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Photoreaction of 4,4′-bis(pentamethyldisilanylethynyl)biphenyl with methanol or acetone

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Abstract

Irradiation of 4,4′-bis(pentamethyldisilanylethynyl) biphenyl **3** with methanol in deaerated methylene chloride yielded two 1:1 photoaddition products **5** and **6** and two photodimers **9** and **10** via silacyclopropene intermediate, while regioselective photoadducts **15** and **16** were obtained with acetone in deaerated methylene chloride. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: 4,4′-Bis(pentamethyldisilanylethynyl) biphenyl; Silacyclopropene

1. Introduction

In an earlier paper, the author reported on the photoreaction of 1,4-bis(pentamethyldisilanylethynyl)benzene with methanol or acetone [1]. It is well known that the photolysis of alkynyl-substituted disilanes yields the highly strained silacyclopropenes and most of the silacyclopropenes are extremely unstable toward atmospheric oxygen and moisture [2,3]. Therefore, the existence of the silacyclopropenes is, in most cases, proved by trapping them with solvents such as methanol or acetone [4]. Irradiation of 1,4-bis(pentamethyldisilanylethynyl)benzene in methanol or acetone was shown to yield the 1:1 photoaddition products via silacyclopropene intermediate.

Along with the studies on the silacyclopropene intermediate formed from the photoreaction of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes [5–7], 1,4-bis(pentamethyldisilanyl)butadiyne [8], 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanyl ethyne [9,10], 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanyl ethyne [11], and 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanyl ethyne [12,13], the present author investigated the photochemistry of 4,4′-bis(pentamethyldisilanylethynyl)biphenyl **3** expecting the formation of two silacyclopropene intermediates in the molecule and reports, in this paper, the novel results about the formation of photodimers **9** and **10** and the regioselective 1:2 photoadduct **16** via two silacyclopropene intermediates.

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H and ^{13}C 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 $CDCl_3$. ^{29}Si NMR spectrum was recorded on Bruker AVANCE 600 high resolution NMR spectrometer with chemical shifts being referenced against TMS as an internal standard. 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 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_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 4,4′-bis(pentamethyldisilanylethynyl)biphenyl **3** was prepared by the reaction of 4,4′-diethynylbiphenyl **2** with

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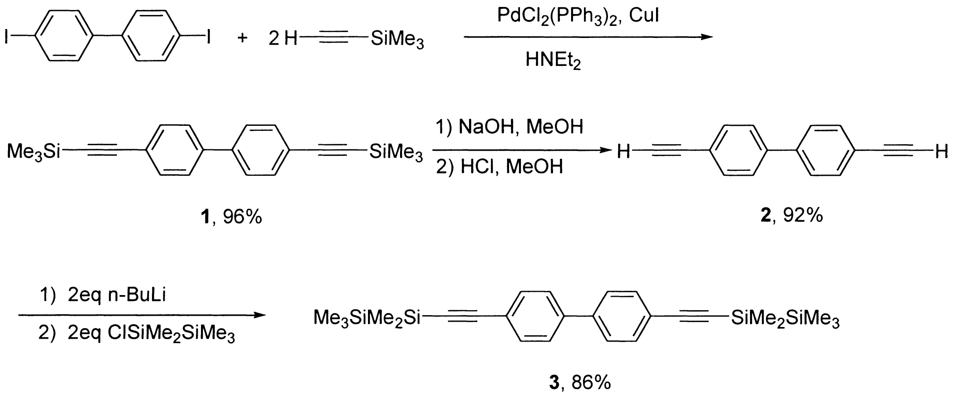


Scheme 1.

chloropentamethyldisilane in 86% yield and recrystallized from methanol (Scheme 1).

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

Trimethylsilylacetylene (1.74 ml, 12.3 mmol) was added dropwise to a deaerated solution of 4,4′-diiodobiphenyl (2 g, 4.93 mmol), bis(triphenylphosphine)palladium dichloride (69 mg, 0.099 mmol) and copper(I) iodide (18.8 mg, 0.099 mmol) in anhydrous diethylamine (40 ml) at room temperature. The reaction mixture was heated at 40°C for 2 h. To this solution, saturated ammonium chloride solution (40 ml) was added and the reaction mixture was extracted with ethyl acetate (3×30 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 *n*-hexane/ethyl acetate (300:1, v/v) as eluents gave **1** (1.64 g, 96% yield).

1: m.p. 158–159°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.26 (18H, s, –Si(C*H*$_3$)$_3$), 7.52(8H, s, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 0.38, 95.6, 105.2, 122.8, 127.1, 132.8, 140.6; UV (CH_2Cl_2) λ_{max} 304 nm; FT-IR (NaCl) 2956.0, 2157.2, 1488.3, 1253.4, 844.5 cm^{-1}; MS (70 eV) *m/z* 346 (M^+); HRMS (M^+) calc. for $C_{22}H_{26}Si_2$ 346.1573, found 346.1561.

