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Notes

A Novel Photoreaction of (2-Hydroxypropoxyphenyl)pentamethyldisilane

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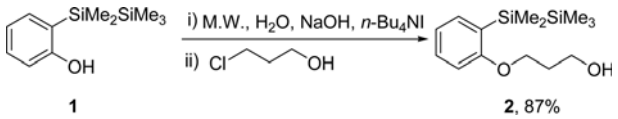
Since the first reports on the photoreactions of 1-phenyl-2-(pentamethyldisilanyl)ethyne[1] and phenylpentamethyldisilane[2] by Ishikawa *et al.*, the intermolecular photolysis of these compounds and their derivatives has been extensively investigated. It is well known that the photolysis of 1-phenyl-2-(pentamethyldisilanyl)ethyne afforded silacyclopropene[3-10] and 1-sila-1,2-propadiene[11-13] intermediate and the photoreaction of phenylpentamethyldisilane gave silatriene[14-20] intermediate. However, relatively little is known about the intramolecular photoreactions of *ortho*-substituted 1-phenyl-2-(pentamethyldisilanyl)ethynes and *ortho*-substituted phenylpentamethyldisilanes.

Recently, we have found that the photolysis of *ortho*-substituted 1-phenyl-2-(pentamethyldisilanyl)ethynes[21] and *ortho*-substituted phenylpenta methyldisilanes[22,23] afforded the novel intramolecular photoproducts *via* silacyclopropene, 1-sila-1,2-propadiene, and silatriene intermediates.

Very recently, we have found that the photoreaction of (2-hydroxymethylphenyl)pentamethyldisilane[24] and (2-hydroxyethoxyphenyl)pentamethyldisilane[25] afforded the novel intramolecular photoproducts *via* silatriene intermediates.

In connection with our ongoing studies for the utility of silacyclopropenes, 1-sila-1,2-propadiene, and silatriene as reaction intermediates in organic synthesis of silicon-containing heterocyclic compounds, we were now interested in the synthesis of silicon-containing large ring compounds *via* the photolysis of *ortho*-substituted phenylpentamethyldisilanes. And, we have investigated the photoreactions of (2-hydroxypropoxyphenyl)pentamethyldisilane **2**, since novel photoproducts from the intramolecular reaction of *ortho*-substituted group with the silatriene intermediate are expected and we would like to report the detailed photochemical study of **2**.

The starting material **2** was prepared by the reaction of (2-hydroxyphenyl)pentamethyldisilane[25] (**1**) with 3-chloro-1-propanol in the presence of sodium hydroxide and tetra-*n*-butyl ammonium iodide using microwave reactor, Micro-SYNTH in water as a solvent as shown in Scheme 1.



1 2, 87%

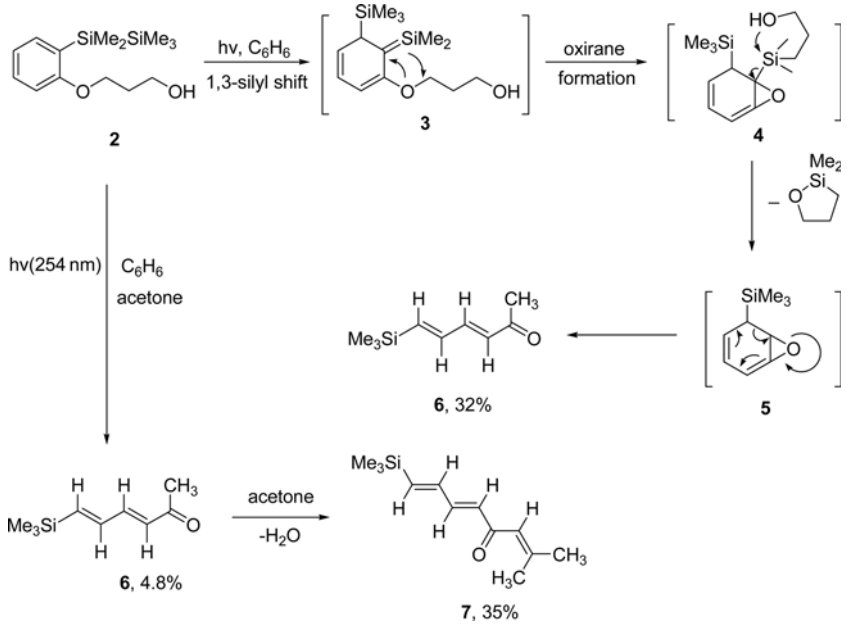
Scheme 1

To investigate whether or not the hydroxypropoxy group as *ortho*-substituent in **2** reacts intramolecularly with silatriene moiety in the reaction intermediate **3** formed in the photoexcited state of **2**, the photoreaction of **2** in benzene was studied.

