

Photoreactions of 1-*o*-substituted-aminophenyl-2-(pentamethyldisilanyl)ethynes

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Abstract

Photolysis of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a** in benzene provides a novel intramolecular cycloaddition product **4** via 1-sila-1,2-propadiene intermediate **3**. Photolysis of 1-*o*-amino-, allylamino-, or methoxycarbonylmethylaminophenyl-2-(pentamethyldisilanyl)ethynes **2b**, **2c**, or **2d** in benzene only provides the reduction product **8**. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the first report on the photolysis of (pentamethyldisilanyl)phenylacetylene in forming 1-silacyclopropene and 1-sila-1,2-propadiene intermediates by Ishikawa et al. [1] and Sakurai et al. [2] in 1977, the synthesis and reactions of 1-silacyclopropene [3–11] and 1-sila-1,2-propadiene [12–19] as useful reaction intermediates for the preparation of silicon-containing ring compounds have been extensively investigated. The reaction of silacyclopropenes with unsaturated functional groups such as C=O, C=C, C≡C or C=N bonds also give five-membered cyclic organosilicon products [20]. We have recently disclosed our investigations related to silacyclopropene intermediates, such as the photoinduced intramolecular reactions of 1-*o*-alkoxyphenyl-2-(pentamethyldisilanyl)ethynes [21–25], 1-*o*-alkoxymethyl-phenyl-2-(pentamethyldisilanyl)ethynes [26], and 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [27,28] affording novel intramolecular photoproducts. In connection with our research program, we were interested in the generation of 1-silacyclopropene and 1-sila-1,2-propadiene intermediates through the photolysis of 1-*o*-substituted-phenyl-2-(pentamethyldisilanyl)ethynes. In this article, we would like to report the photoreaction of 1-*o*-substituted-aminophenyl-2-(pentamethyldisilanyl)ethynes **2a–d** since novel photoproducts from the intramolecular reaction of *ortho*-substituted amino group with the 1-silacyclopropene or 1-sila-1,2-propadiene intermediate

are expected and we describe, in this paper, a detailed photochemical study of 1-*o*-substituted-aminophenyl-2-(pentamethyldisilanyl)ethynes.

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. ¹H and ¹³C NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent CDCl₃. UV absorption spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC-MS by the electron impact (EI) method. FT-IR spectra were recorded on a Bomem MB-100 spectrometer in KBr pellets and NaCl cell. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector. Lichrosorb SI-60 column was used for preparative analyses. Thin layer chromatography (TLC) was performed on Sigma-Aldrich pre-coated silica gel F₂₅₄ aluminum foils. Purification of the reaction products was carried out by flash column chromatography using a glass column dry packed with silica gel (230–400 mesh ASTM). Benzene was distilled from CaH₂ before use. Et₃N was distilled from CaH₂ and stored over KOH pellets. Solvents of reagent grade for chromatography

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were used without further purification. Spectroscopic grade solvents were used for HPLC and UV absorption spectra.

2.2. Synthesis of *o*-acetyl-amino-iodobenzene **1a**

A solution of 2-iodoaniline (1 g, 4.56 mmol) in *N,N*-dimethylformamide (15 ml) was added to a solution of NaH (0.12 g, 5.01 mmol) in DMF (10 ml) at room temperature under nitrogen atmosphere. Acetyl chloride (0.48 ml, 6.84 mmol) was added dropwise to the resulting solution and the mixture was stirred at 40 °C for 2 h. Water (30 ml) was added to the solution and was extracted with ethyl acetate (3 × 20 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 **1a** (1.1 g, 93% yield) as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 2.26 (3H, s), 6.87 (1H, t, *J* = 7.5 Hz), 7.36 (1H, td, *J* = 7.8, 1.2 Hz), 7.43 (1H, s), 7.80 (1H, d, *J* = 7.9 Hz), 8.22 (1H, d, *J* = 7.7 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 25.2, 122.5, 126.3, 126.4, 129.7, 138.6, 139.2, 168.6; UV (CH₂Cl₂) λ_{max} 245 nm; FT-IR (NaCl) 3272.2, 3030.8, 1661.5, 1532.5, 1294.9 cm⁻¹; MS (70 eV), *m/z* 261 (M⁺); HRMS (M⁺) calculated for C₈H₈INO 260.9651, found 260.9641.

