

A Novel Photo reaction of (2-Hydroxyethoxyphenyl)pentamethyldisilane

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Photolysis of (2-hydroxyethoxyphenyl)pentamethyldisilane **2** in benzene provides a novel intramolecular cyclization photoproduct **9** which was probably formed from the intramolecular reaction to form a seven-membered ring in silatriene intermediate **7** and then the photochemical disrotatory ring closure of 1,3-butadiene moiety to cyclobutene. Irradiation of **2** in methanol afforded photoproducts **5** and **6** which were formed by the nucleophilic attack of methanol to β or α silicon atom in pentamethyldisilanyl group of the photoexcited state of **2**. Compounds **10** and **11** were also formed by the same way as in the formation of the photoproducts **5** and **6** in the photolysis of (2-allyloxyethoxyphenyl)pentamethyldisilane **3** in methanol solvent. Photoreaction of (2-acetoxyethoxyphenyl)pentamethyldisilane **4** in methanol gave a photoproduct **12** which was formed *via* the elimination of dimethylsilylene species in the photoexcited state of **4**.

Key Words: (2-Hydroxyethoxyphenyl)pentamethyldisilane, (2-Allyloxyethoxyphenyl)pentamethyldisilane, (2-Acetoxyethoxyphenyl)pentamethyldisilane, Silatriene

Introduction

Since the first report on the photolysis of phenylpentamethyldisilane and (*p*-tolyl)pentamethyldisilane by Ishikawa *et al.*¹ in 1975, photoreactions of arylsilanes have been extensively investigated.²⁻²⁰ However, relatively little is known about the photoreactions of *ortho*-substituted phenylpentamethyldisilanes.

Very recently, we have found that the photolysis of *ortho*-substituted phenylpentamethyldisilanes²¹⁻²³ afforded novel intramolecular photoproducts *via* silatriene intermediates. In connection with our ongoing studies for the utility of silacyclopropenes, 1-silaallenes, and silatrienes as reaction intermediates in organic synthesis of silicon-containing heterocyclic compounds,²⁴ we were now interested in the synthesis of silicon-containing large ring compounds through the photolysis of *ortho*-substituted arylsilanes. And, we have investigated the photoreactions of (2-hydroxyethoxyphenyl)pentamethyldisilane **2**, since novel photoproducts from the intramolecular reaction of *ortho*-substituted group with the silatriene intermediate, which is formed from the radical scission of a silicon-silicon bond followed by migration of the resulting trimethylsilyl radical to the C₆ position of the benzene ring, are expected and we would like to report the detailed photochemical study of (2-hydroxyethoxyphenyl)pentamethyldisilane **2** and its derivatives **3** or **4**.

Experimental

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 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. Microwave-assisted reactions were conducted in a commercially available microwave reactor, MicroSYNTH, equipped with an infrared temperature detector. The temperatures were controlled within less than $\pm 1-2$ °C in the temperature-controlled microwave-assisted reaction. 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).

Materials. Tetrahydrofuran was refluxed over sodium benzophenone and distilled under nitrogen. Methanol (HPLC grade), benzene (HPLC grade), and *n*-hexane (HPLC grade) were 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.

Synthesis of (2-hydroxyphenyl)pentamethyldisilane 1. Triethylamine (0.76 mL, 5.45 mmol) was added to a solution of 2-iodophenol (1 g, 4.54 mmol) in tetrahydrofuran (30 mL) at room temperature under nitrogen atmosphere. Chloropentamethyldisilane (1.05 mL, 5.45 mmol) was added dropwisely to the resulting solution and the mixture was refluxed for 3 h. The reaction mixture was filtered with celite, and concentrated in vacuo. To this reaction residue, THF (30 mL) was added. This resulting reaction solution was added to Mg (0.33 g, 13.6 mmol) at room temperature under nitrogen atmosphere and the mixture was refluxed for 1 h. The reaction mixture was

