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Photochemistry of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes

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All the 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (**1a–d**) synthesized show strong phosphorescence emissions with triplet energies around 218–260 kJ/mol. Laser photolysis of 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1d**) in polar solvents results in the formation of an interesting transient (zwitterion species) through intramolecular electron transfer from disilanyl to the nitro group in the triplet excited state. Irradiation of **1d** in methanol or ethanol gives 1-(*p*-nitrophenyl)-1,3-butadiyne (**8**) through C–Si bond cleavage from the transient. Photolysis of 1-phenyl-4-(pentamethyldisilanyl)-1,3-butadiyne (**1a**), 1-(1-naphthyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1b**), and 1-(*p*-methoxyphenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1c**) in methanol yields photoaddition products (**2–7**) through silacyclopropene intermediates.

Introduction

The excited state chemistry of aryldisilanes has recently been extensively studied because these compounds show dual fluorescence corresponding to two singlet excited states.[1-8] The total emission of aryldisilanes consists of normal (locally excited state, LC) and intramolecular charge-transfer (CT) fluorescence. The CT emission has a broad and structureless band with a large Stokes shift.[1,2] This intramolecular CT state has a strongly polar structure with complete charge separation,[3] which plays an important role in the photochemical reaction.[4,5] Shizuka *et al.* reported that the CT process occurs very rapidly (<10 ps) both in a nonpolar solvent at 293 K and in a polar rigid matrix at 77 K, and the molecular conformation having a planar structure is favorable to the CT process.[5,7] These findings indicate that twisting or internal rotation in the excited state is not necessary for CT process. They suggested that the CT emission is originated from the $^1(2p\pi,3d\pi)$ state produced by the $2p\pi^*$ (aromatic ring) → vacant $3d\pi$ (Si–Si bond) intramolecular charge-transfer transition on the basis of the effect of steric twisting on the emission,[3-7] and the mechanism of the intramolecular CT is very different from that of twisted intramolecular charge transfer (TICT) proposed for dual emission of dialkylaniline derivatives.[5]

On the other hand, Sakurai *et al.* reported that the CT bands of aryldisilanes and related compounds can be explained satisfactorily by the emission from the intramolecular charge-transfer states where σ(Si–Si) and π systems act as donors and acceptors, respectively.[8] They proposed the orthogonal intramolecular charge-transfer (OICT) model as a general term on the basis of both substituent and geometric effects on the dual fluorescence of aryldisilanes.[8] This model is principally similar to (n,π^*) TICT states and sudden polarization in the excited singlet (π,π^*) states. Recently, Horn *et al.* reported electron-transfer fluorescence quenching of electron-deficient benzenes by hexamethyldisilane[9] and an intramolecular CT fluorescence emission of (phenylethynyl)pentamethyldisilanes bearing electron-withdrawing substituents,[10] giving a strong evidence to support the σ(Si–Si) → π^*(aromatic) OICT mechanism.

Although these interesting photophysical properties of aryldisilanes have been extensively investigated, relatively few examples have been reported on the photoreactions involving the intramolecular CT processes.[2,4] Photochemical reactions in the excited singlet states (probably ^{1}CT) of alkynyl-substituted disilane derivatives have been reported to give silacyclopropene derivatives.[2,11] Recently, photoreaction of disilanylquinones and disilanylcyclohexanone have been investigated by Sakurai group. They suggested interesting photoreaction mechanisms involving intramolecular electron-transfer processes in the singlet excited states.[12,13]

We have recently synthesized some 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (**1a–d**) which are a very

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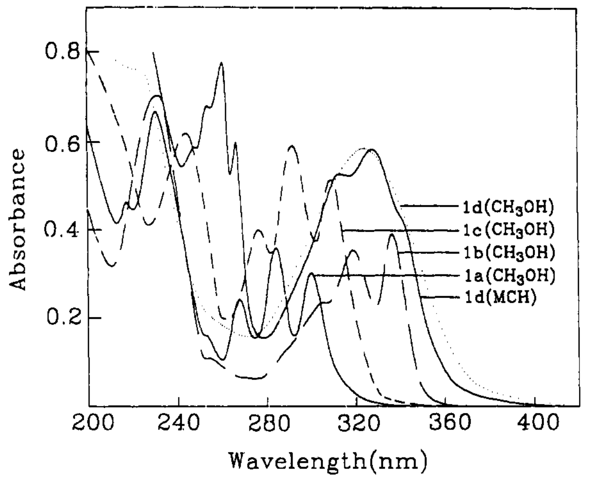

Figure 1. UV absorption spectra of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes in methanol and methylcyclohexane (MCH).

interesting class of organosilicon compounds containing both electron-withdrawing and electron-donating groups in the aryl rings. The photophysical properties of these compounds are investigated and an interesting zwitterionic transient, *via* an intramolecular electron-transfer reaction in the triplet excited state of 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1d**) in ethanol or acetonitrile, is reported in this study.

Results and Discussion

Absorption and Emission Spectra of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes. Figure 1 shows the absorption spectra of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes in methanol and methylcyclohexane. The UV absorption spectra of 1-phenyl-4-(pentamethyldisilanyl)-1,3-butadiyne (**1a**), 1-(1-naphthyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1b**), and 1-(*p*-methoxyphenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1c**) show the characteristic vibrational fine structure corresponding to the vibrational stretching bands of acetylene. The absorption maximum of 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1d**) is shifted to longer wavelength from that of **1a** and **1c**. The absorption spectra of **1d** become broad in polar solvents probably due to a charge-transfer interaction between the nitro and disilanyl group in excited states which are stabilized by polar solvents.