Photolysis of **2** in deaerated benzene with 254 nm UV light gave a novel photoproduct **6** (32% yield) along with some decomposition products of unknown structure as shown in Scheme 2, when 95% of **2** was photolyzed but the expected intramolecular photoproduct was not obtained. The formation of a novel photoproduct **6** can best be explained in terms of the initial formation of silatriene intermediate **3** arising from1,3-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 C_6 position of benzene ring as shown in Scheme 2. The intramolecular reaction to form a oxirane ring in this silatriene intermediate **3** resulted in the formation of the reaction intermediate **4** and then the attack of hydroxyl group to dimethylsilyl group in the side chain of the intermediate **4** gave the reaction intermediate **5** by eliminating the 2-oxasilacyclopentane ring.[26-28] Finally the rearrangement of the reaction intermediate **5** to the more stable compound than the intermediate **5** gave a novel conjugated photoproduct **6**.

To study the further reaction of the photoproduct **6** in the photolysis of **2**, irradiation of the compound **2** in benzene in the presence of acetone was performed and gave the novel photoproducts **6** (4.8% yield) and **7**(35% yield) along with some decomposition products of unknown structure as shown in Scheme 2, when 94.3% of **2** was photolyzed but the expected intramolecular photoproduct was not also obtained. The crossed aldol condensation reaction between the novel photoproduct **6** and acetone afforded the more conjugated and thermodynamically more favorable compound **7** than the photoproduct **6** as a major product in the photolysis of **2** in the presence of acetone.

The structure of these photoproducts **6** and **7** was determined by various physical methods, such as ^{1}H NMR, ^{13}C



Scheme 2

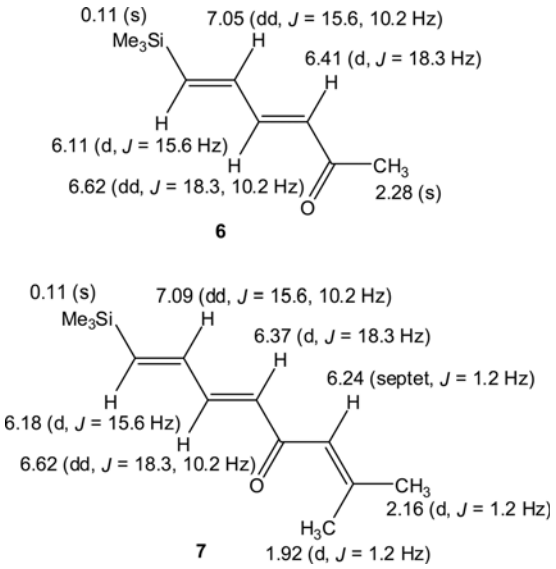
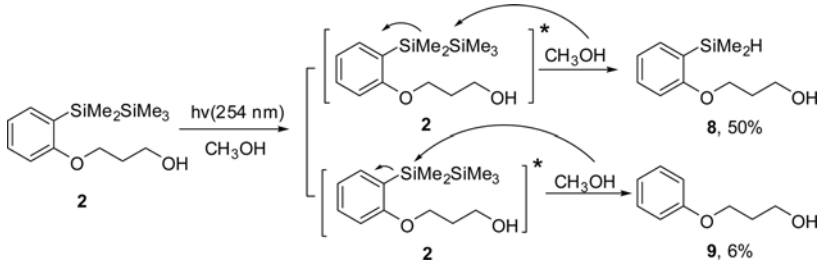


Figure 1. Chemical Shift Comparison in ^{1}H NMR.

NMR, UV, FT-IR, and high resolution mass spectrometry. The absorption maxima (293 nm) in **7** in the UV spectrum was red-shifted compared to that (272 nm) of **6**. The ^{1}H NMR spectra of photoproducts **6** and **7** show the characteristic splitting patterns and coupling constants as shown in Figure 1. The four vinyl protons in **6** split each other into two doublets at 6.11 and 6.41 ppm and two doublet of doublets at 6.62 and 7.05 ppm. The measured coupling constants between the four vinyl protons in **6** are 15.6 and 18.3 Hz, which is the value for *trans* proton-proton coupling constant across a double bond, indicating that the photoproduct **6** is the *trans*, *trans* isomer. The chemical shifts for the vinyl protons and trimethylsilylprotons of **7** in ^{1}H NMR spectrum are very similar to those of **6** but there are new vinyl proton at 6.24 ppm and two methyl protons at 1.92 and 2.16 ppm in **7**. The allylic coupling constant between these new vinyl and methyl protons is 1.2 Hz and the vinyl and trimethylsilyl protons couple each other to give the septet or doublet peaks. One of two methyl protons in **7** shows an upfield shift at 1.92 ppm due to the anisotropy effect of the carbonyl group *cis* to this methyl group.

