

Photoreaction of 3-Allyloxy-2-pentamethyldisilanylpyridine

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It is well established that the photoreactions of phenyl-disilanes proceed through four pathways¹: 1) formation of a silaethene,² Si=C, 2) formation of a silatriene *via* 1,3-trimethylsilyl radical migration,³ 3) elimination of a silylene,⁴ and 4) nucleophilic cleavage of a Si-Si bond in the photo-excited state^{5,6} since the first report on the photolysis of phenylpentamethyldisilane and (*p*-tolyl)pentamethyldisilane by Ishikawa *et al.*⁷ in 1975. However, relatively little is known about the photoreactions of *ortho*-substituted phenylpentamethyldisilanes.

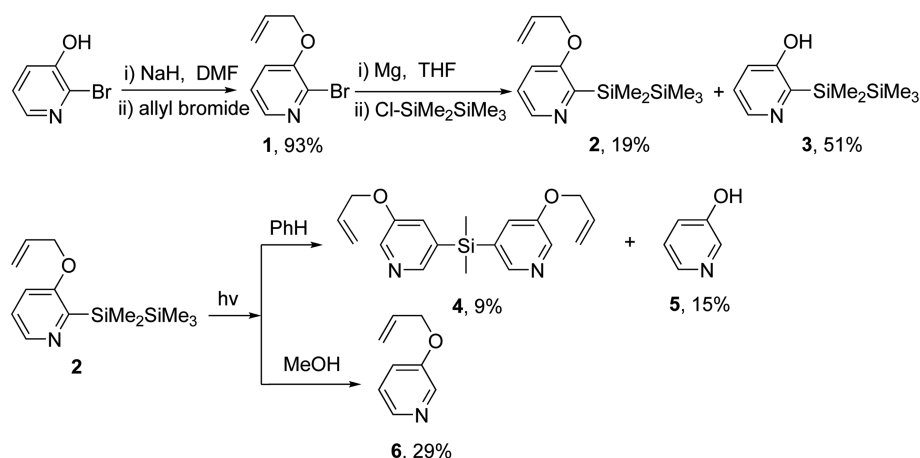
Recently, we have found that the photoreactions of various *ortho*-substituted phenylpentamethyldisilanes⁸ afforded the novel intramolecular photoproducts *via* silatriene intermediates.

As part of our ongoing investigations for the organic synthesis of silicon-containing heterocyclic compounds,⁹ we were, now, interested in the pyridine ring instead of the phenyl ring as an aromatic ring. And, we would like to report detailed photochemical investigations of 3-allyloxy-2-pentamethyldisilanylpyridine **2**, *aza* analogue of (2-allyloxyphenyl)-pentamethyldisilane,¹⁰ since novel photoproducts from the photoreaction of **2** *via* new intermediates are expected. The starting 3-allyloxy-2-pentamethyldisilanylpyridine **2** was prepared by the reaction of pentamethyldisilanyl chloride with 3-allyloxy-2-pyridyl magnesium bromide in tetrahydrofuran as shown in Scheme 1. In this reaction, a compound **3** formed from the allyl group cleavage of **2** was also obtained.

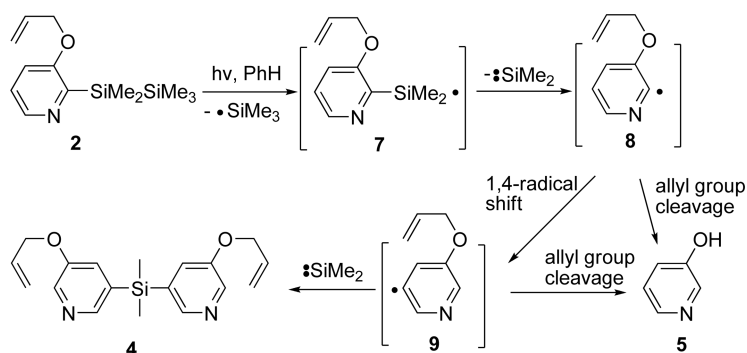
Irradiation of **2** in deaerated benzene with 300nm UV light