The emission spectra of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes were measured over the temperature range from 298 to 77 K in both polar and nonpolar solvents and rigid organic glasses. No fluorescence was observed from **1a**, **1c**, and **1d** even at 77 K but **1b** shows fluorescence with a maximum at 353 nm in methanol. This emission corresponds to that of a locally excited state with a lifetime of ca. 1.0 ns at 298 K in methanol. No charge-transfer emission is observed in any of these compounds. All the 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiyne derivatives show strong phosphorescence with strong 0–0 bands around 460~550 nm at 77 K in organic glasses, indicating the triplet energies of these compounds lie around 218–260 kJ/mol as shown in Table 1. These phosphorescence emissions show the unique vibrational stretching bands at 77 K as reported for (phenylethynyl)pentamethyldisilanes.[10]

Nanosecond Laser Photolysis of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes. Laser excitation (266 nm) of deaerated solutions of **1a**, **1b**, and **1c** in ethanol shows triplet state transients with lifetimes of 8.2, 3.4, and 13.0 μs in ethanol, and they are efficiently quenched by oxygen. The triplet–triplet absorption spectra of **1b** and **1c** show absorption bands at 410 and 480 nm, respectively (Table 1). The absorption maximum in the triplet–triplet absorption spectrum of **1a** is not observed probably because it lies in the wavelength region shorter than 370 nm or is hidden under the strong S_0–S_1 absorption. The laser flash photolysis (using 355 nm) of **1d** in nonpolar solvents results in the formation of a triplet state, and triplet–triplet absorption spectra are dependent of the solvent polarity as shown in Figure 2. The triplet–triplet absorption maximum at 470 nm in methylcyclohexane is shifted to longer wavelength (560 nm in acetone) as the solvent polarity increases. The triplet state lifetime varies from 1.3 to 7.2 μs as the polarity of solvents is changed as shown in Table 2 suggesting a charge transfer (CT) between the nitro and disilanyl group in the triplet excited state, and this CT state is stabilized by increasing the solvent polarity.

Laser photolysis of **1d** in ethanol or acetonitrile results in the formation of a long-lived transient which is observed 500 ns after laser pulsing. The intensity of the transient absorption is decreased in the presence of oxygen, suggesting that the transient is formed from the excited triplet state of **1d**. The absorption maximum appears at 400 nm as shown in Figure 3. The transient species shows complex decay curves in ethanol and acetonitrile. The decay of the transient species in ethanol seems to occur by both first- and second-order processes. Within 5 ms after the laser pulsing, the decay of the transient in ethanol seems to approach the second-order kinetics. After 5 ms, the decay of transient follows the first order kinetics with a rate constant of 7.5×10^1 s^{-1}. The rate constant that followed the first-order kinetics is changed to 2.3×10^2 s^{-1} in the presence of oxygen which indicates very slow oxygen quenching compared to diffusion-controlled oxygen quenching of excited triplet states. It has been reported that the electron transfer from radical anions of nitroaromatic compounds ($ArNO_2^{-\bullet}$) to oxygen takes place very slowly with rate constants in the range of 10^5–10^7 M^{-1} s^{-1},[15] and the decays of the radical anions of $ArNO_2$ show considerable contribution from the second-order kinetics in most cases.[16] In spite of these second-order decays, these radical anions are sufficiently long-lived to engage in subsequent electron-transfer reactions or equilibria.[16] The lifetime and oxygen quenching rate of the long-lived transient are very similar to those of the radical anions of $ArNO_2$, suggesting that the transient is a radical anion species (zwitterion species) of **1d** formed by intramolecular electron transfer from the disilanyl group to the nitro group.

The laser photolysis of 1-(*p*-nitrophenyl)-4-(trimethylsilyl)-1,3-butadiyne was carried out to confirm the

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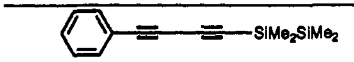
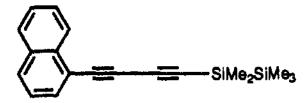
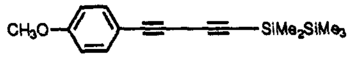
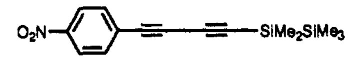
Table 1. Triplet Energy and Lifetime of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes

compounds	phosphorescence λ_{max} (0–0 band), nm EtOH	phosphorescence λ_{max} (0–0 band), nm MCH[a]	triplet energy (kJ/mol) EtOH	triplet energy (kJ/mol) MCH[a]	T–T absorption (λ_{max}), nm	triplet lifetime (μs, at 298 K)
 (1a)	458	460	2621	2612	>370 (EtOH)	8.2 (EtOH)
 (1b)	549	549	218.8	218.8	480 (EtOH)	3.4 (EtOH)
 (1c)	462	464	256.0	258.7	410 (EtOH)	13.0 (EtOH)
 (1d)	498	500	241.1	240.2	470 (MCH[a])	1.3 (MCH[a])

[a] MCH: methylcyclohexane.

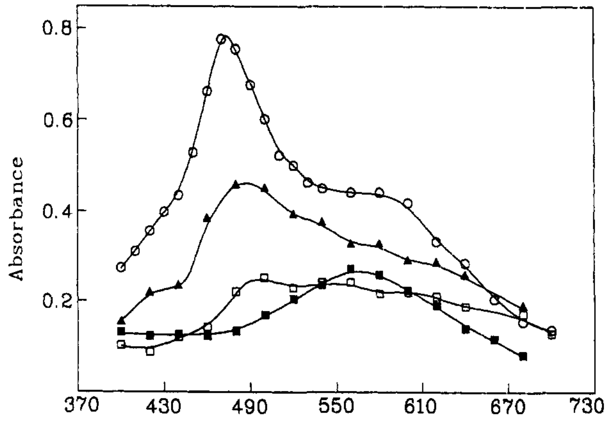


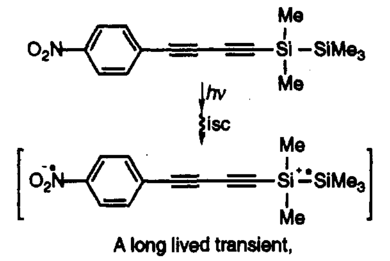
Figure 2. Triplet–triplet absorption spectra of **1d** (4–5 × 10^{-5} M) in various solvents: (○) methylcyclohexane, (▲) ethylacetate, (□) methylene chloride, (■) acetone.