2.3. Synthesis of 4,4′-diethynylbiphenyl **2**

The reaction solution of 4,4′-bis(trimethylsilylethynyl)biphenyl **1** (1.64 g, 4.74 mmol) and sodium hydroxide (0.47 g, 11.8 mmol) in methanol (100 ml) was stirred for 50 min at room temperature. The reaction mixture was acidified with 2 N HCl solution, concentrated in vacuo, and extracted with ethyl acetate (3×50 ml). The combined ethyl acetate solution was dried ($MgSO_4$) and evaporated in vacuo to give a crude product. Flash column chromatography with *n*-hexane/ethyl acetate (90:1, v/v) as eluents gave 4,4′-diethynylbiphenyl **2** (0.88 g, 92% yield).

2: m.p. 162–163°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 3.15 (2H, s, acetylic *H*), 7.55 (8H, td, *J*=8.6, 2.5 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 78.5, 83.8, 121.9, 127.3, 133.1, 140.9; UV (CH_2Cl_2) λ_{max} 290 nm; FT-IR (NaCl) 2921.7, 2105.4, 1487.6, 1392.0, 824.1 cm^{-1}; MS (70 eV) *m/z* 202 (M^+); HRMS (M^+) calc. for $C_{16}H_{10}$ 202.0783, found 202.0782.

2.4. Synthesis of 4,4′-bis(pentamethyldisilanylethynyl)-biphenyl **3**

A solution of 4,4′-diethynylbiphenyl **2** (0.88 g, 4.36 mmol) in THF (30 ml) was treated with *n*-BuLi (3.7 ml, 9.15 mmol) at −78°C followed by chloropentamethyldisilane (1.76 ml, 9.15 mmol). The reaction mixture was warmed at room temperature and stirred for 2.5 h. After evaporation of solvent, the reaction mixture was extracted with ethyl acetate (3×50 ml), washed with water (3×20 ml), and dried with $MgSO_4$, and concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane: ethyl acetate (120:1, v/v) as eluents gave **3** (1.73 g, 86% yield).

3: m.p. 129–130°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.17 (18H, s, –Si(C*H*$_3$)$_3$), 0.28 (12H, s, −Si(C*H*$_3$)$_2$–), 7.51 (8H, s, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −3.02, −2.50, 94.3, 107.0, 122.7, 126.7, 132.3, 140.1; UV (CH_2Cl_2) λ_{max} 310 nm; FT-IR (NaCl) 2951.1, 2149.9, 1491.3, 1397.7, 1243.5, 843.9 cm^{-1}; MS (70 eV) *m/z* 462 (M^+); HRMS (M^+) calc. for $C_{26}H_{38}Si_4$ 462.2051, found 462.2048.

2.5. Irradiation of 4,4′-bis(pentamethyldisilanylethynyl)-biphenyl **3** with methanol

Deaerated solution (5×10^{-4} M) of 4,4′-bis(pentamethyldisilanylethynyl)biphenyl **3** (115.5 mg) and methanol (2 ml) in methylene chloride (500 ml) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 20 min, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **5**, **6**, **9**, and **10** were isolated in (18.5 mg, 15% yield), (13.5 mg, 11% yield), (18.5 mg, 8% yield) and (6.9 mg, 3% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (60:1, v/v) as eluents followed by normal phase HPLC (Lichrospher Si 60) using *n*-hexane/ethyl acetate (20:1) as eluents.

5: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.06 (9H, s, –Si(CH_3)$_3$), 0.21 (9H, s, –Si(CH_3)$_3$), 0.31 (6H, s, –Si(CH_3)$_2$–), 0.33 (6H, s, –Si(CH_3)$_2$–), 3.49 (3H, s, –OCH_3), 7.31 (2H, m, ArH), 7.50 (6H, m, ArH), 7.89 (1H, s, vinylic H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.61, −2.11, −0.50, 2.09, 50.7, 94.5, 107.6, 122.9, 126.7, 127.1, 128.9, 132.7, 139.6, 140.9, 141.9, 145.6, 156.4; UV (CH_2Cl_2) λ_{max} 304 nm; FT-IR (NaCl) 2953.4, 2150.3, 1558.1, 1489.7, 1246.9, 834.3 cm^{-1}; MS (70 eV) *m/z* 494(M^+); HRMS (M^+) calc. for $C_{27}H_{42}OSi_4$ 494.2313, found 494.2312.

