

Novel photoinduced intramolecular cycloaddition reactions of 1-(*o*-alkoxymethylphenyl)-2-pentamethyldisilanyl ethynes

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Abstract

Photolysis of 1-(*o*-hydroxymethyl-, acetoxymethyl-, or allyloxymethylphenyl)-2-pentamethyldisilanyl ethynes **2a**, **2b**, or **2c** in benzene provides novel stereoselective intramolecular cycloaddition products **6**, **8**, or **12** via silacyclopentene intermediates. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the previous papers, the authors reported on the photoinduced intramolecular reactions of 1-(*o*-alkoxyphenyl)-2-pentamethyldisilanyl ethynes affording novel intramolecular photoproducts via silacyclopentene intermediate [1,2]. It is well known that the photolysis of alkynyl-substituted disilanes affords a convenient route to the highly strained silacyclopentenes and these silacyclopentenes react readily with methanol or acetone in the presence of methanol or acetone as trapping agents [3–5]. Silacyclopentenes also react with unsaturated functional groups to give five-membered cyclic organosilicon products in which C=O, C=C, C≡C or C=N bonds are inserted into the Si–C bond of the silacyclopentene ring [6]. Although the chemical properties of silacyclopentenes have been extensively investigated [7–11], relatively few examples have been reported on the intramolecular photoreactions of the system. Along with the studies on the reactions of silacyclopentenes formed from the photolysis of various phenylethynylpentamethyldisilane systems [12–18], we have undertaken the photoreaction of 1-(*o*-alkoxymethylphenyl)-2-pentamethyldisilanyl ethynes **2a–d** since novel photoproducts from the intramolecular reaction of *ortho*-substituted alkoxyethyl group with the silacyclopentene ring are expected and we describe, in this paper, a detailed photochemical study of 1-(*o*-alkoxymethylphenyl)-2-pentamethyldisilanyl ethynes.

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. 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 (HPLC) 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. Thin layer chromatography (TLC) was performed on Sigma-Aldrich pre-coated silica gel F₂₅₄ aluminum foils. Purification of the reaction products was carried out by flash column chromatography using a glass column dry packed with silica gel (230–400 mesh ASTM). Benzene was distilled from CaH₂ before use. Et₃N was distilled from CaH₂ and stored over KOH pellets. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents were used for HPLC and UV absorption spectra.

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2.2. Synthesis of *o*-acetoxyethyl-iodobenzene **1b**

A solution of 2-iodobenzyl alcohol (1 g, 4.27 mmol) in *N,N*-dimethylformamide (15 ml) was added to a solution of NaH (0.11 g, 4.70 mmol) in DMF (10 ml) at room temperature under nitrogen atmosphere. Acetyl chloride (0.45 ml, 6.4 mmol) was added dropwise to the resulting solution and the mixture was stirred at 100°C for 2.5 h. Water (30 ml) was added to the solution and was extracted with ethyl acetate (3×20 ml). The combined ethyl acetate solution was washed with water (20 ml), brine (20 ml) and dried (MgSO₄), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (3:1, v/v) as an eluent gave **1b** (1.07 g, 91% yield) as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 2.17 (3H, s), 5.14 (2H, s), 7.05 (1H, td, *J*=7.2, 2.6 Hz), 7.40 (2H, m), 7.88 (1H, dd, *J*=7.8, 0.8 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 21.4, 70.5, 128.8, 129.9, 130.1, 130.3, 138.7, 139.9, 171.1; UV (CH₂Cl₂) λ_{max} 232 nm; FT-IR (NaCl) 3057.7, 1737.8, 1438.1, 1224.5, 1014.4 cm⁻¹; MS (70 eV) *m/z* 276 (M⁺); HRMS (M⁺) calcd for C₉H₉IO₂ 275.9647, found 275.9666.