Table 2. Triplet Lifetime of 1d in Various Solvents at 298 K

solvents	dielectric constants[a]	triplet lifetimes (μs)
methylcyclohexane	2.02[b]	1.3
ethyl acetate	6.02	1.6
dichloromethane	8.93	4.5
diethyl ketone	17.0	8.5
acetone	20.56	7.2

[a] From ref 14. [b] Dielectric constant of cyclohexane is used for methylcyclohexane.

intramolecular electron-transfer process in **1d**. Laser excitation (355 nm) of deaerated solutions of 1-(*p*-nitrophenyl)-4-(trimethylsilyl)-1,3-butadiyne in ethanol shows only a triplet state transient with lifetime of 1.2 μs, and the triplet–triplet absorption spectrum shows an absorption maximum at 520 nm, indicating that σ(Si–Si) bond of **1d** in polar solvents can be a good electron donor in the excited state.



A long lived transient, λ_{max} 400 nm in EtOH

In order to identify the zwitterion species, the quenching study of the transient by *N,N*-dimethylaniline (DMA), a good electron donor, was carried out. The time trace was recorded at 400 nm following 355 nm excitation of 5 × 10^{-5} M solution of **1d** in the presence of DMA (1 M). As shown in Figure 4, initially formed transient after laser excitation is quenched by DMA and a new transient is formed about 5 ms after laser pulsing. The absorption maximum of the new transient also appears at 400 nm as observed in the long-lived transient, suggesting that both the new transient and long-lived transient (zwitterion species) have a very

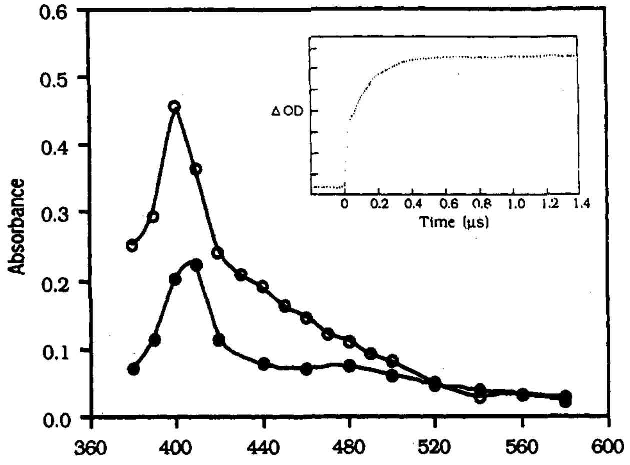


Figure 3. Transient absorption spectra of **1d** (4.6–4.7 × 10^{-5} M) observed 500 ns after laser pulsing in polar solvents: (○) ethanol, (●) acetonitrile. Traces (insert) obtained at 400 nm in ethanol.

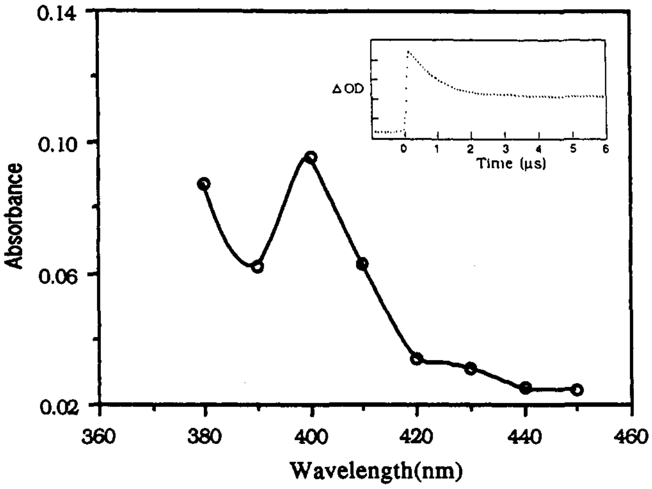


Figure 4. Transient absorption spectrum of **1d** (4.6 × 10^{-5} M) monitored 5 μs after laser pulsing in the presence of *N,N*-dimethylaniline (1 M) and trace (insert) obtained at 400 nm.

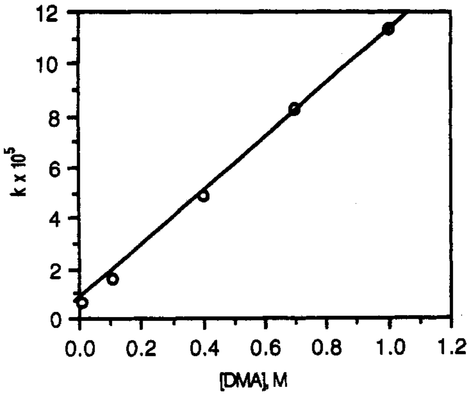


Figure 5. Quenching of the long-lived transient by *N,N*-dimethylaniline (DMA).

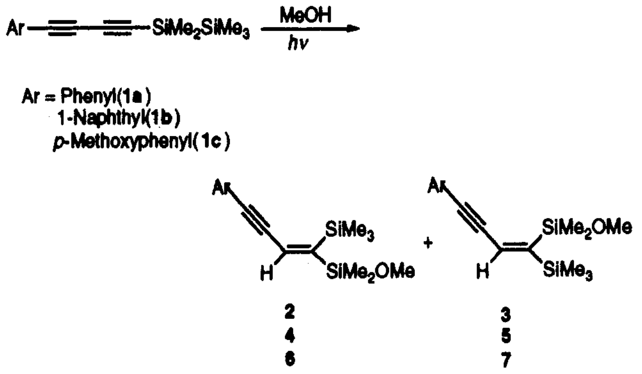
similar chromophore. These can be explained by the electron transfer from *N,N*-dimethylaniline to the disilanyl radical cation center of zwitterionic **1d**, and a new transient formed is very likely to be a radical anion of **1d**. The bimolecular quenching constant by DMA is determined to be 1.1 × 10^7 M^{-1} s^{-1} by plotting the decay rate constant of the long-lived transient based on eq 1in the various

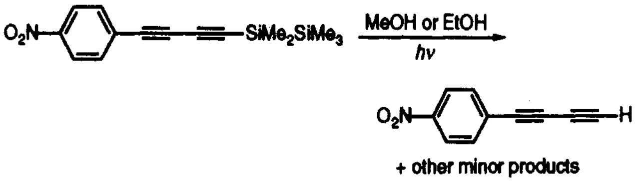
$$k_{obs} = k_o + k_q[\mathrm{DMA}] \qquad (1)$$

concentrations of DMA (10^{-2}–1 M) as shown in Figure 5, where k_{obs} and k_o are pseudo-first-order rate constants for transient decay in the presence and absence of DMA, respectively.