filtered with celite, and concentrated in vacuo. Water (30 mL) was added to the solution and extracted with ethyl acetate (3 × 15 mL). The combined ethyl acetate solution was washed with water (20 mL), brine (20 mL) and dried (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10/1, v/v) as an eluent gave **1** (0.81 g, 80% yield) as a colorless oil: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.11 (9H, s), 0.39 (6H, s), 4.86 (1H, s), 6.68 (1H, dd, *J* = 8.1, 0.9 Hz), 6.96 (1H, td, *J* = 7.4, 0.9 Hz), 7.24 (1H, ddd, *J* = 9, 7.4, 1.8 Hz), 7.37 (1H, dd, *J* = 7.4, 1.8 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -3.49, -1.66, 114.3, 120.8, 125.1, 130.4, 135.6, 160.2; UV (CH₂Cl₂) λ_{max} 286, 279 nm; FT-IR (NaCl) 3536.9, 3066.7, 2950.8, 2893.9, 1592.9, 1437.1, 1275.7, 1243.9, 835.1, 799.2 cm⁻¹; MS (70 eV) *m/z* 224 (M⁻); MS *m/z* (%) 224 (M⁺, 2.5), 209 (100), 193 (70), 151 (19), 133 (33.5), 91 (12); HRMS (M⁺) calcd for C₁₁H₂₀O₂Si₂ 224.1053, found 224.1075.

Synthesis of (2-hydroxyethoxyphenyl)pentamethylidisilane

2. To a solution of (2-hydroxyphenyl)pentamethylidisilane **1** (0.5 g, 2.23 mmol), sodium hydroxide (0.45 g, 11.2 mmol), and tetrabutylammonium iodide (0.082 g, 0.223 mmol) in water (5 mL) was added dropwisely 2-chloroethanol (0.45 mL, 6.69 mmol) at room temperature. The reaction mixture was irradiated in MicroSYNTH operated at 500W for 1 hr at 40 °C temperature. Water (5 mL) was added to the solution and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate solution was washed with water (10 mL), brine (10 mL) and dried (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent gave **2** (0.57 g, 95% yield) as a colorless oil: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.07 (9H, s), 0.37 (6H, s), 1.96 (1H, s), 3.99 (2H, m), 4.11 (2H, m), 6.83 (1H, d, *J* = 8.4 Hz), 6.98 (1H, t, *J* = 7.5 Hz), 7.34 (2H, m); ¹³C NMR (CDCl₃, 75 MHz) δ_C -2.99, -1.60, 61.7, 69.0, 110.1, 121.1, 127.4, 130.5, 135.6, 163.1; UV (CH₂Cl₂) λ_{max} 286, 279 nm; FT-IR (NaCl) 3359.3, 3062.9, 2949.3, 2892.7, 1585.1, 1436.5, 1232.0, 793.7 cm⁻¹; MS (70 eV) *m/z* 268 (M⁻); MS *m/z* (%) 268 (M⁺, 0.1), 252 (14), 223 (18), 209 (30), 179 (100), 133 (44), 123 (29), 73 (14); HRMS (M⁻) calcd for C₁₃H₂₄O₂Si₂ 268.1315, found 268.1370.

Synthesis of (2-allyloxyethoxyphenyl)pentamethylidisilane

3. To a solution of (2-hydroxyethoxyphenyl)pentamethylidisilane **2** (0.5 g, 1.86 mmol), sodium hydroxide (0.37 g, 9.32 mmol), and tetrabutylammonium iodide (0.068 g, 0.186 mmol) in water (5 mL) was added dropwisely allyl bromide (0.48 mL, 5.59 mmol) at room temperature. The reaction mixture was irradiated in MicroSYNTH operated at 500 W for 45 min at 66 °C temperature. Water (5 mL) was added to the solution and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate solution was washed with water (10 mL), brine (10 mL) and dried (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (15/1, v/v) as an eluent gave **3** (0.54 g, 94% yield) as a colorless oil: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.09 (9H, s), 0.39 (6H, s), 3.85 (2H, t, *J* = 3.9 Hz), 4.09 (2H, d, *J* = 4.2 Hz), 4.17 (2H, t, *J* = 3.9 Hz), 5.24 (1H, d, *J* = 7.8 Hz), 5.35 (1H, dd, *J* = 12.9, 1.2 Hz), 5.98 (1H, m), 6.84 (1H, d, *J* = 6 Hz), 6.98 (1H, t, *J* = 5.4 Hz), 7.34 (1H, td, *J* = 6,