Photoreaction of **6** in deaerated methanol with 254 nm UV light gave **8** (50% yield) and **9** (6% yield) along with some decomposition products of unknown structure as shown in Scheme 3, when 95% of **2** was photolyzed but the expected intramolecular photoproduct was not also obtained. The formation of a photoproduct **8** or **9** 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. The structure of the photoproduct **8** was deter-



Scheme 3

mined by the ^{1}H NMR and IR absorption spectra. These spectra of **8** show a septet resonance at δ 4.48 and a characteristic absorption at 2117.5 cm^{-1}, respectively, due to a Si-H proton and a Si-H stretching mode in the dimethylsilyl group of **8**.

In conclusion, the photoreaction of **2** in benzene gave the novel conjugated photoproduct **6** *via* the reaction intermediate **3**. The transformation of **3** to the photoproduct **6** is explained by the oxirane formation of **3** followed by the removal of 2-oxasilacyclopentane ring in **4**, and then the rearrangement of **5** to the conjugated compound **6**. Photolysis of **2** in the presence of acetone afforded **6** and the more conjugated photoproduct **7**. The crossed aldol condensation reaction between the photoproduct **6** and acetone gave the more conjugated, thermodynamically favorable photoproduct **7**. Irradiation **2** in methanol provided **8** or **9**, respectively, which were probably formed through the β or α silicon atom attack of methanol to pentamethyldisilanyl group in photo-excited state of **2** but the expected intramolecular photoproducts were not obtained in the photolysis of **2** in methanol solvent. To study whether or not the thermal reactions of **2** gave the same products as the photolysis of **2**, the reactions of **2** in benzene, benzene in the presence of acetone, or methanol as a solvent were investigated but it did not give any products in the same reaction conditions without the irradiation of 254 nm light, indicating that the photolysis of **2** only afforded the various photoproducts.

Experimental

Synthesis of (2-Hydroxypropoxyphenyl)pentamethyldisilane 2. To a solution of (2-hydroxyphenyl)pentamethyldisilane (**1**) (0.50 g, 2.2 mmol), sodium hydroxide (0.45 g, 11.2 mmol), and tetrabutylammonium iodide (80 mg, 0.2 mmol) in water (5 mL) was added dropwisely 3-chloro-1-propanol (0.56 mL, 6.7 mmol) at room temperature. The reaction mixture was irradiated in MicroSYNTH operated at 500W for 1 h at 60 °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 over $MgSO_4$. The solvent was evaporated *in vacuo* to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (3/1, v/v) as an eluent gave **2** (0.55 g, 87% yield) as a colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.06 (9H, s), 0.36 (6H, s), 2.09 (2H, quintet, J = 6.3 Hz), 2.11 (1H, s), 3.87 (2H, t, J = 6.3 Hz), 4.11 (2H, t, J = 6.3 Hz), 6.85 (1H, d, J = 8.1 Hz), 6.96 (1H, td, J = 7.2, 0.9 Hz), 7.33 (2H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −3.16, −1.65, 32.2, 59.9, 64.6, 109.8, 120.6, 127.1, 130.4, 135.3, 163.3; UV (CH_2Cl_2) λ_{max} 280, 287 nm; FT-IR (NaCl) 3332.4, 3008.4, 2948.6, 2891.7, 1584.2, 1435.7, 1226.5, 796.5 cm^{-1}; MS (70 eV) *m/z* 282 (M^+); MS *m/z* (%) 282 (M^+, 0.2), 209 (22), 193 (100), 163 (23), 151 (33), 133 (25), 117 (37), 91 (15); HRMS (M^+) calcd for $C_{14}H_{26}O_2Si_2$ 282.1471, found 282.1401.

Irradiation of 2 in Benzene. A solution (5 × 10^{-4} M) of **2** (141 mg) in benzene (1 L) was deaerated by nitrogen purging for 1 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 1.5 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproduct, 6-trimethylsilyl-3,5-hexadien-2-one **6** was isolated in 32% (27 mg) yield in addition to 5% (7 mg) of the starting material **2** by column chromatography with *n*-hexane/ethyl acetate (30/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (20/1, v/v) as an eluent. **6**; ^{1}H NMR ($CDCl_3$, 300MHz) δ_H 0.11 (9H, s), 2.28 (3H, s), 6.11 (1H, d, J = 15.6 Hz), 6.41 (1H, d, J = 18.3 Hz), 6.62 (1H, dd, J = 18.3, 10.2 Hz), 7.05 (1H, dd, J = 15.6, 10.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −1.53, 27.3, 130.7, 141.8, 145.2, 146.5, 199.1; UV (CH_2Cl_2) λ_{max} 272 nm; FT-IR (NaCl) 3061.4, 2923.6, 2852.2, 1734.7, 1372.1, 1240.0, 1021.1, 735.7 cm^{-1}; MS (70 eV) *m/z* 168 (M^+); MS *m/z* (%) 168 (M^+, 1.4), 153 (100), 125 (13), 99 (3), 95 (7), 75 (64), 69 (2); HRMS (M^+) calcd for $C_9H_{16}OSi$ 168.097, found 168.0921.