2.3. Synthesis of *o*-allyloxymethyl-iodobenzene **1c**

This compound was prepared according to the procedure described for the preparation of **1b**, except allyl chloride (0.52 ml, 6.4 mmol) was used. Chromatography (*n*-hexane/ethyl acetate, 10:1, v/v) provided 1.15 g (98% yield) of **1c** as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 4.12 (2H, dt, *J*=5.4, 1.2 Hz), 4.51 (2H, s), 5.25 (1H, dq, *J*=10.3, 1.2 Hz), 5.37 (1H, dq, *J*=17.5, 1.5 Hz), 6.00 (1H, m), 6.99 (1H, td, *J*=7.6, 1.8 Hz), 7.35 (1H, td, *J*=7.6, 1.2 Hz), 7.47 (1H, dd, *J*=7.6, 1.8 Hz), 7.83 (1H, dd, *J*=7.6, 1.2 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 71.6, 75.8, 97.6, 117.3, 128.2, 128.7, 129.1, 134.6, 139.2, 140.6; UV (CH₂Cl₂) λ_{max} 232 nm; FT-IR (NaCl) 3064.4, 2852.0, 1585.9, 1460.9, 1261.9, 1116.9 cm⁻¹; MS (70 eV) *m/z* 274 (M⁺); HRMS (M⁺) calcd for C₁₀H₁₁IO 273.9855, found 273.9850.

2.4. Synthesis of *o*-methoxycarbonylmethoxymethyl-iodobenzene **1d**

This compound was prepared according to the procedure described for the preparation of **1b**, except methyl bromoacetate (0.4 ml, 6.4 mmol) was used. Chromatography (*n*-hexane/ethyl acetate, 3:1, v/v) provided 1.16 g (89% yield) of **1d** as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 3.79 (3H, s), 4.22 (2H, s), 4.64 (2H, s), 7.00 (1H, td, *J*=7.6, 1.6 Hz), 7.36 (1H, td, *J*=7.5, 1.0 Hz), 7.49 (1H, dd, *J*=7.6, 1.6 Hz), 7.82 (1H, dd, *J*=7.5, 1.0 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 52.4, 68.2, 98.2, 116.7, 128.8, 129.4, 129.9, 139.6, 139.9, 171.0; UV (CH₂Cl₂) λ_{max} 232 nm; FT-IR (NaCl) 2951.4, 1755.2, 1436.5, 1210.3, 1138.2 cm⁻¹; MS (70 eV) *m/z* 306 (M⁺); HRMS (M⁺) calcd for C₁₀H₁₁IO₃ 305.9753, found 305.9741.

2.5. Synthesis of 1-(*o*-hydroxymethylphenyl)-2-pentamethyldisilanyl ethyne **2a**

To a deaerated solution of 2-iodobenzyl alcohol (0.5 g, 2.14 mmol), bis(triphenylphosphine)palladium dichloride (15 mg, 0.02 mmol) and copper(I) iodide (3.8 mg, 0.02 mmol) in anhydrous triethylamine (10 ml) were added dropwise pentamethyldisilanylethyne (0.45 ml, 2.5 mmol) at room temperature. The reaction mixture was heated at 40°C for 2 h. To this solution saturated ammonium chloride solution (20 ml) was added and the reaction mixture was extracted with ethyl acetate (3×20 ml). The combined ethyl acetate solution was washed with H₂O (10 ml), brine (10 ml), and dried (MgSO₄), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (3:1, v/v) as an eluent gave **2a** (0.5 g, 90% yield) as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 0.22 (9H, s), 0.33 (6H, s), 2.70 (1H, s), 4.84 (2H, s), 7.24 (1H, td, *J*=7.41, 1.07 Hz), 7.33 (1H, td, *J*=7.51, 1.28 Hz), 7.43 (1H, dd, *J*=7.53, 0.57 Hz), 7.48 (1H, dd, *J*=7.53, 1.04 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -2.29, -1.80, 64.5, 99.3, 105.3, 121.9, 127.6, 127.9, 129.4, 133.1, 143.7; UV (CH₂Cl₂) λ_{max} 262 nm; FT-IR (NaCl) 3344.2, 3067.6, 2953.2, 2148.7, 1480.1, 1245.9, 852.9 cm⁻¹; MS (70 eV) *m/z* 262 (M⁺); HRMS (M⁺) calcd for C₁₄H₂₂OSi₂ 262.1209, found 262.1243.

