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Photoreactions of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne, aza analogue of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne

Seung Ki Park*, Dong Jae Baek

Department of Chemistry, College of Natural Sciences, The University of Suwon, P.O. Box 77, Suwon 445-743, South Korea

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Abstract

Photolysis of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1**, aza analogue of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne, in benzene provides novel intramolecular cycloaddition products **6** and **8** via silacyclopropene intermediate **3** but affords a novel intramolecular cycloaddition product **10** via 1-silaallene intermediate **9** in addition to **6** and **8** in methylene chloride.

Keywords: 1-(3-Hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne; Silacyclopropene; 1-Silaallene

1. Introduction

The formation of silacyclopropene, an unsaturated three-membered ring containing one silicon atom and one C=C bond, and 1-silaallene, a compound containing cumulated double bonds to silicon, as reaction intermediates is a general feature of the photochemistry of alkynyldisilanes [1–16] since the earliest report on the photolysis of 1-phenyl-2-(pentamethyldisilanyl)ethyne by Ishikawa et al. [17]. Most of the silacyclopropenes or 1-silaallenes are extremely unstable toward atmospheric oxygen and moisture. Therefore, the existence of the silacyclopropene or 1-silaallene intermediates is, in most cases, proved by trapping them with solvents such as methanol or acetone. Leigh and co-workers recently reported the direct detection and characterization of transient 1-silaallene derivatives in a laser flash photolysis study of 1-phenyl-2-(pentamethyldisilanyl)ethyne and ((trimethylsilyl)ethynyl)pentamethyldisilane [18,19]. Also, isolable 1-silaallene derivative [20] and a ruthenium complex of a 1-silaallene [21] were recently reported.

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 or 1-silaallene intermediates [22–25]. 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-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1**, aza analogue of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [26,27], containing the nitrogen atom in the benzene ring. Therefore, we have studied the photochemistry of **1**, since it is expected to affect the photochemical behavior of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne by the introduction of nitrogen atom in phenyl ring and we describe, in this paper, detailed photoreactions of **1** in various solvents.

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H- 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

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* Corresponding author. Tel.: +82-331-220-2153; fax: +82-331-220-2153.
E-mail address: skpark@mail.suwon.ac.kr (S.K. Park).

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on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector. Lichrosorb SI-60 column was used for preparative analyses. Thin layer chromatography (TLC) was performed on Sigma–Aldrich pre-coated silica gel 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. $NHEt_2$ 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-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1***

To a deaerated solution of 2-bromo-3-pyridinol (0.5 g, 2.87 mmol), bis(triphenylphosphine)palladium dichloride (21 mg, 0.03 mmol) and copper(I) iodide (5.7 mg, 0.03 mmol) in anhydrous diethylamine (10 ml) were added dropwise pentamethyldisilanylethyne (0.59 ml, 3.4 mmol) at room temperature. The reaction mixture was heated at 45 °C for 3 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 (3:1, v/v) as an eluent gave **1** (0.19 g, 27% yield) and **2** (0.22 g, 31% yield). **1**; m.p. 121–122 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 0.21 (9H, s), 0.35 (6H, s), 5.93 (1H, s), 7.20 (1H, dd, $J = 8.3, 4.6$ Hz), 7.29 (1H, dd, $J = 8.3, 1.2$ Hz), 8.19 (1H, dd, $J = 4.6, 1.2$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ_C −2.81, −2.15, 100.4, 103.6, 122.1, 125.0, 130.9, 142.7, 154.4; UV (CH_2Cl_2) λ_{max} 303, 243 nm; FT-IR (NaCl) 3443.0, 2955.9, 2150.8, 1570.8, 1458.5, 1266.4, 838.0 cm^{-1}; MS (70 eV) *m/z* 249 (M^+); HRMS (M^+) calcd. for $C_{12}H_{19}NOSi_2$ 249.1005, found 249.1001. Anal. calcd. for $C_{12}H_{19}NOSi_2$: C, 57.78; H, 7.68; N, 5.61. Found: C, 57.94; H, 7.53; N, 5.46. **2**; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 0.13 (9H, s), 0.40 (6H, s), 7.11 (1H, s), 7.16 (1H, dd, $J = 8.2, 4.7$ Hz), 7.72 (1H, d, $J = 8.2$ Hz), 8.50 (1H, d, $J = 4.7$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ_C −4.50, −2.00, 117.7, 118.2, 118.8, 145.7, 148.8, 151.3, 169.5; UV (CH_2Cl_2) λ_{max} 298, 252 nm; FT-IR (NaCl) 3060.6, 2953.7, 1409.9, 1262.3, 1247.4, 835.2 cm^{-1}; MS (70 eV) *m/z* 249 (M^+); HRMS (M^+) calcd. for $C_{12}H_{19}NOSi_2$ 249.1005, found 249.1000.

