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# Solvent effects on the photochemical behavior of 1-($n$-pyridyl)-2-(pentamethyldisilanyl)ethynes ($n = 2, 3$, or 4), aza analogs of 1-phenyl-2-(pentamethyldisilanyl)ethyne

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## Abstract

Photolysis of 1-($n$-pyridyl)-2-(pentamethyldisilanyl)ethynes ($n = 2, 3$, or 4) **1**, **9**, or **20**, respectively, aza analogs of 1-phenyl-2-(pentamethyldisilanyl)ethyne, was performed in both non-polar and polar solvents. In benzene, they provide silacyclopropene and 1-sila-1,2-propadiene intermediates but afford only silacyclopropene intermediate in methanol.

*Keywords:* 1-($n$-Pyridyl)-2-(pentamethyldisilanyl)ethynes; Silacyclopropene; 1-Sila-1,2-propadiene

## 1. Introduction

The photochemical behavior of 1-phenyl-2-(pentamethyldisilanyl)ethyne and its derivatives has been extensively investigated because of the photochemical and photophysical interests in the synthesis of highly strained silacyclopropenes [1–15]. Ishikawa et al. [1] first reported that the photolysis of 1-phenyl-2-(pentamethyldisilanyl)ethyne in benzene or methanol solvent afforded silacyclopropene and 1-sila-1,2-propadiene intermediates 25 years ago. These intermediates are extremely unstable toward atmospheric oxygen and moisture. Therefore, the existence of the silacyclopropene and 1-sila-1,2-propadiene intermediates is proved by trapping them with solvents such as methanol or acetone. Sakurai et al. [2] also independently reported the photolysis of 1-phenyl-2-(pentamethyldisilanyl)ethyne in benzene or methanol solvent and a variety of reactions of the photochemically generated silacyclopropene intermediate. In connection with these intermediates, we have recently found that the photolysis of *ortho*-substituted 1-phenyl-2-(pentamethyldisilanyl)ethynes afforded novel intramolecular photoproducts via silacyclopropene intermediate [16–22].

Although the excited-state properties of 1-phenyl-2-(pentamethyldisilanyl)ethyne and its *ortho*-substituted derivatives have been extensively studied, relatively little is known about the excited state behavior of 1-($n$-pyridyl)-2-(pentamethyldisilanyl)ethynes ($n = 2, 3$, or 4) **1**, **9**, or **20**, respectively, aza analogs of 1-phenyl-2-(pentamethyldisilanyl)ethyne, containing the nitrogen atom in the benzene ring. Therefore, we would like to report the photochemistry of **1**, **9**, or **20**, since it is expected to affect the photochemical behavior of 1-phenyl-2-(pentamethyldisilanyl)ethyne by the introduction of nitrogen atom to phenyl ring and we describe, in this paper, solvent effects on the photochemical behavior of **1**, **9**, or **20**.

## 2. Experimental

### 2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. $^1H$ 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 $CDCl_3$. 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

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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 $F_{254}$ 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 $CaH_2$ before use. $Et_3N$ was distilled from $CaH_2$ 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.

### 2.2. Synthesis of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne *1*

To a deaerated solution of 2-bromopyridine (0.5 g, 3.16 mmol), bis(triphenylphosphine) palladium dichloride (22 mg, 0.03 mmol) and copper(I) iodide (6.0 mg, 0.03 mmol) in anhydrous triethylamine (10 ml) were added dropwise pentamethyldisilanylethyne (0.66 ml, 3.80 mmol) at room temperature. The reaction mixture was heated at 45 °C for 4 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 $H_2O$ (10 ml), brine (10 ml), and dried ($MgSO_4$), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent gave **1** (0.55 g, 75% yield) as a colorless oil; $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.11 (9H, s), 0.23 (6H, s), 7.12 (1H, ddd, $J = 7.6, 4.9, 1.0$ Hz), 7.35 (1H, d, $J = 7.8$ Hz), 7.54 (1H, td, $J = 7.7, 1.7$ Hz), 8.48 (1H, d, $J = 4.4$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −2.89, −2.17, 94.4, 106.3, 123.1, 127.6, 136.3, 143.7, 150.2; UV ($CH_2Cl_2$), $\lambda_{max}$: 283, 248 nm; FT-IR (NaCl): 2953.8, 2895.3, 2159.3, 1581.1, 1461.0, 1246.6, 849.7, 799.6 cm$^{-1}$; MS (70 eV), *m/z*: 233 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{19}NSi_2$ 233.1056, found 233.1055.

### 2.3. Synthesis of 1-(3-pyridyl)-2-(pentamethyldisilanyl)ethyne *9*

This reaction was carried out according to the same procedure described for the preparation of **1**, except 3-bromopyridine (0.5 g, 3.16 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 5/1, v/v) to afford colorless oil of **9** (0.6 g, 81% yield); $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.12 (9H, s), 0.23 (6H, s), 7.14 (1H, ddd, $J = 7.8, 4.9, 0.7$ Hz), 7.64 (1H, dt, $J = 7.9, 1.9$ Hz), 8.44 (1H, dd, $J = 4.9, 1.6$ Hz), 8.62 (1H, d, $J = 1.3$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −2.83, −2.21, 97.8, 103.9, 120.9, 123.1, 138.9, 148.8, 152.9; UV ($CH_2Cl_2$), $\lambda_{max}$: 258 nm; FT-IR (NaCl): 2953.7, 2895.3, 2154.9, 1560.1, 1474.4, 1246.4, 844.6, 800.2 cm$^{-1}$; MS (70 eV), *m/z*: 233 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{19}NSi_2$ 233.1056, found 233.1050.