2.6. Synthesis of 1-(*o*-acetoxyethylphenyl)-2-pentamethyldisilanyl ethyne **2b**

This reaction was carried out using the same procedure described for the preparation of **2a**, except *o*-acetoxyethyl-iodobenzene **1b** (0.5 g, 1.81 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 3:1, v/v) to afford colorless oil of **2b** (0.48 g, 88% yield); ¹H NMR (CDCl₃, 300 MHz) δ_H 0.20 (9H, s), 0.31 (6H, s), 2.14 (3H, s), 5.30 (2H, s), 7.26 (1H, td, *J*=7.4, 1.4 Hz), 7.32 (1H, dd, *J*=7.4, 1.4 Hz), 7.38 (1H, td, *J*=7.6, 1.4 Hz), 7.50 (1H, dd, *J*=7.6, 1.4 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -2.6, -2.1, 21.3, 65.2, 99.2, 104.4, 123.3, 128.4, 128.6, 128.9, 132.9, 138.1, 171.1; UV (CH₂Cl₂) λ_{max} 262, 226 nm; FT-IR (NaCl) 2953.5, 2149.7, 1744.8, 1484.2, 1245.6, 1229.2, 835.9 cm⁻¹; MS (70 eV) *m/z* 304 (M⁺); HRMS (M⁺) calcd for C₁₆H₂₄O₂Si₂ 304.1315, found 304.1329.

2.7. Synthesis of 1-(*o*-allyloxymethylphenyl)-2-pentamethyldisilanyl ethyne **2c**

This reaction was carried out using the same procedure described for the preparation of **2a**, except *o*-allyloxymethyl-iodobenzene **1c** (0.5 g, 1.82 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 10:1, v/v) to afford colorless oil of **2c** (0.5 g, 92% yield); ¹H NMR (CDCl₃, 300 MHz) δ_H 0.17 (9H, s), 0.28 (6H, s), 4.10 (2H, d, *J*=5.7 Hz), 4.71 (2H, s), 5.22 (1H, dd, *J*=10.5, 1.2 Hz), 5.34

(1H, dd, $J=17.5, 1.5$ Hz), 5.99 (1H, m), 7.22 (1H, m), 7.33 (1H, td, $J=7.8, 1.2$ Hz), 7.47 (2H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.16, -2.67, 70.08, 71.62, 98.16, 104.56, 117.10, 121.84, 127.07, 127.17, 128.60, 132.33, 134.83, 140.56; UV (CH_2Cl_2) λ_{max} 262, 251 nm; FT-IR (NaCl) 2953.1, 2149.3, 1482.1, 1245.8, 1084.2, 853.5 cm^{-1} ; MS (70 eV) m/z 302 (M^+); HRMS (M^+) calcd for $\text{C}_{17}\text{H}_{26}\text{OSi}_2$ 302.1522, found 302.1546.

2.8. Synthesis of 1-(*o*-methoxycarbonylmethoxymethylphenyl)-2-pentamethyldisilanyl ethyne **2d**

This reaction was carried out using the same procedure described for the preparation of **2a**, except *o*-methoxycarbonylmethoxymethyl-iodobenzene **1d** (0.5 g, 1.63 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 5:1, v/v) to afford colorless oil of **2d** (0.46 g, 85% yield); ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.11 (9H, s), 0.23 (6H, s), 3.72 (3H, s), 4.13 (2H, s), 4.76 (2H, s), 7.18 (1H, t, $J=7.1$ Hz), 7.28 (1H, t, $J=7.1$ Hz), 7.40 (1H, d, $J=7.6$ Hz), 7.46 (1H, d, $J=7.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.06, -2.56, 51.8, 67.7, 71.3, 98.4, 104.3, 122.0, 127.4, 127.5, 128.6, 132.3, 139.1, 170.6; UV (CH_2Cl_2) λ_{max} 262 nm; FT-IR (NaCl) 2953.4, 2149.3, 1759.7, 1437.7, 1246.3, 835.8 cm^{-1} ; MS (70 eV) m/z 334 (M^+); HRMS (M^+) calcd for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Si}_2$ 334.1420, found 334.1415.

2.9. Irradiation of 1-(*o*-hydroxymethylphenyl)-2-pentamethyldisilanyl ethyne **2a** in benzene

Deaerated solution (5×10^{-4} M) of **2a** (131 mg) in benzene (1 L) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 4 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **4a**, **6**, and **8** were isolated in 21 mg (21% yield), 22 mg (17% yield), and 4 mg (3% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (10/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (8/1, v/v) as an eluent.