2.3. Synthesis of *o*-allyl-amino-iodobenzene **1c**

This compound was prepared according to the procedure described for the preparation of **1a**, except allyl chloride (0.56 ml, 6.84 mmol) was used. Chromatography (*n*-hexane/ethyl acetate, 80:1, v/v) provided 1.05 g (89% yield) of **1c** as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 3.86 (2H, d, *J* = 4.9 Hz), 4.37 (1H, s), 5.23 (1H, dd, *J* = 10.3, 1.2 Hz), 5.33 (1H, dd, *J* = 18.4, 1.5 Hz), 6.00 (1H, m), 6.48 (1H, td, *J* = 7.8, 1.0 Hz), 6.59 (1H, dd, *J* = 7.8, 1.0 Hz), 7.23 (1H, td, *J* = 7.8, 1.0 Hz), 7.69 (1H, dd, *J* = 7.8, 1.0 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 46.9, 85.8, 111.3, 116.9, 119.2, 129.8, 135.0, 139.4, 147.4; UV (CH₂Cl₂) λ_{max} 303, 251 nm; FT-IR (NaCl) 3396.1, 2980.3, 1590.3, 1505.4 cm⁻¹; MS (70 eV), *m/z* 259 (M⁺); HRMS (M⁺) calculated for C₉H₁₀IN 258.9858, found 258.9898.

2.4. Synthesis of *o*-methoxycarbonylmethoxyamino-iodobenzene **1d**

This compound was prepared according to the procedure described for the preparation of **1a**, except methyl bromoacetate (0.65 ml, 6.84 mmol) was used. Chromatography (*n*-hexane/ethyl acetate, 10:1, v/v) provided 1.1 g (83% yield) of **1d** as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 3.83 (3H, s), 3.98 (2H, s), 4.85 (1H, s), 6.46 (1H, dd, *J* = 8.1, 1.3 Hz), 6.52 (1H, td, *J* = 7.6, 1.3 Hz), 7.23 (1H, td, *J* = 8.1, 1.4 Hz), 7.71 (1H, dd, *J* = 7.8, 1.4 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 46.3, 52.8, 85.8, 110.9, 119.9, 129.8, 139.6, 146.6, 171.3; UV (CH₂Cl₂) λ_{max} 299,

247 nm; FT-IR (NaCl) 3379.0, 2956.9, 1736.5, 1590.8, 1198.0, 1169.9 cm⁻¹; MS (70 eV), *m/z* 291 (M⁺); HRMS (M⁺) calculated for C₉H₁₀INO₂ 290.9756, found 290.9728.

2.5. Synthesis of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a**

To a deaerated solution of *o*-acetyl-amino-iodobenzene **1a** (0.5 g, 1.92 mmol), bis(triphenylphosphine)palladium dichloride (15 mg, 0.02 mmol) and copper(I) iodide (3.8 mg, 0.02 mmol) in anhydrous triethylamine (10 ml) were added dropwise pentamethyldisilanyl ethyne (0.4 ml, 2.3 mmol) at room temperature. The reaction mixture was heated at 45 °C for 2.5 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 H₂O (10 ml), brine (10 ml), and dried (MgSO₄), 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 **2a** (0.45 g, 81% yield) as a colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 0.20 (9H, s), 0.34 (6H, s), 2.22 (3H, s), 7.03 (1H, t, *J* = 7.5 Hz), 7.33 (1H, td, *J* = 7.9, 1.4 Hz), 7.42 (1H, dd, *J* = 7.8, 1.3 Hz), 8.0 (1H, s), 8.41 (1H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -2.58, -2.12, 25.2, 101.8, 102.6, 112.3, 119.3, 123.5, 130.2, 132.0, 139.7, 168.5; UV (CH₂Cl₂) λ_{max} 309, 300, 273, 264, 238 nm; FT-IR (NaCl) 3397.1, 2959.1, 2140.1, 1706.2, 1518.6, 848 cm⁻¹; MS (70 eV), *m/z* 289 (M⁺); HRMS (M⁺) calculated for C₁₅H₂₃NOSi₂ 289.1318, found 289.1365.