The laser photolysis studies indicate that the triplet excited state of **1d** has charge-transfer character which results in the formation of a long-lived transient by intramolecular electron transfer from the disilanyl group to the nitro group in polar solvents. This intramolecular electron-transfer reaction seems to be strongly dependent on solvent polarity. The observed transient is considered to be a zwitterionic triplet (triplet biradical) species since the transient is formed from the triplet excited state and the lifetime is very long. Recently, Sakurai *et al.* have reported an interesting intermediate showing triplet electron spin resonance (ESR) spectra in the photoreaction of disilanylcyclohexenone at 77 K.[13] However, they did not explain why the observed intermediate gives triplet ESR spectra in spite of the photoreaction proceedings from the singlet excited state. The results of ESR spectra suggest that this intermediate may be derived from the triplet excited state, supporting that the σ(Si–Si) bond in the disilane compounds can be a good electron donor in the triplet excited state.

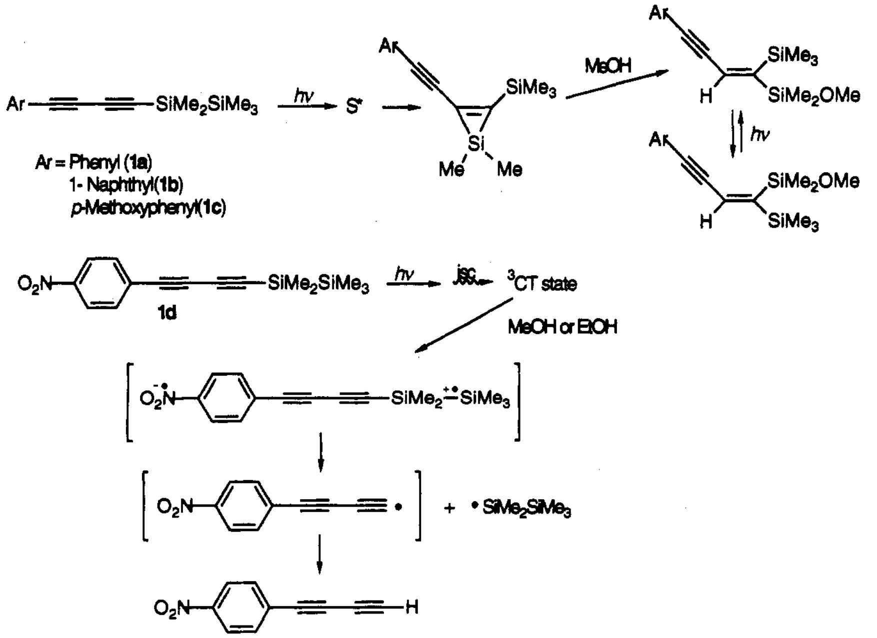
Photochemical Reaction. Irradiation of **1a–c** in methanol gives the photoaddition products (**2–7**) in 15–25% yields, while photolysis of **1d** in methanol or ethanol results in the formation of 1-(*p*-nitrophenyl)-1,3-butadiyne (**8**) through C–Si bond cleavage. Many photoproducts are observed in very low yields by photoreaction of **1d**. Dark yellow products (probably oligomers) are obtained as the major byproduct.





The structure of these photoproducts is determined by various physical methods such as ^1H and ^{13}C NMR spectroscopy. The UV absorption spectra of these photoproducts (**2–7**) do not show the characteristic vibrational

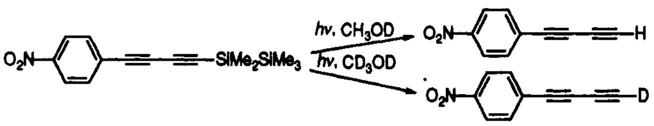
Scheme 1. Plausible Photoreaction Mechanisms of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes



fine structure of conjugated diynes. The absorption maxima are red-shifted compared to parent diynes. Mass spectra of **2**–**7** show the molecular ion (M^+) peaks indicating that the photoproducts are formed by addition of one methanol molecule to parent diynes. In the ^{13}C NMR spectra of photoadducts **2**–**7**, trimethylsilyl-substituted sp^2 carbon (C4) peaks appear at 157–160 ppm. In the distortionless enhancement by polarization transfer (DEPT) experiments of **2**–**7**, these sp^2 peaks are assigned to be quaternary carbons indicating that the dimethylmethoxysilyl group in the photoproducts is attached to the C4 carbon. The structure of photoisomers **2**, **4**, and **6** could be distinguished from that of **3**, **5**, and **7**, respectively, on the basis of the ^1H NMR spectra of the isomer pairs. The ^1H NMR spectra of *cis* isomers **3**, **5**, and **7** show an upfield shift for the dimethylmethoxysilyl group due to the ring current of the phenyl or naphthyl ring, while their isomers show the upfield shift for the trimethylsilyl group but not the dimethylmethoxysilyl group. The ^1H NMR spectrum of photoproduct **8** shows the acetylenic proton at 2.62 ppm.