4a: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.29 (9H, s), 2.31 (1H, s), 4.83 (2H, s), 7.26 (1H, td, $J=7.44, 1.26$ Hz), 7.35 (1H, td, $J=7.49, 1.30$ Hz), 7.43 (1H, dd, $J=7.35, 0.56$ Hz), 7.49 (1H, dd, $J=7.51, 0.91$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 0.34, 64.5, 100.0, 102.9, 121.5, 127.6, 127.8, 129.4, 132.8, 143.5; UV (CH_2Cl_2) λ_{max} 262, 251 nm; FT-IR (NaCl) 3343.4, 3067.3, 2959.4, 2155.6, 1480.4, 1249.9, 867.0 cm^{-1} ; MS (70 eV) m/z 204 (M^+); HRMS (M^+) calcd for $\text{C}_{12}\text{H}_{16}\text{OSi}$ 204.0970, found 204.0945. **6**: colorless oil; UV (CH_2Cl_2) λ_{max} 268, 229 nm; FT-IR (NaCl) 3453.5, 3067.6, 2954.4, 1455.6, 1250.6, 871.9 cm^{-1} ; MS (70 eV) m/z 262 (M^+); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}_2$ 262.1209, found 262.1252. **8**: colorless oil; UV (CH_2Cl_2) λ_{max} 305, 295, 271, 260 nm; FT-IR (NaCl) 3252.6, 2953.9, 1459.0, 1246.1, 884.1 cm^{-1} ; MS

(70 eV) m/z 262 (M^+); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}_2$ 262.1209, found 262.1219.

2.10. Irradiation of 1-(*o*-acetoxyethylphenyl)-2-pentamethyldisilanyl ethyne **2b** in benzene

This reaction was carried out using the same procedure described for the photolysis of **2a** in benzene (1 L), except 1-(*o*-acetoxyethylphenyl)-2-pentamethyldisilanyl ethyne **2b** (152 mg, 5×10^{-4} mol) and RUL 300 nm lamps were used. The photoadducts **4b**, **6**, and **8** were isolated in 17 mg (14% yield), 26 mg (20% yield), and 4 mg (3% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (15/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (8/1, v/v) as an eluent. **4b**: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.27 (9H, s), 2.15 (3H, s), 5.28 (2H, s), 7.34 (3H, m), 7.50 (1H, dd, $J=7.3, 1.1$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 0.29, 21.3, 65.2, 100.1, 102.4, 122.9, 128.4, 128.6, 129.1, 132.9, 138.3, 171.1; UV (CH_2Cl_2) λ_{max} 262, 251 nm; FT-IR (NaCl) 2958.4, 2157.6, 1746.4, 1485.2, 1249.3, 1229.3, 868.6 cm^{-1} ; MS (70 eV) m/z 246 (M^+); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Si}$ 246.1076, found 246.1072.

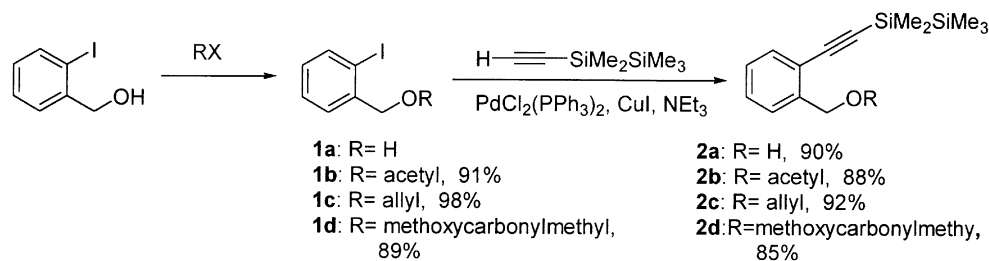
2.11. Irradiation of 1-(*o*-allyloxymethylphenyl)-2-pentamethyldisilanyl ethyne **2c** in benzene

This reaction was carried out using the same procedure described for the photolysis of **2a** in benzene (1 L), except 1-(*o*-allyloxymethylphenyl)-2-pentamethyldisilanyl ethyne **2c** (151 mg, 5×10^{-4} mol) was used. The photoadducts **4c** and **12** were isolated in 6 mg, 5% yield and 29 mg, 19% yield, respectively, by column chromatography with *n*-hexane/ethyl acetate (90/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (60/1, v/v) as an eluent.

