

Photoreaction of 1,4-bis(pentamethyldisilanylethynyl)benzene with methanol or acetone

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Abstract

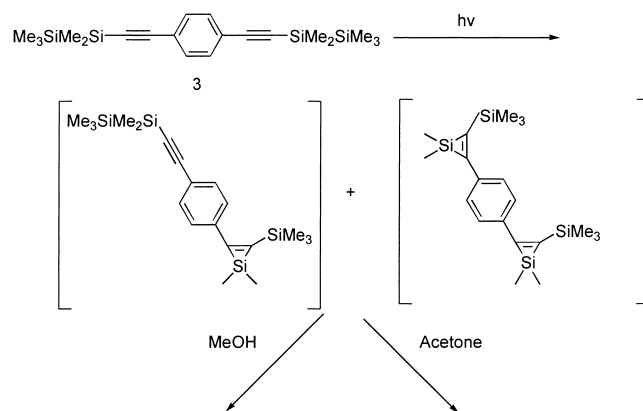
Irradiation of 1,4-bis(pentamethyldisilanylethynyl)benzene **3** in methanol yields two 1 : 1 photoaddition products, **4** and **5**, via silacyclopropene intermediate, while regioselective photoadducts, **9** and **10**, were obtained with acetone in deaerated methylene chloride. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: 1,4-Bis(pentamethyldisilanylethynyl)benzene; Silacyclopropene

1. Introduction

The photolysis of alkynyl-substituted disilanes affords a convenient route to the highly strained silacyclopropenes [1,2]. Most of the silacyclopropenes are extremely unstable toward atmospheric oxygen and moisture and they are trapped by solvents such as methanol or acetone [3]. Silacyclopropenes also react with unsaturated functional groups to give five-membered cyclic organosilicon products [4]. We have recently reported the photochemical behavior of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes [5–7], 1,4-bis(pentamethyldisilanyl)butadiyne [8], and 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanyl ethyne [9,10] in connection with this silacyclopropene intermediates.

In the course of our research, we investigated the photochemistry of 1,4-bis(pentamethyldisilanylethynyl)benzene **3** expecting the formation of two silacyclopropene intermediates in the molecule and extending the interest and utility of the chemistry of silacyclopropenes.



2. Experimental

2.1. General methods

¹H and ¹³C NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent CDCl₃. UV absorption spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC-MS by the electron impact (EI) method. FT-IR spectra were recorded on a Bomem MB-100 spectrometer in KBr pellets and NaCl cell. High-performance liquid chromatography was performed

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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 and Lichrospher RP-18 were used for preparative analyses. Methylene chloride was dried with P_2O_5 followed by fractional distillation prior to use. Acetone was dried with K_2CO_3 followed by fractional distillation immediately prior to use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia) were used for HPLC and UV absorption spectra.

The starting 1,4-bis(pentamethyldisilylethynyl)benzene **3** was prepared by the reaction of 1,4-diethynylbenzene **2** with chloropentamethyldisilane in 89% yield and recrystallized from methanol (Scheme 1).

2.2. Synthesis of 1,4-bis(trimethylsilylethynyl)benzene **1**

To a deaerated solution of 1,4-diiodobenzene (2 g, 6.06 mmol), bis(triphenylphosphine)palladium dichloride (340 mg, 0.48 mmol) and copper(I) iodide (46.2 mg, 0.24 mmol) in anhydrous diethylamine (40 ml) was added dropwise trimethylsilylacetylene (2.14 ml, 15.15 mmol) at room temperature. The reaction mixture was heated at 40°C for 1 h. To this solution saturated ammonium chloride solution (40 ml) was added and the reaction mixture was extracted with ethyl acetate (3 ml \times 30 ml). The combined ethyl acetate solution was washed with H_2O (20 ml), brine (20 ml), and dried ($MgSO_4$), and concentrated in vacuo to give the crude product. Flash column chromatography with ethyl acetate/*n*-hexane (80 : 1, v/v) as eluents gave **1** (1.6 g, 95% yield).

mp 118–119°C; 1H NMR ($CDCl_3$, 300 MHz) δ_H 0.25 (18H, s, $-Si(CH_3)_3$), 7.40 (4H, s, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 0.30, 96.7, 104.9, 123.5, 132.1; UV (CH_2Cl_2) λ_{max} 294 nm ($\epsilon = 71,016 M^{-1} cm^{-1}$), 279 nm ($\epsilon = 57,727 M^{-1} cm^{-1}$); FT-IR (NaCl) 2963.7, 2156.5, 1494.1, 1265.0 cm^{-1} ; MS (70 eV) *m/z* 270 (M^+); HRMS (M^+) calc. $C_{16}H_{22}Si_2$ 270.1260, found 270.1212.