Photoreaction Mechanism. Photochemical reactions of (phenylethynyl)disilanes in the presence of methanol were reported to give mainly photoaddition products through the silacyclopropene intermediates in the singlet excited states.[2,11] The major addition product has *trans* configuration between the phenyl and dimethylmethoxysilyl groups and isomerizes to give *cis* isomer on further irradiation.[2,16] The silacyclopropene intermediates cannot be isolated in general because of the high reactivity toward air and moisture except for some cases. In the photoreactions of **1a**–**c** in methanol, no silacyclopropene photoproduct was isolated. After irradiation of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (2 mM) in 5 mL of dry benzene in the absence of methanol for 2 h, 0.5 mL of methanol was added to the reaction mixture to identify the formation of silacyclopropene as the intermediate. The addition products **2**, **4** and **6** having a *trans* configuration were detected by HPLC from **1a**, **1b**, and **1c**, strongly supporting the formation of silacyclopropene photoproducts but not from **1d**. The photoreactions of **1a**–**c** in methanol are not quenched by oxygen suggesting the photoreactions to proceed *via* silacyclopropene intermediates in the singlet excited state as shown in Scheme 1.

Irradiation of **1d** in methanol or ethanol yields 1-(*p*-nitrophenyl)-1,3-butadiyne (**8**). Irradiation of **1d** in CH_3OD does not give any deuterium incorporation in the acetylenic hydrogen while photoreaction in CD_3OD yields deuterium-incorporated product, indicating a radical mechanism for the photoreaction since methyl hydrogens instead of the hydroxyl proton in methanol are abstracted.



The photoreaction of **1d** and the long-lived transient in ethanol are efficiently quenched by amines such as *N,N*-dimethylaniline and triethylamine, indicating that the transient is the precursor of the photoproduct **8**. A plausible mechanism involving an intramolecular electron-transfer process in polar solvents is proposed in Scheme 1. The triplet charge-transfer state of **1d** results in the formation of a long-lived transient (zwitterion species) in polar solvents, the C–Si bond is cleaved homolytically from the transient, and the radical abstracts a hydrogen from the methyl group of methanol.

Conclusion

All the 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (**1a**–**d**) show strong phosphorescence emission at 77 K. The triplet energies of these compounds lie around 218–260 kJ/mol above the ground state. Laser flash photolysis of **1d** indicated that both the triplet–triplet absorption and triplet lifetime are dependent on the solvent polarity due to the charge-transfer (CT) character of the excited triplet state between the nitro and disilanyl group. Laser photolysis of **1d** in ethanol results in the formation of an interesting transient which is observed 500 ns after laser pulsing and quenched by oxygen (electron acceptor) and *N,N*-dimethylaniline (electron donor). The transient is probably formed by an intramolecular electron-transfer process from the disilanyl to nitro the group in polar solvents such as ethanol or acetonitrile. Irradiation of **1d** in methanol or ethanol gives 1-(*p*-nitrophenyl)-1,3-butadiyne (**8**) through C–Si bond cleavage. The photoproduct **8** is formed from the triplet excited state of **1d**, and the photoreaction proceeds through a radical mechanism from the transient. Irradiation of **1a**–**c** in methanol gives the photoaddition products **2**–**7** through silacyclopropene intermediates from the singlet excited states.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-300, Bruker AC-200, and Varian FT80 A spectrometers in $CDCl_3$. Laser photolysis studies were carried out by using the third (355 nm) and fourth (266 nm) harmonic of a Nd:YAG laser (Model HY 500 from JK Laser Ltd.); the duration was ca. 20 ns and the energies of the third and fourth harmonic are, respectively, ca. 100 and 60 mJ/pulse. The detection system of the transient spectra has been previously reported.[17] Laser photolysis was carried out by using a quartz cell with a optical path length of 1 cm. All the sample solutions were degassed on a vacuum line. The concentrations of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes were $1-7 \times 10^{-5}$ M range. A chromatography column of silica gel was prepared with Kieselgel (70–230 mesh). (*Z*)-1-Methoxybut-1-en-3-yne was purchased from Aldrich and purified according to the literature procedure prior to use.[18] Bis(triphenylphosphine)palladium dichloride,[19] pentamethylchlorodisilane,[20] and 1-(trimethylsilyl)-1,3-butadiyne[21] were prepared by the reported methods. Aryl iodides (iodobenzene, 1-iodonaphthalene, 4-iodoanisole, and 1-iodo-4-nitrobenzene) were purchased from Aldrich and used without further purification. THF was freshly distilled from sodium and benzophenone prior to use. Triethylamine, methanol, and ethanol were used after distillation.[22] Solvents of reagent grade were used for chromatography without further purification. Spectroscopic grade solvents (Merck) were used for HPLC and absorption and emission measurements.

Synthesis of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (1a–d). Some 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (**1a**–**d**) were prepared, as shown in Scheme 2, by the use of (*Z*)-1-methoxybut-1-en-3-yne as a diyne source. Aryl

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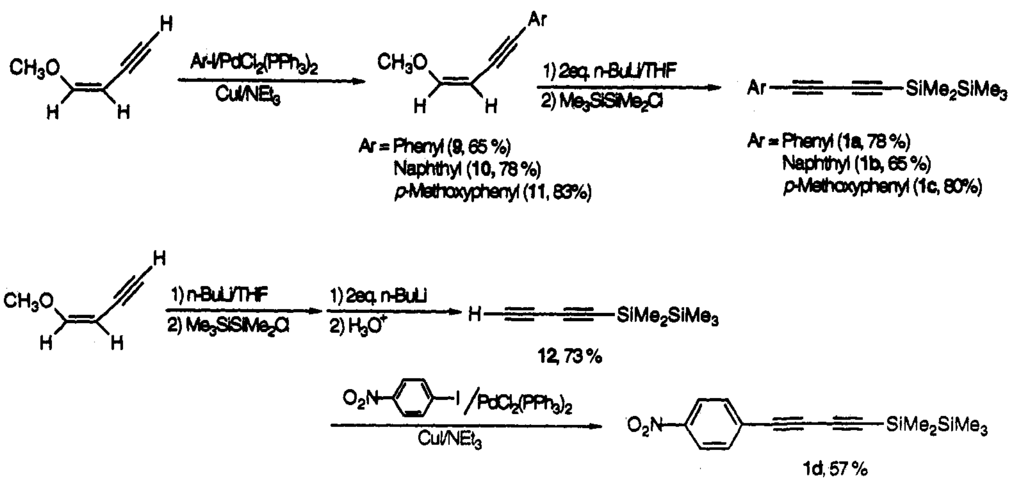
Scheme 2. Synthetic Routes for 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes



groups were introduced by using $PdCl_2(PPh_3)_2$ as a catalyst. *n*-BuLi (Aldrich) was used for preparing butadiynes.