2.6. Synthesis of 1-*o*-aminophenyl-2-(pentamethyldisilanyl)ethyne **2b**

This reaction was carried out according to the same procedure described for the preparation of **2a**, except 2-iodoaniline **1b** (0.5 g, 2.28 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 30:1, v/v) to afford colorless oil of **2b** (0.46 g, 82% yield); ¹H NMR (CDCl₃, 300 MHz) δ_H 0.20 (9H, s), 0.32 (6H, s), 4.26 (2H, s), 6.69 (2H, td, *J* = 8.0, 0.8 Hz), 7.14 (1H, td, *J* = 7.7, 1.5 Hz), 7.32 (1H, dd, *J* = 7.7, 1.5 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C -2.36, -2.05, 99.1, 104.2, 108.6, 114.6, 118.1, 130.2, 132.7, 148.6; UV (CH₂Cl₂) λ_{max} 324, 265, 258, 234 nm; FT-IR (NaCl) 3474.8, 3376.5, 2953.0, 2140.8, 1613.9, 1489.8, 834.4 cm⁻¹; MS (70 eV), *m/z* 247 (M⁺); HRMS (M⁺) calculated for C₁₃H₂₁NSi₂ 247.1213, found 247.1204.

2.7. Synthesis of 1-*o*-allylaminophenyl-2-(pentamethyldisilanyl)ethyne **2c**

This reaction was carried out according to the same procedure described for the preparation of **2a**, except *o*-allyl-amino-iodobenzene **1c** (0.5 g, 1.93 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl

acetate, 250:1, v/v) to afford colorless oil of **2c** (0.5 g, 90% yield); ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.20 (9H, s), 0.32 (6H, s), 3.86 (2H, d, $J = 5.1$ Hz), 4.83 (1H, s), 5.22 (1H, dd, $J = 10.3, 1.2$ Hz), 5.34 (1H, dd, $J = 17.2, 1.3$ Hz), 6.0 (1H, m), 6.62 (2H, m), 7.20 (1H, td, $J = 7.8, 1.2$ Hz), 7.33 (1H, dd, $J = 7.0, 1.1$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -2.32, -2.07, 46.4, 99.6, 104.4, 108.3, 110.1, 116.5, 116.7, 130.4, 132.6, 135.3, 149.5 UV (CH_2Cl_2) λ_{max} 337, 263, 238 nm; FT-IR (NaCl) 3403.3, 2953.3, 2138.0, 1601.2, 1509.2, 835.6 cm^{-1} ; MS (70 eV), m/z 287 (M^+); HRMS (M^+) calculated for $\text{C}_{16}\text{H}_{25}\text{NSi}_2$ 287.1526, found 287.1525.

2.8. Synthesis of 1-*o*-methoxycarbonylmethoxyamino-2-(pentamethyldisilanyl)ethyne **2d**

This reaction was carried out according to the same procedure described for the preparation of **2a**, except *o*-methoxycarbonylmethoxyamino-iodobenzene **1d** (0.5 g, 1.72 mmol) was used. The crude product was chromatographed (*n*-hexane/ethyl acetate, 10:1, v/v) to afford colorless oil of **2d** (0.39 g, 71% yield); ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.20 (9H, s), 0.35 (6H, s), 3.81 (3H, s), 3.97 (2H, s), 5.27 (1H, s), 6.46 (1H, d, $J = 8.2$ Hz), 6.67 (1H, t, $J = 7.5$ Hz), 7.20 (1H, td, $J = 7.8, 1.4$ Hz), 7.34 (1H, dd, $J = 7.6, 1.4$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -2.38, -2.07, 45.7, 52.7, 100.1, 103.8, 108.9, 109.8, 117.4, 130.4, 132.7, 148.4, 171.2; UV (CH_2Cl_2) λ_{max} 332, 268, 261, 237 nm; FT-IR (NaCl) 3389.1, 2952.9, 2140.2, 1751.2, 1512.0, 1246.1, 835.4 cm^{-1} MS (70 eV), m/z 319 (M^+); HRMS (M^+) calculated for $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{Si}_2$ 319.1424, found 319.1424.