2.3. Synthesis of 1,4-diethynylbenzene **2**

The reaction solution of 1,4-bis(trimethylsilylethynyl)benzene **1** (1.6 g, 5.91 mmol) and sodium hydroxide (0.434 g, 10.8 mmol) in methanol (100 ml) was stirred for 30 min at room temperature. The reaction mixture was acidified with 2N HCl solution, concentrated in vacuo, and extracted with ethyl acetate (3 \times 50 ml). The combined ethyl acetate solution was dried ($MgSO_4$) and evaporated in vacuo to give crude product. Purification by eluents to give 1,4-diethynylbenzene **2** (0.48 g, 94% yield).

1H NMR ($CDCl_3$, 300 MHz) δ_H 3.19 (2H, s, $-C\equiv C-H$), 7.46 (4H, s, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 79.5, 83.4, 123.0, 132.4; UV (CH_2Cl_2) λ_{max} 274 nm

($\epsilon = 22,889 M^{-1} cm^{-1}$), 261 nm ($\epsilon = 21,133 M^{-1} cm^{-1}$); FT-IR (NaCl) 2961.7, 2154.1, 1495.1, 1241.1 cm^{-1} ; MS (70 eV) *m/z* 126 (M^+); HRMS (M^+) calc. for $C_{10}H_6$ 126.0470, found 126.0402.

2.4. Synthesis of 1,4-bis(pentamethyldisilylethynyl)benzene **3**

A solution of 1,4-diethynylbenzene **2** (0.48 g, 3.85 mmol) in THF (30 ml) was treated with *n*-BuLi (7.75 mmol) at 0°C followed by pentamethylchlorodisilane (1.59 ml, 8.30 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min. After evaporation of solvent, the reaction mixture was extracted with ethyl acetate (3 \times 50 ml), washed with water (3 \times 20 ml), and dried with $MgSO_4$. The solvent was removed by column chromatography using *n*-hexane: ethyl acetate (40 : 1, v/v) as an eluent to give **3** (1.26 g, 89% yield).

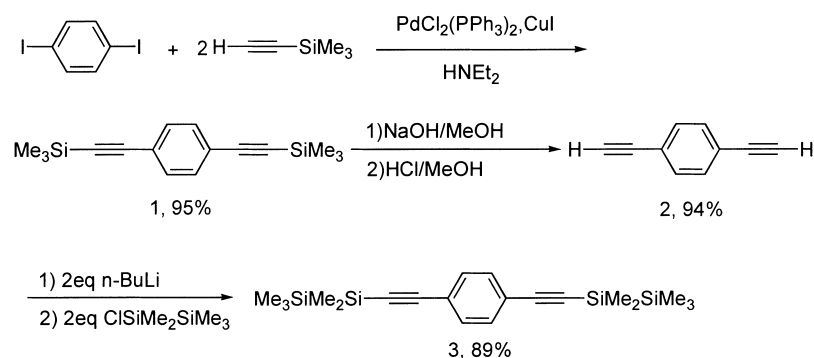
mp 115–116°C; 1H NMR ($CDCl_3$, 300 MHz) δ_H 0.18 (18H, s, $-Si(CH_3)_3$), 0.29 (12H, s, $-Si(CH_3)_2-$), 7.38 (4H, s, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C -2.68, -2.12, 95.8, 107.2, 123.7, 132.1; UV (CH_2Cl_2) λ_{max} 304 nm ($\epsilon = 26,445 M^{-1} cm^{-1}$), 289 nm ($\epsilon = 25,327 M^{-1} cm^{-1}$); FT-IR (NaCl) 2953.6, 2154.3, 1497.7, 1243.2 cm^{-1} ; MS (70 eV) *m/z* 386 (M^+); HRMS (M^+) calc. for $C_{20}H_{34}Si_4$ 386.1738, found 386.1777.