afforded a novel photoproduct **4** (9%yield) in addition to **5** (15%yield) along with several decomposition products of unknown structure as shown in Scheme 1, when 92% of **2** was photolyzed. Indeed, the atomic charges of 2-, 3-, and 4-pyridyl radical site (+0.015, -0.268, and -0.007, respectively) have been calculated at the BPW91/cc-pVDZ//BPW91/cc-pVDZ.¹¹ In this paper, it is revealed that 2-pyridyl radical with a partial positive charge behaves like an electrophilic radical, but 3- and 4-pyridyl radical behave like a nucleophilic radical. And, the relative energies of 2-, 3-, and 4-pyridyl radical (0, 26, and 21 kJ/mol, respectively) have been calculated by G3B3¹². Therefore, it is revealed that 2-pyridyl radical is more stable than the 4-isomer, which is in turn more stable than 3-isomer in this paper. These above results suggested that the photoproduct **4** is formed from the reaction of electrophilic silylene and 2 mol of nucleophilic, unstable 3-pyridyl radical **9**, formed *via* 1,4-radical shift from the electrophilic, stable 2-pyridyl radical **8** (Scheme 2). In this case, it is thought that the reaction of nucleophilic 4-pyridyl radical and electrophilic silylene was not occurred because of the steric hindrance of the allyloxy group. The formation of **5** is explained by the allyl group cleavage from the radical intermediates, **8** or **9** as shown in Scheme 2.

The structure of the photoproduct **4** was determined by various physical methods. The ¹H NMR spectrum of the photoproduct **4** shows the characteristic 3,5-disubstituted pyridine structure. The two protons (2 and 6 positions in the



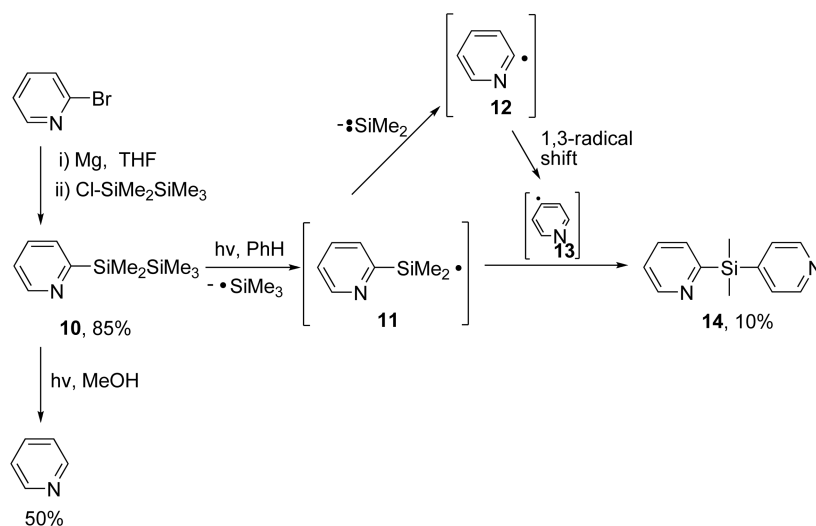
Scheme 1



Scheme 2

pyridine ring) in **4** show two singlets at 8.22 and 8.33 ppm. The proton (4 position in the pyridine ring) in **4** shows a triplet splitting pattern at 7.23 ppm. The ^{13}C NMR spectrum of the photoproduct **4** shows 9 peaks indicating that the photoproduct **4** has the symmetric structure. Photoreaction of **2** in deaerated methanol with 300 nm UV light gave **6** (29% yield) along with several decomposition products of unknown structure as shown in Scheme 1, when 97% of **2** was photolyzed but the expected intramolecular photoproduct was not also obtained. The formation of a photoproduct **6** can best be explained in terms of the nucleophilic attack at α silicon atom of pentamethyldisilanyl group in the photoexcited state of **2** by methanol. The ^1H NMR spectrum of the photoproduct **6** shows the characteristic 3-substituted pyridine structure. In order to obtain the more information about the formation of a novel photoproduct **4** obtained from the photoreaction of **2**, we planned the synthesis and the photoreaction of **10** which does not have the allyloxy group in **2**. The starting 2-pentamethyldisilanylpyridine **10** was also prepared by the same method as the synthesis of **2** as shown in Scheme 3. A novel photoproduct **14** (10% yield) was obtained from the photoreaction of **10** in deaerated benzene solution with 300 nm UV light, when 93% of **10** was photolyzed. Several decomposition compounds of unknown struc-