4c: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.28 (9H, s), 4.14 (2H, d, $J=5.4$ Hz), 4.71 (2H, s), 5.24 (1H, dd, $J=10.4, 1.2$ Hz), 5.36 (1H, dd, $J=17.2, 1.5$ Hz), 6.00 (1H, m), 7.24 (1H, t, $J=7.1$ Hz), 7.35 (1H, td, $J=7.2, 1.1$ Hz), 7.49 (2H, t, $J=8.1$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 0.38, 70.50, 72.08, 99.38, 103.05, 117.47, 122.07, 127.50, 127.82, 129.11, 132.63, 135.17, 140.99; UV (CH_2Cl_2) λ_{max} 262, 250 nm; FT-IR (NaCl) 2948.9, 2150.2, 1449.4, 1243.7, 831.4 cm^{-1} ; MS (70 eV) m/z 244 (M^+); HRMS (M^+) calcd for $\text{C}_{15}\text{H}_{20}\text{OSi}$ 244.1283, found 244.1271. **12**: colorless oil; UV (CH_2Cl_2) λ_{max} 269 nm; FT-IR (NaCl) 2953.9, 1499.3, 1250.8, 1074.9, 871.3 cm^{-1} ; MS (70 eV) m/z 302 (M^+); HRMS (M^+) calcd for $\text{C}_{17}\text{H}_{26}\text{OSi}_2$ 302.1522, found 302.1533.

2.12. Irradiation of 1-(*o*-methoxycarbonylmethoxymethylphenyl)-2-pentamethyldisilanyl ethyne **2d** in benzene

This reaction was carried out using the same procedure described for the photolysis of **2a** in benzene (1 L), except



Scheme 1.

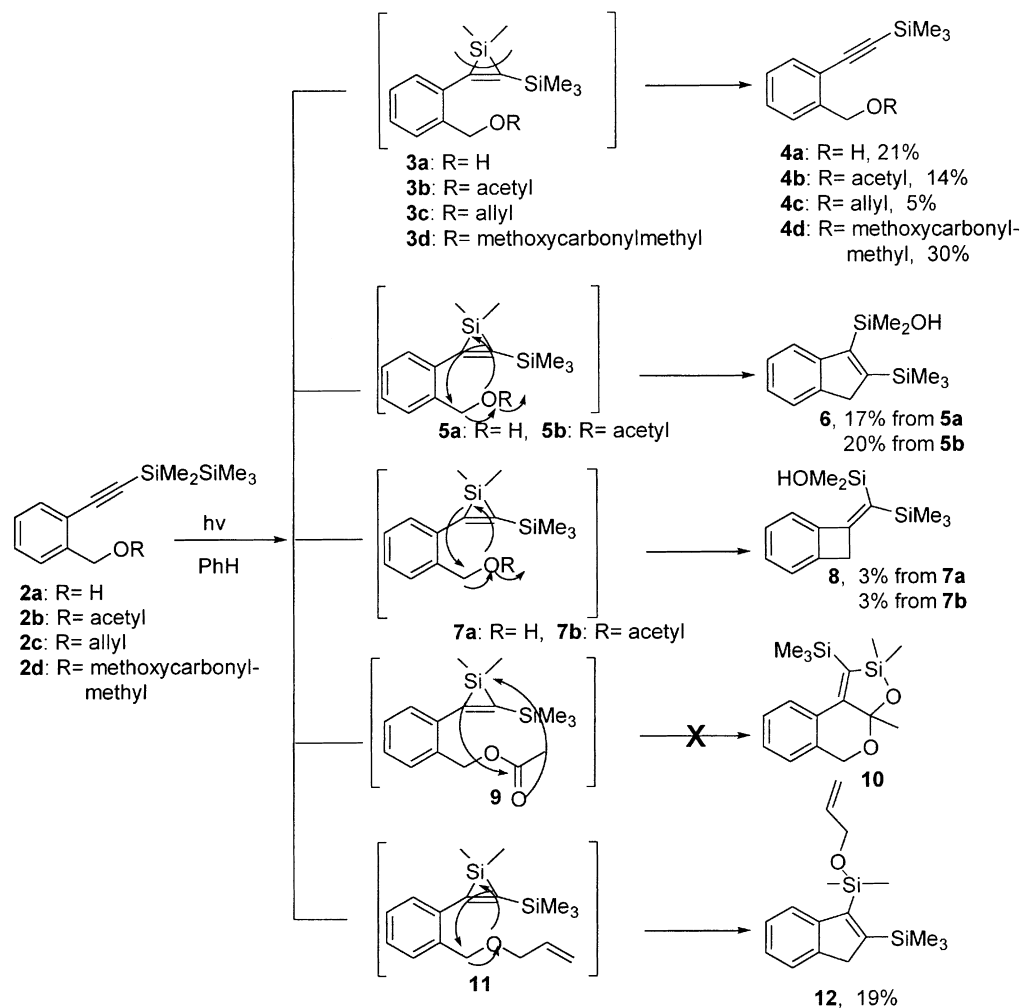
1-(*o*-methoxycarbonylmethoxymethylphenyl)-2-pentamethyldisilanyl ethyne **2d** (167 mg, 5×10^{-4} mol) and RUL 300 nm lamps were used. The photoadduct **4d** was isolated in 41 mg, 30% yield, by column chromatography with *n*-hexane/ethyl acetate (10/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (8/1, v/v) as an eluent. **4d**: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.28 (9H, s), 3.79 (3H, s), 4.20 (2H, s), 4.83 (2H, s), 7.26 (1H, td, $J=7.5$, 1.1 Hz), 7.36 (1H, td, $J=7.5$, 1.3 Hz), 7.48 (1H, dd, $J=7.6$, 1.1 Hz), 7.52 (1H, d, $J=7.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 0.34, 52.2, 68.2, 71.7, 99.6, 102.9, 122.4, 127.9, 128.2, 129.2, 132.7, 139.8, 171.1; UV (CH_2Cl_2) λ_{max} 262, 250 nm; FT-IR (NaCl) 2955.9, 2156.9, 1740.1, 1455.2, 1249.4, 867.7 cm^{-1} ; MS (70 eV) m/z 276 (M^+); HRMS (M^+) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Si}$ 276.1182, found 276.1175.