2.5. Irradiation of 1,4-bis(pentamethyldisilylethynyl)benzene **3** in methanol

Deaerated solution ($5 \times 10^{-4} M$) of 1,4-bis(pentamethyldisilylethynyl)benzene **3** (96 mg) in methanol (500 ml) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 1.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, **4** and **5**, were isolated in (19.8 mg, 19% yield) and (15.6 mg, 15% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (80/1) as an eluent followed by reverse phase HPLC (Lichrospher RP-18) using methanol as an eluent.

4 1H NMR ($CDCl_3$, 300 MHz) δ_H 0.02 (9H, s, $-Si(CH_3)_3$), 0.19 (9H, s, $-Si(CH_3)_3$), 0.29 (6H, s, $-Si(CH_3)_2-$), 0.31 (6H, s, $-Si(CH_3)_2-$), 3.47 (3H, s, $-OCH_3$), 7.17 (2H, d, $J = 8.1$ Hz, ArH), 7.42 (2H, d, $J = 8.1$, ArH), 7.81 (1H, s, vinylic H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C -2.59, -2.09, -0.54, 2.06, 50.8, 94.0, 107.6, 122.7, 128.2, 131.8, 142.6, 146.1, 156.2; UV (CH_2Cl_2) λ_{max} 285 nm; FT-IR (NaCl) 2953.6, 2151.2, 1567.0, 1497.5, 1246.9 cm^{-1} ; MS (70 eV) *m/z* 418 (M^+); HRMS (M^+) calc. for $C_{21}H_{38}OSi_4$ 418.2000, found 418.2001.

5 1H NMR ($CDCl_3$, 300 MHz) δ_H 0.06 (6H, s, $-Si(CH_3)_2-$), 0.18 (9H, s, $-Si(CH_3)_3$), 0.20 (9H, s, $-Si(CH_3)_3$), 0.29 (6H, s, $-Si(CH_3)_2-$), 3.30 (3H, s, $-OCH_3$), 7.21 (2H, d, $J = 8.1$ Hz, ArH), 7.40 (2H, d, $J = 8.1$, ArH), 7.68 (1H, s, vinylic H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C -2.60,



–2.10, 0.59, 0.79, 50.2, 94.1, 110.0, 122.7, 128.3, 131.7, 142.3, 147.6, 155.0; UV (CH_2Cl_2) λ_{max} 282 nm; FT-IR (NaCl) 2953.8, 2151.1, 1564.9, 1497.2, 1248.4 cm^{-1} ; MS (70 eV) m/z 418 (M^+); HRMS (M^+) calc. for $\text{C}_{21}\text{H}_{38}\text{OSi}_4$ 418.2000, found 418.2006.

2.6. Irradiation of 1,4-bis(pentamethyldisilanyl)ethynylbenzene **3** with acetone

Deaerated solution (5×10^{-4} M) of 1,4-bis(pentamethyldisilanyl)ethynylbenzene **3** (19 mg) and acetone (34 mM) in methylene chloride (500 ml) was irradiated in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamp. After irradiation for 30 min, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, **9** and **10**, were isolated in (2.2 mg, 10% yield) and (3.1 mg, 16% yield), respectively, by silica gel column chromatography with *n*-hexane/ethyl acetate (90/1, v/v) as an eluent. The products were purified by normal phase HPLC (Lichrosper Si 60) using *n*-hexane/ethyl acetate (60/1, v/v) as an eluent.

9 ^1H NMR (CDCl_3 , 500 MHz) δ_{H} –0.22 (9H, s, –Si(CH₃)₃), 0.15 (9H, s, –Si(CH₃)₃), 0.25 (6H, s, –Si(CH₃)₂–), 0.29 (6H, s, –Si(CH₃)₂–), 1.25 (6H, s, dimethyl), 6.99 (2H, d, $J=8.3$ Hz, ArH), 7.38 (2H, d, $J=8.3$ Hz, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} –3.02, –2.51, 0.27, 2.05, 29.1, 29.7, 87.7, 93.5, 107.0, 122.0, 126.7, 128.4, 131.1, 131.6, 136.6, 142.0, 175.9; UV (CH_2Cl_2) λ_{max} 267, 255 nm; FT-IR (NaCl) 2958.9, 2155.1, 1554.0, 1248.3 cm^{-1} ; MS (70 eV) m/z : 444 (M^+); HRMS (M^+) calc. for $\text{C}_{23}\text{H}_{40}\text{OSi}_4$ 444.2156, found 444.2156.