(*Z*)-1-Methoxy-4-arylbut-1-en-3-ynes (9–11). A deaerated solution of (*Z*)-1-methoxybut-1-en-3-yne (32 mmol) and aryl iodide (30 mmol) in deaerated anhydrous triethylamine (80 mL) were added to bis(triphenylphosphine)palladium dichloride (421 mg, 0.6 mmol) and copper(I) iodide (228 mg, 1.2 mmol) under nitrogen atmosphere. The mixture was heated and maintained at 30 °C for 50 min. After evaporation of solvent, the reaction mixture was extracted with petroleum ether and decolorized with activated charcoal. The reaction mixture was filtered and concentrated. **9**, **10**, and **11** were separated in 65, 78, and 83% yields, respectively, by column chromatography using the following conditions. Eluents: **9**, *n*-hexane/diethyl ether (10/1, v/v); **10**, *n*-hexane/diethyl ether (5/1, v/v); **11**, *n*-hexane/diethyl ether (2/1, v/v). **9**: ^1H NMR (300 MHz) δ 7.56 (m, 2H), 7.41 (m, 3H), 6.40 (d, 1H), 4.85 (d, 1H), 3.87 (s, 3H) ppm; MS, *m/e* 158 (M^+, 100%), 115 ($M^+ - C_2H_3O$, 83.4%); HRMS (M^+) calcd for $C_{11}H_{10}O$ 158.0732, found 158.0733. **10**: ^1H NMR (80 MHz) δ 7.3 (m, 7H), 6.4 (d, 1H), 5.0 (d, 1H), 3.8 (s, 3H) ppm; MS, *m/e* 208 (M^+, 100%), 165 ($M^+ - C_2H_3O$, 66.8%); HRMS (M^+) calcd for $C_{15}H_{12}O$ 208.0888, found 208.0886. **11**: ^1H NMR (300 MHz) δ 7.30 (d, 2H), 6.73 (d, 2H), 6.20 (d, 1H), 4.64 (d, 1H), 3.69 (s, 6H) ppm; ^{13}C NMR (75 MHz) δ 158.9, 155.6, 132.5, 115.7, 113.6, 92.4, 85.3, 82.3, 76.9, 60.4, 54.9 ppm; MS, *m/e* 188 (M^+, 100%), 145 ($M^+ - C_2H_3O$, 61.3%); HRMS (M^+) calcd for $C_{11}H_{10}O$ 188.0837, found 188.0835.

1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (1a–c). A solution of (*Z*)-1-methoxy-4-arylbut-1-en-3-yne (20 mmol) in THF (50 mL) was treated with *n*-BuLi (40 mmol) at −40 to −45 °C followed by pentamethylchlorodisilane (25 mmol). The reaction mixture was warmed to room temperature and stirred for 1 h. After evaporation of solvent, the reaction mixture was extracted with petroleum ether and dried with $MgSO_4$. Compound **1a** (colorless liquid) was separated in 78% yield by column chromatography using *n*-hexane as eluent. **1b** and **1c** were separated in 65 and 80% yields as white solids, respectively, by column chromatography using the following conditions. Eluents: **1b**, *n*-hexane; **1c**, *n*-hexane/diethyl ether (20/1, v/v). Pure **1b** and **1c** were obtained by crystallization from methanol. **1a**: ^1H NMR (300 MHz) δ 7.46–7.32 (m, 5H), 0.25 (s, 6H), 0.16 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 132.6, 129.2, 128.4, 121.6, 90.2, 89.8, 76.6, 74.5, −2.6, −3.4 ppm; UV (MeOH) λ_{max} 300.4, 283.0, 267.5, 253.0, 231.7 nm; MS, *m/e* 256 (M^+, 17.2%), 241 ($M^+ - CH_3$, 100%), 183 ($M^+ - SiMe_3$, 23.2%); HRMS (M^+) calcd for $C_{15}H_{20}Si_2$ 256.1104, found 256.1093. Anal. Calcd for $C_{15}H_{20}Si_2$: C, 70.24; H, 7.86. Found: C, 70.73; H, 7.82. **1b**: mp 58–59 °C; ^1H NMR (300 MHz) δ 8.37–7.26 (m, 7H), 0.33 (s, 6H), 0.25 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 134.0, 133.0, 132.2, 129.7, 128.4, 127.2, 126.6, 126.1, 125.1, 119.2, 91.4, 89.9, 79.1, 74.9, −2.5, −3.3 ppm; UV (MeOH) λ_{max} 337.8, 318.8, 304.2, 255.9, 234.8 nm; MS, *m/e* 306 (M^+, 26.3%), 291 ($M^+ - CH_3$, 49.6%), 233 ($M^+ - SiMe_3$, 30.5%), 73 ($SiMe_3^+$, 100%); HRMS (M^+) calcd for $C_{19}H_{22}Si_2$ 306.1260, found 306.1267. Anal. Calcd for $C_{19}H_{22}Si_2$: C, 74.44; H, 7.23. Found: C, 74.58; H, 7.28. **1c**: mp 69 °C; ^1H NMR (300 MHz) δ 7.43 (d, 2H), 6.83 (d, 2H), 3.81 (s, 3H), 0.25 (s, 6H), 0.18 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 160.4, 134.2, 114.1, 113.4, 90.1, 89.4, 76.6, 73.4, 55.2, −2.6, −3.3 ppm; UV (MeOH) λ_{max} 309.7, 292.2, 276.5, 243.4 nm; MS, *m/e* 286 (M^+, 31.4%), 291 ($M^+ - CH_3$, 100%), 233 ($M^+ - SiMe_3$, 16.8%); HRMS (M^+) calcd for $C_{16}H_{22}OSi_2$ 286.1209, found 286.1202. Anal. Calcd for $C_{16}H_{22}OSi_2$: C, 67.07; H, 7.74. Found: C, 67.08; H, 7.72.