0.9 Hz), 7.38 (1H, dd, *J* = 5.4, 0.9 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -3.50, -1.81, 66.4, 68.5, 72.1, 109.5, 117.2, 120.5, 127.2, 130.1, 134.5, 135.1, 162.9; UV (CH₂Cl₂) λ_{max} 286, 280 nm; FT-IR (NaCl) 3063.4, 2949.3, 2892.8, 1585.4, 1436.4, 1231.8, 1128.7, 926.6 cm⁻¹; MS (70 eV) *m/z* 308 (M⁺); MS *m/z* (%) 308 (M⁺, 2), 267 (7), 235 (30), 192 (100), 164 (52), 150 (17), 118 (8), 74 (55); HRMS (M⁺) calcd for C₁₆H₂₈O₂Si₂ 308.1628, found 308.1637.

Synthesis of (2-acetoxyethoxyphenyl)pentamethylidisilane

4. A solution of (2-hydroxyethoxyphenyl)pentamethylidisilane **2** (0.5 g, 1.86 mmol) in *N,N*-dimethylformamide (5 mL) was added to a solution of NaH (0.05 g, 2.23 mmol) in DMF (5 mL) at room temperature under nitrogen atmosphere. Acetyl chloride (0.27 mL, 3.73 mmol) was added dropwise to the resulting solution and the reaction mixture was irradiated in MicroSYNTH operated at 500 W for 1 hr at 80 °C temperature. Water (10 mL) was added to the solution and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate solution was washed with water (10 mL), brine (10 mL) and dried (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent gave **4** (0.32 g, 55% yield) as a colorless oil: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.043 (9H, s), 0.34 (6H, s), 2.09 (3H, s), 4.18 (2H, m), 4.44 (2H, m), 6.78 (1H, d, *J* = 8.1 Hz), 6.97 (1H, td, *J* = 7.5, 0.9 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -3.23, -1.53, 21.2, 63.1, 65.5, 109.7, 112.1, 121.2, 130.5, 135.6, 156.1, 168.6; UV (CH₂Cl₂) λ_{max} 286, 279 nm; FT-IR (NaCl) 3063.3, 2950.2, 2893.3, 1745.8, 1585.6, 1437.0, 1220.2, 1067.5, 793.7 cm⁻¹; MS (70 eV) *m/z* 310 (M⁻); MS *m/z* (%) 310 (M⁻, 0.8), 267 (2), 237 (100), 193 (30), 179 (55), 151 (17), 87 (76), 75 (12); HRMS (M⁻) calcd for C₁₅H₂₆O₃Si₂ 310.1420, found 310.1401.

Irradiation of (2-hydroxyethoxyphenyl)pentamethylidisilane

2 in methanol. A solution (5 × 10⁻¹ M) of (2-hydroxyethoxyphenyl)pentamethylidisilane **2** (134 mg) in methanol (1 L) was deaerated by nitrogen purging for 1 hr and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 1 hr, the resulting photoreaction mixture was concentrated in vacuo. The photoproducts **5** and **6** were isolated in (53.9 mg, 55% yield) and (3.5 mg, 5% yield), respectively, in addition to 2% (2.7 mg) of the starting material **2** by column chromatography with *n*-hexane/ethyl acetate (4/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1, v/v) as an eluent. **5:** ¹H NMR (CDCl₃, 300 MHz) δ_H 0.37 (6H, d, *J* = 3 Hz), 1.98 (1H, s), 3.98 (2H, m), 4.12 (2H, m), 4.46 (1H, septet, *J* = 3 Hz), 6.84 (1H, d, *J* = 6 Hz), 6.99 (1H, t, *J* = 5.4 Hz), 7.37 (1H, td, *J* = 6, 1.2 Hz), 7.45 (1H, dd, *J* = 5.4, 1.2 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -3.46, 61.8, 69.3, 110.6, 121.3, 125.7, 131.5, 136.0, 163.3; UV (CH₂Cl₂) λ_{max} 284, 278 nm; FT-IR (NaCl) 3376.5, 3063.5, 2955.7, 2876.5, 2117.6, 1587.4, 1437.3, 1235.8, 1082.3, 783.7 cm⁻¹; MS (70 eV) *m/z* 196 (M⁺); MS *m/z* (%) 196 (M⁺, 12), 179 (81), 162 (100), 136 (14), 134 (5), 102 (38), 92 (26), 76 (4), 54 (3); HRMS (M⁺) calcd for C₁₀H₁₆O₂Si 196.0920, found 196.0936. **6:** ¹H NMR (CDCl₃, 300 MHz) δ_H 2.52 (1H, s), 3.96 (2H, m), 4.08 (2H, m), 6.94 (3H, m), 7.30 (2H, m); ¹³C NMR (CDCl₃, 75 MHz) δ_C 61.7, 69.3, 114.8, 121.4, 129.8, 158.8; UV (CH₂Cl₂) λ_{max} 278, 271