### 2.4. Synthesis of 1-(4-pyridyl)-2-(pentamethyldisilanyl)ethyne *20*

This reaction was carried out according to the same procedure described for the preparation of **1**, except 4-bromopyridine hydrochloride (0.5 g, 2.57 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 3/1, v/v) to afford colorless oil of **20** (89.9 mg, 15% yield); $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.18 (9H, s), 0.29 (6H, s), 7.29 (2H, d, $J = 5.8$ Hz), 8.56 (2H, d, $J = 5.8$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −2.94, −2.19, 99.8, 104.6, 126.1, 131.9, 150.1; UV ($CH_2Cl_2$), $\lambda_{max}$: 258, 248 nm; FT-IR (NaCl): 2953.9, 2895.4, 2158.7, 1592.4, 1405.1, 1246.7, 847.2, 799.7 cm$^{-1}$; MS (70 eV), *m/z*: 233 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{19}NSi_2$ 233.1056, found 233.1078.

### 2.5. Irradiation of 1-(2-pyridyl)-2-(pentamethyldisilanyl)-ethyne *1* in benzene in the presence of water

Deaerated solution ($5 \times 10^{-4}$ M) of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** (116.5 mg) and water (0.5 ml) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 1 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **4**–**6** were isolated in 30.1 mg (24% yield), 7.9 mg (9% yield), and 26.4 mg (21% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (5/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1, v/v) as an eluent. Compound **4**: UV ($CH_2Cl_2$), $\lambda_{max}$: 286, 247 nm; FT-IR (NaCl): 3350.5, 2954.1, 1542.1, 1425.6, 1249.3, 836.4 cm$^{-1}$; MS (70 eV), *m/z*: 251 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{21}NOSi_2$ 251.1162, found 251.1145. Compound **5**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.30 (9H, s), 7.24 (1H, ddd, $J = 7.6, 4.9, 1.0$ Hz), 7.47 (1H, d, $J = 7.8$ Hz), 7.66 (1H, td, $J = 7.7, 1.7$ Hz), 8.59 (1H, d, $J = 4.1$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −0.07, 95.2, 104.1, 123.2, 127.7, 136.4, 143.5, 150.3; UV ($CH_2Cl_2$), $\lambda_{max}$: 287, 279, 247 nm; FT-IR (NaCl): 2959.3, 2167.6, 1581.9, 1462.1, 1250.3, 866.8, 799.5 cm$^{-1}$; MS (70 eV), *m/z*: 175 ($M^+$); HRMS ($M^+$) calc. for $C_{10}H_{13}NSi$ 175.0817, found 175.0836. Compound **6**: UV ($CH_2Cl_2$), $\lambda_{max}$: 276, 246 nm; FT-IR (NaCl): 3312.9, 2955.5, 1542.2, 1425.8, 1249.7, 838.1 cm$^{-1}$; MS (70 eV), *m/z*: 251 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{21}NOSi_2$ 251.1162, found 251.1156.

### 2.6. Irradiation of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne *1* in methanol

A solution ($5 \times 10^{-4}$ M) of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** (116.5 mg) in methanol (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 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **7** and **8** were isolated in 51.7 mg (39% yield) and 13.2 mg (10% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (5/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1, v/v) as an eluent. Compound **7**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.16 (9H, s), 0.33 (6H, s), 3.48 (3H, s), 7.17 (1H, ddd, $J = 7.8, 4.8, 0.9$ Hz), 7.28 (1H, d, $J = 7.8$ Hz), 7.66 (1H, td, $J = 7.8, 1.7$ Hz), 7.73 (1H, s), 8.58 (1H, d, $J = 4.8$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −0.45, 2.47, 50.7, 122.6, 124.5, 136.4, 148.7, 149.6, 153.7, 157.6; UV ($CH_2Cl_2$), $\lambda_{max}$: 289, 248 nm; FT-IR (NaCl): 2953.8, 2898.1, 1577.2, 1426.2, 1250.3, 838.4 cm$^{-1}$; MS (70 eV), *m/z*: 265 ($M^+$); HRMS ($M^+$) calc. for $C_{13}H_{23}NOSi_2$ 265.1318, found 265.1311. Compound **8**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.16 (9H, s), 0.28 (6H, s), 4.71 (3H, s), 7.21 (1H, d, $J = 5.0$ Hz), 7.44 (1H, s), 8.49 (1H, d, $J = 5.0$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −2.85, −2.11, 63.5, 94.7, 106.3, 120.7, 125.0, 143.8, 150.3, 171.5; UV ($CH_2Cl_2$), $\lambda_{max}$: 283, 250 nm; FT-IR (NaCl): 2953.7, 2895.6, 2154.9, 1599.0, 1470.7, 1246.9, 836.5, 802.6 cm$^{-1}$; MS (70 eV), *m/z*: 263 ($M^+$); HRMS ($M^+$) calc. for $C_{13}H_{21}NOSi_2$ 263.1162, found 263.1127.