*2.3. Irradiation of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in benzene*

Deaerated solution (5×10^{-4} M) of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** (125 mg) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 2 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **2**, **4**, **5**, **6** and **8** were isolated in 5 mg (4% yield), 14.3 mg (15% yield), 3.8 mg (4% yield), 19.9 mg (16% yield), and 13.7 mg (11% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (8:1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (4:1, v/v) as an eluent. **4**; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 0.32 (9H, s), 5.96 (1H, s), 7.21 (1H, dd, $J = 8.5, 4.5$ Hz), 7.30 (1H, d, $J = 8.5$ Hz), 8.19 (1H, d, $J = 4.5$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ_C −0.05, 98.2, 103.7, 122.2, 125.0, 130.4, 142.6, 154.3; UV (CH_2Cl_2) λ_{max} 299, 241 nm; FT-IR (NaCl) 3422.9, 2964.0, 2162.0, 1567.1, 1462.5, 1253.2, 850.6 cm^{-1}; MS (70 eV) *m/z* 191 (M^+); HRMS (M^+) calcd. for $C_{10}H_{13}NOSi$ 191.0766, found 191.0769. **5**; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 0.37 (9H, s), 7.21 (1H, dd, $J = 8.2, 4.7$ Hz), 7.15 (1H, s), 7.77 (1H, d, $J = 8.2$ Hz), 8.59 (1H, d, $J = 4.7$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ_C −1.61, 117.2, 118.2, 118.9, 145.9, 148.7, 153.2, 171.5; UV (CH_2Cl_2) λ_{max} 297, 247 nm; FT-IR (NaCl) 3060.6, 2959.9, 1409.0, 1253.1, 845.7 cm^{-1}; MS (70 eV) *m/z* 191 (M^+); HRMS (M^+) calcd. for $C_{10}H_{13}NOSi$ 191.0766, found 191.0770. **6**; UV (CH_2Cl_2) λ_{max} 317, 230 nm; FT-IR (NaCl) 2957.4, 1576.7, 1541.9, 1431.9, 1283.0, 958.9, 861.1 cm^{-1}; MS (70 eV) *m/z* 249 (M^+); HRMS (M^+) calcd. for $C_{12}H_{19}NOSi_2$ 249.1005, found 249.1003. **8**; UV (CH_2Cl_2) λ_{max} 332, 246 nm; FT-IR (NaCl) 2957.2, 1578.9, 1457.1, 1260.8, 1103.2, 867.0 cm^{-1}; MS (70 eV) *m/z* 249 (M^+); HRMS (M^+) calcd. for $C_{12}H_{19}NOSi_2$ 249.1005, found 249.1008.

*2.4. Irradiation of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in methanol*

A solution (5×10^{-4} M) of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** (125 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 300 nm lamps. After irradiation for 0.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **2**, **4**, **5**, **6** and **7** were isolated in 6.2 mg (5% yield), 16.2 mg (17% yield), 5.7 mg (6% yield), 24.9 mg (20% yield), and 8.8 mg (7% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (8:1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (4:1, v/v) as an eluent. **7**; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 0.12 (9H, s), 0.32 (3H, s), 0.36 (3H, s), 0.44 (1H, dd, $J = 13.5, 3.9$ Hz), 3.0 (1H, dd, $J = 15.9, 13.5$ Hz), 3.19 (1H, dd, $J = 15.9, 3.9$ Hz), 7.09 (1H, dd, $J = 8.2, 4.6$ Hz), 7.13 (1H, d, $J = 8.2$ Hz), 8.07 (1H, d, $J = 4.6$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ_C −0.82, −0.25, 1.06, 12.30, 30.7, 123.2, 126.4, 140.9, 150.9, 151.5; UV (CH_2Cl_2) λ_{max} 279 nm; FT-IR (NaCl) 3064.6, 2955.2, 1433.9, 1272.1, 824.4 cm^{-1}; MS (70 eV) *m/z* 251

(M^+); HRMS (M^+) calcd. for $C_{12}H_{21}NOSi_2$ 251.1162, found 251.1166.