6: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.11 (6H, s, –Si(CH_3)$_2$–), 0.21 (9H, s, –Si(CH_3)$_3$), 0.24 (9H, s, –Si(CH_3)$_3$), 0.32 (6H, s, –Si(CH_3)$_2$–), 3.33 (3H, s, –OCH_3), 7.36 (2H, m, ArH), 7.55 (6H, m, ArH), 7.77 (1H, s, vinylic H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.60, −2.11, 0.65, 0.83, 50.1, 94.5, 107.6, 122.8, 126.6, 127.0, 129.0, 132.7, 139.6, 140.9, 141.7, 146.9, 155.3; UV (CH_2Cl_2) λ_{max} 305 nm; FT-IR (NaCl) 2953.2, 2150.6, 1558.8, 1489.8, 1246.5, 833.8 cm^{-1}; MS (70 eV) *m/z* 494 (M^+); HRMS (M^+) calc. for $C_{27}H_{42}OSi_4$ 494.2313, found 494.2309.

9: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.06 (18H, s, –Si(CH_3)$_3$), 0.20 (18H, s, –Si(CH_3)$_3$), 0.31 (12H, s, –Si(CH_3)$_2$–), 0.36 (12H, s, –Si(CH_3)$_2$–), 7.30 (4H, m, ArH), 7.58 (10H, m, ArH), 7.91 (2H, s, ArH), ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.58, −2.08, 1.95, 2.23, 94.5, 107.6, 122.8, 126.7, 127.1, 128.9, 132.7, 139.6, 140.9, 141.9, 146.9, 155.7; UV (CH_2Cl_2) λ_{max} 307 nm; FT-IR (NaCl) 2953.9, 2895.4, 2150.5, 1558.5, 1490.0, 1246.8, 833.8 cm^{-1}; MS (70 eV) *m/z* 924 (M^+); HRMS (M^+) calc. for $C_{52}H_{76}Si_8$ 924.4101, found 924.4161.

10: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.19 (12H, s, –Si(CH_3)$_2$–), 0.20 (18H, s, –Si(CH_3)$_3$), 0.26 (18H, s, –Si(CH_3)$_3$), 0.31 (12H, s, –Si(CH_3)$_2$–), 7.34 (4H, m, ArH), 7.56 (10H, m, ArH), 7.76 (2H, s, ArH), ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.58, −2.08, 0.67, 3.63, 94.6, 107.5, 122.9, 127.0, 127.1, 128.7, 132.8, 139.8, 140.7, 141.9, 148.3, 154.5; ^{29}Si NMR ($CDCl_3$, 119 MHz) δ −6.16, −9.39, −18.57, −36.64; UV (CH_2Cl_2) λ_{max} 310 nm; FT-IR (NaCl) 2953.9, 2895.8, 2150.2, 1604.6, 1491.5, 1246.8, 844.1 cm^{-1}; MS (70 eV) *m/z* 924 (M^+); HRMS (M^+) calc. for $C_{52}H_{76}Si_8$ 924.4101, found 924.4133.

2.6. Irradiation of 4,4′-bis(pentamethyldisilanylethynyl)-biphenyl **3** *with acetone*

Deaerated solution (5×10^{-4} M) of 4,4′-bis(pentamethyldisilanylethynyl)biphenyl **3** (115.5 mg) and acetone (2 ml) in methylene chloride (500 ml) was irradiated in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamp. After irradiation for 20 min, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **1**, **15**, and **16** were isolated in (0.9 mg, 1% yield), (11.5 mg, 10% yield), and (36.1 mg, 25% yield), respectively, by silica gel column chromatography with *n*-hexane/ethyl acetate (40:1, v/v) as eluents. The products were purified by normal phase HPLC (Lichrosper Si 60) using *n*-hexane/ethyl acetate (15:1, v/v) as eluents.

15: m.p. 124–125°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H −0.17 (9H, s, –Si(CH_3)$_3$), 0.29 (9H, s, –Si(CH_3)$_3$), 0.35 (6H, s, –Si(CH_3)$_2$–), 1.35 (6H, s, dimethyl), 7.16 (2H, m, ArH), 7.58 (6H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 0.40, 0.70, 2.50, 29.6, 88.1, 95.3, 105.4, 122.5, 126.4, 127.1, 129.4, 132.8, 136.9, 139.1, 141.0, 141.6, 176.6; UV (CH_2Cl_2) λ_{max} 289 nm; FT-IR (NaCl) 2964.7, 2930.2, 2157.2, 1488.5, 1248.9, 868.6 cm^{-1}; MS (70 eV) *m/z* 462 (M^+); HRMS (M^+) calc. for $C_{27}H_{38}OSi_3$ 462.2230, found 462.2223.

16: m.p. 252–253°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H −0.15 (18H, s, –Si(CH_3)$_3$), 0.35 (12H, s, –Si(CH_3)$_2$–), 1.35 (12H, s, dimethyl), 7.17 (4H, m, ArH), 7.61 (4H, m, ArH), ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 0.74, 2.52, 29.6, 88.2, 126.3, 129.3, 136.7, 139.4, 141.2, 176.7; UV (CH_2Cl_2) λ_{max} 271 nm; FT-IR (NaCl) 2953.4, 2923.0, 1554.5, 1488.2, 1247.1, 867.6 cm^{-1}; MS (70 eV) *m/z* 578 (M^+); HRMS (M^+) calc. for $C_{32}H_{50}O_2Si_4$ 578.2888, found 578.2887.

