# Photochemistry of 1,4-Bis(pentamethyldisilanyl)butadiyne: Formation of Silacyclopropene Intermediates[†]

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*Received October 30, 1995*[⊗]

*Summary: Irradiation of 1,4-bis(pentamethyldisilanyl)-butadiyne (**BPDB**) in methanol yields two 1:1 photoaddition products (**1** and **2**) and one 1:2 photoadduct (**3**). Adduct **1** is the primary photoproduct while **2** and **3** are the secondary products, **3** being formed via two silacyclopropene intermediates. Irradiation of **BPDB** with acetaldehyde and acetone in deaerated methylene chloride yields only 1:1 photoadducts (**4**−**6**), probably due to the steric effects of the initially formed 1-oxa-2-silacyclopent-3-ene ring preventing the formation of the second silacyclopropene intermediate from the 1:1 photoadducts.*

## Introduction

The chemical properties of silacyclopropenes have been extensively investigated[1] since the first report on the silacyclopropene structure by Vol'pin *et al.* in 1962,[2] although the proposed structure was soon shown to be incorrect, with the actual structure being the dimer of silacyclopropene, 1,4-disilacyclohexa-2,5-diene.[3] Interestingly, photolysis of alkynyl-substituted disilane derivatives affords a convenient route to the silacyclopropenes.[4−6] In general, most of the silacyclopropenes are thermally stable, but they are extremely reactive toward atmospheric oxygen and moisture. These silacyclopropenes formed from the photolysis of alkynyl-substituted disilanes in methanol or acetone react readily with methanol or acetone. We have recently reported the photophysical and photochemical properties of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes.[7] Silacyclopropenes are formed from singlet excited states of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes, except 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)-1,3-butadiyne, which gives silacyclopropenes from the triplet excited state. In the course of our study, we investigated the photochemistry of 1,4-bis(pentamethyldisilanyl)butadiyne (**BPDB**) expecting formation of two successive silacyclopropene groups as shown in Scheme 1.

## Results and Discussion

Irradiation of **BPDB** in methanol affords two 1:1 photoaddition products (**1** and **2**) and one 1:2 photoadduct (**3**) (Scheme 2).

The structure of these photoproducts is determined by various physical methods such as $^1$H NMR, $^{13}$C NMR, and mass spectrometry. The photoisomers **1** and **2** can be distinguished by nuclear Overhauser effects (NOE). In photoadduct **1**, saturation of methoxy protons enhances the intensity of the olefinic proton, but no NOE enhancement of the olefinic proton is observed in photoadduct **2**. The structure of photoisomers **1** could also be distinguished from that of photoadduct **2** on the basis of the $^1$H NMR spectra of the isomer pair.[4a] The $^1$H NMR of photoadduct **2** showed a downfield shift for the dimethylmethoxysilyl group due to the anisotropy effect of the C≡C triple bond *cis* to this dimethylmethoxysilyl group compared to photoadduct **1**. In the $^1$H NMR spectrum of photoadduct **3**, the chemical shifts of dimethylmethoxysilyl group are similar to those of (*E*)-1-(dimethylmethoxysilyl)-1-(trimethylsilyl)-2-phenylethylene[4a] and photoadduct **1**, suggesting that this dimethylmethoxysilyl group is *trans* to the C=C double bond. If this dimethylmethoxysilyl group was *cis* to the C=C double bond, $^1$H NMR of photoadduct **3** would show an upfield shift for the dimethylmethoxysilyl group due to the anisotropy effect of the C=C double bond. Mass spectra of photoproducts **1**−**3** show the molecular ion peaks ($M^+$) at 342, 342, and 374, respectively, indicating that **1** and **2** are formed by the addition of one methanol molecule to the parent diyne and **3** is a 1:2 photoadduct.

Photochemical reactions of (arylethynyl)disilanes[5,6] and 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes[7] in the presence of methanol were reported to give mainly photoaddition products through the silacyclopropene intermediates formed in the singlet excited states. After irradiation of **BPDB** in dry benzene, methanol was added to the reaction mixture and we observed the formation of methanol addition product **1**. The results