### *2.7. Irradiation of 1-(3-pyridyl)-2-(pentamethyldisilanyl)-ethyne **9** in benzene in the presence of water*

Deaerated solution ($5 \times 10^{-4}$ M) of 1-(3-pyridyl)-2-(pentamethyldisilanyl)ethyne **9** (116.5 mg) and water (0.5 ml) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 1 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, a mixture of **12** and **13**, **14**, and a mixture of **15** and **16**, were isolated in 55.2 mg (44% yield), 7 mg (8% yield), and 26.4 mg (21% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (3/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (1/1, v/v) as an eluent. A mixture of **12** and **13**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): −0.04 (9H, s), 0.07 (6H, s), 0.22 (9H, s), 0.31 (6H, s), 7.23 (2H, m), 7.48 (1H, d, $J = 7.8$ Hz), 7.56 (1H, d, $J = 7.8$ Hz), 7.60 (1H, s), 7.79 (1H, s), 8.40 (1H, s), 8.45 (3H, d, $J = 2.9$ Hz); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): 0.54, 1.89, 2.14, 3.63, 135.6, 135.7, 138.4, 148.3, 148.4, 148.8, 148.9, 150.4, 151.2, 151.3, 152.2; UV ($CH_2Cl_2$), $\lambda_{max}$: 237 nm; FT-IR (NaCl): 3253.3, 2954.8, 1588.5, 1553.2, 1250.0, 920.5 cm$^{-1}$; MS (70 eV), *m/z*: 251 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{21}NOSi_2$ 251.1161, found 251.1139. Compound **14**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.29 (9H, s), 7.25 (1H, dd, $J = 7.7, 4.9$ Hz), 7.75 (1H, d, $J = 7.9$ Hz), 8.55 (1H, d, $J = 2.7$ Hz), 8.71 (1H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): 0.20, 98.6, 101.9, 120.7, 123.2, 139.2, 149.1, 153.1; UV ($CH_2Cl_2$), $\lambda_{max}$: 247 nm; FT-IR (NaCl): 2958.1, 2162.9, 1474.7, 1250.9, 801.1 cm$^{-1}$; MS (70 eV), *m/z*: 175 ($M^+$); HRMS ($M^+$) calc. for $C_{10}H_{13}NSi$ 175.0817, found 175.0839. A mixture of **15** and **16**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.17 (9H, s), 0.22 (6H, s), 0.23 (9H, s), 0.30 (6H, s), 6.38 (1H, s), 6.54 (1H, s), 7.19 (2H, s), 7.36 (1H, d, $J = 7.7$ Hz), 7.41 (1H, d, $J = 7.7$ Hz), 8.24 (1H, s), 8.32 (1H, s), 8.38 (2H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): 1.10, 1.15, 2.21, 2.26, 123.2, 134.4, 134.5, 146.6, 146.8, 147.1, 147.4, 151.1, 153.4, 159.8, 161.7; UV ($CH_2Cl_2$), $\lambda_{max}$: 242 nm; FT-IR (NaCl): 3241.8, 3082.6, 2953.9, 1570.8, 1407.9, 1251.7, 931.5 cm$^{-1}$; MS (70 eV), *m/z*: 251 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{21}NOSi_2$ 251.1161, found 251.1142.

### *2.8. Irradiation of 1-(3-pyridyl)-2-(pentamethyldisilanyl)ethyne **9** in methanol*

A solution ($5 \times 10^{-4}$ M) of 1-(3-pyridyl)-2-(pentamethyldisilanyl)ethyne **9** (116.5 mg) in methanol (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 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, a mixture of **17** and **18**, were isolated in 116.6 mg (88% yield) by column chromatography with *n*-hexane/ethyl acetate (3/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (1/1, v/v) as an eluent. A mixture of **17** and **18**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.01 (9H, s), 0.07 (6H, s), 0.23 (9H, s), 0.32 (6H, s), 3.27 (3H, s), 3.49 (3H, s), 7.27 (2H, m), 7.52 (1H, d, $J = 7.7$ Hz), 7.60 (1H, d, $J = 7.7$ Hz), 7.67 (1H, s), 7.78 (1H, s), 8.55 (4H, m); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −0.59, 0.49, 0.85, 2.02, 50.1, 50.8, 122.9, 123.0, 135.3, 135.4, 148.7, 149.1, 149.2, 149.3, 150.4, 151.4, 152.4; UV ($CH_2Cl_2$), $\lambda_{max}$: 241 nm; FT-IR (NaCl): 3030.4, 2954.4, 2899.7, 2830.2, 1586.1, 1572.8, 1470.9, 1250.8, 1187.2, 921.0, 836.2, 798.3 cm$^{-1}$; MS (70 eV), *m/z*: 265 ($M^+$); HRMS ($M^+$) calc. for $C_{13}H_{23}NOSi_2$ 265.1318, found 265.1362.

### *2.9. Reduction of photoproducts, a mixture of **17** and **18***

A solution of a mixture of **17** and **18** (100 mg, 0.38 mmol) and 5% Pd/C (5 mg) in methanol (7 ml) under hydrogen atmosphere was stirred for 3 h at room temperature. To this solution water (10 ml) was added and the resulting solution was extracted with ethyl acetate (3 × 10 ml). The organic extract was washed with $H_2O$ (10 ml), brine (10 ml), and dried ($MgSO_4$). Filtration and evaporation of the solvent and flash column chromatography with *n*-hexane/ethyl acetate (3/1) as an eluent gave **19** (95.7 mg, 95% yield) as a colorless oil; $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.05 (9H, s), 0.07 (3H, s), 0.11 (3H, s), 0.46 (1H, t, $J = 6.9$ Hz), 2.81 (1H, dd, $J = 14.8, 6.5$ Hz), 2.87 (1H, dd, $J = 14.8, 7.5$ Hz), 3.34 (3H, s), 7.21 (1H, t, $J = 6.2$ Hz), 7.55 (1H, d, $J = 7.8$ Hz), 8.43 (1H, d, $J = 3.7$ Hz), 8.50

(1H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −0.88, −0.77, 0.19, 17.4, 28.6, 50.3, 123.5, 136.2, 140.1, 147.4, 150.3; UV ($CH_2Cl_2$), $\lambda_{max}$: 265 nm; FT-IR (NaCl): 2953.6, 1575.0, 1422.6, 1250.9, 836.4 cm$^{-1}$; MS (70 eV), *m/z*: 267 ($M^+$); HRMS ($M^+$) calc. for $C_{13}H_{25}NOSi_2$ 267.1475, found 267.1435.