10 ^1H NMR (CDCl_3 , 500 MHz) δ_{H} –0.23 (9H, s, –Si(CH₃)₃), 0.23 (9H, s, –Si(CH₃)₃), 0.28 (6H, s, –Si(CH₃)₂–), 1.25 (6H, s, dimethyl), 7.00 (2H, d, $J=8.3$ Hz, ArH), 7.40 (2H, d, $J=8.3$ Hz, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} –0.06, 0.26, 2.04, 29.1, 30.6, 87.7, 94.4, 104.8, 121.7, 126.7, 128.4, 131.2, 131.7, 136.7, 142.2, 175.8; UV (CH_2Cl_2) λ_{max} 268, 256 nm; FT-IR (NaCl) 2956.4, 2159.1, 1557.0, 1249.2 cm^{-1} ; MS (70 eV) m/z : 386 (M^+); HRMS (M^+) calc. for $\text{C}_{21}\text{H}_{34}\text{OSi}_3$ 386.1918, found 386.1938.

3. Results and discussion

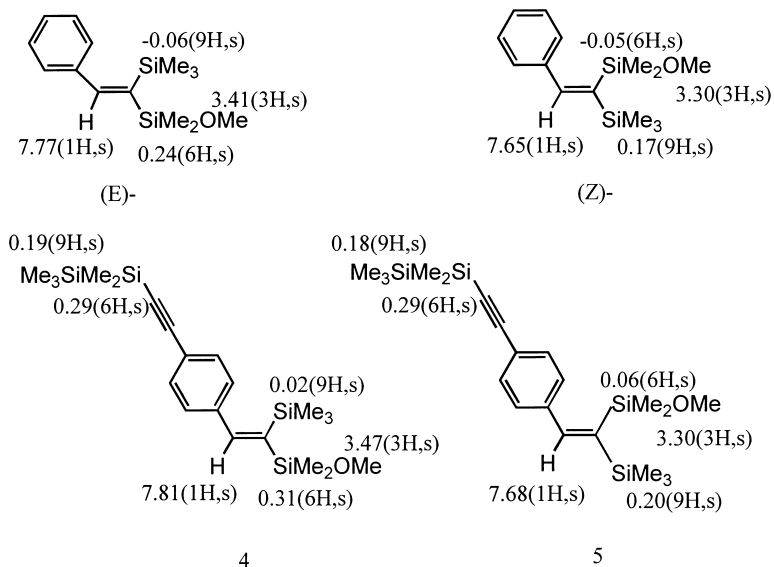
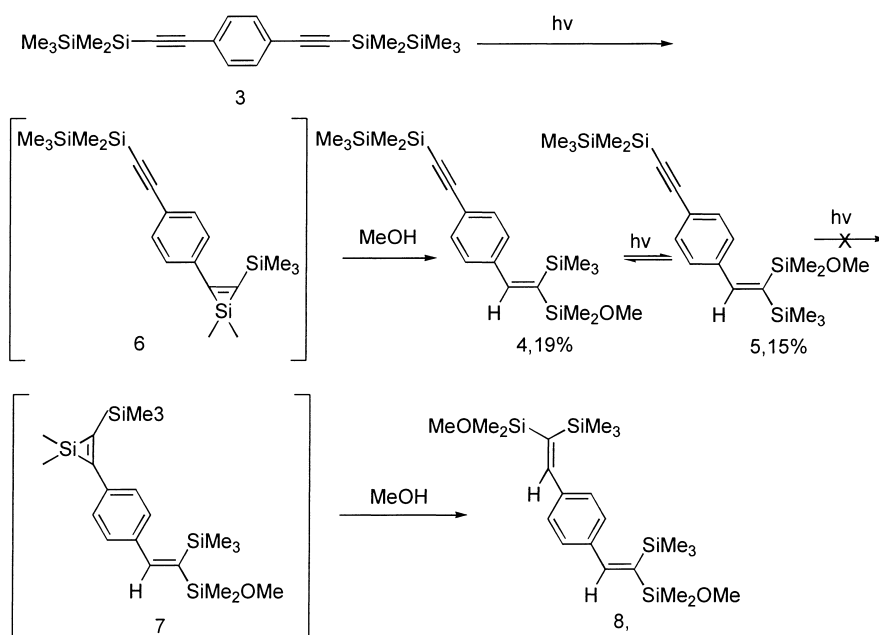
3.1. Photoreaction of 1,4-bis(pentamethyldisilanyl)ethynylbenzene **3** with methanol

Irradiation of **3** in methanol affords two 1 : 1 photoaddition products **4** and **5** but the expected successive reaction of the photoproduct **4** or **5** to give the compound **8** was not observed (Scheme 2).