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[†] Dedicated to Professor Pill-Soon Song on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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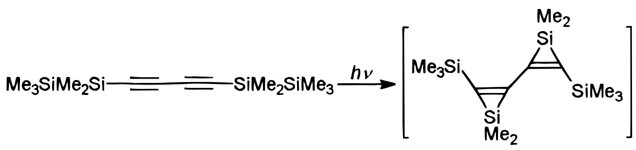
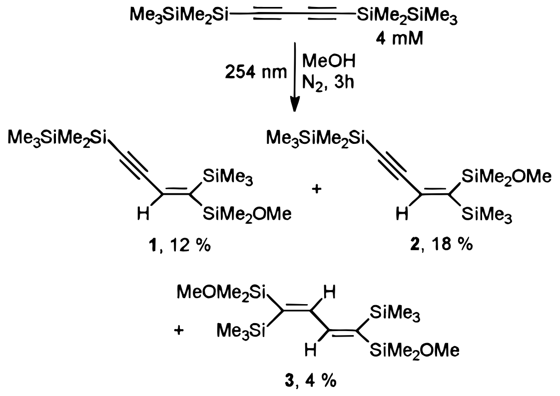
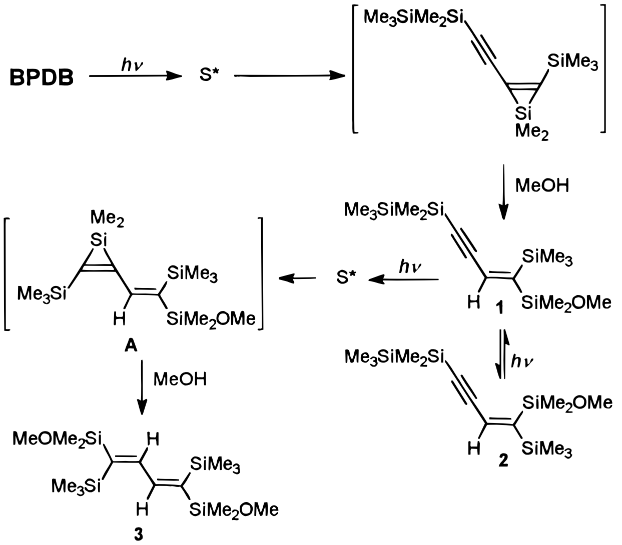
**Scheme 1**



**Scheme 2**



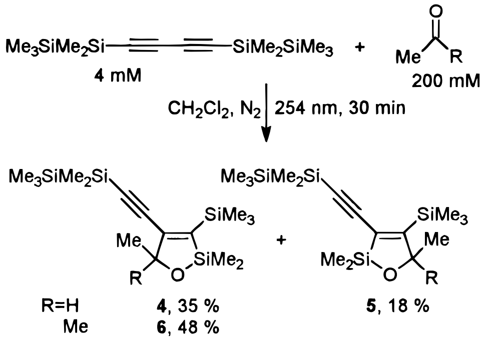
**Scheme 3**



strongly support the formation of silacyclopropene intermediate from **BPDB** and indicate the reaction of the silacyclopropene with methanol is not a photochemical but a thermal reaction. In this experiment, only adduct **1** was detected and further irradiation of the reaction mixture gives the equilibrium mixture of **1**−**3** indicating that adduct **1** is the primary photoproduct and adducts **2** and **3** are the secondary photoproducts. Irradiation of pure adduct **1** gives the same mixture of **1**−**3**, strongly supporting this mechanism. Photolysis of pure adduct **2** in methanol gives the same mixture of **1**−**3**. The photoreaction of **BPDB** in methanol is not quenched by oxygen suggesting that the silacyclopropene intermediate is formed from the singlet excited state of **BPDB**.

From these results, we propose the following reaction mechanism shown in Scheme 3. A silacyclopropene intermediate is formed from the singlet excited state of **BPDB** and reacts with methanol to give a primary photoproduct **1**. Geometrical C=C bond photoisomerization of **1** yields **2**, and another silacyclopropene **A** is formed upon irradiation of **1** and reacts with methanol to give the 1:2 photoadduct **3**.

**Scheme 4**



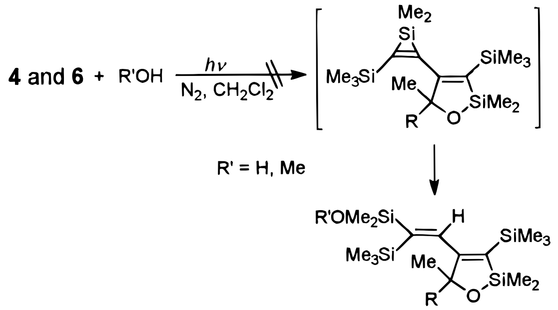
Irradiation of **BPDB** with acetaldehyde and acetone in deaerated methylene chloride yields 1:1 photoadducts **4**−**6** (Scheme 4).