1-(Pentamethylsilanyl)-1,3-butadiyne (12). A solution of (*Z*)-1-methoxybut-1-en-3-yne (30 mmol) in THF (60 mL) was treated with n-BuLi (30 mmol) at −78 °C followed by pentamethylchlorodisilane (32 mmol). The mixture was warmed to 0 °C and stirred for 1 h. Compound **12** was prepared by treatment of the mixture at −40 to −45 °C with *n*-BuLi (60 mmol) for 30 min followed by pouring into 1 N HCl solution. After extraction with *n*-pentane, the solvent was removed under the reduced pressure and the residue was purified by column chromatography using *n*-pentane as an eluent to give **12** in 73% yield. **12**: ^1H NMR (300 MHz) δ 2.08 (s, 1H), 0.19 (s, 6H), 0.11 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 89.4, 84.2, 68.6, 66.5, −2.7, −3.6 ppm; MS, *m/e* 180 (M^+, 18.6%), 165 ($M^+ - CH_3$, 100%); HRMS (M^+) calcd for $C_9H_{16}Si_2$ 180.0791, found 180.0785.

1-(*p*-Nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (1d) and 1-(*p*-Nitrophenyl)-4-(trimethylsilyl)-1,3-butadiyne. A deaerated solution of substituted 1,3-butadiynes (**12** or 1-(trimethylsilyl)-1,3-butadiyne, 18 mmol) and 1-iodo-4-nitrobenzene (15 mmol) in deaerated anhydrous triethylamine (80 mL) were added to bis(triphenylphosphine)palladium dichloride (253 mg, 0.36 mmol) and copper(I) iodide (137 mg, 0.72 mmol) under nitrogen atmosphere. The mixture was heated and maintained at 30 °C for 30 min. After evaporation of solvent, the reaction mixture was extracted with petroleum ether and decolorized with activated charcoal. The reaction mixture was filtered and concentrated and separated by column chromatography using *n*-hexane/diethyl ether (30/1, v/v) as an eluent to give **1d** and **1-(*p*-nitrophenyl)-4-(trimethylsilyl)-1,3-butadiyne** in 57 and 59% yield as white solids, respectively. Pure **1d** and **1-(*p*-nitrophenyl)-4-(trimethylsilyl)-1,3-butadiyne** were obtained by crystallization from methanol. **1d**: mp 111–112 °C; ^1H NMR (300 MHz) δ 8.15 (d, 2H), 7.50 (d, 2H), 0.24 (s, 6H), 0.14 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 147.4, 133.3, 128.6, 123.6, 94.2, 88.9, 79.3, 74.1, −2.6, −3.8 ppm; UV (MeOH) λ_{max} 325.7 nm; MS, *m/e* 301 (M^+, 19.8%), 286 ($M^+ - CH_3$, 100%), 228 ($M^+ - SiMe_3$, 10.4%); HRMS (M^+) calcd for $C_{15}H_{19}NO_2Si_2$ 301.0954, found 301.0927. Anal. Calcd for $C_{15}H_{19}NO_2Si_2$: C, 59.76; H, 6.35; N, 4.65. Found: C, 59.92; H, 6.33; N, 4.66.
1-(*p*-Nitrophenyl)-4-(trimethylsilyl)-1,3-butadiyne: ^1H NMR (200 MHz) δ 8.15 (d, 2H), 7.59 (d, 2H), 0.22 (s, 3H) ppm; ^{13}C NMR (50 MHz) δ 147.6, 133.4, 128.4, 123.6, 94.2, 86.9, 79.0, 74.1, −0.6 ppm; UV (EtOH) λ_{max} 317.8 nm; MS, *m/e* 243 (M^+, 27.0%), 228 ($M^+ - CH_3$, 100%); HRMS (M^+) calcd for $C_{12}H_{12}NO_2Si$ 243.0716, found 243.0729.