2.9. Irradiation of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a** in benzene

Deaerated solution (5×10^{-4} M) of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a** (144 mg) in benzene (1 l) was 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 photoadducts **4** and **6** were isolated in 88.1 mg (61% yield) and 3.4 mg (3% 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. **4**: colorless oil; UV (CH_2Cl_2) λ_{max} 326, 261, 229 nm; FT-IR (NaCl) 2950.2, 1656.5, 1605.8, 1260.9, 804.8 cm^{-1} ; MS (70 eV), m/z 289 (M^+) HRMS (M^+) calculated for $\text{C}_{15}\text{H}_{23}\text{NOSi}_2$ 289.1318, found 289.1301. **6**: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.30 (9H, s), 2.21 (3H, s), 7.02 (1H, td, $J = 7.5, 0.9$ Hz), 7.33 (1H, td, $J = 7.9, 1.5$ Hz), 7.41 (1H, dd, $J = 7.7, 1.5$ Hz), 7.99 (1H, s), 8.39 (1H, d, $J = 8.3$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 0.35, 25.2, 100.7, 102.7, 112.2, 119.3, 123.5, 130.4, 131.8, 139.9, 168.5 UV (CH_2Cl_2) λ_{max} 308, 299,

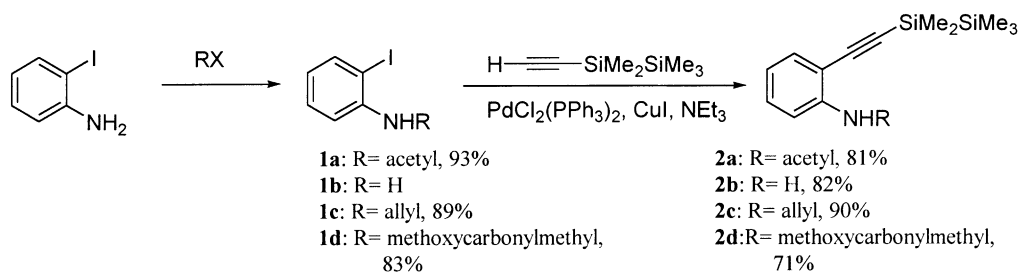
272, 261, 237 nm; FT-IR (NaCl) 3393.1, 2959.2, 2151.1, 1706.0, 1580.1, 863.1 cm^{-1} ; MS (70 eV), m/z 231 (M^+); HRMS (M^+) calculated for $\text{C}_{13}\text{H}_{17}\text{NOSi}$ 231.1079, found 231.1078.

2.10. Irradiation of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a** with acetone

A solution (5×10^{-4} M) of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a** (144 mg) and acetone (2 ml) 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 photoadducts **4**, **6**, and **7** were isolated in 60.7 mg (42% yield), 15 mg (13% yield), and 22.5 mg (13% 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. **7**: ^1H NMR (CDCl_3 , 300 MHz) δ_{H} -0.16 (9H, s), 0.37 (6H, s), 1.25 (3H, s), 1.38 (3H, s), 2.09 (3H, s), 6.99 (1H, dd, $J = 7.6, 1.5$ Hz), 7.07 (1H, t, $J = 7.4$ Hz), 7.17 (1H, s), 7.31 (1H, td, $J = 7.6, 1.5$ Hz), 8.25 (1H, d, $J = 8.2$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} 0.07, 2.35, 2.96, 25.1, 29.5, 30.1, 89.0, 120.9, 123.6, 128.8, 129.1, 130.8, 134.9, 142.6, 167.7, 172.9; UV (CH_2Cl_2) λ_{max} 379, 260, 237 nm; FT-IR (NaCl) 3308.5, 3093.2, 2974.7, 1638.2, 1572.7, 1518.9, 1224.6, 747.8 cm^{-1} ; MS (70 eV), m/z 347 (M^+); HRMS (M^+) calculated for $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{Si}_2$ 347.1737, found 347.1740.