*2.5. Irradiation of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in methylene chloride*

Deaerated solution (5×10^{-4} M) of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** (125 mg) in methylene chloride (1 l) was irradiated in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 5 min, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **2**, **4**, **5**, **6**, **8** and **10**, were isolated in 5 mg (4% yield), 15.3 mg (16% yield), 7.6 mg (8% yield), 21.2 mg (17% yield), 14.9 mg (12% yield), and 3.7 mg (3% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (8:1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (4:1, v/v) as an eluent. **10**; UV (CH_2Cl_2) λ_{max} 310, 230 nm; FT-IR (NaCl) 3052.6, 2955.6, 1577.9, 1528.7, 1423.7, 1281.4, 839.0 cm^{-1}; MS (70 eV) *m/z* 249 (M^+); HRMS (M^+) calcd. for $C_{12}H_{19}NOSi_2$ 249.1005, found 249.1009.

3. Results and discussion

The starting 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1**, aza analogue of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne, was prepared by the reaction of 2-bromo-3-pyridinol with pentamethyldisilanyl ethyne in the presence of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in diethylamine (Scheme 1). In this reaction, a compound **2** formed from the cyclization of **1** was also obtained.

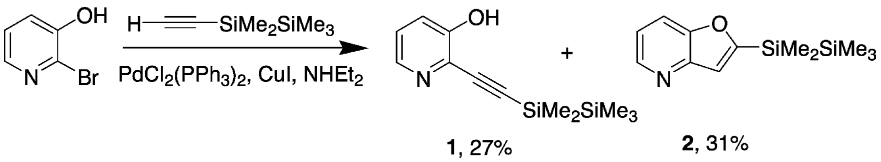
*3.1. Photoreaction of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in benzene*

Irradiation of **1** in deaerated benzene with 300 nm UV light provided five compounds **2** (4% yield), **4** (15% yield), **5** (4% yield), **6** (16% yield), and **8** (11% yield) along with some products of unknown structure as shown in Scheme 2. The formation of novel cycloaddition photoproducts **6** and **8** can be rationalized in terms of the initial formation of silacyclopropene intermediate **3** upon irradiation followed by the concerted intramolecular cycloaddition reaction (paths **b** and **c**, respectively) between the hydroxy group in *ortho*-substituent and Si–C bond of silacyclopropene intermediate **3** formed. The formation of photoproduct **2** or **5** can be explained in terms of the intramolecular cyclization reaction between the hydroxy group in *ortho*-substituent and the C≡C bond of pentamethyldisilanylethynyl or trimethylsilylethynyl group in **1** or **4**, respectively. Liberation of dimethylsilylene species from the silacyclopropene intermediate **3** (path **a**) resulted in the formation of **4**.