### 2.10. Irradiation of 1-(4-pyridyl)-2-(pentamethyldisilanyl)ethyne **20** in benzene in the presence of water

Deaerated solution ($5\times10^{-4}$ M) of 1-(4-pyridyl)-2-(pentamethyldisilanyl)ethyne **20** (116.5 mg) and water (0.5 ml) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 0.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, a mixture of **23** and **24**, **25**, and a mixture of **26** and **27**, were isolated in 43.9 mg (35% yield), 3.5 mg (4% yield), and 20.1 mg (16% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (3/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (1/1, v/v) as an eluent. A mixture of **23** and **24**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): −0.006 (9H, s), 0.10 (6H, s), 0.22 (9H, s), 0.33 (6H, s), 7.10 (2H, d, $J$ = 5.1 Hz), 7.15 (2H, d, $J$ = 5.1 Hz), 7.57 (1H, s), 7.74 (1H, s), 8.53 (4H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): 0.45, 1.85, 2.07, 3.56, 123.1, 123.2, 149.5, 149.6, 150.6, 150.8, 150.9, 151.3, 152.3, 152.7; UV ($CH_2Cl_2$), $\lambda_{max}$: 237 nm; FT-IR (NaCl): 3177.4, 2954.8, 1600.0, 1540.9, 1248.8, 836.5 cm$^{-1}$; MS (70 eV), *m/z*: 251 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{21}NOSi_2$ 251.1161, found 251.1173. Compound 25; $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.24 (9H, s), 7.29 (2H, d, $J$ = 4.6 Hz), 8.56 (2H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): 0.06, 100.3, 102.4, 126.3, 131.6, 150.0; UV ($CH_2Cl_2$), $\lambda_{max}$: 256, 244 nm; FT-IR (NaCl): 2961.1, 2166.3, 1592.1, 1405.2, 1245.7, 800.7 cm$^{-1}$; MS (70 eV), *m/z*: 175 ($M^+$); HRMS ($M^+$) calc. for $C_{10}H_{13}NSi$ 175.0817, found 175.0891. A mixture of **26** and **27**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): −0.04 (9H, s), 0.07 (6H, s), 0.18 (9H, s), 0.31 (6H, s), 6.29 (1H, s), 6.39 (1H, s), 6.95 (2H, d, $J$ = 4.6 Hz), 6.97 (2H, d, $J$ = 4.6 Hz), 8.47 (4H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): 1.17, 1.41, 1.98, 2.16, 122.0, 122.9, 144.3, 144.8, 148.9, 149.0, 150.6, 150.8, 150.9, 151.3, 152.3, 152.7; UV ($CH_2Cl_2$), $\lambda_{max}$: 231 nm; FT-IR (NaCl): 3233.7, 2961.1, 1599.2, 1539.9, 1247.2, 837.2 cm$^{-1}$; MS (70 eV), *m/z*: 251 ($M^+$); HRMS ($M^+$) calc. for $C_{12}H_{21}NOSi_2$ 251.1161, found 251.1174.

### 2.11. Irradiation of 1-(4-pyridyl)-2-(pentamethyldisilanyl)ethyne **20** in methanol

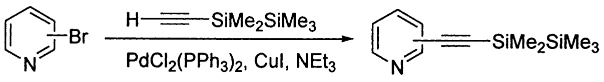
A solution ($5 \times 10^{-4}$ M) of 1-(4-pyridyl)-2-(pentamethyldisilanyl)ethyne **20** (116.5 mg) in methanol (1 l) was deaerated by nitrogen purging for 1 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 0.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts, a mixture of **28** and **29**, were isolated in 108.7 mg (82% yield) by column chromatography with *n*-hexane/ethyl acetate (3/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (1/1, v/v) as an eluent. A mixture of **28** and **29**: $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.01 (9H, s), 0.07 (6H, s), 0.23 (9H, s), 0.32 (6H, s), 3.29 (3H, s), 3.49 (3H, s), 7.13 (2H, d, $J$ = 5.3 Hz), 7.17 (2H, d, $J$ = 5.4 Hz), 7.61 (1H, s), 7.74 (1H, s), 8.57 (4H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −0.65, 0.40, 0.80, 1.95, 50.1, 50.8, 123.1, 149.3, 149.8, 149.9, 150.5, 151.2, 152.2, 153.2; UV ($CH_2Cl_2$), $\lambda_{max}$: 239 nm; FT-IR (NaCl): 2955.2, 2899.3, 1601.1, 1565.2, 1249.1, 836.7 cm$^{-1}$; MS (70 eV), *m/z*: 265 ($M^+$); HRMS ($M^+$) calc. for $C_{13}H_{23}NOSi_2$ 265.1318, found 265.1371.

### 2.12. Reduction of photoproducts, a mixture of **28** and **29**

This reaction was carried out according to the same procedure described for the reduction of photoproducts, a mixture of **17** and **18**, except a mixture of **28** and **29** (100 mg, 0.38 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 3:1, v/v) to afford colorless oil of **30** (81.6 mg, 81% yield); $^1$H NMR ($CDCl_3$, 600 MHz), $\delta_H$ (ppm): 0.05 (9H, s), 0.08 (3H, s), 0.11 (3H, s), 0.48 (1H, t, $J$ = 6.8 Hz), 2.78 (1H, dd, $J$ = 14.9, 6.3 Hz), 2.84 (1H, dd, $J$ = 14.9, 7.3 Hz), 3.34 (3H, s), 7.17 (2H, d, $J$ = 4.4 Hz), 8.50 (2H, s); $^{13}$C NMR ($CDCl_3$, 150 MHz), $\delta_C$ (ppm): −0.88, −0.77, 0.20, 16.6, 30.9, 50.4, 124.3, 149.9, 154.1; UV ($CH_2Cl_2$), $\lambda_{max}$: 252 nm; FT-IR (NaCl): 2954.0, 1599.5, 1415.7, 1251.4, 834.4 cm$^{-1}$; MS (70 eV), *m/z*: 267 ($M^+$); HRMS ($M^+$) calc. for $C_{13}H_{25}NOSi_2$ 267.1475, found 267.1421.