nm; FT-IR (NaCl) 3377.4, 2935.7, 1598.9, 1496.5, 1245.5, 1082.1, 916.1, 754.5 cm^{-1} ; MS (70 eV) m/z 138 (M^+); MS m/z (%) 138 (M^+ , 1), 135 (26), 119 (37), 88 (45), 86 (40), 76 (60), 74 (100), 60 (53); HRMS (M^+) calcd for $C_8H_{10}O_2$ 138.0681, found 138.0623.

Irradiation of (2-hydroxyethoxyphenyl)pentamethyldisilane 2 in benzene. A solution (5×10^{-4} M) of (2-hydroxyethoxyphenyl)pentamethyldisilane **2** (134 mg) in benzene (1 L) was deaerated by nitrogen purging for 1 hr and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 2 hr, the resulting photoreaction mixture was concentrated in vacuo. The photoproduct **9** was isolated in (34.8 mg, 26% yield) in addition to 6% (8 mg) of the starting material **2** by column chromatography with *n*-hexane/ethyl acetate (4/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1, v/v) as an eluent. **9**: UV (CH_2Cl_2) λ_{max} 273 nm; FT-IR (NaCl) 3050.8, 2954.3, 2864.1, 1587.6, 1438.7, 1249.3, 1118.9, 928.6, 848.7 cm^{-1} ; MS (70 eV) m/z 268 (M^+); MS m/z (%) 268 (M^+ , 0.6), 225 (7), 195 (25), 147 (100), 135 (32), 95 (17), 73 (80), 59 (9); HRMS (M^+) calcd for $C_{13}H_{24}O_2Si_2$ 268.1315, found 268.1346.

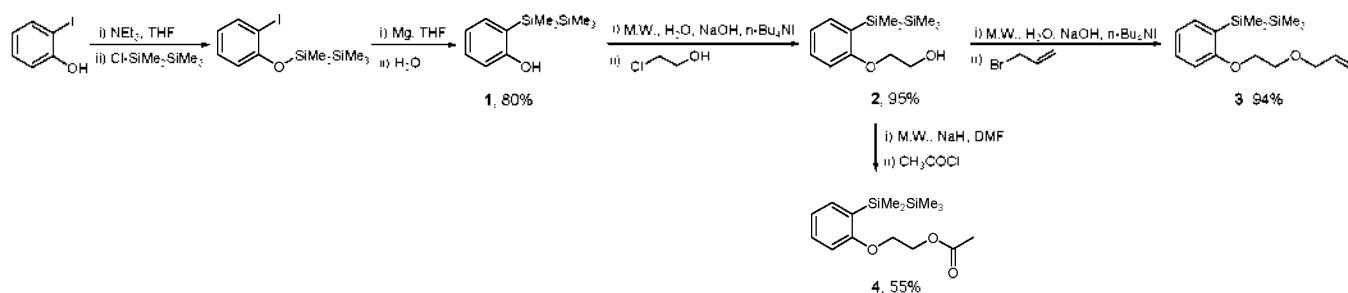
Irradiation of (2-allyloxyethoxyphenyl)pentamethyldisilane 3 in methanol. A solution (5×10^{-4} M) of (2-allyloxyethoxyphenyl)pentamethyldisilane **3** (154 mg) in methanol (1 L) was deaerated by nitrogen purging for 1 hr and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 30 min, the resulting photoreaction mixture was concentrated in vacuo. The photoproducts **10** and **11** were isolated in (53.1 mg, 45% yield) and (2.7 mg, 3% yield), respectively, in addition to 4% (6.2 mg) of the starting material **3** by column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1, v/v) as an eluent. **10**: ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.36 (6H, d, $J = 3.9$ Hz), 3.83 (2H, t, $J = 4.8$ Hz), 4.10 (2H, dt, $J = 5.7, 1.5$ Hz), 4.14 (2H, t, $J = 4.8$ Hz), 4.42 (1H, septet, $J = 3.9$ Hz), 5.21 (1H, dq, $J = 10, 1.2$ Hz), 5.32 (1H, dq, $J = 17, 1.5$ Hz), 5.95 (1H, m), 6.83 (1H, d, $J = 8.1$ Hz), 6.96 (1H, td, $J = 7.2, 0.9$ Hz), 7.35 (1H, ddd, $J = 9.3, 7.5, 1.8$ Hz), 7.45 (1H, dd, $J = 7.2, 1.8$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.75, 67.0, 68.6, 72.3, 110.1, 117.1, 120.6, 125.6, 131.1, 134.6, 135.9, 163.4; UV (CH_2Cl_2) λ_{max} 285, 278 nm; FT-IR (NaCl) 3065.0, 2956.2, 2870.7, 2115.7, 1587.5, 1437.4, 1238.6, 1130.9, 889.4 cm^{-1} ; MS (70 eV) m/z 236 (M^+); MS m/z (%) 236 (M^+ , 2.5), 235 (15), 191 (31), 179 (84), 151 (100), 135 (68), 115 (38), 91 (54), 77 (24), 59 (9);

