (9 H, s, Me₅Si), 7.2-7.7 (15 H, m, ring protons). Anal. Calcd for C₂₃H₂₄Si₂: C, 77.47; H, 6.78. Found: C, 77.36; H, 7.02.

Photolysis of 1 in the Presence of Acetone. A mixture of 1.0020 g (4.31 mmol) of 1 and 0.4 mL of acetone 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 2 h with a slow stream of nitrogen bubbling through the mixture. After the solvent was evaporated off, the residue was analyzed by VPC using octadecane as an internal standard, as 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclopent-3-ene (5) (51% yield), 2,2,5,5-tetramethyl-3-phenyl-4-trimethylsilyl-1-oxa-2-silacyclopent-3-ene (6) (2% yield), phenyltrimethylsilylacetylene (10% yield), 1-phenyl-1-trimethylsilyl-3-methyl-1,2-butadiene (7) (5% yield), and 19% of the starting 1. Compounds 5-7 were distilled under reduced pressure and isolated pure by preparative VPC. For 5: mass spectrum m/e 290; ¹H NMR δ (ppm) -0.25 (9 H, s, Me₃Si), 0.26 (6 H, s, Me₂Si), 1.24 (6 H, s, Me₂C) 6.9-7.4 (5 H, m, ring protons). Anal. Calcd for C₁₆H₂₆OSi₂: C, 66.14; H, 9.02. Found: C, 65.97; H, 9.04. For 6: ¹H NMR δ (ppm) -0.10 (9 H, s, Me₃Si), 0.16 (6 H, s, Me₂Si), 1.40 (6 H, s, Me₂C), 6.9-7.4 (5 H, m, ring protons); exact mass 290.1545 (calcd 290.1522). For 7: ¹H NMR δ (ppm) 0.19 (9 H, s, Me₃Si), 1.77 (6 H, s, Me₂C), 7.14 (5 H, broad s, ring protons); exact mass 216.1341 (calcd 216.1334).

Protodesilylation of 5. In a 50-mL, two-necked flask fitted with a gas inlet tube and a reflux condenser was placed 0.1820 g (0.63 mmol) of 5 dissolved in 25 mL of dry ether. Dry hydrogen chloride gas was introduced into the solution with ice-cooling. The progress of the reaction was monitored by VPC analysis of small aliquots extracted periodically from the reaction mixture. The starting compound was completely cleaved by hydrogen chloride after 7 h. At this stage, VPC analysis showed that 77% of 9 was produced. After further introduction of hydrogen chloride gas for 74 h, compound 10 was produced in 33% yield, in addition to a 31% yield of 9. The reaction mixture was washed with water and neutralized with sodium bicarbonate solution. The organic layer was separated and dried over calcium chloride. After the solvent ether was evaporated, the residue was distilled under reduced pressure. Pure 9 and 10 were isolated by preparative VPC. For 9: ¹H NMR δ (ppm) 0.26 (6 H, s, Me₂Si), 1.34 (6 H, s, Me₂C), 5.73 (1 H, s, vinylic proton), 7.23 (5 H, s, ring protons). Anal. Calcd for C13H18OSi: C, 71.50; H, 8.31. Found: C, 71.32; H, 8.55. The IR and ¹H NMR spectra of 10 were identical with those of the authentic sample:¹⁷ ¹H NMR δ (ppm) 1.97 (3 H, broad s, Me), 5.04 (4 H, m, vinylic protons), 7.19 (5 H, broad s, ring protons).

Photolysis of 1 in the Absence of a Trapping Agent. A mixture of 0.2733 g (1.18 mmol) of 1 and 0.0468 g (0.25 mmol) of tridecane as an internal standard in 25 mL of dry benzene was photolyzed for 50 min at room temperature. VPC analysis of the mixture showed that silacy-clopropene 8 and phenyltrimethylsilylacetylene were formed in 49 and 10% yields, respectively, in addition to 7% of unchanged 1. The solvent benzene was evaporated under a nitrogen atmosphere and the residue was distilled under reduced pressure to give a slightly yellow liquid boiling over a range of 79–90 °C (2 mm). Product 8 was isolated by VPC using a glass column containing 30% Silicone SE-30 on Chromosorb W (column temperature 130 °C): IR 1950, 1573, 965 cm⁻¹; ¹H NMR δ (ppm) 0.23 (6 H, s, Me₃Si), 0.30 (9 H, s, Me₃Si), 7.0–7.7 (m, ring protons); exact mass 232.1095 (calcd 232.1104).

Photolysis of 1 in Diethylmethylsilane. A mixture of 0.2601 g (1.12 mmol) of 1 and 0.0301 g (0.16 mmol) of tridecane as an internal

standard in 25 mL of diethylmethylsilane was irradiated with a lowpressure mercury lamp for 50 min. The photolysis mixture was analyzed by VPC as being 8 (52% yield), 1,1-diethyl-1,2,2-trimethyldisilane (13% yield), and phenyltrimethylsilylacetylene (25% yield), in addition to 5% of the starting compound 1. Pure 8 and 1,1-diethyl-1,2,2-trimethyldisilane were isolated by preparative VPC. The ¹H NMR, mass, and IR spectra of 1,1-diethyl-1,2,2-trimethyldisilane were identical with those of an authentic sample.¹⁸