3. Results and discussion

The starting 1-(*o*-alkoxymethylphenyl)-2-pentamethyldisilanyl ethynes **2a–d** were prepared by the reaction of *o*-alkoxymethyl-iodobenzenes **1a–d** with pentamethyldisilanyl ethyne in the presence of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in triethylamine (Scheme 1). Irradiation of **2a** in deaerated benzene with 254 nm UV light provided novel cycloaddition products **6** (17% yield) and **8** (3% yield) in addition to **4a** (21% yield) along with some decomposition products of unknown structure as shown in Scheme 2. The formation of photoproducts **6** and **8** can be rationalized in terms of the initial formation of silacyclopropene intermediates **5a** and **7a** upon irradiation followed by the concerted intramolecular cycloaddition reaction between the hydroxy group in *ortho* substituent and Si–C bond of silacyclopropene formed. Liberation of dimethylsilylene species from the silacyclopropene intermediate **3a** resulted in the formation of **4a**. In order to check whether or not the C=O bond in the *ortho* substituent inserts intramolecularly into Si–C bond of the silacyclopropene ring, we have synthesized 1-(*o*-acetoxymethylphenyl)-2-pentamethyldisilanyl ethyne **2b** which has the acetoxymethyl group as *ortho* substituent to phenylethynylpentamethyldisilane and investigated the photolysis of **2b** in benzene with 300 nm UV light to obtain the same photoproducts **6** (20% yield) and **8** (3% yield) as

in the case of the photolysis of **2a**, in addition to **4b** (14% yield) instead of the expected intramolecular cycloaddition product **10** via silacyclopropene intermediate **9** (Scheme 2). To investigate the reactivity difference between the benzylic and allylic positions in the *ortho* substituent, we have synthesized 1-(*o*-allyloxymethylphenyl)-2-pentamethyldisilanyl ethyne **2c** which has the allyloxymethyl group as *ortho* substituent to phenylethynylpentamethyldisilane. When a benzene solution of **2c** was irradiated at room temperature with 254 nm UV light under a purified nitrogen atmosphere, **12** and **4c** in 19 and 5% yield, respectively, were obtained via silacyclopropene intermediate **11** and **3c**, respectively, but the other possible photoproducts were not observed (Scheme 2). The result indicates the initial formation of silacyclopropene intermediate **11** upon irradiation followed by the novel intramolecular cycloaddition reaction of Si–C (silacyclopropene ring) to C–O (benzylic position) via oxygen–silicon bond formation to give the novel photoproduct **12**. In the case of the photolysis of **2d** in benzene with 300 nm UV light, **4d** was only obtained in 30% yield but the expected intramolecular cycloaddition reaction of Si–C (silacyclopropene ring) to C=O (carbonyl group in the *ortho* substituent) was not occurred probably due to the long distance between Si–C (silacyclopropene ring) and C=O bonds.