HRMS (M^+) calcd for $C_{13}H_{20}O_2Si_2$ 236.1233, found 236.1258. **11**: ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 3.82 (2H, m), 4.13 (4H, m), 5.23 (1H, dq, $J = 10, 1.2$ Hz), 5.34 (1H, dq, $J = 17, 1.5$ Hz), 5.96 (1H, m), 6.96 (3H, m), 7.30 (2H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 67.3, 68.6, 72.4, 114.6, 117.4, 120.9, 129.5, 134.6, 158.8; UV (CH_2Cl_2) λ_{max} 278, 272 nm; FT-IR (NaCl) 3064.5, 2926.9, 2870.2, 1598.6, 1495.9, 1244.9, 1113.0, 915.3 cm^{-1} ; MS (70 eV) m/z 178 (M^+); MS m/z (%) 178 (M^+ , 66), 133 (17), 120 (100), 92 (32), 78 (77), 66 (19); HRMS (M^+) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0921.

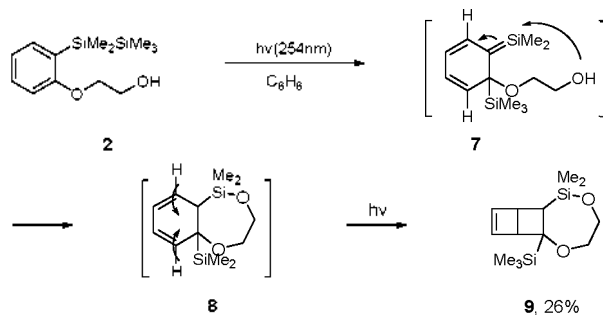
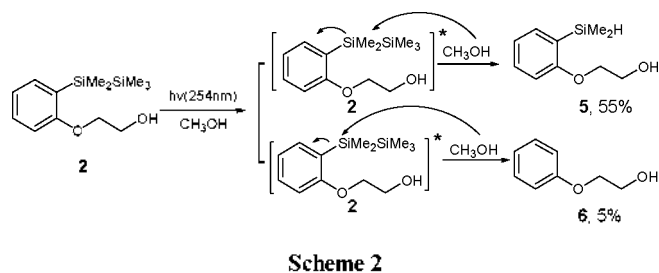
Irradiation of (2-acetoxyethoxyphenyl)pentamethyldisilane 4 in methanol. A solution (5×10^{-4} M) of (2-acetoxyethoxyphenyl)pentamethyl disilane **4** (155 mg) in methanol (1 L) was deaerated by nitrogen purging for 1 hr and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 2 hr, the resulting photoreaction mixture was concentrated in vacuo. The photoproducts **12** were isolated in (48 mg, 38% yield) in addition to 9% (14 mg) of the starting material **4** by column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1, v/v) as an eluent. **12**: ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.34 (9H, s), 2.09 (3H, s), 4.18 (2H, m), 4.44 (2H, m), 6.79 (1H, d, $J = 8.1$ Hz), 6.97 (1H, td, $J = 7.5, 0.9$ Hz), 7.34 (2H, m); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.47, 21.2, 63.1, 65.8, 110.2, 114.9, 121.3, 131.5, 136.4, 159.4, 169.9; UV (CH_2Cl_2) λ_{max} 285, 278 nm; FT-IR (NaCl) 3055.1, 2983.9, 1735.8, 1587.7, 1438.1, 1265.8, 1046.6, 739.4 cm^{-1} ; MS (70 eV) m/z 252 (M^+); MS m/z (%) 252 (M^+ , 6), 224 (63), 211 (22), 149 (100), 117 (11), 98 (6), 74 (90), 60 (25); HRMS (M^+) calcd for $C_{13}H_{20}O_3Si_2$ 252.1182, found 252.1102.