ture were also obtained in this reaction. The formation of the photoproduct **14** is also most likely explained by the reaction of electrophilic silyl radical **11** and nucleophilic, unstable 4-pyridyl radical **13**, formed *via* 1,3-radical shift from the electrophilic, stable 2-pyridyl radical **12** as shown in Scheme 3. The structure of the photoproduct **14** was also determined by various physical methods. The ^1H NMR spectrum of the photoproduct **14** shows the characteristic A_2X_2 splitting pattern and 2-substituted pyridine structure. The two groups of two protons in the A_2X_2 pattern of **14** show two doublet of doublets (dd) at 7.38 and 7.60 ppm. The other aromatic protons in **14** show similar splitting patterns and the chemical shifts to **10**. The ^{13}C NMR spectrum of the photoproduct **14** shows 9 peaks indicating that the photoproduct **14** has the unsymmetric structure. Photoreaction of **10** in deaerated methanol with 300nm UV light gave pyridine (50% yield) along with several decomposition products of unknown structure as shown in Scheme 3, when 91% of **10** was photolyzed. The formation of pyridine can best be explained in terms of the nucleophilic attack at α silicon atom of pentamethyldisilanyl group in the photoexcited state of **10** by methanol. In conclusion, the photoreaction of **2** in benzene gave the novel photoproduct **4** in addition to **5** *via* several radical intermediates **7**, **8**, and **9**. The formation of a novel photo-



Scheme 3

product **14** from **10** is also explained by the radical intermediates **11**, **12**, and **13**.

Experimental

Synthesis of 3-Allyloxy-2-bromopyridine 1. A solution of 2-bromo-3-pyridinol (0.5 g, 2.87 mmol) in *N,N*-dimethylformamide (5 mL) was added to a solution of NaH (75.8 mg, 3.16 mmol) in DMF (10 mL) at room temperature under nitrogen atmosphere. Allyl bromide (0.37 mL, 4.3 mmol) was added dropwise to the resulting solution and the mixture was stirred at 70 °C for 2 h. Water (20 mL) was added to the solution and was extracted with ethyl acetate (3 × 15 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 **1** (0.57 g, 93% yield) as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 4.51 (2H, dt, *J* = 5.1, 1.5 Hz), 5.22 (1H, dq, *J* = 10.5, 1.5 Hz), 5.37 (1H, dq, *J* = 17.1, 1.5 Hz), 5.92 (1H, ddt, *J* = 17.1, 10.5, 5.1 Hz), 7.04 (1H, dd, *J* = 8.1, 1.5 Hz), 7.10 (1H, dd, *J* = 8.1, 4.5 Hz), 7.84 (1H, dd, *J* = 4.5, 1.5 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 69.5, 118.2, 119.9, 123.3, 131.5, 132.7, 141.1, 151.7; UV (CH₂Cl₂) λ_{max} 282 nm; FT-IR (NaCl) 3062.4, 2984.3, 1561.1, 1407.8, 1281.5, 1052.9 cm⁻¹; MS (70 eV) *m/z* 213 (M⁺); MS *m/z* (%) 213 (M⁺, 30), 134 (100), 107 (7.5), 93 (4), 79 (3), 65 (6); HRMS (M⁺) calcd for C₈H₈BrNO 212.9789, found 212.9701.

Synthesis of 3-Allyloxy-2-pentamethyldisilanylpuridine 2. A solution of 3-allyloxy-2-bromopyridine (0.5 g, 2.35 mmol) in tetrahydrofuran (5 mL) was added to a solution of magnesium (74.2 mg, 3.05 mmol) in THF (15 mL) at room temperature under nitrogen atmosphere. Chloropentamethyl disilane (0.47 g, 2.82 mmol) was added dropwise to the resulting solution and the mixture was refluxed for 2 h. The reaction solution was filtered through Celite and then hydrolyzed with water (20 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The organic layer and the extracts were combined, washed with water (20 mL), brine (20 mL) and dried (MgSO₄). The solvent was evaporated *in vacuo* to give the crude products. The products **2** and **3** were isolated in (0.12 g, 19% yield) and (0.27 g, 51% yield) by column chromatography with *n*-hexane/ethyl acetate (10/1, v/v) as an eluent as a colorless oil; **2**: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.036 (9H, s), 0.386 (6H, s), 4.53 (2H, dt, *J* = 5.4, 1.5 Hz), 5.29 (1H, dq, *J* = 10.5, 1.5 Hz), 5.36 (1H, dq, *J* = 17.4, 1.5 Hz), 6.02 (1H, ddt, *J* = 17.4, 10.5, 5.4 Hz), 6.99 (1H, dd, *J* = 8.4, 1.2 Hz), 7.11 (1H, dd, *J* = 8.4, 4.5 Hz), 8.36 (1H, dd, *J* = 4.5, 1.2 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -3.97, -1.63, 68.8, 115.9, 118.5, 122.9, 132.8, 142.6, 157.8, 160.0; UV (CH₂Cl₂) λ_{max} 286 nm; FT-IR (NaCl) 3050.6, 2950.6, 1573.6, 1410.7, 1244.8, 1028.8, 793.6, 765.6 cm⁻¹; MS (70 eV) *m/z* 265 (M⁺); MS *m/z* (%) 265 (M⁺, 0.7), 251 (22.5), 225 (100), 211 (5.5), 151 (4), 89 (10.5), 73 (46), 61 (41); HRMS (M⁺) calcd for C₁₃H₂₃NOSi₂ 265.1318, found 265.1391. **3**: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.107 (9H, s), 0.428 (6H, s), 7.07 (2H,