Irradiation of 2 in Benzene in the Presence of Acetone. A solution (5 × 10^{-4} M) of **2** (141 mg) and acetone (5.5 mL, 75 mmol) in benzene (1 L) was deaerated by nitrogen purging for 1 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 1.5 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts **6** and 2-methyl-8-trimethylsilyl-2,5,7-octatrien-4-one **7** were isolated in 4.8% (4 mg) and 35% (36 mg) yield, respectively, in addition to 5.7% (8 mg) of the starting material **2** by column chromatography with *n*-hexane/ethyl acetate (30/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (20/1, v/v) as an eluent. **7**; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.11 (9H, s), 1.92 (3H, d, J = 1.2 Hz), 2.16 (3H, d, J = 1.2 Hz), 6.18 (1H, d, J = 15.6 Hz), 6.24 (1H, septet, J = 1.2 Hz), 6.37 (1H, d, J = 18.3 Hz), 6.62 (1H, dd, J = 18.3, 10.2 Hz), 7.09 (1H, dd, J = 15.6, 10.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ_C −1.46, 21.1, 27.9, 123.3, 132.0, 142.2, 143.7, 145.4, 156.1, 190.9; UV (CH_2Cl_2) λ_{max} 293 nm; FT-IR (NaCl) 3030.6, 2955.4, 1727.9, 1650.8, 1623.8, 1246.7, 1005.7, 837.9 cm^{-1}; MS (70 eV) *m/z* 208 (M^+); MS *m/z* (%) 208 (M^+, 1.2), 178 (29), 167 (22), 149 (100), 121 (25), 105 (16), 75 (33); HRMS (M^+) calcd for $C_{12}H_{20}OSi$ 208.1283, found 208.1215.

Irradiation of 2 in Methanol. A solution (5 × 10^{-4} M) of **2** (141 mg) in methanol (1 L) was deaerated by nitrogen purging for 1h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 1.5 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts, (2-hydroxypropoxyphenyl)dimethylsilane **8** and 1-hydroxy-3-phenoxypropane **9** were isolated in 50% (52.5 mg) and 6% (4.6 mg) yield, respectively, in addition to 5% (7 mg) of the starting material **2** by column chromatography with *n*-hexane/ethyl acetate (10/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (5/1, v/v) as an eluent. **8**; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.39 (6H, d, J = 3.6 Hz), 2.08 (2H, quintet, J = 6.0 Hz), 2.74 (1H, s), 3.89 (2H, t, J = 6.0 Hz), 4.12 (2H, t, J = 6.0 Hz), 4.48 (1H, septet,

J = 3.6 Hz), 6.87 (1H, d, J = 8.4 Hz), 6.99 (1H, t, J = 7.2 Hz), 7.39 (1H, ddd, J = 8.4, 7.2, 1.8 Hz), 7.47 (1H, dd, J = 7.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −3.69, 32.2, 59.9, 64.9, 110.1, 120.6, 125.2, 131.2, 135.7, 163.4; UV (CH_2Cl_2) λ_{max} 279, 285 nm; FT-IR (NaCl) 3365.2, 3051.8, 2955.4, 2117.5, 1587.1, 1437.7, 1232.3, 1055.8, 877.5, 734.7 cm^{-1}; MS (70 eV) *m/z* 210 (M^+); MS *m/z* (%) 210 (M^+, 19), 209 (100), 163 (37), 151 (43), 149 (25), 135 (28), 133 (22), 91 (19), 77 (15), 75 (27), 73 (21); HRMS (M^+) calcd for $C_{11}H_{18}O_2Si$ 210.1076, found 210.1021.

9: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.03 (2H, quintet, J = 6.0 Hz), 2.05 (1H, s), 3.85 (2H, t, J = 6.0 Hz), 4.10 (2H, t, J = 6.0 Hz), 6.92 (3H, m), 7.28 (2H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 31.9, 60.5, 65.6, 114.5, 120.9, 129.6, 158.6; UV (CH_2Cl_2) λ_{max} 272, 279 nm; FT-IR (NaCl) 3348.8, 2950.6, 1598.7, 1495.5, 1241.9, 1056.8, 752.1 cm^{-1}; MS (70 eV) *m/z* 152 (M^+); MS *m/z* (%) 152 (M^+, 15), 134 (7), 94 (100), 77 (6), 66 (11), 65 (4); HRMS (M^+) calcd for $C_9H_{12}O_2$ 152.0837, found 152.0881.

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