2.7. Synthesis of 4-pentamethyldisilanylethynyl-4′-ethynylbiphenyl **20**

A solution of 4,4′-diethynylbiphenyl **2** (0.5 g, 2.48 mmol) in THF (25 ml) was treated with *n*-BuLi (1.1 ml, 2.7 mmol) at −78°C followed by chloropentamethyldisilane (0.52 ml, 2.7 mmol). The reaction mixture was warmed at room temperature and stirred for 2 h. After evaporation of solvent, the reaction mixture was extracted with ethyl acetate (3×30 ml), washed with water (3×20 ml), and dried with $MgSO_4$, and concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane:ethyl acetate (120:1, v/v) as eluents gave **20** (0.74 g, 90% yield).

20: m.p. 61–62°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.21 (9H, s, –Si(CH_3)$_3$), 0.32 (6H, s, –Si(CH_3)$_2$–), 3.17 (1H, s, acetylic H), 7.56 (8H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.60, −2.08, 78.4, 83.8, 94.9, 107.4, 121.8, 123.3, 127.2, 127.3, 132.8, 133.0, 140.4, 141.1; UV (CH_2Cl_2) λ_{max} 302 nm; FT-IR (NaCl) 2952.2, 2150.9, 1489.2, 1395.5, 1246.4, 824.3 cm^{-1}; MS (70 eV) *m/z* 332 (M^+); HRMS (M^+) calc. for $C_{21}H_{24}Si_2$ 332.1417, found 332.1419.

2.8. Synthesis of 4-pentamethyldisilanylethynyl-4′-trimethylsilanylethynylbiphenyl **17**

A solution of 4-pentamethyldisilanylethynyl, 4′-ethynylbiphenyl **20** (0.74 g, 2.23 mmol) in THF (30 ml) was treated with *n*-BuLi (0.98 ml, 2.45 mmol) at −78°C followed by trimethylsilane (0.31 ml, 2.45 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. After evaporation of solvent, the reaction mixture was extracted with ethyl acetate (3×40 ml), washed with water

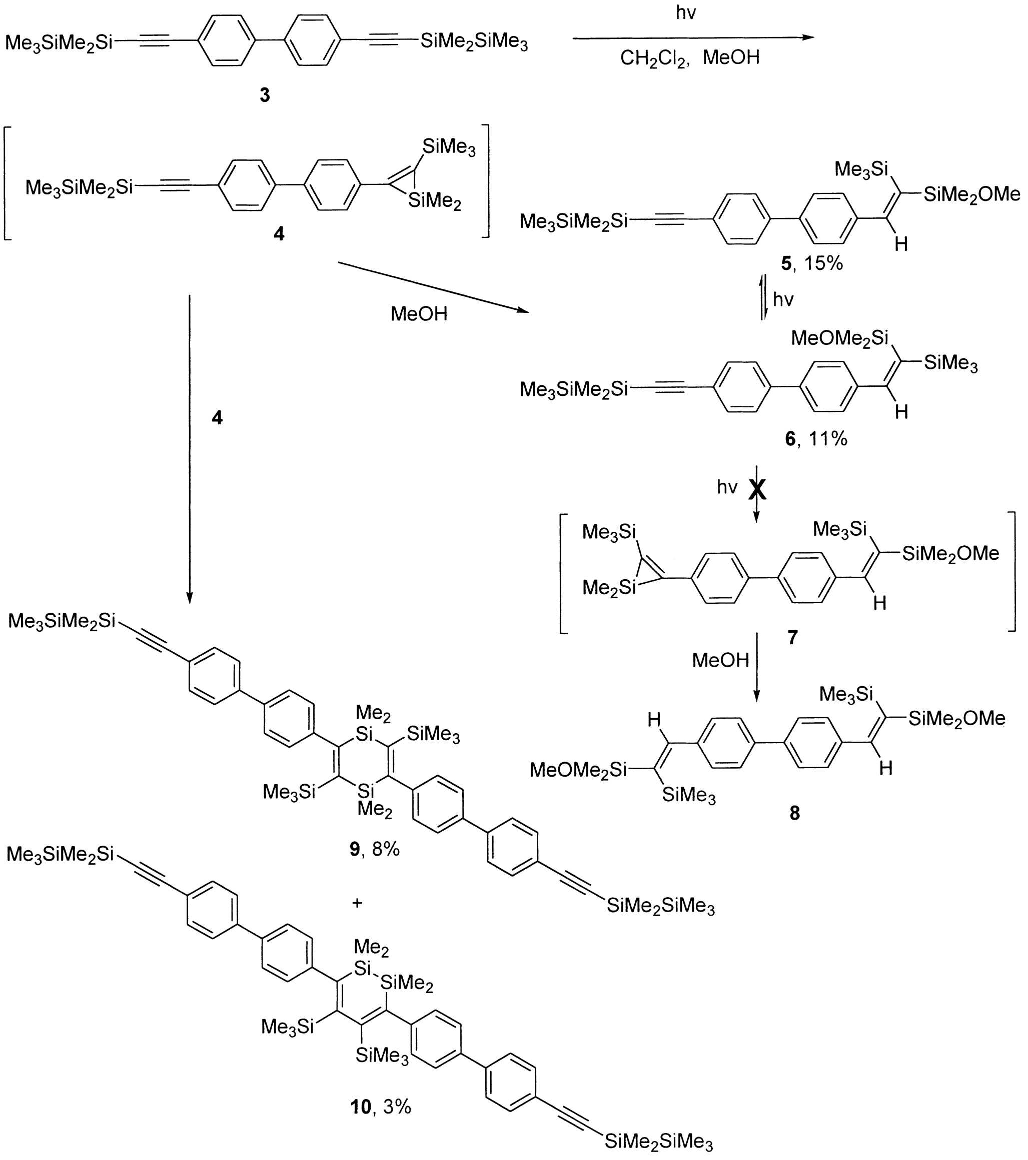
(3×20 ml), and dried with $MgSO_4$, and concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane: ethyl acetate (90:1, v/v) as eluents gave **17** (0.84 g, 93% yield).