Results and Discussion

(2-Hydroxyphenyl)pentamethyldisilane **1** was prepared by the 1,3-migration of pentamethyldisilyl group in 2-(pentamethyldisilyloxy)phenylmagnesium iodide in tetrahydrofuran. The starting (2-hydroxyethoxyphenyl)pentamethyldisilane **2** was prepared by the reaction of 2-chloroethanol with (2-hydroxyphenyl)pentamethyldisilane **1** under microwave irradiation using MicroSYNTH in water. The starting (2-allyloxyethoxyphenyl)pentamethyldisilane **3** or (2-acetoxyethoxyphenyl)pentamethyldisilane **4** were also prepared by the reaction of allyl bromide or acetyl chloride with (2-hydroxyethoxyphenyl)pentamethyldisilane **2** under microwave irradiation using MicroSYNTH (Scheme 1).



Scheme 1



Photoreactions of (2-hydroxyethoxyphenyl)pentamethyldisilane 2. To investigate whether or not the hydroxyethoxy group as *ortho* substituent in **2** reacts intramolecularly with silatriene moiety formed in the photoexcited state of **2**, the photolysis of **2** was performed.

Irradiation of **2** in deaerated methanol with 254 nm UV light afforded **5** (55% yield) and **6** (5% yield) along with some decomposition products of unknown structure as shown in Scheme 2, when 98 % of **2** was photolyzed but the expected intramolecular photoproduct was not obtained. Indeed, it is well known that the photolysis of substituted phenylpentamethyldisilanes has four reaction pathways:²⁵ (path a) formation of a silene compound and a trimethylsilane², (path b) formation of a silatriene compound arising from 1,3-shift of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon bond to the C₆ position of benzene ring,³⁻¹⁵ (path c) formation of a trimethylsilyl compound *via* elimination of a silylene,^{3,18} (path d) formation of a direct solvolysis compound accompanied by the formation of trimethylalkoxysilane and

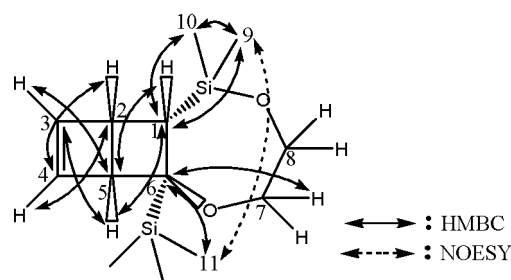


Figure 1. Important correlations observed in HMBC and NOESY spectra of the photoproduct **9**.

trimethylsilane.^{19,26} The formation of a photoproduct **5** or **6** can best be explained in terms of the nucleophilic attack at β or α silicon atom of pentamethyldisilanyl group in the photoexcited state of **2** by methanol (path d). The structure of the photoproduct **5** was determined by the ¹H NMR and IR absorption spectra of **5** showing a septet resonance at δ 4.46 and a characteristic absorption at 2117.6 cm⁻¹, respectively, due to a Si-H proton and a Si-H stretching mode in the dimethylsilyl group of **5**.