The structure of these photoproducts is determined by various physical methods such as ^1H NMR, ^{13}C NMR, UV, FT-IR, and mass spectrometry. The UV absorption spectra of both photoproducts are very similar and the absorption maxima in **4** and **5** were blue-shifted compared to that of **3**. The molecular ion peaks (M^+) of **4** and **5** indicate that the photoproducts are formed by the addition of one methanol molecule to **3**. FT-IR spectra of **4** and **5** show the typical ethynyl absorption at 2151.2 and 2151.1 cm^{-1} , respectively indicating that one of the two ethynyl groups is sustained. The photoisomers **4** and **5** can be distinguished by comparison with the literature data (Fig. 1) [11]. The chemical shifts for the vinylic protons of **4** and **5** are similar to those of (*E*) and (*Z*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene [11]. The structure of photoisomer **4** could also be distinguished from that of **5** on the basis of the ^1H NMR spectra of the isomer pair. The ^1H NMR of photoadduct **5** show an upfield shift for the dimethylmethoxysilyl group due to the ring current of the phenyl ring, while its isomer **4** shows the upfield shift for the trimethylsilyl group but not the dimethylmethoxysilyl group, and *E* structure to **4** and *Z* structure to **5** could be assigned (Fig. 1).

The ^{13}C NMR of photoadduct **4** also shows an upfield shift for the trimethylsilyl group due to the anisotropy effect of the phenyl ring *cis* to this trimethylsilyl group compared to photoadduct **5** and the ^{13}C NMR of photoadduct **5** also shows an upfield shift for the dimethylmethoxysilyl group.

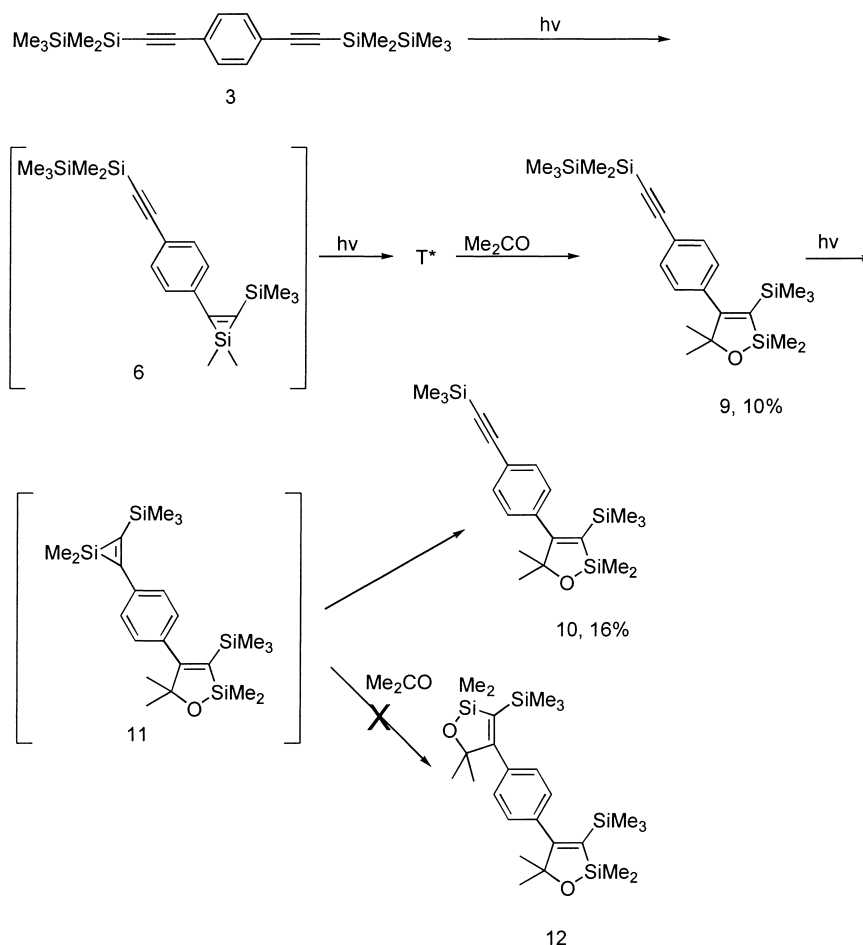
Photochemical reactions of phenylethynylpentamethyldisilane in the presence of methanol were reported to give mainly photoaddition products through the silacyclopentene