Mass spectra of photoproducts **4**−**6** show the molecular ion peaks ($M^+$) at 354, 354, and 368, respectively, indicating that adducts are formed by the addition of one acetone molecule to the parent diyne. The $^{13}C$ NMR spectra of **4**−**6** show the characteristic methyl-substituted $sp^3$ carbons at 83.2, 83.0, and 87.8 ppm, respectively, supporting the 1-oxa-2-silacyclopent-3-ene moiety. The presence of 1-oxa-2-silacyclopent-3-ene and the location of the trimethylsilyl group on the five-membered ring were determined by comparison with the literature data.[5−7] After irradiation of **BPDB** in dry benzene for 30 min, acetone was added to the reaction mixture but no acetone addition product was obtained. In (arylethynyl)disilanes[5,6] and 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes,[7] the addition reaction between the corresponding silacyclopropenes and acetone proceeded photochemically but not in the dark. The results are the same for **BPDB**. The quantum yield of photoproduct **6** decreased to 5% in aerated solution indicating that triplet excited states are involved in this reaction. Since silacyclopropene intermediate is formed from the singlet excited state of **BPDB**, this process is not quenched by oxygen efficiently indicating that the triplet excited state is involved in the reaction of silacyclopropene intermediate with acetone. Although Seyferth et al. had proposed a mechanism involving $(n, \pi^*)^3$ of the C=O bond which is similar to the photoinduced cycloaddition of carbonyl compounds to simple alkenes,[1c] we have recently proven that the excited triplet state of the silacyclopropene intermediate reacts with acetone to give the addition products.[7b,c]

Photoreaction of **BPDB** with methanol gives 1:1 and 1:2 photoadducts *via* two silacyclopropene units as expected, but with acetaldehyde and acetone only 1:1 photoadducts are obtained probably due to the steric effects of the 1-oxa-2-silacyclopent-3-ene ring which prevents the formation of silacyclopropene from the 1:1 photoadducts. Irradiation of the 1:1 adducts **4** and **6** with methanol or water did not give any methanol or water addition product, and all the starting materials **4** and **6** are recovered, suggesting that the formation of a silacyclopropene intermediate from the adducts **4** and **6** is difficult (Scheme 5).

The electronic and steric factors seem to be important in the chemistry of silacyclopropenes,[1d] but not many examples are available. Both the formation and reaction of silacyclopropene may be affected by the terminal aromatic ring through electronic effects and the intramolecular electron or charge transfer between the

**Scheme 5**



aromatic ring and the disilanyl group.[5,7] The substitution of the aryl ring by the disilanyl group is, therefore, expected to alter the photochemistry of 1,4-bis(pentamethyldisilanyl)butadiyne. But there was no significant difference in photochemical behavior between 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes and **BPDB** indicating that electronic effects are not very significant and steric effects play a more important role. Further studies on the substituent effects (electronic and steric) on the formation and reaction of silacyclopropenes are in progress in our laboratory.

## Experimental Section

**General Comments.** $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC-200 spectrometer with chemical shifts being referenced against the signal of the solvent CDCl$_3$. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector. Lichrosorb Si-60 column was used for preparative analyses. Methylene chloride was dried with P$_2$O$_5$ and followed by fractional distillation immediately prior to use. Acetone was dried with K$_2$CO$_3$ and followed by fractional distillation prior to use. Acetaldehyde was dried with CaSO$_4$ and followed by fractional distillation before use. Oxygen quenching experiments were carried out as described in the literature.[7b]

**Preparation of 1,4-Bis(pentamethyldisilanyl)butadiyne.** 1,4-Bis(pentamethyldisilanyl)butadiyne was prepared by the reported method[8] using chloropentamethyldisilane in 73% yield and recrystallized in methanol: White solid; mp 147−148 °C; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 0.17 (s, 12H), 0.10 (s, 18H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 90.6, 84.8, −2.5, −3.4 ppm; UV (*n*-hexane) $\lambda_{max}$ 290.6, 273.8, 259.1, 229.2 nm; IR (IBr) 2954.8, 2859.4, 2095.5, 1407.1, 1246.1, 836.2, 797.9 cm$^{-1}$; HRMS (M$^+$) calcd for C$_{14}$H$_{30}$Si$_4$ 310.1424, found 310.1424. Anal. Calcd for C$_{14}$H$_{30}$Si$_4$: C, 54.17; H, 9.75. Found: C, 54.16; H, 9.75.

**Irradiation of 1,4-Bis(pentamethyldisilanyl)butadiyne with Methanol.** Deaerated solution of 1,4-bis(pentamethyldisilanyl)butadiyne (4 mM) in methanol was irradiated at 254 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with an RUL 254 nm lamp. After irradiation for 3 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **1**−**3** were isolated in 12%, 18%, and 4% yields, respectively, by silica gel column chromatography using *n*-hexane/diethyl ether (30/1, v/v) as an eluent. The products were purified by normal-phase HPLC using the following eluents: (**1**) *n*-hexane/diethyl ether (60/1, v/v); (**2**) *n*-hexane/diethyl ether (90/1, v/v); (**3**) *n*-hexane/diethyl ether (60/1, v/v).