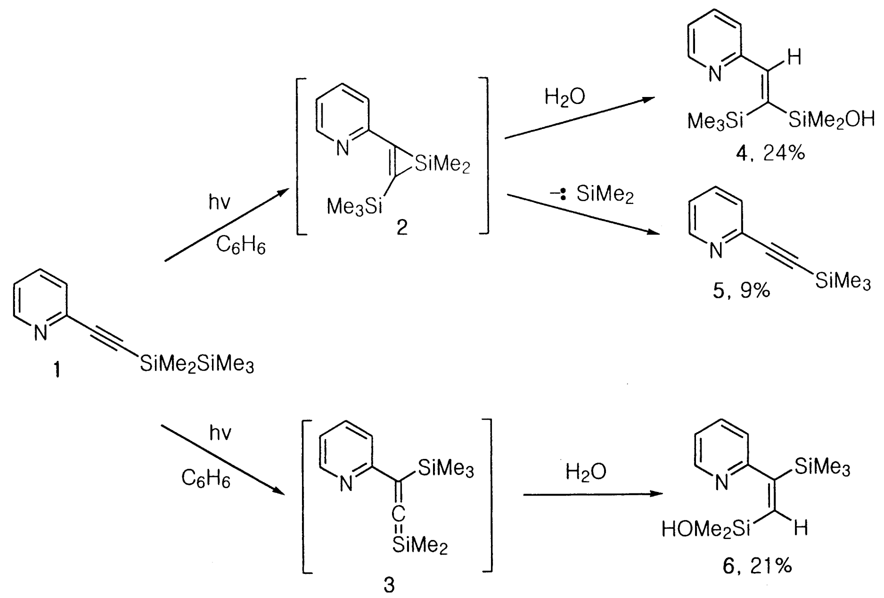
## 3. Results and discussion

The starting 1-(*n*-pyridyl)-2-(pentamethyldisilanyl)ethynes ($n$ = 2, 3, or 4) **1**, **9**, or **20**, respectively, aza analogs of 1-phenyl-2-(pentamethyldisilanyl)ethyne, were prepared by the reaction of *n*-bromopyridine ($n$ = 2, 3, or 4, respectively) with pentamethyldisilanylethyne in the presence of bis(triphenylphosphine) palladium dichloride and copper(I) iodide in triethylamine (Scheme 1).

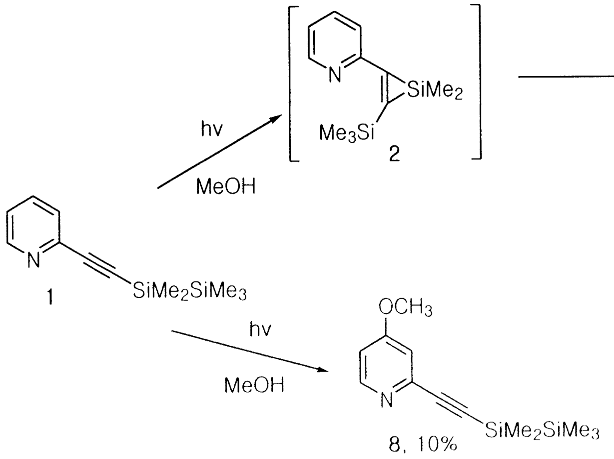


**1**: 2-Pyridyl, 75%
**9**: 3-Pyridyl, 81%
**20**: 4-Pyridyl, 15%

Scheme 1.



Scheme 2.



Scheme 3.

### 3.1. *Photoreaction of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in benzene or methanol*

Irradiation of **1** in deaerated benzene in the presence of water as a trapping agent with 254 nm UV light provided two compounds **4** (24% yield) and **6** (21% yield) which can be expected from the reaction of the silacyclopropene **2** or 1-sila-1,2-propadiene **3** with water, respectively, in addition to **5** (9% yield) which was formed by the liberation of dimethylsilylene species from **2** as shown in Scheme 2. Photolysis of **1** in methanol gave the regioselective photoproduct **7** (39% yield) via silacyclopropene intermediate **2** and a nucleophilic aromatic substitution product **8** (10% yield) along with some decomposition products of unknown structure shown in Scheme 3. In this case, 1-sila-1,2-propadiene intermediate **3** was not observed. In these reactions, prolonged irradiation of **1** did not afford the stereoisomers of **4**, **6**, or **7**. From these results, it is thought that the interaction between the nitrogen atom at 2-position in pyridine ring and the alkylated silicon atom at (*Z*) position of pyridine ring in **4**, **6**, or **7** prohibits photoisomerization to its stereoisomers because **12** and **13**, **15** and **16**, **17** and **18**, **23** and **24**, **26** and **27**, and **28** and **29** which are formed from the photoreaction of **9** or **20** in benzene or methanol were obtained as isomer mixtures.[1] The structures of the photoproducts **4** and **6** were determined by various spectroscopic methods including $^{1}$H–$^{1}$H and $^{1}$H–$^{13}$C correlation spectroscopy (COSY), HMBC, nuclear overhauser and exchange

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[1] A mixture of **12** and **13** was not separated by silica gel column chromatography, normal phase HPLC (column; LiChrospher Si 60) or inverse phase HPLC (column; LiChrospher RP-18) and other isomer pairs (**15** and **16**, **17** and **18**, **23** and **24**, **26** and **27**, **28** and **29**) were also not separated.

Table 1
$^1$H NMR (600 MHz), $^{13}$C NMR (150 MHz), and HMBC data for photoproduct **4** in $CDCl_3$[a]

| Position | $\delta_C$ (ppm) | M[b] | $\delta_H$ (ppm) | *I*[c] | *M*[d] | $J_{H–H}$ (Hz) | HMBC[e] |
|---|---|---|---|---|---|---|---|
| 1 | 136.5 | d | 7.67 | 1H | td | 7.6 ($J_{1H–2H, 5H}$), 1.1 ($J_{1H–3H}$) | H3 |
| 2 | 122.6 | d | 7.17 | 1H | dd | 7.1 ($J_{2H–1H}$), 4.9 ($J_{2H–3H}$) | H3, H5 |
| 3 | 148.7 | d | 8.58 | 1H | d | 4.0 ($J_{3H–2H}$) | H1, H2 |
| 4 | 157.7 | s | | | | | H1, H3, H5, H6 |
| 5 | 124.4 | d | 7.27 | 1H | d | 7.8 ($J_{5H–1H}$) | H2, H6 |
| 6 | 152.9 | d | 7.78 | 1H | s | | H5 |
| 7 | 150.8 | s | | | | | H8, H9 |
| 8 | 1.90 | q | 0.37 | 6H | s | | |
| 9 | 2.58 | q | 0.15 | 9H | s | | |
| –OH | | | 1.91 | 1H | | | |