m), 8.08 (1H, d, *J* = 4.2 Hz), 9.89 (1H, broad singlet); ¹³C NMR (CDCl₃, 75 MHz) δ_C -4.44, -1.84, 112.0, 119.9, 123.2, 135.4, 154.5; UV (CH₂Cl₂) λ_{max} 289 nm; FT-IR (NaCl) 3513.7, 2994.9, 1455.0, 1374.0, 1231.3, 1056.8, 851.4 cm⁻¹; MS (70 eV) *m/z* 225 (M⁺); MS *m/z* (%) 225 (M⁺, 100), 223 (5), 221 (16), 193 (19), 176 (83), 170 (6), 152 (10), 120 (4); HRMS (M⁺) calcd for C₁₀H₁₉NOSi₂ 225.1005, found 225.1091.

Irradiation of 3-Allyloxy-2-pentamethyldisilanyl Pyridine 2 in Benzene. A solution (1 × 10⁻³ M) of 3-allyloxy-2-pentamethyldisilanylpyridine **2** (265 mg) in benzene (1 L) was deaerated by nitrogen purging for 0.5 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 3 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts **4** and **5** were isolated in (29.3 mg, 9% yield) and (14.3 mg, 15% yield) in addition to 8% (21.2 mg) of the starting material **2** by column chromatography with *n*-hexane/ethyl acetate (1/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (1/1, v/v) as an eluent. **4**: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.51 (3H, s), 4.58 (2H, dt, *J* = 5.1, 1.5 Hz), 5.33 (1H, dq, *J* = 10.5, 1.5 Hz), 5.43 (1H, dq, *J* = 17.1, 1.5 Hz), 6.03 (1H, ddt, *J* = 17.1, 10.5, 5.1 Hz), 7.23 (1H, t, *J* = 2.1 Hz), 8.22 (1H, s), 8.33 (1H, s); ¹³C NMR (CDCl₃, 75 MHz) δ_C -1.32, 69.1, 118.4, 121.8, 124.1, 132.5, 138.0, 142.0, 154.9; UV (CH₂Cl₂) λ_{max} 279 nm; FT-IR (NaCl) 3005.5, 2989.1, 1475.3, 1275.7, 1258.3, 1026.9, 835.0 cm⁻¹; MS (70 eV) *m/z* 326 (M⁺); MS *m/z* (%) 326 (1), 320 (0.8), 268 (5), 209 (6), 175 (46), 135 (100), 107 (0.7), 100 (1); HRMS (M⁺) calcd for C₁₈H₂₂N₂O₂Si 326.1451, found 326.1401. **5**: ¹H NMR (CDCl₃, 300 MHz) δ_H 7.05 (1H, ddd, *J* = 8.4, 4.5, 0.9 Hz), 7.10 (1H, ddd, *J* = 8.4, 2.7, 1.8 Hz), 7.94 (1H, dd, *J* = 4.5, 1.5 Hz), 8.11 (1H, d, *J* = 1.8 Hz), 9.54 (1H, broad singlet); ¹³C NMR (CDCl₃, 75 MHz) δ_C 123.3, 124.3, 137.5, 139.4, 154.4; FT-IR (NaCl) 3733.5, 3099.1, 2924.5, 1578.5, 1457.9, 1278.6, 870.7 cm⁻¹; UV (CH₂Cl₂) λ_{max} 277 nm; MS (70 eV) *m/z* 95 (M⁺); MS *m/z* (%) 95 (M⁺, 100), 94 (12), 85 (16); HRMS (M⁺) calcd for C₅H₅NO 95.0371, found 95.0312.