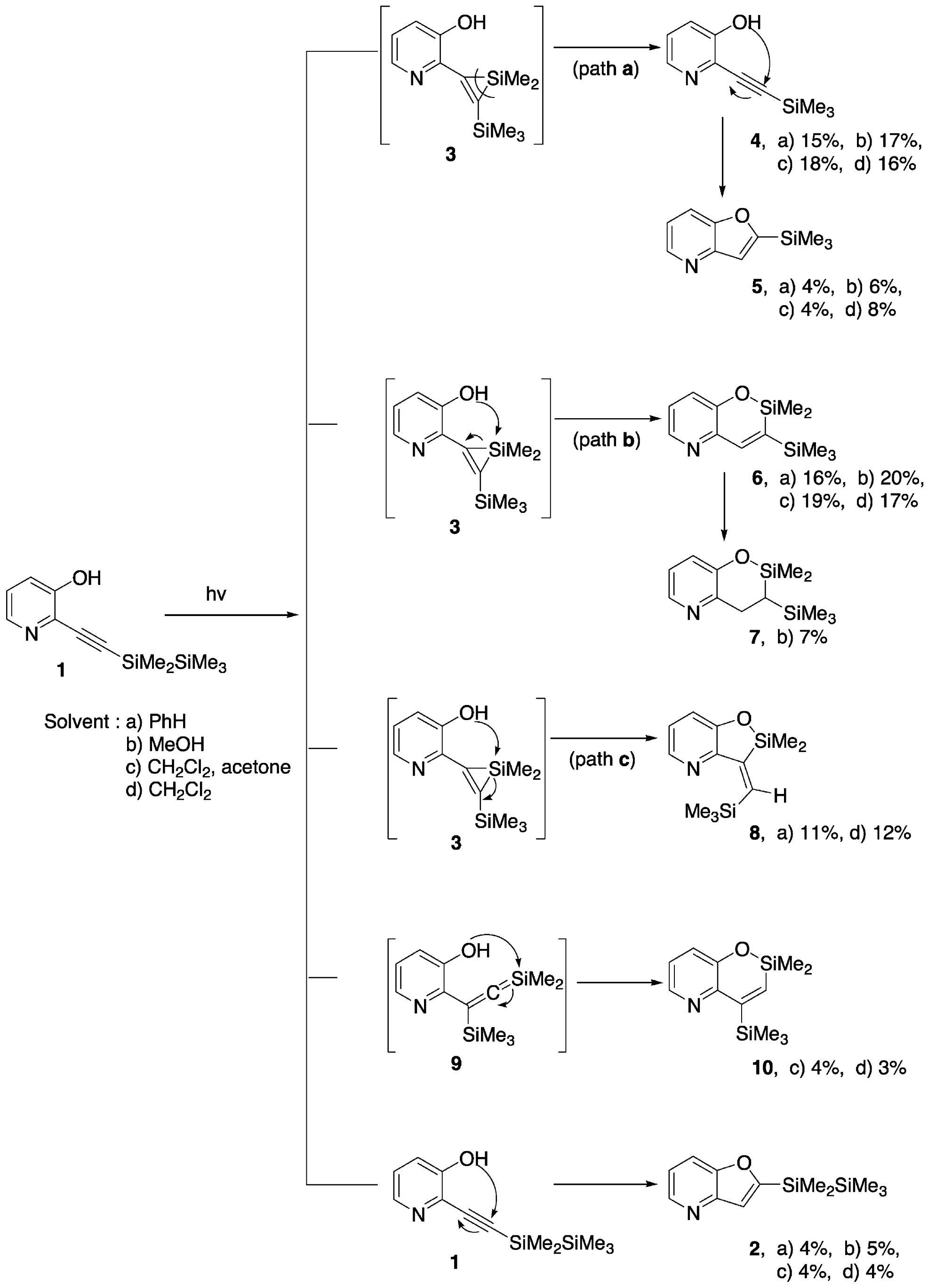
The structures of the photoproducts **6** and **8** were determined by various spectroscopic methods including ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY), HMBC, nuclear overhauser and exchange spectroscopy (NOESY) (Tables 1 and 2). The ^1H–^1H and ^1H–^{13}C correlation spectroscopy spectra of **6** and **8** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **6** and **8**, 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 **6** and **8** were taken. The presence of the cross-peak due to the vicinal coupling between the proton of C(7) and the quaternary carbon C(5) in **6** showed the connectivity of the carbon C(7) to the pyridine ring. In the same manner, the connectivity of the carbon C(6) to the trimethylsilyl and the dimethylsilyl groups in **6** was established. The presence of the cross-peak due to the vicinal coupling between the protons of C(8) and the quaternary carbon C(7) in **8** showed the connectivity of the carbon C(7) to the trimethylsilyl group. In the same manner, the connectivity of the carbon C(6) to the dimethylsilyl group in **8** was established. The 3D structures of **6** and **8** were determined by a nuclear overhauser and exchange spectroscopy. In particular, the presence of the cross-peak between the protons of C(8) and the protons of C(9) in **6** showed the close proximity of the protons of C(8) to the protons of C(9) 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) or C(9) in **8** indicating that these protons are located on the same side of the molecule. Thus, the skeletal structures of **6** and **8** were unambiguously established as shown in Fig. 1.