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

spectroscopy (NOESY) (Tables 1 and 2). The $^1$H–$^1$H and $^1$H–$^{13}$C COSY spectra of **4** and **6** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **4** and **6**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Tables 1 and 2. In order to determine the location of the quaternary carbons, the HMBC spectra of **4** and **6** were taken. The presence of the cross-peaks due to the vicinal coupling between the proton of C(5) and the quaternary carbon C(6) in **4** showed the connectivity of the carbon C(6) to the pyridine ring. In the same manner, the connectivity of the carbon C(7) to the trimethylsilyl and the hydroxydimethylsilyl groups in **4** was established. The presence of the cross-peaks due to the vicinal coupling between the protons of C(5) and C(8) and the quaternary carbon C(6) in **6** showed the connectivity of the C(6) to the pyridine ring and trimethylsilyl group. In the same manner, the connectivity of the C(7) to the hydroxydimethylsilyl group in **6** was established. The 3D structure of **4** and **6** was determined by a NOESY. In particular, the presence of the cross-peaks between a proton of C(6) and the protons of C(8) in **4** showed the close proximity of a proton of C(6) to the protons of C(8) indicating that these protons are located on the same side of the molecule. In the same manner, the close proximity of a proton of C(7) to the protons of C(8) in **6** indicating that these protons are located on the same side of the molecule. Thus, the skeletal structures of **4** and **6** were unambiguously established as shown in Fig. 1.

### *3.2. Photoreaction of 1-(3-pyridyl)-2-(pentamethyldisilanyl)ethyne **9** in benzene or methanol*

Irradiation of **9** in deaerated benzene in the presence of water as a trapping agent with 254 nm UV light afforded a mixture of **12** and **13** (44% yield), and **14** (8% yield) via silacyclopropene intermediate **10**, and a mixture of **15** and **16** (21% yield) via 1-sila-1,2-propadiene intermediate **11** as shown in Scheme 4. The $^1$H NMR spectrum of a mixture

Table 2
$^1$H NMR (600 MHz), $^{13}$C NMR (150 MHz), and HMBC data for photoproduct **6** in $CDCl_3$[a]

| Position | $\delta_C$ (ppm) | M[b] | $\delta_H$ (ppm) | *I*[c] | M[d] | $J_{H–H}$ (Hz) | HMBC[e] |
|---|---|---|---|---|---|---|---|
| 1 | 136.7 | d | 7.62 | 1H | td | 7.7 ($J_{1H–2H, 5H}$), 1.6 ($J_{1H–3H}$) | H3 |
| 2 | 121.1 | d | 7.10 | 1H | dd | 6.8 ($J_{2H–1H}$), 5.3 ($J_{2H–3H}$) | H3, H5 |
| 3 | 148.5 | d | 8.51 | 1H | d | 4.1 ($J_{3H–2H}$) | H1, H2 |
| 4 | 167.7 | s | | | | | H1, H3, H7 |
| 5 | 121.2 | d | 7.14 | 1H | d | 7.8 ($J_{5H–1H}$) | H2 |
| 6 | 165 | s | | | | | H5, H7, H8 |
| 7 | 149.1 | d | 6.59 | 1H | s | | H9 |
| 8 | 1.35 | q | 0.24 | 9H | s | | |
| 9 | 2.24 | q | 0.34 | 6H | s | | |
| –OH | | | 2.28 | 1H | | | |

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

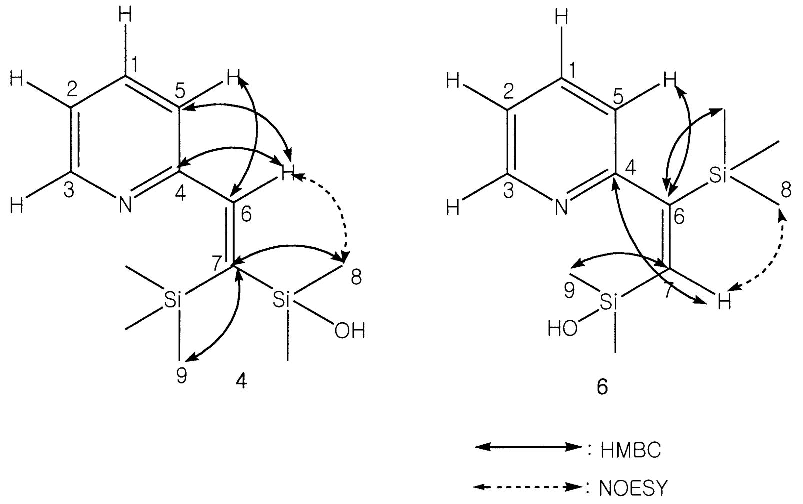
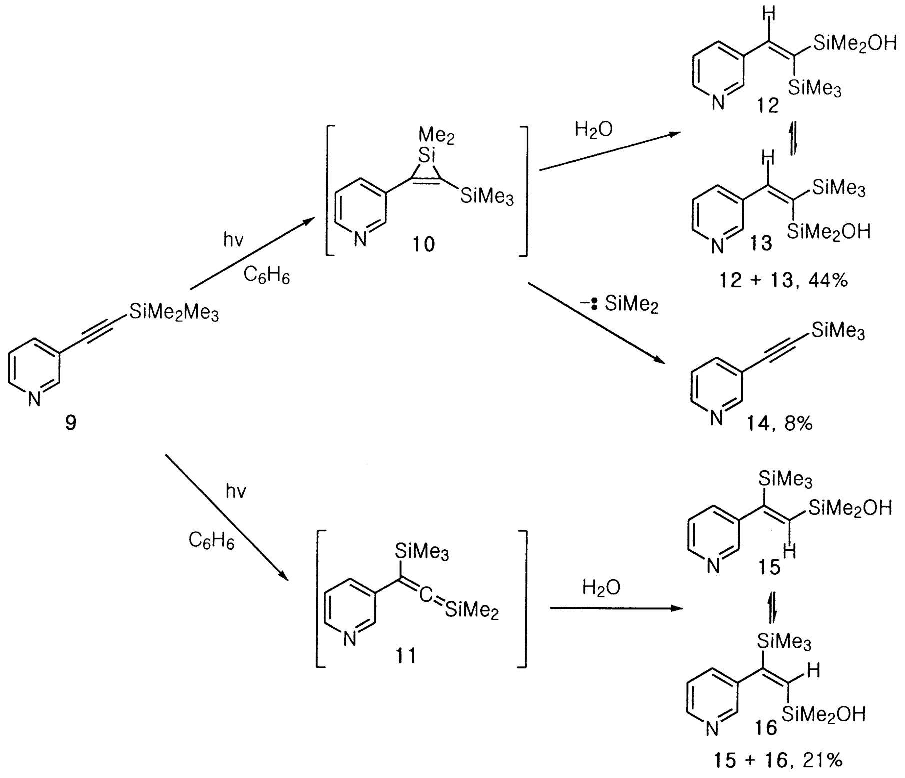
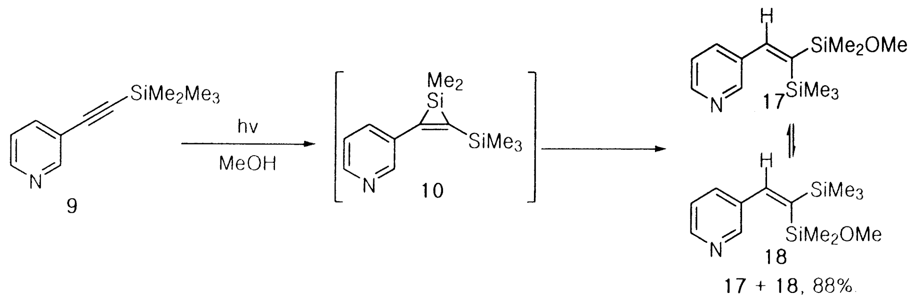


Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproducts **4** and **6**.

of **12** and **13** showed two pairs of all relevant signals in a 1.3:1 ratio. The photoproducts **12** and **13**, and other isomer pairs (**15** and **16**, **17** and **18**, **23** and **24**, **26** and **27**, **28** and **29**) can be distinguished by comparison with the literature data [1,2,7,8,12,14,15]. In particular, the vinylic protons of isomer pairs showed a difference in the chemical shift. Two singlets of **12** and **13** were observed at 7.79 and 7.60 ppm in a 1.3:1 ratio. The $^1$H NMR spectrum of a mixture of **15** and **16** also showed two pairs of all relevant signals in a 0.8:1 ratio. Two singlets from the vinylic protons of **15** and **16** were observed at 6.38 and 6.54 ppm in a 0.8:1 ratio. In the case of using methanol as solvent, a mixture of **17** and **18** (88% yield), via **10** was obtained from the photolysis of **9** as shown in Scheme 5 but 1-sila-1,2-propadiene intermediate **11** was also not observed. The $^1$H NMR spectrum of a mixture of **17** and **18** also showed two pairs of all relevant signals in a 1.06:1 ratio. Two singlets from the vinylic protons of **17** and **18** were observed at 7.78 and 7.67 ppm in a 1.06:1 ratio.

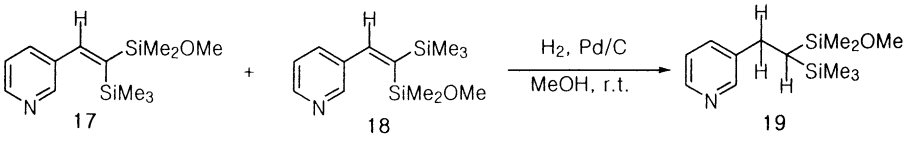


Scheme 4.



Scheme 5.

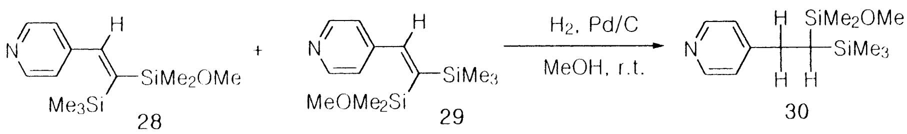
From the fact that a sole reduction product **19** was obtained from the reaction of a mixture of **17** and **18** in reduction reaction condition ($H_2$, Pd/C, MeOH), the structures of a mixture of **17** and **18** were differentiated from the photoproducts which are expected from the reaction of the 1-sila-1,2-propadiene intermediate **11** with methanol:The methylene protons located on a benzylic carbon adjacent to a stereocenter in **19** is diastereotopic, and they not only have different chemical shifts (2.81 and 2.87 ppm in $^1$H NMR) but also show splitting interaction (the coupling constant for geminal coupling is 14.8 Hz). In the case of splitting pattern for the proton located on a stereocenter in **19**, the two doublets overlap by coincidence and appear as a triplet. As with diastereotopic hydrogens, the two methyl groups in methoxydimethylsilyl group in **19** have also slightly different chemical shifts (0.07 and 0.11 ppm in $^1$H NMR) because the adjacent carbon atom is a stereocenter.

