Photochemistry of 1-(*o*-Hydroxyphenyl)-2-pentamethyldisilanylethyne : Photoreaction in a Concentrated Benzene Solution and Photoreaction with Methanol or Acetone†

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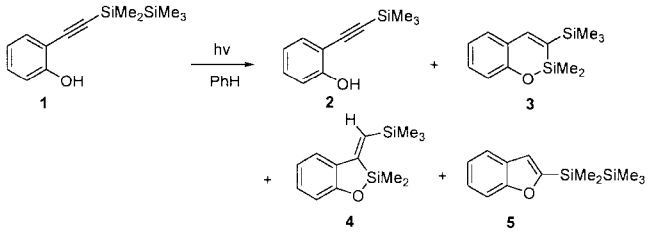
Irradiation of 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne **1** in a concentrated benzene solution has provided photodimer product **7** along with other reported photoproducts. Irradiation of **1** in methanol yields 1-(*o*-hydroxyphenyl)-2-trimethylsilylethyne **2** and its reduction product **13**. *via* silacyclopropene intermediate **10**. and the reduction product **8** and two methanol addition products, **11** and **12**, *via* *o*-hydroxyphenylethyne. Photolysis of **1** with acetone in deaerated methylene chloride affords site specific and regioselective 1 : 1 adduct **16** *via* silacyclopropene intermediate **10**.

Keywords : 1-(*o*-Hydroxyphenyl)-2-pentamethyldisilanylethyne, Silacyclopropene, Photoreaction.

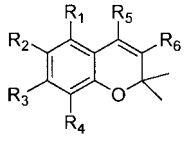
Introduction

The photolysis of alkynyl-substituted disilanes is a convenient route to the highly strained silacyclopropenes[1-6] and these silacyclopropenes react readily with methanol or acetone in the presence of methanol or acetone as trapping agents.[7-9] In the course of my research in connection with these silacyclopropene intermediates.[10-17] I very recently reported that the photolysis of **1** gave the novel photoproducts **2**, **3**, and **4** *via* silacyclopropene intermediate and the cyclization product **5**.[18]



1 2 3 4 5

Among these photoproducts, **3** is an especially attractive molecule because this compound has a 2-sila-2,2-dimethyl-2H-benzopyrane moiety, the silicon analog of the 2,2-dimethylbenzopyrane template, **6**, a structural motif found in some natural products.[19]



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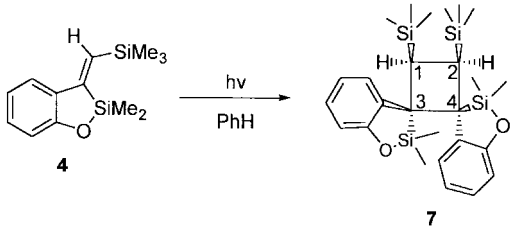
In the present study, the photoreaction of **1** in a concentrated benzene solution to obtain the improved chemical yield of **3** and the photoreaction of **1** in the presence of trapping agents, such as methanol or acetone to investigate the reaction intermediate in this photoreaction are reported.

Results and Discussion

The starting 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne **1** was prepared by the reaction of *o*-iodophenol with pentamethyldisilanylethyne in the presence of *bis*(triphenylphosphine)palladium dichloride and copper(I) iodide in triethylamine, as reported previously.[18]

Photoreaction of 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne 1 in a concentrated benzene solution. Irradiation of **1** in the concentrated benzene solution (3×10^{-3} M solution) to improve the chemical yield of **3** afforded the photodimer product **7** (13% yield) along with the reported photoproducts **2**, **3**, **4**, and **5** in 18, 25, 10, and 13% yields, respectively, but the chemical yield of **3** did not improved in this photoreaction (yield of **3**, 35%[18] → 25%).



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To learn more about the formation of **7**, the photolysis of **3**, **4** or **5**, individually under the same conditions as the photolysis of **1** was carried out, with the compound **7** being formed from the photolysis of **4** and not from the photolysis of **3** or **5**. Compound **3** or **5** was inert in this photoreaction condition. The structure of this photodimer **7** was determined by various physical methods, such as ^{1}H NMR, ^{13}C NMR, 2D NMR (^{1}H-^{1}H COSY and NOESY), UV, FT-IR, and high resolution mass spectrometry. The high resolution mass spectrum of the photodimer **7** showed the parent peak at

†This paper is dedicated to Prof. Sang Chul Shim on the occasion of his 65th birthday.

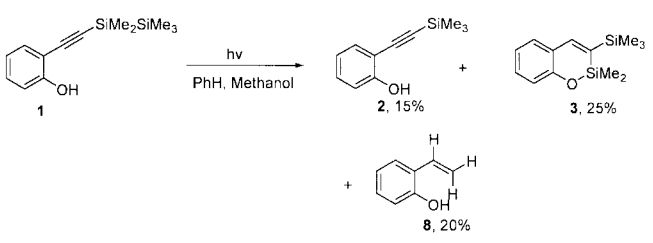
496.2123, corresponding to the calculated molecular weight for **7** (496.2105), indicating that **7** was formed by the dimerization of **4**. The ^{1}H NMR spectrum of **7** showed six singlets in the ratio of 1/3/1/3/1/1, as expected in the structure of **7**, at δ −0.11, 0.24,, 0.32, 0.41, 0.46, and 0.54 indicating that the chemical environment of the trimethylsilyl group is similar but that of the dimethylsilylene group is different. And, the analysis of the ^{1}H NMR spectrum revealed the presence of two *cis* hydrogens (H-1 and H-2 in **7**), characterized by two doublet signals at δ 1.48 (J = 13.2 Hz) and δ 2.28 (J = 13.2 Hz).