17: m.p. 85–86°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.20 (9H, s, $-Si(CH_3)_3$), 0.29 (9H, s, $-Si(CH_3)_3$), 0.31 (6H, s, $-Si(CH_3)_2-$), 7.54 (4H, s, ArH), 7.55 (4H, s, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.60, −2.08, 0.40, 94.8, 95.6, 105.2, 107.4, 122.8, 123.2, 126.3, 127.1, 132.8, 132.9, 140.4, 140.7; UV (CH_2Cl_2) λ_{max} 307 nm; FT-IR (NaCl) 2955.6, 2155.4, 1489.6, 1397.9, 1248.3, 845.8 cm^{-1}; MS (70 eV) *m/z* 404 (M^+); HRMS (M^+) calc. for $C_{24}H_{32}Si_3$ 404.1872, found 404.1820.

3. Results and discussion

3.1. Photoreaction of 4,4′-bis(pentamethyldisilanylethynyl)biphenyl **3** with methanol

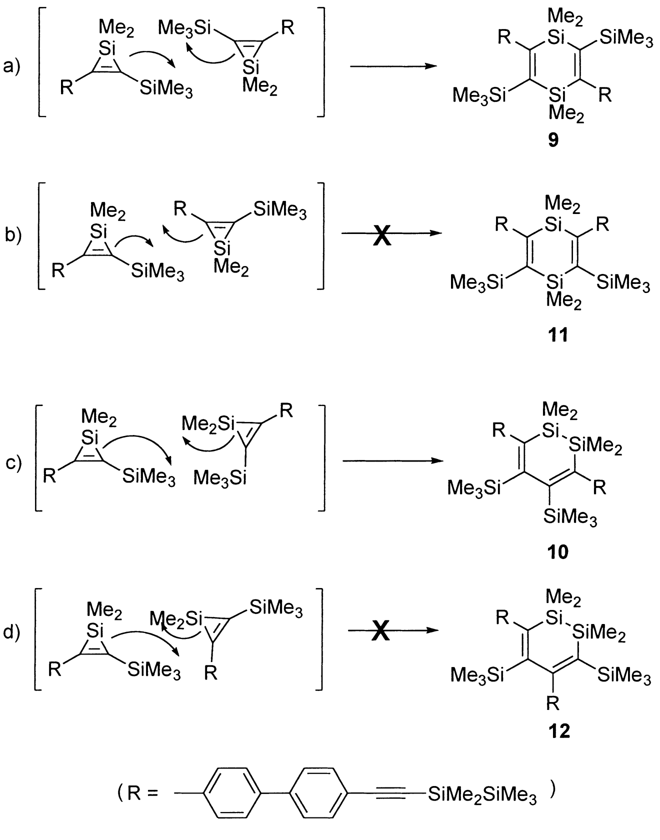
Irradiation of **3** with 300 nm UV light in the presence of a large excess of methanol in deaerated methylene chloride afforded two 1:1 photoaddition products **5** and **6** in 15 and 11% yield, respectively, and two photodimers **9** and **10** in 8 and 3% yield, respectively, but the expected successive reaction of the photoproduct **5** or **6** to give the compound **8** was not observed (Scheme 2). The products **5** and **6** were probably formed by the addition reaction of the silacyclopropene



Scheme 2.

intermediate **4** arising from a 1,2-trimethylsilyl shift to the ethynyl group when the compound **3** was photolyzed with methanol. Photochemical reactions of phenylethynyl pentamethyldisilane in the presence of methanol were reported to give the photoaddition products through the silacyclopropene intermediates [2–4].