2.11. Irradiation of 1-*o*-amino-, allylamino-, or methoxycarbonylmethylaminophenyl-2-(pentamethyldisilanyl)ethynes **2b**, **2c**, or **2d** in benzene

Deaerated solution (5×10^{-4} M) of **2b**, **2c**, or **2d** (123, 143, or 159 mg, respectively) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254, 300, or 254 nm lamps, respectively. After irradiation for 2.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadduct **8** was isolated in 24.9 mg (20% yield), 27.4 mg (22% yield), or 37.3 mg (30% yield), respectively, by column chromatography with *n*-hexane/ethyl acetate (20/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (10/1, v/v) as an eluent. **8**: colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 0.13 (9H, s), 0.25 (6H, s), 3.80 (2H, s), 6.41 (1H, d, $J = 18.9$ Hz), 6.70 (1H, dd, $J = 8.0, 0.9$ Hz), 6.80 (1H, td, $J = 7.6, 0.6$ Hz), 6.93 (1H, d, $J = 18.9$ Hz), 7.10 (1H, td, $J = 7.6, 1.5$ Hz), 7.34 (1H, dd, $J = 7.6, 1.3$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.72, -1.80, 116.6, 119.4, 125.9, 127.6, 129.0, 131.1, 139.4, 143.7; UV (CH_2Cl_2) λ_{max} 323, 267 nm; FT-IR (NaCl) 3470.2, 3382.4, 3066.4, 2950.4, 1620.1, 1487.8, 836.0 cm^{-1} ; MS (70 eV), m/z 249 (M^+); HRMS (M^+) calculated for $\text{C}_{13}\text{H}_{23}\text{NSi}_2$ 249.1369, found 249.1361.



Scheme 1.

3. Results and discussion

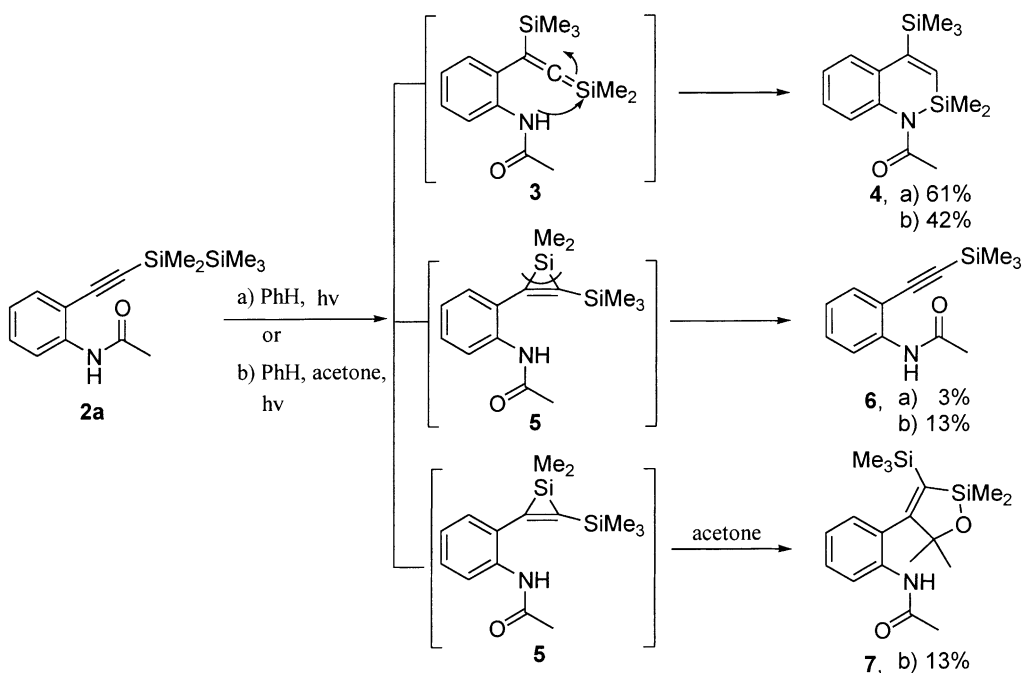
The starting 1-*o*-substituted-aminophenyl-2-(pentamethyldisilanyl)ethynes **2a–d** were prepared by the reaction of *o*-substituted-amino-iodobenzenes **1a–d** with pentamethyldisilanyl ethyne in the presence of bis(triphenylphosphine) palladium dichloride and copper(I) iodide in triethylamine (Scheme 1).