Irradiation of **2** in deaerated benzene with 254 nm UV light afforded a novel intramolecular photoproduct **9** (26% yield) along with some decomposition products of unknown structure as shown in Scheme 3, when 94% of **2** was photolyzed. The formation of a novel photoproduct **9** can best be explained in terms of the initial formation of silatriene intermediate **7** arising from 1,3-migration of trimethylsilyl radical, which is formed *via* the homolytic cleavage of silicon-silicon bond of pentamethyldisilanyl group in the photoexcited state of **2** to the C₆ position of benzene ring (path b). The intramolecular reaction to form a seven-membered ring in this silatriene intermediate **7** resulted in the formation of the reaction intermediate **8** and then the photochemical disrotatory ring closing of 1,3-butadiene moiety in **8** to cyclobutene gave the novel compound **9**. Relatively little is known about the synthesis of the highly strained bicyclo[2.2.0]hex-2-ene moiety in **9** from the photolysis of benzene but the two valence isomers, benzvalene²⁷ and Dewar benzene,²⁸⁻³⁰ are reported in benzene photochemistry. In relation to the bicyclo[2.2.0]hex-2-ene moiety in **9** similar to Dewar benzene structure, McDonald

Table 1. ¹H NMR (500 MHz), ¹³C NMR (125 MHz), and HMBC data for the photoproduct **9** in CDCl₃^a

Position	δ_C (ppm)	M ^b	δ_H (ppm)	I ^c	M ^d	J _{H-H} (Hz)	HMBC ^e
1	28.8	d	1.58	1H	d	7.2 (<i>J</i> _{1H-2H})	H3, H5, H9, H10
2	36.6	d	2.10	1H	dt	7.2 (<i>J</i> _{2H-1H}), 2.7 (<i>J</i> _{2H-3H,5H})	H3, H4, H5
3	133.9	d	5.38	1H	dq	5.5 (<i>J</i> _{3H-4H}), 1.2 (<i>J</i> _{3H-1H,2H,5H})	H1, H4, H5
4	126.5	d	5.59	1H	dt	5.5 (<i>J</i> _{4H-3H}), 2.4 (<i>J</i> _{4H-2H,5H})	H2, H3
5	38.4	d	1.98	1H	m		H1, H3, H4
6	60.6	s					H1, H5, H7, H11
7	69.5	t	3.67	2H	m		H8
8	65.1	t	3.93	2H	m		H7
9	-0.2	q	0.15	3H	s		H10
10	0.07	q	0.18	3H	s		H9
11	-3.44	q	0.004	3H	s		

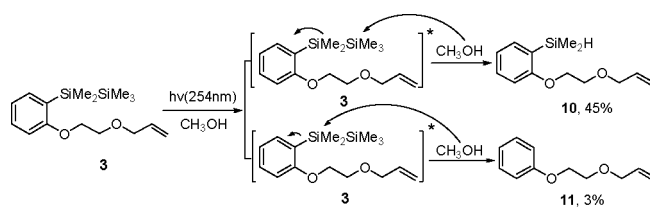
^aAll these assignments were confirmed by ¹H-¹H and ¹H-¹³C COSY and NOESY, HMBC spectra. ^bMultiplicities were determined by DEPT spectrum. ^cIntegrated intensity. ^dMultiplicities. ^eProtons correlated to carbon resonances in ¹³C column.

and Reineke³¹ found that the photoreaction of *cis*-1,2-dihydrophthalic anhydride gave bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride and the intramolecular electrocyclic [4 π]-ring closure of 2-pyridone to 3-oxo-2-azabicyclo[2.2.0]-5-hexene³²⁻³⁶ was reported. The structure of the photoproduct **9** was determined by various physical methods, such as ¹H NMR, ¹³C NMR, 2D NMR (¹H-¹H COSY, ¹H-¹³C HETCO, HMBC, and NOESY), UV, FT-IR, and high resolution mass spectrometry. The ¹H NMR spectrum of **9** shows one double bond (at 5.38 and 5.59 ppm) and three aliphatic protons (at 1.58, 1.98, and 2.10 ppm) and *cis* coupling constant ($J = 7.2\text{Hz}$) between proton 1 and proton 2 in the cyclobutane ring in **9**. From the correlated peaks in the ¹H-¹³C HETCO spectrum of **9**, we have been able to identify the pairs of protons directly attached to the individual carbons as shown in Table 1. To obtain the informations about the structure skeleton of **9**, the HMBC spectrum of **9** was obtained. The connectivity of the carbon C (1) to the dimethylsilyl group in **9** was established by the presence of the cross-peaks due to the vicinal coupling between the protons of C (9) and C (10) and the carbon C (1) in **9**. In the same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C (7) and C (11) and the quaternary carbon C (6) in **9** showed the connectivity of the carbon C (6) to the seven-membered ring and trimethylsilyl group in **9**. The two methyl protons of carbon C (9) and carbon C (10) located on the same silicon atom adjacent to a stereocenter (carbon 1) in **9** are diastereotopic, and they not only have different chemical shifts (0.15 and 0.18 ppm, respectively, in ¹H NMR) but they also show the presence of the cross-peaks due to the vicinal coupling between the protons of C (10) and the carbon C (9), the protons of C (9) and the carbon C (10) in the HMBC spectrum of **9**. From the presence of the cross-peaks between the protons of C (9), C (10) and the protons of C (11) which is showed in a nuclear overhauser and exchange spectroscopy (NOESY) of **9**, it was determined that these protons are located on the same side of the molecule. Thus, the skeletal structure of **9** was unambiguously established as shown in Figure 1.