The structures of these photoproducts **6**, **8**, and **12** were determined by various physical methods, such as ^1H NMR, ^{13}C NMR, 2D NMR (^1H – ^1H , ^1H – ^{13}C COSY, HMBC, NOESY), UV, FT-IR, and high resolution mass spectrometry. FT-IR spectra of **6** and **8** showed the typical hydroxy absorption at 3453.5 and 3252.6 cm^{-1} , respectively, but the FT-IR spectrum of **12** did not show the –OH absorption. The ^1H , ^{13}C , and 2D NMR spectra of **6** were very similar to those of **12** except that the photoproduct **12** has the allyloxy group instead of the hydroxy group in **6**. The ^1H – ^1H and ^1H – ^{13}C correlation spectroscopy (COSY) spectra of **6**, **8**, and **12** were studied to identify the protons directly attached to the individual carbons. From the correlated peaks in **6**, **8**, and **12**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Tables 1–3. In order to locate the quaternary carbons, the HMBC spectra of **6**, **8**, and **12** were taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(1), C(9), C(10) and the quaternary carbon C(7) in **6** and **12** showed the connectivity of the carbon C(7) to the benzene



Scheme 2.

Table 1

¹H NMR (600 MHz), ¹³C NMR (150 MHz), and HMBC data for photoproduct **6** in CDCl₃^a

Position	δ _C (ppm)	M ^b	δ _H (ppm)	I ^c	M ^d	J _{H-H} (Hz)	HMBC ^e
1	122.3	d	7.59	1H	d	7.5 (<i>J</i> _{1H-2H})	H2
2	124.8	d	7.21	1H	td	7.3 (<i>J</i> _{2H-1H,3H}), 1.0 (<i>J</i> _{2H-4H})	H1, H3
3	126.4	d	7.30	1H	td	7.3 (<i>J</i> _{3H-2H,4H}), 1.0 (<i>J</i> _{3H-1H})	H1, H2, H4
4	123.8	d	7.55	1H	d	7.5 (<i>J</i> _{4H-3H})	H2, H3, H9
5	149.8	s					H3, H9
6	146.6	s					H2, H9
7	153.2	s					H1, H9, H10
8	161.0	s					H9, H11
9	48.2	t	3.61	2H	s		H4
10	2.67	q	0.53	6H	s		
11	1.34	q	0.35	9H	s		
-OH			1.91	1H			

^a All these assignments were confirmed by ¹H-¹H and ¹H-¹³C COSY and NOESY, HMBC spectra.^b Multiplicities were determined by DEPT spectrum.^c Integrated intensity.^d Multiplicities.^e Protons correlated to carbon resonances in ¹³C column.

Table 2

¹H NMR (600 MHz), ¹³C NMR (150 MHz), and HMBC data for photoproduct **8** in CDCl₃^a

Position	δ _C (ppm)	M ^b	δ _H (ppm)	I ^c	M ^d	J _{H–H} (Hz)	HMBC ^e
1	122.4	d	7.24	1H	m		H3
2	127.6	d	7.24	1H	m		H4
3	129.6	d	7.24	1H	m		H4
4	122.9	d	7.44	1H	dd	6.8 (J _{4H–3H}), 2.2 (J _{4H–2H})	H9
5	147.8	s					H3
6	147.5	s					H2
7	160.1	s					H1, H9
8	132.9	s					H9, H10, H11
9	44.3	t	3.76	2H	s		H4
10	2.24	q	0.41	6H	s		
11	2.21	q	0.25	9H	s		
–OH			1.78	1H			

^a All these assignments were confirmed by ¹H–¹H and ¹H–¹³C COSY and NOESY, HMBC spectra.^b Multiplicities were determined by DEPT spectrum.^c Integrated intensity.^d Multiplicities.^e Protons correlated to carbon resonances in ¹³C column.