Fig. 1. Chemical Shift Comparison in ^1H NMR.

intermediates in the singlet excited states [12]. The major addition product has *E* configuration between the phenyl and dimethylmethoxysilyl groups and isomerize to give *Z* isomer on further irradiation. After irradiation of **3** in dry benzene in the absence of methanol for 15 min, methanol was added to the reaction mixture to identify the formation of silacyclopropene as the intermediate. The addition product **4** having an *E* configuration was detected by HPLC from **3**, strongly supporting the formation of silacyclopropene intermediate. In this experiment, only photoadduct **4** was detected and further irradiation of the reaction mixture gives

the compound **5** indicating that adduct **4** is a primary photoproduct and the compound **5** is a secondary photoproduct. The photoreaction of **3** in methanol is not quenched by oxygen suggesting the photoreaction to proceed via silacyclopropene intermediate in the singlet excited state.

From these results, the reaction mechanism is proposed as shown in Scheme 2. A silacyclopropene intermediate is formed from the singlet excited state of **3** and reacts with methanol to give the primary photoproduct **4**. Geometrical C=C bond isomerization of **4** yields **5** upon irradiation of **4**, but another silacyclopropene **7** is not formed



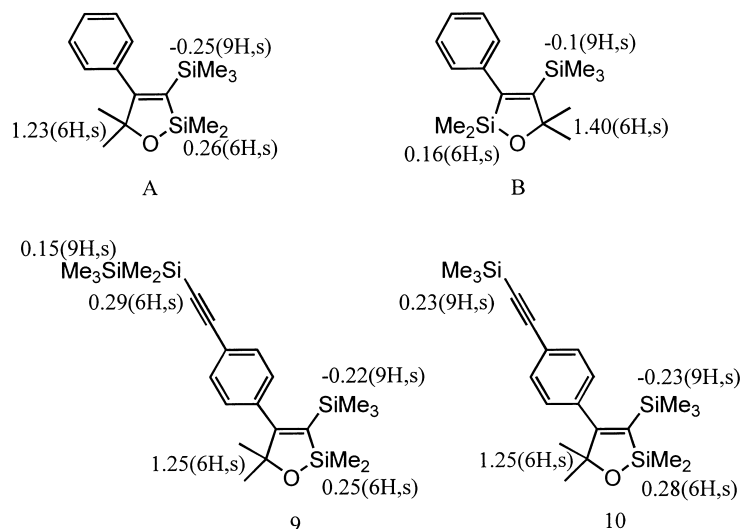
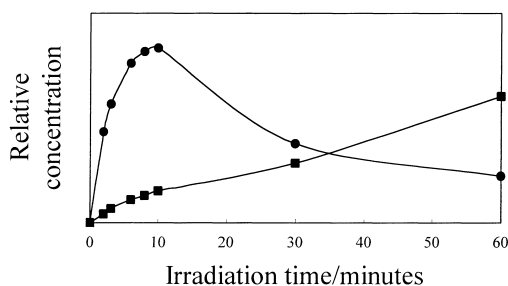
Scheme 3.

upon irradiation of **4**, suggesting that the formation of silacyclopentene may be affected by the newly formed double bond at 4 position of benzene ring in the photoproduct **4** through electronic effect. In relation to this results, we have reported previously some results for the photoreaction of 1-aryl-4-pentamethyldisilanyl-1,3-butadiyne containing both electron-donating and electron-withdrawing group in the aryl group with methanol [5]. The compound with an electron-donating group gave the photoaddition products via silacyclopentene intermediate but the photolysis of the compound with a nitro group as an electron-withdrawing group results in the 1-(*p*-nitrophenyl)-1,3-butadiyne through C–Si bond cleavage. From these results, it is thought that the photolysis of the compound **4** in methanol did not give the silacyclopentene intermediate **7** because of the newly formed substituted double bond in the compound **4**.

3.2. Photoreaction of 1,4-bis(pentamethyldisilanylethynyl)benzene **3** with acetone

Irradiation of **3** with acetone in deaerated methylene chloride yields site specific and regioselective photoadducts, **9** and **10**, but the expected compound **12** is not observed (Scheme 3).