Photolysis of 2. A mixture of 0.2509 g (0.85 mmol) of 2 and 0.0298 g (0.13 mmol) of cetane in 25 mL of hexane was irradiated with a low-pressure mercury lamp for 1 h at room temperature. VPC analysis of the mixture showed that silacyclopropene 12 and 1,2-disilacyclobutene 13, whose retention time on VPC was identical with that of the authentic sample, were formed in 54 and 2% yield, respectively, in addition to 14% yield of phenyl(phenyldimethylsilyl)acetylene and 2% of unchanged 2. After evaporation of the solvent, the residue was distilled under reduced pressure. Product 12 was isolated by VPC using a glass column (column temperature 200 °C): ¹H NMR δ (ppm) 0.29 (6 H, s, Me₂Si), 0.59 (6 H, s, Me₂Si), 6.9–7.9 (m, ring protons); exact mass 294.1270 (calcd 294.1260).

Photolysis of 3. A. Determination of a Yield of 14. A solution of 0.2466 g (0.84 mmol) of 3 and 0.0272 g (0.12 mmol) of cetane in 25 mL of hexane was photolyzed for 45 min at room temperature. After irradiation was stopped, 0.5 mL of dry methanol was added to the mixture. VPC analysis of the mixture showed that methoxysilanes 16 and 17 were formed in 46 and 20% yields, in addition to 10% yield of phenyltrimethylsilylacetylene and 2% yield of the starting 3. Compounds 16 and 17 were isolated by preparative VPC. For 16: IR 1090 cm⁻¹; mass spectrum m/e 326; ¹H NMR δ (ppm) -0.13 (9 H, s, Me₃Si), 0.52 (3 H, s, MeSi), 3.48 (3 H, s, MeO), 7.1-7.6 (10 H, m, ring protons), 7.82 (1 H, s, HC=C). Anal. Calcd for C₁₉H₂₆OSi₂: C, 69.88; H, 8.02. Found: C, 70.05; H, 8.06. For 17: IR 1090 cm⁻¹; ¹H NMR δ (ppm) -0.18 (9 H, s, MeO), 6.45 (1 H, s, HC=C), 6.8-7.5 (10 H, m, ring protons). Anal. Calcd for C₁₉H₂₆OSi₂: C, 69.88; H, 8.02. Found: C, 69.88; H, 8.02. Found: C, 70.15; H, 8.16.

B. Isolation of 14. A solution of 0.2233 g (0.76 mmol) of 3 in 25 mL of hexane was irradiated for 50 min. At this stage, the starting 3 was completely photolyzed. The solvent hexane was distilled off under a nitrogen atmosphere, and the residue was distilled through a short column under reduced pressure to give 0.065 g (29% yield) of 14: ¹H NMR δ (ppm) 0.37 (9 H, s, Me₃Si), 0.60 (3 H, s, MeSi), 6.9–7.9 (m, ring protons).

Photolysis of 4. A. Determination of a Yield of 15. A solution of 0.3203 g (0.90 mmol) of 4, 0.0469 g (0.24 mmol) of tetradecane, and 0.0328 g (0.12 mmol) of eicosane as internal standards in 25 mL of hexane was photolyzed for 45 min at room temperature. After irradiation was stopped, 0.5 mL of methanol was added to the photolysis mixture. VPC analysis of the mixture showed methoxysilanes 18 and 19

were produced in 43 and 18% yield, in addition to 11% yield of phenyltrimethylsilylacetylene. Compounds **18** and **19** were isolated by preparative VPC. For **18**: IR 1090 cm⁻¹; ¹H NMR δ (ppm) -0.13 (9 H, s, Me₃Si), 3.59 (3 H, s, MeO), 7.1-7.7 (15 H, m, ring protons), 7.80 (1 H, s, HC=C). Anal. Calcd for C₂₄H₂₈OSi₂: C, 74.17; H, 7.26. Found: C, 73.92; H, 7.38. For **19**: IR 1090 cm⁻¹; ¹H NMR δ (ppm) -0.16 (9 H, s, Me₃Si), 3.42 (3 H, s, MeO), 6.58 (1 H, s, HC=C), 6.8-7.6 (15 H, m, ring protons); exact mass 388.1678 (calcd 388.1679).

B. Isolation of 15. A solution of 0.7066 g (1.98 mmol) of 4 in 80 mL of hexane was irradiated for 1.4 h. At this stage, the starting 4 was photolyzed completely. The solvent hexane was evaporated under a nitrogen atmosphere and the residue was distilled under reduced pressure through a short column to give 0.194 g (27% yield) of 15: ¹H NMR δ (ppm) 0.36 (9 H, s, Me₃Si), 6.9–8.1 (m, ring protons).

Absorption and Emission Spectra of 1. The experimental apparatus and procedures were the same as reported elsewhere.²⁷ Methylcyclohexane (M) and isopentane (P) were purified by passing them through a silica gel column. A 2×10^{-5} M MP (M:P = 3:1) solution of 1 was thoroughly degassed by freeze-pump-thaw cycles. Fluorescence quantum yields were determined by comparison with that of toluene at 260 nm and 300 K ($\Phi_F = 0.14$).²⁸ The phosphorescence quantum yield was evaluated from the relative intensities of the total emission spectrum and the corresponding fluorescence quantum yield at 77 K. A cryostat (Oxford DN 704) for optical spectroscopy was employed at 77 K.

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