**1**: colorless oil; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 6.67 (s, 1H), 3.36 (s, 3H), 0.23 (s, 9H), 0.20 (s, 6H), 0.16 (s, 6H), 0.10 (s, 9H) ppm; $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 157.4, 133.8, 107.7, 101.1, 50.3, −0.2, −1.6, −2.5, −3.4 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 266.6 nm; IR (NaCl) 2955.5, 2897.4, 2143.2, 1517.3, 1249.5, 1090.2, 839.5, 800.4 cm$^{-1}$; MS (70 eV) *m*/*z* 342 (M$^+$); HRMS (M$^+$) calcd for C$_{15}$H$_{34}$OSi$_4$ 342.1687, found 342.1700.

**2**: colorless oil; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 6.54 (s, 1H), 3.42 (s, 3H), 0.30 (s, 6H), 0.19 9s, 6H), 0.10 (s, 9H), 0.08 (s, 9H) ppm; $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 160.4, 131.5, 107.8, 99.2, 50.0, −0.7, −1.2, −2.5, −3.3 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 268.1 nm; IR (NaCl) 2935.1, 2128.7, 1523.7, 1245.7, 1094.2, 832.5, 781.6 cm$^{-1}$; MS (70 eV) *m*/*z* 342 (M$^+$); HRMS (M$^+$) calcd for C$_{15}$H$_{34}$OSi$_4$ 342.1687, found 342.1680.

**3**: white solid; mp 85−86 °C; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 7.19 (s, 2H), 3.38 (s, 6H), 0.25 (s, 12H), 0.12 (s, 18H) ppm; $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 154.3, 148.7, 49.8, 0.6, −0.1 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 260.2 nm; IR (NaCl) 2931.0, 1247.9, 1085.4, 905.5, 840.8, 774.4 cm$^{-1}$; MS (70 eV) *m*/*z* 374 (M$^+$); HRMS (M$^+$) calcd for C$_{16}$H$_{38}$O$_2$Si$_4$ 374.1949, found 374.1929.

**Irradiation of 1,4-Bis(pentamethyldisilanyl)butadiyne with Acetone and Acetaldehyde.** Deaerated solution of 1,4-bis(pentamethyldisilanyl)butadiyne (4 mM) and acetone or acetaldehyde (200 mM) in methylene chloride was irradiated at 254 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 30 min, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts (**4**−**6**) were isolated in 35%, 18%, and 48% yields, respectively, by silica gel column chromatography using *n*-hexane/diethyl ether (30/1, v/v) as an eluent. The products were purified by normal-phase HPLC using *n*-hexane/diethyl ether (90/1, v/v) as an eluent.

**4**: colorless oil; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 4.94 (q, 1H), 1.25 (d, 3H), 0.34 (s, 3H), 0.28 (s, 3H), 0.26 (s, 3H), 0.25 (s, 3H), 0.16 (s, 9H), 0.10 (s, 9H) ppm; $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 175.4, 133.2, 104.7, 103.9, 83.2, 24.6, 0.8, −0.01, −0.59, −1.3, −3.2, −3.8 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 272.4 nm; IR (NaCl) 2958.4, 2124.9, 1248.9, 984.2, 838.5, 798.5 cm$^{-1}$; MS (70 eV) *m*/*z* 354 (M$^+$); HRMS (M$^+$) calcd for C$_{16}$H$_{34}$O$_1$Si$_4$ 354.1687, found 354.1665.

**5**: colorless oil; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 4.68 (q, 1H), 1.35 (d, 3H), 0.24 (s, 3H), 0.21 (s, 3H), 0.20 (s, 6H), 0.17 (s, 9H), 0.10 (s, 9H) ppm; $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 160.1, 153.0, 124.8 (two acetylenic carbons), 83.0, 23.1, 2.2, 1.0, −0.7, −2.5, −3.4 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 266.5 nm; IR (NaCl) 2957.5, 2138.1, 1522.8, 1248.4, 1096.9, 835.9, 800.5 cm$^{-1}$; MS (70 eV) *m*/*z* 354 (M$^+$); HRMS (M$^+$) calcd for C$_{16}$H$_{34}$O$_1$Si$_4$ 354.1687, found 354.1665.

**6**: colorless oil; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 1.37 (s, 6H), 0.21 (s, 6H), 0.20 (s, 6H), 0.16 (s, 9H), 0.10 (s, 9H) ppm; $^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 156.9, 144.9, 105.0, 101.5, 87.8, 29.3, 1.8, −0.7, −2.6, −3.4 ppm; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 267.2 nm; IR (NaCl) 2958.3, 2135.2, 1519.2, 1248.2, 836.9, 800.4 cm$^{-1}$; MS (70 eV) *m*/*z* 368 (M$^+$); HRMS (M$^+$) calcd for C$_{17}$H$_{36}$O$_1$Si$_4$ 368.1843, found 368.1862.

**Acknowledgment.** This investigation was supported by OCRC-KOSEF and the Korea Advanced Institute of Science and Technology.

OM950855Y

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