*3.2. Photoreaction of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in methanol*

The photolysis of 1-phenyl-2-(pentamethyldisilanyl)ethyne [17,28] and its *ortho*-substituted compound [29] in methanol affords two reaction intermediates, silacyclopropene and 1-silaallene. To investigate whether or not the



Scheme 1.



Scheme 2.

photolysis of **1** in methanol gives two reaction intermediates, the photolysis of **1** in methanol solvent was carried out. In this study, methanol was used to trap the highly reactive reaction intermediates, and the reaction intermediates were confirmed from the existence of the methanol addition photoproducts.

Irradiation of **1** (124 mg, 0.5 mmol) in deaerated methanol (1 l) with 300 nm UV light afforded the reduction product **7** (8.8 mg, 7% yield) in addition to the same photoproducts **2**, **4**, **5** and **6** (5, 17, 6 and 20% yields, respectively) as in the case of benzene solvent as shown in Scheme 2, but the expected methanol addition photoproducts via silacyclopropene **3** or 1-silaallene intermediate **9** were not obtained. This result indicates that the intramolecular reaction of *ortho*-substituted hydroxy group of **1** with silacyclopropene or 1-silaallene intermediate to give the cycloaddition products is much faster than the intermolecular reaction of methanol solvent with sialcyclopropene or 1-silaallene intermediate. But, the photolysis of 1-(*o*-allyloxyphenyl)-2-(pentamethyldisilanyl)ethyne

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

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	$J_{H–H}$ (Hz)	HMBC[e]
1	126.9	d	7.16	1H	d	8.1 ($J_{1H–2H}$)	H3
2	124.5	d	7.08	1H	dd	8.1 ($J_{2H–1H}$), 4.5 ($J_{2H–3H}$)	H3
3	142.0	d	8.18	1H	d	4.5 ($J_{3H–2H}$)	H1
4	143.7	s					H3, H7
5	151.3	s					H2, H7
6	143.5	s					H7, H8, H9
7	152.8	d	7.66	1H	s		
8	−0.33	q	0.20	9H	s		
9	2.33	q	0.39	6H	s		

[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.

Table 2
^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz), and HMBC data for photoproduct **8** in $CDCl_3$[a]

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	$J_{H–H}$ (Hz)	HMBC[e]
1	122.8	d	7.18	1H	dd	8.1 ($J_{1H–2H}$), 1.2 ($J_{1H–3H}$)	H3
2	124.6	d	7.10	1H	dd	8.1 ($J_{2H–1H}$), 4.6 ($J_{2H–3H}$)	H3
3	141.8	d	8.15	1H	dd	4.6 ($J_{3H–2H}$), 1.2 ($J_{3H–1H}$)	H1
4	150.1	s					H1, H3, H7
5	155.4	s					H2
6	149.2	s					H7, H9
7	145.1	d	7.85	1H	s		H8
8	0.13	q	0.22	9H	s		
9	0.84	q	0.55	6H	s		

[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.

having an allyloxy group as the *ortho*-substituted group in methanol gave the methanol addition photoproducts to silacyclopropene intermediate [29], indicating that the hydroxy group is much more reactive than the allyloxy group in the intramolecular reaction. It is thought that a compound **7** was, probably, formed from the reduction of the photoproduct **6** in methanol solvent. The photolysis of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne in methanol [27] also afforded the reduction photoproduct in addition to the methanol addition products to *o*-hydroxyphenylethyne, which is formed from the C–Si bond cleavage of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne, but the expected compounds formed from the photoaddition reaction of the reaction intermediate, silacyclopropene or 1-silaallene with methanol were also not obtained.