Irradiation of 3-Allyloxy-2-pentamethyldisilanyl Pyridine 2 in Methanol. A solution (1 × 10⁻³ M) of 3-allyloxy-2-pentamethyldisilanylpyridine **2** (265 mg) in methanol (1 L) was deaerated by nitrogen purging for 0.5 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 4 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproduct **6** was isolated in (39.2 mg, 29% yield) in addition to 3% (8 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 (8/1, v/v) as an eluent. **6**: ¹H NMR (CDCl₃, 300 MHz) δ_H 4.53 (2H, dt, *J* = 5.4, 1.5 Hz), 5.27 (1H, dq, *J* = 10.5, 1.5 Hz), 5.37 (1H, dq, *J* = 17.1, 1.5 Hz), 5.99 (1H, ddt, *J* = 17.1, 10.5, 5.4 Hz), 7.15 (2H, m), 8.17 (1H, s), 8.28 (1H, s); ¹³C NMR (CDCl₃, 75 MHz) δ_C 68.9, 118.2, 121.4, 123.8, 132.4, 138.1, 142.1, 154.1; UV (CH₂Cl₂) λ_{max} 278 nm; FT-IR (NaCl) 3053.7, 2986.2, 1574.6, 1476.2, 1422.2, 1284.1, 731.9 cm⁻¹; MS (70 eV) *m/z* 135 (M⁺); MS *m/z* (%) 135 (M⁺,

100), 134 (1.9), 108 (1.7), 107 (14.4), 105 (1), 101 (1.1); HRMS (M^+) calcd for C_8H_9NO 135.0684, found 135.0691.

Synthesis of 2-Pentamethyldisilanylpyridine 10. This compound was prepared according to the procedure described for the preparation of **2** except 2-bromopyridine (0.5 g, 3.16 mmol), magnesium (99.8 mg, 4.11 mmol), and chloropentamethyldisilane (0.63 g, 3.79 mmol) were used. Chromatography (*n*-hexane/ethyl acetate (10/1, v/v) gave **10** (0.56 g, 85% yield) as a colorless oil; 1H NMR ($CDCl_3$, 300 MHz) δ_H 0.047 (9H, s), 0.376 (6H, s), 7.12 (1H, ddd, $J = 7.5, 4.8, 1.5$ Hz), 7.41 (1H, dt, $J = 7.5, 1.2$ Hz), 7.53 (1H, td, $J = 7.5, 1.5$ Hz), 8.73 (1H, ddd, $J = 4.8, 1.5, 0.9$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C -4.42, -2.12, 122.3, 129.4, 134.0, 149.9, 168.5; UV (CH_2Cl_2) λ_{max} 287, 264 nm; FT-IR (NaCl) 3064.3, 2985.3, 2950.6, 1573.6, 1242.9, 830.2, 798.4 cm^{-1} ; MS (70 eV) m/z 209 (M^+); MS m/z (%) 209 (M^+ , 100), 194 (27), 154 (8), 136 (7); HRMS (M^+) calcd for $C_{10}H_{19}NSi_2$ 209.1056, found 209.1011.

Irradiation of 2-Pentamethyldisilanylpyridine 10 in Benzene. This photoreaction was proceeded according to the photoreaction described for **2** in benzene except 2-pentamethyldisilanylpyridine **10** (209 mg) was used and irradiated for 7 h. Chromatography (*n*-hexane/ethyl acetate (10/1, v/v) gave **14** (21.4 mg, 10 % yield) in addition to 7% (14.6 mg) of the starting material **10**. **14**; 1H NMR ($CDCl_3$, 300 MHz) δ_H 0.628 (6H, s), 7.20 (1H, ddd, $J = 7.5, 4.8, 1.5$ Hz), 7.38 (2H, dd, $J = 5.1, 2.1$ Hz), 7.44 (1H, dt, $J = 7.5, 1.2$ Hz), 7.55 (1H, td, $J = 7.5, 1.5$ Hz), 7.60 (2H, dd, $J = 5.1, 1.5$ Hz), 8.80 (1H, ddd, $J = 4.8, 1.5, 0.9$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C -3.02, 122.9, 128.0, 129.4, 129.9, 134.3, 137.3, 150.4, 166.7; UV (CH_2Cl_2) λ_{max} 256 nm; FT-IR (NaCl) 3067.2, 2955.4, 1573.6, 1428.0, 1245.8, 815.7, 779.1 cm^{-1} ; MS (70 eV) m/z 214 (M^+); MS m/z (%) 214 (M^+ , 100), 178

(8), 155 (15), 154 (94), 136 (39); HRMS (M^+) calcd for $C_{12}H_{14}N_2Si$ 214.0926, found 214.0990.

Irradiation of 2-Pentamethyldisilanylpyridine 10 in Methanol. This photoreaction was proceeded according to the photoreaction described for **2** in methanol except 2-pentamethyldisilanylpyridine **10** (209 mg) was used and irradiated for 6 h. Chromatography (*n*-hexane/ethyl acetate (10/1, v/v) gave pyridine (39.5 mg, 50 %yield) in addition to 9% (18.8 mg) of the starting material **10**.

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