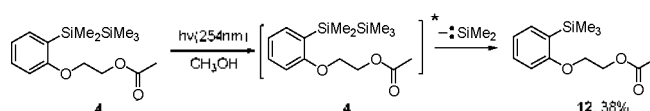
Photoreaction of (2-allyloxyethoxyphenyl)pentamethyldisilane 3. To investigate whether or not the allyloxyethoxy group as *ortho* substituent in **3** reacts intramolecularly with silatriene moiety formed in the photoexcited state of **3**, the photolysis of **3** was performed.

Photolysis of **3** in deaerated methanol with 254 nm UV light gave **10** (45% yield) and **11** (3% yield) along with some decomposition products of unknown structure as shown in Scheme 4, when 96% of **3** was photolyzed but the expected intramolecular photoproduct was not obtained. The formation of a photoproduct **10** or **11** can also be explained by the same way as the formation of a photoproduct **5** or **6** (path d). The structure of the photoproduct **10** was also determined by the ¹H NMR and IR absorption spectra of **10** showing a septet resonance at δ 4.42 and a characteristic absorption at 2115.7 cm^{-1} , respectively, due to a Si-H proton and a Si-H stretching mode in the dimethylsilyl group of **10**.

Photoreaction of (2-acetoxyethoxyphenyl)pentamethyldisilane 4. To investigate whether or not the acetoxyethoxy group as *ortho* substituent in **4** reacts intramolecularly with



Scheme 4



Scheme 5

silatriene moiety formed in the photoexcited of **4**, the photolysis of **4** was performed.

Photolysis of **4** in deaerated methanol with 254 nm UV light gave **12** (38% yield) along with some decomposition products of unknown structure as shown in Scheme 5, when 91% of **4** was photolyzed but the expected intramolecular photoproduct was not obtained. Liberation of dimethylsilylene species from the photoexcited state of **4** resulted in the formation of **12** (path c). In contrast to the photoreaction of **3** or **4** in methanol, no product was detected in the photolysis of **3** or **4** in deaerated benzene, indicating that the hydroxyethoxy group is much more reactive than the allyloxyethoxy or acetoxyethoxy group as the *ortho*-substituted group to phenyl-pentamethyldisilane in this intramolecular photoreaction.

In conclusion, irradiation of **2** in benzene gave the novel intramolecular cyclization photoproduct **9**. It is thought that the cyclization photoproduct **9** was probably formed *via* silatriene intermediate **7**, seven-membered ring compound **8** having the 1,3-butadiene moiety, and then the photochemical disrotatory ring closure of 1,3-butadiene to cyclobutene. The photolysis of **2** or **3** in methanol provided **5** and **6**, or **10** and **11**, respectively, which were probably formed through the β or α silicon atom attack of methanol to pentamethyldisilanyl group in photoexcited state of **2** or **3**. The formation of **12** in the photoreaction of **4** in methanol can be rationalized in terms of the elimination of dimethylsilylene species in the excited state of **4** but the expected intramolecular photoproducts from the reaction of the silatriene intermediate with *ortho* substituents were not obtained in the photolysis of **2**, **3**, and **4** in methanol solvent.

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