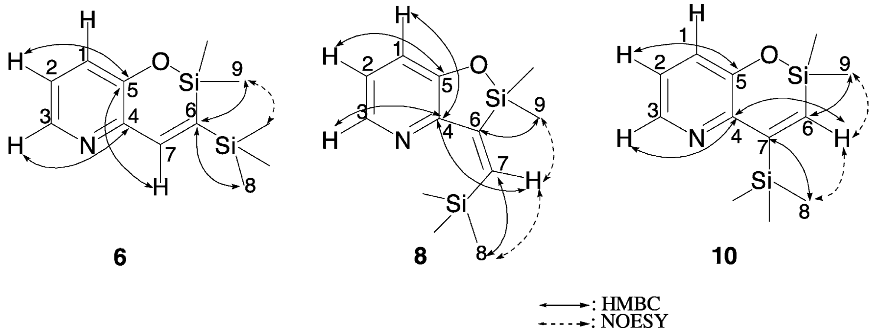
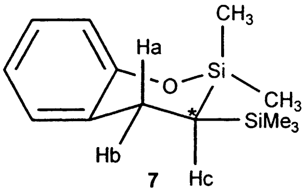


Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproducts **6**, **8** and **10**.

The structure of the photoproduct **7** was determined by various physical methods, such as ^1H NMR, ^{13}C NMR, UV, FT-IR, and high resolution mass spectrometry. The two methylene protons (Ha and Hb) located on a benzylic carbon adjacent to a stereocenter (the chemical shift of Hc is 0.44 ppm in ^1H NMR) in **7** is diastereotopic, and they not only have different chemical shifts (3.0 and 3.19 ppm, respectively, in ^1H NMR) but they also show splitting interactions ($^2J_{Ha–Hb,gem} = 15.9$ Hz, $^3J_{Ha–Hc,vic} = 13.5$ Hz, $^3J_{Hb–Hc,vic} = 3.9$ Hz). The splitting patterns for the protons (Ha, Hb and Hc) in **7** appear as three doublet of doublets (dd). As with diastereotopic hydrogen, the two methyl groups in dimethylsilyl group in **7** have also slightly different chemical shifts (0.32 and 0.36 ppm in ^1H NMR) because the adjacent carbon atom is a stereocenter.



7

3.3. *Photoreaction of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** in methylene chloride*

To trap the reaction intermediates formed from the photolysis of **1**, acetone was used as a trapping agent in methylene chloride solvent. Irradiation of **1** (124 mg, 0.5 mmol) in deaerated methylene chloride (1 l) with acetone with 300 nm UV light yielded a novel cycloaddition photoproduct **10** (5.0 mg, 4% yields) in addition to the same photoproducts **2**, **4**, **5** and **6** (4, 18, 4 and 19% yields, respectively) as in the case of benzene solvent as shown in Scheme 2, but the expected acetone photoaddition products to silacyclopropene **3** or 1-silaallene intermediate **9** were not also obtained like the photolysis of **1** in methanol solvent. In the case of the photolysis of **1** in the absence of acetone in methylene chloride solvent, **8** (12% yield) in addition to **2**, **4**, **5**, **6** and **10** (4, 16, 8, 17 and 3% yields, respectively) was obtained. The formation of photoproduct **10** can be rationalized in terms of the initial formation of 1-silaallene intermediate **9** upon irradiation followed by the concerted intramolecular cycloaddition of a hydroxy group in *ortho*-substituent to Si=C bond of 1-silaallene formed.

The structure of the photoproduct **10** was determined by various spectroscopic methods including ^1H–^1H and ^1H–^{13}C correlation spectroscopy, HMBC, nuclear overhauser and exchange spectroscopy (NOESY) (Table 3). The ^1H–^1H and ^1H–^{13}C correlation spectroscopy spectra of **10** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **10**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Table 3. In order to determine the location of the quaternary carbons, the HMBC spectra of **10** were taken.

The presence of the cross-peak due to the vicinal coupling between the proton of C(6) and the quaternary carbon C(4) in **10** showed the connectivity of the carbon C(7) to the pyridine ring. The presence of the cross-peaks due to the vicinal couplings between the protons of C(9) and the quaternary carbon C(6), and between the protons of C(8) and the quaternary carbon C(7) in **10** showed the connectivity of the carbon C(6) to the dimethylsilyl group, and the carbon C(7) to the trimethylsilyl group. The 3D structure of **10** was determined by a nuclear overhauser and exchange spectroscopy. In particular, the presence of the cross-peak between the proton of C(6) and the protons of C(9) in **10** showed the close proximity of the proton of C(6) to the protons of C(9) indicating that these protons are located on the same side of the molecule. In the same manner, the close proximity of the proton of C(6) to the protons of C(8) in **10** indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **10** was unambiguously established as shown in Fig. 1.