Irradiation of **2a** in deaerated benzene with 254 nm UV light provided a novel intramolecular cycloaddition product **4** (61% yield) along with **6** (3% yield) as indicated in Scheme 2. The formation of photoproduct **4** can be rationalized in terms of the initial formation of 1-sila-1,2-propadiene intermediate **3** upon irradiation followed by the intramolecular cycloaddition of an amino group in *ortho* substituent to Si=C bond of 1-sila-1,2-propadiene formed. Subsequent liberation of dimethylsilylene species from the silacyclopropene intermediate **5** resulted in the formation of **6**. To trap the reaction intermediates **3** or **5**, we investigated the photolysis of **2a**

in the presence of a trapping agent, acetone, to obtain the same photoproducts **4** (42% yield) and **6** (13% yield) and also acetone-addition photoproduct **7** (13% yield).

Based on these observations, a plausible photoreaction mechanism is proposed as illustrated in Scheme 2. The photolysis of **2a** has been found to proceed simultaneously by two different routes leading to the formation of 1-sila-1,2-propadiene **3** and 1-silacyclopropene intermediate **5**. Subsequent intramolecular cyclization of **3** resulted in the production of **4**. The photoproduct **6** was formed from the liberation of dimethylsilylene in **5** and compound **7** was formed from the photoreaction of 1-silacyclopropene intermediate **5** with acetone.

The structures of these photoproducts **4**, **6**, and **7** were unambiguously supported by various spectroscopic methods such as ^1H NMR, ^{13}C NMR, 2D NMR (^1H - ^1H , ^1H - ^{13}C COSY, HMBC, NOESY), UV, FT-IR, and high resolution mass spectrometry. The ^1H - ^1H and ^1H - ^{13}C correlation spectroscopy (COSY) spectra of **4** were carried out to



Scheme 2.

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

Position	δ_{C} (ppm)	M^b	δ_{H} (ppm)	I^c	M^d	$J_{\text{H-H}}$ (Hz)	HMBC ^e
1	123.4	d	7.47	1H	d	7.4 ($J_{\text{H-2H}}$)	H3
2	127.5	d	7.14	1H	t	7.8 ($J_{\text{2H-1H,3H}}$)	H4
3	130.8	d	7.26	1H	t	7.8 ($J_{\text{3H-2H,4H}}$)	H1
4	125.9	d	7.12	1H	d	7.8 ($J_{\text{4H-3H}}$)	H2
5	138.8	s					H1, H3
6	121.7	s					H2, H4, H8
7	155.7	s					H1, H8
8	95.1	d	5.08	1H	s		H11
9	158.8	s					H10
10	21.4	q	2.16	3H	s		
11	-3.08	q	0.21	6H	s		H8
12	-1.70	q	0.08	9H	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.

identify the protons directly attached to the individual carbons. According to the correlated peaks in **4**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Table 1. In order to determine the location of the quaternary carbons, the HMBC spectrum of **4** was taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(1), C(8), C(12) and the quaternary carbon C(7) in **4** showed the connectivity of the carbon C(7) to the benzene ring, trimethylsilyl, and the carbon C(8). In the same manner, the connectivity of the carbon C(8) to the carbon C(7) and the dimethylsilyl group in **4** was established. The three-dimensional structure of **4** was determined by a nuclear overhauser and exchange spectroscopy (NOESY). In particular, the presence of the cross-peaks between a proton of C(1) and the protons of C(12) showed the close proximity of a proton of C(1) to the protons of C(12) indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **4** was unambiguously established as shown in Fig. 1.