Table 3

¹H NMR (600 MHz), ¹³C NMR (150 MHz), and HMBC data for photoproduct **12** in CDCl₃^a

Position	δ _C (ppm)	M ^b	δ _H (ppm)	I ^c	M ^d	J _{H–H} (Hz)	HMBC ^e
1	122.09	d	7.62	1H	d	7.7 (J _{1H–2H})	H2
2	124.23	d	7.18	1H	t	7.3 (J _{2H–1H,3H})	H1, H3
3	125.96	d	7.27	1H	t	7.3 (J _{3H–2H,4H})	H1, H2, H4
4	123.21	d	7.52	1H	d	7.3 (J _{4H–3H})	H2, H3, H9
5	149.54	s					H3, H9
6	146.11	s					H2, H9
7	151.45	s					H1, H9, H10
8	161.31	s					H9, H11
9	47.90	t	3.58	2H	s		H4
10	0.86	q	0.47	6H	s		
11	0.57	q	0.30	9H	s		
12	63.92	t	4.25	2H	d	5.4 (J _{12H–13H})	H14
13	137.20	d	6.00	1H	m		H12, H14
14 _α	115.13	t	5.13	1H	dd	10.3 (J _{14αH–13H}), 1.6 (J _{14αH–14βH})	H12
14 _β	115.13	t	5.28	1H	dd	17.1 (J _{14βH–13H}), 1.6 (J _{14βH–14αH})	H12

^a All these assignments were confirmed by ¹H–¹H and ¹H–¹³C COSY and NOESY, HMBC spectra.^b Multiplicities were determined by DEPT spectrum.^c Integrated intensity.^d Multiplicities.^e Protons correlated to carbon resonances in ¹³C column.

ring, hydroxysilyl or allyloxysilyl group, and the carbon(8). In the same manner, the connectivity of the carbon C(8) to the carbon C(9) and the trimethylsilyl group in **6** and **12** was established. The presence of the cross-peaks due to the vicinal coupling between the protons of C(9), C(10), C(11) and the quaternary carbon C(8) in **8** showed the connectivity of the carbon C(8) to the carbon C(7), hydroxysilyl, and trimethylsilyl group. In the same manner, the connectivity of the carbon C(7) to the benzene ring in **8** was established. The 3D-structures of **6**, **8**, and **12** were determined by a nuclear overhauser and exchange spectroscopy (NOESY) spectrum. In particular, the presence of the cross-peaks between a proton of C(10) and the protons of C(11) showed

the close proximity of a proton of C(10) to the protons of C(11), indicating that these protons are located on the same side of the molecule. In the same manner, the presence of the cross-peaks between a proton of C(9) and the protons of trimethylsilyl group in **8** showed the close proximity of a proton of C(9) to the protons of trimethylsilyl group, indicating that the stereochemistry of **8** is **Z** form. Thus, the skeletal structures of **6**, **8**, and **12** were established as shown in Fig. 1.

In conclusion, the photoinduced intramolecular cycloaddition reactions of various *ortho*-substituted pentamethylid-silanyl ethynes afforded the novel photoproducts **6**, **8**, and **12** via silacyclopentene intermediates. The formation of

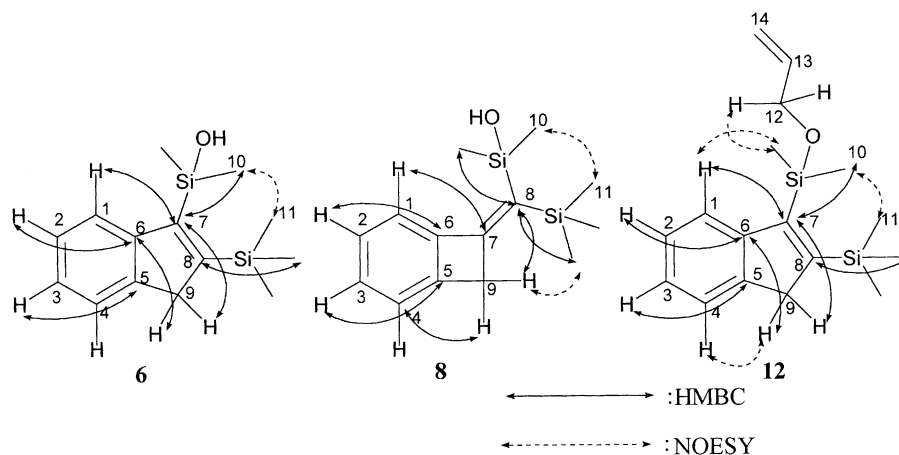


Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproducts **6**, **8**, and **12**.

the photoproducts **6**, **8**, and **12** was explained by the concerted intramolecular cycloaddition reactions as shown in Scheme 2.

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