The major addition product has *E* configuration between the phenyl and dimethylmethoxysilyl groups and isomerizes to give *Z* isomer on further irradiation. After irradiation of **3** in dry methylene chloride in the absence of methanol for 20 min, methanol was added to the reaction mixture to identify the formation of silacyclopropene as the intermediate. The addition product **5** having an *E* configuration was detected by HPLC from **3**, strongly supporting the formation of silacyclopropene intermediate. In this experiment, only photoadduct **5** was detected and further irradiation of the reaction mixture gave the compound **6** indicating that the adduct **5** is a primary photoproduct and the compound **6** is a secondary photoproduct. The formation of photodimers **9** and **10** can best be explained in terms of the dimerization of the silacyclopropene intermediate **4**. Indeed, it is well known that 1,4-disilacyclohexa-2,5-dienes like photodimer **9** can always be produced in the palladium(II) catalyzed reaction of the silacyclopropenes [14–16]. For example, Ishikawa et al. [17] found that the treatment of 1,1-dimethyl-2-phenyl-3-(substituted-dimethylsilyl)-1-silacyclopropenes with a catalytic amount of dichlorobis-(triethylphosphine)palladium(II) in the presence or absence of phenyl(trimethylsilyl)acetylene gave the respective 1,4-disilacyclohexa-2,5-dienes as the sole product with high regio and stereoselectivity. Although the transition metal catalyzed reactions of the silacyclopropenes have been extensively investigated [18–20], relatively few examples have been reported in the absence of a transition metal catalyst [21]. Interestingly, irradiation of **3** in the absence of a palladium(II) catalyst yielded two photodimers **9** and **10** in addition to the products **5** and **6**. The formation of compound **9** was explained by the cycloaddition reaction of two silacyclopropene intermediates, while the compound **10** was probably obtained through the silicon–silicon bond formation (Scheme 3). Neither compound **11** nor compound **12** was probably formed by the steric hindrance between the pentamethyldisilanyl ethynylbiphenyl group and trimethylsilyl group.



Scheme 3.