The ^{13}C NMR spectrum of photoadduct **7** shows the characteristic dimethyl substituted sp^3 carbons at δ 89.0, supporting the 1-oxa-2-silacyclopent-3-ene moiety. The location of the dimethylmethylene group on the five-membered ring was confirmed by comparison with the reported results [1,2,14,23,29,30]. The formation of photoproduct **7** is understood by assuming the intermediacy of silacyclopropene **5**. Insertion of acetone into the silicon-carbon bond in **5** generates a five-membered ring compound **7**.

Irradiation of **2b-d** in deaerated benzene with 254 or 300 nm UV light only provided the reduction product **8** (20–30% yield) along with several unknown products as shown in Scheme 3. However, the photoinduced intramolecular cycloaddition products via 1-silacyclopropene or 1-sila-1,2-propadiene intermediate were not detected.

The structure of the photoproduct **8** was unambiguously supported by various spectroscopic methods, such as ^1H NMR, ^{13}C NMR, UV, FT-IR, and high resolution mass spectrometry. The vinyl protons in the ^1H NMR spectrum

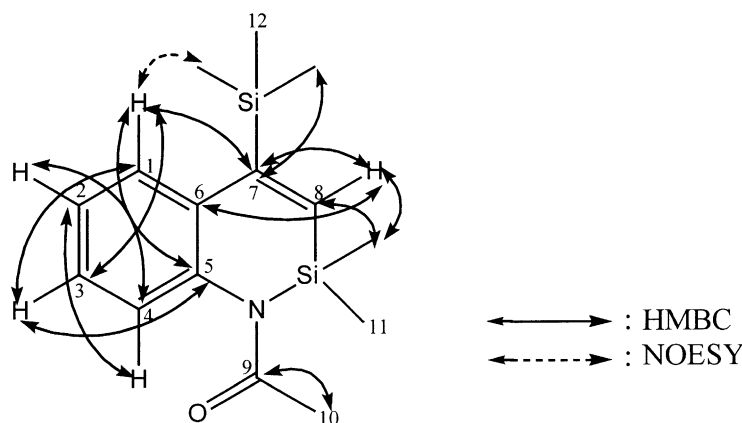
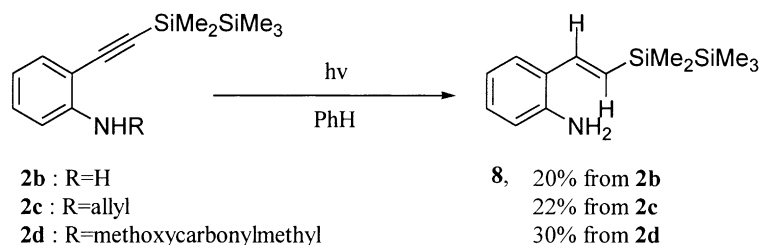


Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **4**.



Scheme 3.

of **8** showed *trans* coupling constant ($J = 18.9$ Hz) at 6.41 and 6.93 ppm and FT-IR spectrum of **8** showed the typical $-\text{NH}_2$ absorption at 3470.2 and 3382.4 cm^{-1} .

In conclusion, the photoinduced intramolecular cycloaddition reaction of 1-*o*-acetylaminophenyl-2-(pentamethyldisilanyl)ethyne **2a** afforded the novel photoproduct **4** via 1-sila-1,2-propadiene intermediate **3**. The formation of the photoproduct **7** was explained by the photoaddition reaction of the silacyclopentene intermediate **5** with acetone. Irradiation of **2b–d** in deaerated benzene only provided the reduction product **8**, but the expected photoinduced intramolecular cycloaddition products via 1-silacyclopentene or 1-sila-1,2-propadiene intermediate were not obtained.

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