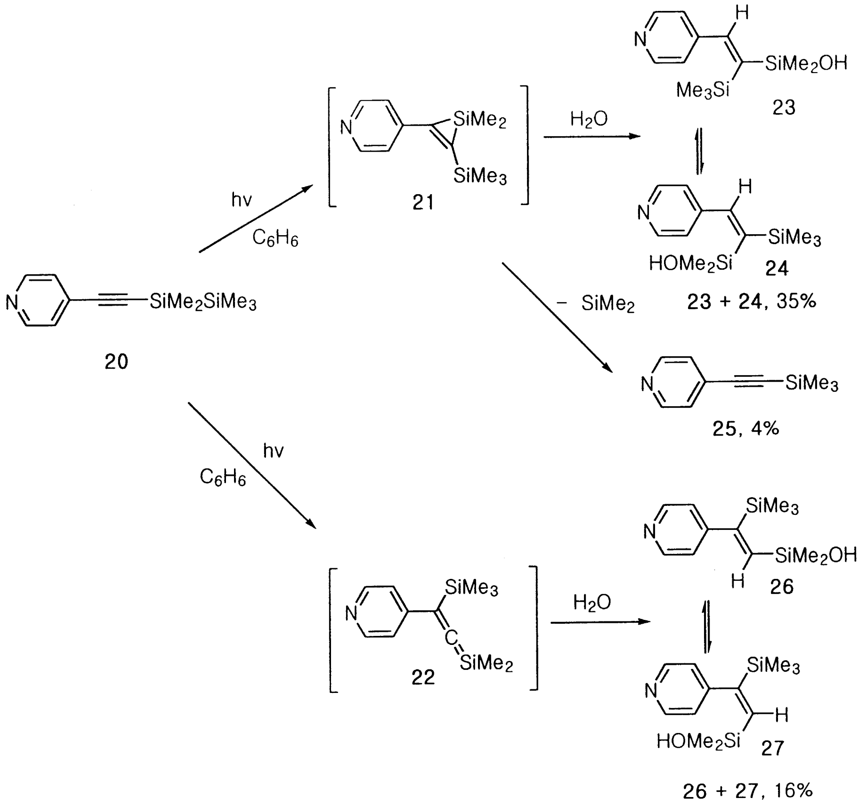


### 3.3. Photoreaction of 1-(4-pyridyl)-2-(pentamethyldisilanyl)ethyne **20** in benzene or methanol

In the case of **20**, the same results as in the photolysis of **9** were also obtained as shown in Schemes 6 and 7. A mixture of **23** and **24** (35% yield), **25** (4% yield), and a mixture of **26** and **27** (16% yield) were obtained via silacyclopropene intermediate **21** or 1-sila-1,2-propadiene intermediate **22**, respectively, from the photoreaction of **20** in deaerated benzene in the presence of water as a trapping agent with 254 nm UV light.

Photolysis of **20** in methanol also afforded a mixture of **28** and **29** (82% yield) via silacyclopropene intermediate **21** and the photoproducts which are expected from the reaction of the 1-sila-1,2-propadiene intermediate **22** with methanol were also not detected. Indeed, research has established that the photolysis of phenylethynylpentamethyldisilane [1], 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane [3], or 1-(trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane [23] in the presence of methanol were reported to give the photoproducts via silacyclopropene or 1-sila-1,2-propadiene intermediates. In contrast, the photolysis of (pentamethyldisilanyl)phenylacetylene [2], 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes [7], 1,4-bis(pentamethyldisilanyl)butadiyne [8], 1-(*ortho*-allyloxyphenyl)-2-pentamethyldisilanylethyne [12], 1,4-bis(pentamethyldisilanylethynyl) benzene [14], or 4,4′-bis(pentamethyldisilanylethynyl)biphenyl [15] in the presence of methanol were reported to afford the photoproducts only via silacyclopropene intermediate. In comparison with the above results, it is thought that 1-sila-1,2-propadiene intermediates formed, probably, from the photolysis of **1**, **9**, or **20** in methanol as minor photoproducts may undergo fast polymerization to give non-volatile substances [23] even in the presence of a trapping agent, methanol, and the photoproducts formed from the reaction of 1-sila-1,2-propadiene intermediates with methanol were not detected. The structures of photoisomers, **23**, **26**, and **28**, could be distinguished from those of **24**, **27**, and **29**, respectively, on the basis of comparison of the $^1$H NMR spectra of the isomer pairs [1,2,7,8,12,14,15]. Singlets from the vinylic protons of **23**, **26**, and **28** were observed at 7.74, 6.29, and 7.74 ppm, respectively, while its isomers **24**, **27**, **29** showed the vinylic protons at 7.57, 6.39, and 7.61 ppm, respectively:

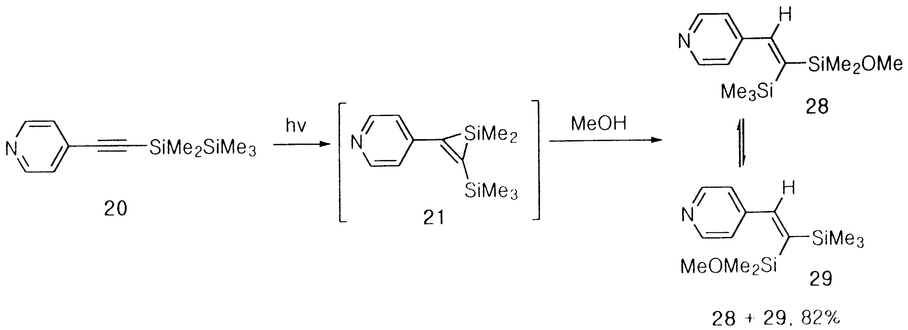




Scheme 6.

Subsequent reduction of a mixture of **28** and **29** gave the same reduction product **30**. The chemical shifts and coupling patterns in **30** are similar as in **19**, and the structure of **30** was unambiguously determined.

In conclusion, irradiation of **1** in benzene, non-polar solvent, provided two compounds **4** and **6** which can be expected from the reaction of the silacyclopropene **2** or 1-sila-1,2-propadiene **3** with water, respectively, in addition to **5**. Irradiation of **9** in benzene afforded a mixture of **12** and **13**, and **14** via silacyclopropene intermediate **10**, and a mixture of **15** and **16** via 1-sila-1,2-propadiene intermediate **11**. A mixture of **23** and **24**, **25**, and a mixture of **26** and **27** were obtained via silacyclopropene intermediate **21** or 1-sila-1,2-propadiene intermediate **22**, respectively, from the photoreaction of **20** in benzene. Whereas the photolysis of **9** or **20** in methanol almost quantitatively afforded a mixture of **17** and **18**, or a mixture of **28** and **29** via the silacyclopropene intermediate **10** or **21**, respectively, the photolysis of **1** gave several other products of unknown structure in addition to the photoproduct **7** in moderate yields formed from the reaction of **2** with methanol and the nucleophilic aromatic substitution product **8** in low yields formed from the reaction of **1** with methanol. These results indicate that the formation of silacyclopropene intermediate **2** from the photolysis of **1** in methanol is much more difficult than in the case of **9** or **20**. It is, therefore, thought that



Scheme 7.

the photolysis of **1** proceed simultaneously by two different routes, the major route, one of which, leads to the production of the silacyclopropene intermediate **2**, and the minor route is the nucleophilic aromatic substitution of methanol at the γ-position in pyridine ring of **1**, and the photoproduct **8** was obtained only in the photolysis of **1**.

## Acknowledgements

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