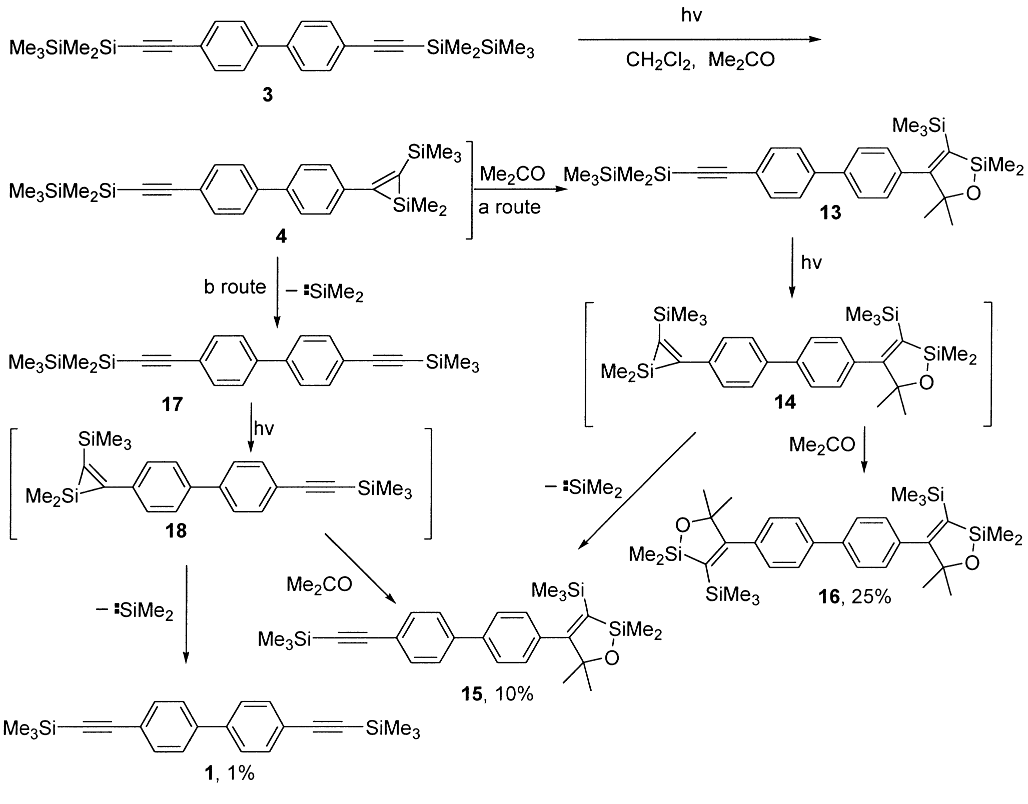
The structure of these photoproducts **5**, **6**, **9**, and **10** was determined by various physical methods such as ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, UV, FT-IR, and mass spectrometry. The molecular ion peaks (M^+) of **5** and **6** indicated that the photoproducts were formed by the addition of one methanol molecule to **3**. The high resolution mass spectra of two photodimers **9** and **10** showed the parent peak at 924.4161 and 924.4133, respectively, corresponding to the calculated molecular weight for **9** and **10** (924.4101). FT-IR spectra of **5**, **6**, **9**, and **10** showed the typical ethynyl absorption at 2150.3, 2150.6, 2150.5, and 2150.2 cm^{-1}, respectively, indicating that one of the two ethynyl groups is sustained. The structure of photoisomer **5** could be distinguished from that of **6** on the basis of the ^{1}H NMR spectra of the isomer pair. The chemical shifts (7.89 and 7.77 ppm, respectively) for the vinylic protons of **5** and **6** are similar to those (7.77 and 7.65 ppm, respectively) of (*E*) and (*Z*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene [2] and those (7.81 and 7.68 ppm, respectively) of (*E*) and (*Z*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-(4-pentamethyldisilanylethynylphenyl)ethylene [1]. Also, the chemical shifts (0.31 and 0.11 ppm, respectively) for the dimethyl protons in the dimethylmethoxysilyl group of **5** and **6** are similar to those (0.24 and −0.05 ppm, respectively) of (*E*) and (*Z*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene [2] and those (0.31 and 0.06 ppm, respectively) of (*E*) and (*Z*)-1-methoxydimethylsilyl-1-trimethylsilyl-2-(4-pentamethyldisilanyl ethynylphenyl)ethylene [1]. The ^{1}H NMR of photo-adduct **6** showed an upfield shift for the dimethylmethoxysilyl group due to the ring current of the phenyl ring, while its isomer **5** showed the upfield shift for the trimethylsilyl group but not for the dimethylmethoxysilyl group, and *E* structure to **5** and *Z* structure to **6** could be assigned. The ^{13}C NMR spectra of photoadducts **5** and **6** also showed similar pattern for the chemical shifts of dimethylmethoxysilyl group and trimethylsilyl group as compared to the literature data [1]. The ^{1}H NMR spectrum of photodimer **9** having a center of symmetry showed four singlets in the ratio of 3/3/2/2, as expected in the structure of **9**, at 0.06, 0.20, 0.31, and 0.36 ppm, due to the Me_3Si at 1,4-disilacyclohexa-2,5-diene ring, the Me_3Si, the Me_2Si, and the Me_2Si at 1,4-disilacyclohexa-2,5-diene ring, respectively. The 1,4-disilacyclohexa-2,5-diene unit of **9** was confirmed by comparison with reported results [17]. The ^1H NMR spectrum of photodimer **10** having a symmetry plane also showed four singlets in the ratio of 2/3/3/2, as expected in the structure of **10** at 0.19, 0.20, 0.26, and 0.31 ppm due to the Me_2Si at 1,2-disilacyclohexa-3,5-diene ring, the Me_3Si, the Me_3Si at 1,2-disilacyclohexa-3,5-diene ring, and the Me_2Si, respectively. In order to differentiate the photodimer structure between **10** and **11**, the ^{29}Si NMR spectrum of **10** was obtained. As expected, the proton-decoupled ^{29}Si NMR spectrum of photodimer **10** showed four peaks at −6.16, −9.39, −18.57, and −36.64 ppm, due to the Me_3Si at 1,2-disilacyclohexa-3,5-diene ring, the Me_2Si at 1,2-disilacyclohexa-3,5-diene ring, the Me_2Si, and the Me_3Si, respectively, indicating that some possibility of the structure **11** for **10** was ruled out since the five peaks were expected in the proton-decoupled ^{29}Si NMR spectrum of **11**. The photolysis of **3** in deaerated methylene chloride in the absence of methanol afforded only two photodimers **9** and **10**, as expected, in 6 and 1% yield, respectively, along with some products, probably polymers.

From these results, the reaction mechanism is proposed as shown in Scheme 2. A silacyclopropene intermediate **4** is formed from the photolysis of **3** and reacts with methanol to give the primary photoproduct **5**. Geometrical C=C bond isomerization of **5** yields **6** upon irradiation of **5**, but another silacyclopropene **7** is not formed upon irradiation of **5**, suggesting that the formation of silacyclopropene **7** may be blocked by the facile photo-induced *cis–trans* isomerization, and two photodimers **9** and **10** are formed from the dimerization of a silacyclopropene intermediate **4** in two different ways (a) and (c), respectively, as shown in Scheme 3.