The UV absorption spectrum of both photoproducts is very similar and the UV absorption maxima in **9** and **10** were blue-shifted compared to that of **3**. The FT-IR spectrum of photoproducts **9** and **10** shows the ethynyl absorption at 2155.1 and 2159.1 cm^{-1} , respectively indicating that one of the two ethynyl group is sustained. Mass spectrum of **9** shows the molecular ion (M^+) peak indicating that the photoproduct **9** is formed by the addition of one acetone molecule to **3** and the mass spectrum of **10** shows the molecular ion (M^+) peak indicating that the photoproduct **10** is formed by the removal of dimethylsilyl group in photoproduct **9**. The photoproduct **9** and **10** can be distinguished by comparison with the literature data (Fig. 2) [11]. The chemical shifts for the trimethylsilyl, dimethylsilyl and dimethylmethylene protons of **9** and **10** are similar to those of 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclopent-3-ene (Compound A) [11]. The ^{13}C NMR spectra of photoadduct **9** and **10** show the characteristic dimethyl substituted sp^3 carbons at δ 87.7 and 87.7, respectively supporting the 1-oxa-2-silacyclopent-3-ene moiety. The ^{13}C NMR spectra of photoadduct **9** and **10** show an ethynyl carbon at δ 93.5, 107.0 and 94.4, 104.8, respectively, indicating that one of the two ethynyl group in **3** remains intact. The chemical shifts of **9** in ^1H and ^{13}C NMR

Fig. 2. Chemical Shift Comparison in ^1H NMR.Fig. 3. Kinetics of the photoreaction of **3** with acetone: ●, **9**; ■, **10**.

spectrum are very similar to those of **10** except that there is not dimethylsilyl group in photoproduct **10**. Therefore, the structures of photoproduct **9** and **10** could be assigned like as Fig. 2.

After irradiation of **3** in dry benzene for 10 min, acetone was added to the reaction mixture but no acetone addition product was obtained. In aryloxydisilanes [12], 1-aryl-4-pentamethyldisilanyl-1,3-butadiynes [5–7], and 1,4-bis(pentamethyldisilanyl)butadiyne [8], the addition reaction between the corresponding silacyclopropenes and acetone proceeded photochemically but not in the dark. The results are the same for **3**. The quantum yield of photoproduct **9** and **10** decreased to 15 and 5%, respectively in aerated solution indicating that the triplet excited state is involved in the reaction of silacyclopropene intermediate with acetone. As shown in Fig. 3, the photoadduct **9** is initially formed and prolonged irradiation of the solution results in the formation of the photoadduct **10** indicating that **9** is the primary and **10** is the secondly photoproduct. Photolysis of pure **9** in deaerated methylene chloride results in the formation of **10**, strongly supporting the mechanism.

From these results, we propose a plausible photoreaction mechanism as shown in Scheme 3. The silacyclopropene intermediate **6** formed from the compound **3**

absorb the light and react with acetone in the triplet manifold to give the acetone addition photoadduct **9** having the 1-oxo-2-silacycloprop-3-ene moiety. The photoadduct **9** absorbs the light and gives the silacyclopropene intermediate **11** and this intermediate ejects dimethylsilylene to give the photoproduct **10**, but the expected photoproduct **12** from the reaction of silacyclopropene intermediate **11** with acetone is not detected, suggesting that the formation of the photoproduct **12** may be also affected by the substitution of the aryl group by the 1-oxa-2-silacycloprop-3-ene ring through electronic effect. The electronic and steric factors seem to be important in the chemistry of silacyclopropenes [13], but not many examples are available. Both the formation and reaction of silacyclopropene may be affected by the substitution of the aromatic ring through electronic effects and the intramolecular electron or charge transfer between the substituted aromatic ring and the disilanyl group [14]. The substitution of the phenyl ring by the 1-oxa-2-silacycloprop-3-ene ring is, therefore, expected to alter the photochemistry of photoproduct **9**. In relation to this substitution effect, we have reported previously that 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne substituted with a methoxy group as an electron-donating group gave the acetone addition photoproduct via silacyclopropene intermediate in lower yield than the compound having a nitro group as an electron-withdrawing group [6]. In the case of the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne with dimethyl fumarate [6], the compound with a methoxy group did not give photoproduct via silacyclopropene intermediate but the compound having a nitro group gave the photoadduct via silacyclopropene intermediate.

From these results, it is thought that the silacyclopropene intermediate **11** formed from **9** is rather unstable due to the electron-donating 1-oxa-2-silacycloprop-3-ene ring and the photoproduct **12** is not obtained.

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