Table 3
^1H NMR (600 MHz), ^{13}C NMR (150 MHz), and HMBC data for photoproduct **10** in $CDCl_3$[a]

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	$J_{H–H}$ (Hz)	HMBC[e]
1	126.9	d	7.14	1H	d	8.1 ($J_{1H–2H}$)	H3
2	123.4	d	7.02	1H	dd	8.1 ($J_{2H–1H}$), 4.5 ($J_{2H–3H}$)	H1, H3
3	141.0	d	8.18	1H	d	4.5 ($J_{3H–2H}$)	H1, H2
4	146.8	s					H1, H3, H6
5	149.9	s					H1, H2
6	138.5	d	6.65	1H	s		H9
7	164.0	s					H6, H8
8	0.15	q	0.27	9H	s		
9	1.42	q	0.35	6H	s		

[a] All these assignments were confirmed by ^1H–^1H and ^1H–^{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.

3.4. Differences in photochemistry between 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **1** and 1-o-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne

3.4.1. In benzene solvent

A photoproduct **8** obtained via path **c** in the photolysis of **1** has an *E*-configuration, while a corresponding photoproduct obtained in the photolysis of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [26] has a *Z*-configuration. From this result, it is thought that the interaction between the nitrogen atom at 1-position in pyridine ring and the silicon atom of trimethylsilyl group at *Z* position of pyridine ring in **8** leads to the formation of *E*-photoproduct **8** in the photolysis of **1**.

3.4.2. In methanol solvent

The reduction product **7** in addition to the same photoproducts **2**, **4**, **5** and **6** as in the case of benzene solvent were obtained in the photolysis of **1**, while the much different photoproducts from the photoproducts in the benzene solvent were obtained in the case of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [27]. This result indicates that the intramolecular reaction of *ortho*-substituted hydroxy group of **1** with silacyclopropene or 1-silaallene intermediate is much faster than the intramolecular reaction of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne. In the photolysis of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)-ethyne, four reduction photoproducts were obtained, but the intramolecular photoproducts were not obtained.

3.4.3. In methylene chloride solvent in the presence of acetone

An intramolecular photoproduct **10** in addition to the same photoproducts **2**, **4**, **5** and **6** as in the case of benzene solvent were obtained in the photolysis of **1**, while site specific and regioselective acetone-addition photoproduct was obtained as the only product in the case of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [27]. This result was explained by the same reasons as in the methanol solvent.

3.4.4. In methylene chloride solvent

In the photolysis of **1**, a photoproduct **8** was characteristically obtained in benzene or methylene chloride solvent, but not formed in methanol solvent or in the presence of acetone. This results probably indicate that the unstable photoproduct **8** was easily transformed into the some products of unknown structure in the presence of nucleophile, such as methanol or acetone, like the corresponding photoproduct in the photolysis of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [26].

In conclusion, the photolysis of **1** in benzene gave five compounds **2**, **4**, **5**, **6** and **8**. The formation of novel cycloaddition photoproducts **6** and **8** can be rationalized in terms of the concerted intramolecular cycloaddition reaction between the hydroxy group in *ortho*-substituent and Si–C bond of silacyclopropene intermediate **3**. The formation of **2** or **5** can be explained in terms of the intramolecular cyclization between the hydroxy group in *ortho*-substituent and the carbon–carbon triple bond of **1** or **4**, respectively. But the photoproduct via 1-silaallene intermediate **9** was not obtained. Irradiation of **1** in methanol afforded the reduction product **7** in addition to the same photoproducts **2**, **4**, **5** and **6** as in the case of benzene solvent, but the expected methanol addition photoproducts via silacyclopropene **3** or 1-silaallene intermediate **9** were not obtained. Irradiation of **1** with acetone in methylene chloride yielded a novel cycloaddition photoproduct **10** in addition to the same photoproducts **2**, **4**, **5** and **6** as in the case of benzene solvent, but the expected acetone photoaddition products to silacyclopropene **3** or 1-silaallene intermediate **9** were not also obtained. The formation of photoproduct **10** can be rationalized in terms of the concerted intramolecular cycloaddition of a hydroxy group in *ortho*-substituent to Si=C bond of 1-silaallene intermediate **9** formed.

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