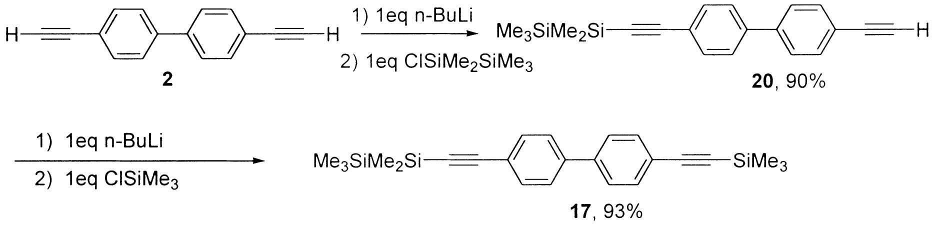
3.2. Photoreaction of 4,4′-bis(pentamethyldisilanylethynyl)biphenyl **3** *with acetone*

When a deaerated methylene chloride solution of **3** in the presence of acetone was irradiated at room temperature with 300 nm UV lamp under a purified nitrogen atmosphere, site specific and regioselective photoadducts **15** and **16** were obtained in 10 and 25% yield, respectively, in addition to 1% yield of **1**. The formation of products **15**, **16**, and **1** can be best understood by assuming intermediacy of silacyclopropenes **4**, **14**, and **18** (Scheme 4).

Insertion of acetone into the silicon–carbon bond in silacyclopropene **4** generated five-membered compound **13**. Further irradiation of **13** yielded silacyclopropene intermediate **14**, which was reacted with acetone to give the novel photoproduct **16** which can be expected from the reaction of two silacyclopropene moieties with acetone. Liberation of dimethylsilylene species from the intermediate **14** or insertion of acetone into the silicon–carbon bond in



Scheme 4.



Scheme 5.

silacyclopropene intermediate **18** resulted in the formation of **15**. Compound **1** can be rationalized in terms of loss of dimethylsilylene species in silacyclopropene intermediate **18** arising from the photolysis of **17**, which was formed from the photolysis of **3** by loss of dimethylsilylene species. To establish whether or not the compound **17** was formed in the photolysis of **3** and the compounds **1** and **15** were formed from the photolysis of **17**, the compound **17** was synthesized (Scheme 5) and was irradiated with 300 nm UV lamp in the presence of acetone in deaerated methylene chloride solution to obtain, as expected, the compound **1** and **15** in 9 and 21% yields, respectively.

The structure of these photoproducts **15** and **16** was determined by various physical methods such as ^{1}H NMR, ^{13}C NMR, UV, FT-IR, and mass spectrometry. The high resolution mass spectrum of the photoproduct **15** showed the parent peak at 462.2223 corresponding to the calculated molecular weight for **15** (462.2230) and that of the photoproduct **16** showed the parent peak at 578.2887 corresponding to the calculated molecular weight for **16** (578.2888) indicating that the photoproduct **15** was formed by the removal of dimethylsilyl group in silacyclopropene intermediate **14** and **16** was formed by the stepwise addition of two acetone molecules to **4**, and then **14**. FT-IR spectrum of photoproduct **15** showed the typical ethynyl absorption at 2157.2 cm^{-1} indicating that one of the two ethynyl groups is sustained but that of **16** did not show the ethynyl absorption at 2000–2200 cm^{-1} range. The photoproducts **15** and **16** can be distinguished by comparison with the literature data [1,2]. The chemical shifts for the trimethylsilyl, dimethylsilyl and dimethylmethylene protons of **15** and **16** are patterns similar to those of 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclopent-3-ene [2] and 2,2,5,5-tetramethyl-3-trimethylsilyl-4-(4′-pentamethyldisilanylethynyl)phenyl-1-oxa-2-silacyclopent-3-ene [1]. The ^{1}H NMR spectrum of photoadduct **16** having a center of symmetry showed three singlets in the ratio of 3/2/2, as expected in the structure of **16**, at −0.15, 0.35, and 1.35 ppm, due to the Me_3Si, the Me_2Si, and the Me_2C at l-oxa-2-silacyclopenta-3-ene ring, respectively. The ^{13}C NMR spectra of photoadducts **15** and **16** showed the characteristic dimethyl substituted sp^3 carbons at δ 88.1 and 88.2, respectively, supporting the l-oxa-2-silacyclopent-3-ene moiety. The ^{13}C NMR spectrum of photoadduct **15** showed an ethynyl carbon at δ 95.3 and 105.4 indicating that one of the two ethynyl groups in **3** remains intact but that of **16** did not show the ethynyl carbon.

From these results, a plausible photoreaction mechanism as shown in Scheme 4 is proposed. The photolysis of **3** has been found to proceed simultaneously by two different routes, one of which, a main route, leads to the production of **13**, and the other, a minor one, comprises the formation of **17**. The silacyclopropene intermediate **14** arising from further irradiation of **13** afforded the novel photoproduct **16**, which was formed from the insertion of acetone into the silicon–carbon bond in silacyclopropene **14** and the photoproduct **15** formed from the liberation of dimethylsilylene. Further photolysis of **17** gave the product **15** formed from the insertion of acetone into the silicon–carbon bond in silacyclopropene intermediate **18** and the compound **1** was formed from the loss of dimethylsilylene species in **18**.

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