Irradiation of 1-Aryl-4-(pentamethyldisilanyl)-1,3-butadiynes (1a–d) in Methanol. Deaerated solutions (2 mM) of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes **1a–c** in methanol were irradiated with 300-nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300-nm lamps. After irradiation for 24 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts (**2**–**3** and **4**–**5**) of **1a** and **1b** were isolated in 13, 17, 25, and 25% yields, respectively, by column chromatography with *n*-hexane/diethyl ether (50/1, v/v) as an eluent followed by normal-phase HPLC using *n*-hexane/diethyl ether (60/1, v/v) as an eluent. **2**: ^{1}H NMR (300 MHz) δ 7.47–7.45 (m, 2H), 7.37–7.33 (m, 3H), 6.79 (s, 1H), 3.49 (s, 3H), 0.41 (s, 6H), 0.18 (s, 9H) ppm; ^{13}C NMR (50 MHz) δ 159.8, 132.8, 131.3, 128.4, 123.3, 94.3, 90.4, 50.1, −0.6, −0.9 ppm; UV (MeOH) λ_{max} 304.8, 286.9 nm; MS, *m/e* 288 (M$^+$, 8.0%), 273 (M$^+$ − CH$_3$, 76.1%), 159 (M$^+$ − C$_4$H$_9$Si$_2$O, 100%); HRMS (M$^+$) calcd for C$_{16}$H$_{24}$OSi$_2$ 288.1366, found 288.1331. **3**: ^{1}H NMR (300 MHz) δ 7.48–7.45 (m, 2H), 7.37–7.34 (m, 3H), 6.92 (s, 1H), 3.43 (s, 3H), 0.34 (s, 9H), 0.27 (s, 6H) ppm; ^{13}C NMR (75 MHz) δ 157.3, 133.4, 131.3, 128.5, 128.4, 123.3, 95.8, 90.4, 50.4, 0.0, −1.5 ppm; UV (MeOH) λ_{max} 306.1, 288.7 nm; MS, *m/e* 288 (M$^+$, 6.4%), 273 (M$^+$ − CH$_3$, 51.6%), 159 (M$^+$ − C$_4$H$_9$Si$_2$O, 100%); HRMS (M$^+$) calcd for C$_{16}$H$_{24}$OSi$_2$ 288.1366, found 288.1400. **4**: ^{1}H NMR (300 MHz) δ 8.45–8.42 (m, 1H), 7.90–7.85 (m, 2H), 7.74–7.71 (m, 1H), 7.63–7.45 (m, 3H), 7.01 (s, 1H), 3.55 (s, 3H), 0.51 (s, 6H), 0.26 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 159.6, 133.2, 131.5, 130.4, 128.9, 128.2, 126.7, 126.4, 126.3, 125.3, 121.0, 95.0, 92.6, 50.1, −0.6, −0.7 ppm; UV (MeOH) λ_{max} 342.0, 326.2, 230.0 nm; MS, *m/e* 338 (M$^+$, 28.9%), 273 (M$^+$ − CH$_3$, 63.6%), 209 (M$^+$ − C$_4$H$_9$Si$_2$O, 96.8%); HRMS (M$^+$) calcd for C$_{20}$H$_{26}$OSi$_2$ 338.1522, found 338.1500. **5**: ^{1}H NMR (300 MHz) δ 8.36–8.33 (m, 1H), 7.86–7.81 (m, 2H), 7.69–7.66 (m, 1H), 7.57–7.41 (m, 3H), 7.07 (s, 1H), 3.45 (s, 3H), 0.35 (s, 9H), 0.28 (s, 6H) ppm; ^{13}C NMR (75 MHz) δ 157.2, 133.5, 133.2, 133.1, 130.3, 128.9, 128.3, 126.7, 126.4, 126.2, 125.3, 121.0, 95.0, 94.1, 50.4, 0.1, −1.5 ppm; UV (MeOH) λ_{max} 342.8, 327.1, 229.0 nm; MS, *m/e* 338 (M$^+$, 26.7%), 273 (M$^+$ − CH$_3$, 55.0%), 209 (M$^+$ − C$_4$H$_9$Si$_2$O, 100%); HRMS (M$^+$) calcd for C$_{20}$H$_{26}$OSi$_2$ 338.1522, found 338.1528.

The photoadducts (**6** and **7**) were isolated in 13 and 12% yields by column chromatography with *n*-hexane/diethyl ether (30/1, v/v) as an eluent followed by normal-phase HPLC using *n*-hexane/diethyl ether (40/1, v/v) as an eluent. **6**: ^{1}H NMR (300 MHz) δ 7.36 (d, 2H), 6.84 (d, 2H), 6.74 (s, 1H), 3.80 (s, 3H), 3.45 (s, 3H), 0.35 (s, 6H), 0.12 (s, 9H) ppm; ^{13}C NMR (75 MHz) δ 159.8, 158.2, 132.8, 131.7, 115.4, 114.1, 94.5, 89.5, 55.3, 50.1, −0.6, −0.8 ppm; UV (MeOH) λ_{max} 316.3, 301.8 nm. MS, *m/e* 318 (M$^+$, 21.2%), 303 (M$^+$ − CH$_3$, 27.2%), 189 (M$^+$ − C$_4$H$_9$Si$_2$O, 100%); HRMS (M$^+$) calcd for C$_{17}$H$_{26}$O$_2$Si$_2$ 318.1471, found 318.1477. **7**: ^{1}H NMR (300 MHz) δ 7.40 (d, 2H), 6.90 (s, 1H), 6.87 (d, 2H), 3.83 (s, 3H), 3.42 (s, 3H), 0.32 (s, 9H), 0.24 (s, 6H) ppm; ^{13}C NMR (50 MHz) δ 159.8, 155.6, 133.8, 132.8, 115.4, 114.1, 96.1, 89.4, 55.3, 50.3, 0.0, −1.5 ppm; UV (MeOH) λ_{max} 317.8, 303.7 nm; MS, *m/e* 318 (M$^+$, 18.3%), 303 (M$^+$ − CH$_3$, 30.1%), 189 (M$^+$ − C$_4$H$_9$Si$_2$O, 100%); HRMS (M$^+$) calcd for C$_{17}$H$_{26}$O$_2$Si$_2$ 318.1471, found 318.1478.

Irradiation of 1-(*p*-Nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne in Methanol or Ethanol. A deaerated solution (2 mM) of 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1d**) in methanol or ethanol was irradiated with 350-nm UV light in a Rayonet photochemical reactor equipped with RUL 350-nm lamps. After irradiation for 24 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproduct **8** was isolated in 50–60% yields by column chromatography with *n*-hexane/diethyl ether (10/1, v/v) as an eluent. **8**: ^{1}H NMR (300 MHz) δ 8.19 (d, 2H), 7.65 (d, 2H), 2.62 (s, 1H) ppm; UV (MeOH) λ_{max} 306.0 nm; MS, *m/e* 171 (M$^+$, 100%), 141 (M$^+$ − NO, 26.5%), 125 (M$^+$ − NO$_2$, 33.5%); HRMS (M$^+$) calcd for C$_{10}$H$_5$NO$_2$ 171.0320, found 171.0321.

Irradiation of 1-(*p*-Nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne in CD$_3$OD or CH$_3$OD. Deaerated solutions of 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne (**1d**, 5 mg) in CD$_3$OD (5 mL, 99.8 atom %) and CH$_3$OD (5 mL, 99.5+ atom %) were irradiated with 350-nm UV light, respectively. After irradiation for 2 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproducts were isolated by column chromatography with *n*-hexane/diethyl ether (10/1, v/v) as an eluent in the darkroom. The deuterium incorporation was identified by comparing with the ^{1}H NMR spectra of the photoproducts. The photoproduct formed in CD$_3$OD only showed a trace at 2.62 ppm.

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