The presence of the cross-peaks due to the vicinal coupling and the close proximity between protons of C(1) and C(2) in the ^{1}H-^{1}H correlation spectroscopy (COSY) and nuclear overhauser and exchange spectroscopy (NOESY) spectra all indicated the *cis* configulation between the two protons (H-1 and H-2).

The ^{13}C NMR spectrum of **7** displayed signals for 21 different carbon atoms ; the signal at 27.6 ppm corresponds to the carbon 1 or 2 and twelve signals between δ 120 and 170 correspond to the carbon atoms of two benzene rings which are in the different chemical environments. These results are consistent with the unsymmetrical structure proposed for compound **7**.

Photoreaction of 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne 1 with methanol. The photolysis of (pentamethyldisilanyl)phenylacetylene affords two reaction intermediates, silacyclopropene and 1-sila-1,2-propadiene.[7,12] To investigate whether or not the photolysis of **1** gives two reaction intermediates like (pentamethyldisilanyl)phenylacetylene, the photolysis of **1** in various solvent systems was carried out. In this study, methanol was used to trap the highly reactive reaction intermediates, and the reaction intermediate was confirmed from the existence of the methanol addition photoproducts .

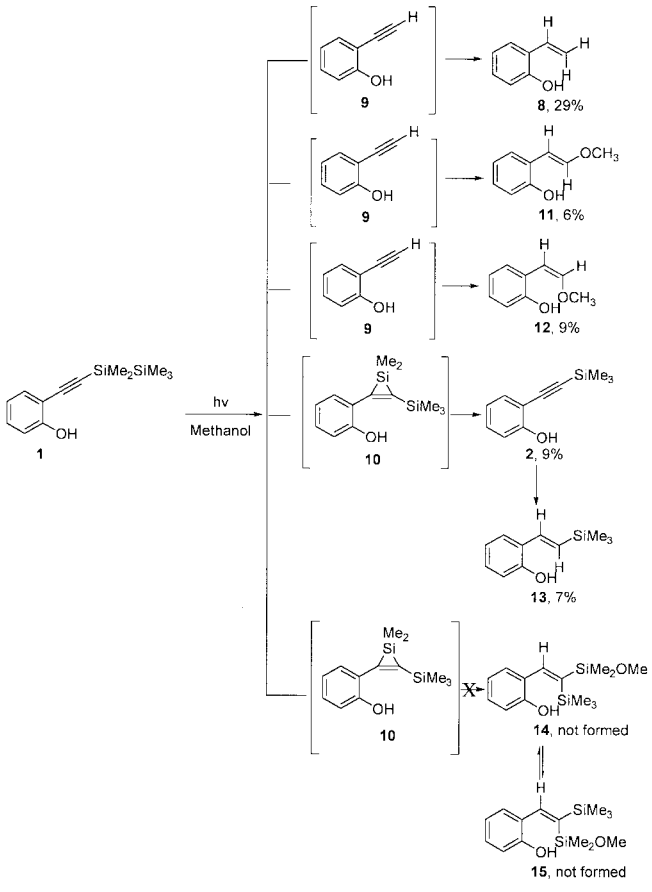
Irradiation of **1** (124 mg, 0.5 mmol) in deaerated benzene (1 L) in the presence of a trapping agent, methanol (1.2 mL, 30 mmol) with 300 nm UV light to determine the reaction intermediate afforded the reduction product **8** 12 mg (0.1 mmol, 20%) along with the reported photoproducts **2** 14.3 mg (0.07 mmol, 15%) and **3** 31 mg (0.1 mmol, 25%), but the expected methanol addition photoproducts like **14** or **15** *via* silacyclopropene intermediate **10** were not obtained. In the case of methylene chloride as solvent in the above reaction condition, only compound **8** was obtained, in 45% yield, along with some other products of unknown structure, but the expected methanol addition photoproducts also were not obtained.



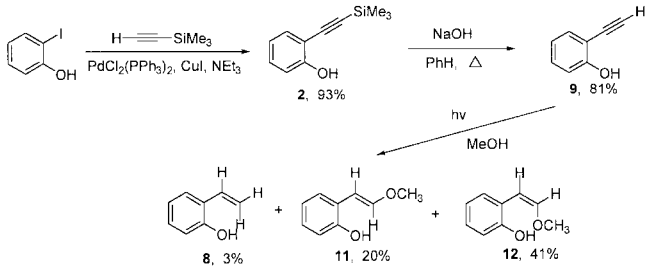
When a solution of **1** in methanol was irradiated with 300 nm UV light, five products, **2**, **8**, **11**, **12**, and **13** were obtained in 9, 29, 6, 9, and 7% yields, respectively, but the expected compounds **14** or **15** formed from the photoaddition reaction of the reaction intermediate, silacyclopropene, and methanol were not obtained. The formation of photoproducts **8**, **11**, and **12** can be rationalized from the initial formation of o-hydroxyphenylethyne **9** upon irradiation followed by the reduction or methanol addition reaction. Liberation of dimethylsilylene species from the silacyclopropene intermediate **10** upon irradiation resulted in the formation of **2**, and then further reduction afforded **13** (Scheme 1).

To establish whether or not compound **9** was formed in the photolysis of **1** and compounds **8**, **11**, and **12** were formed from the photolysis of **9**, compound **9** was synthesized (Scheme 2) and irradiated with 300 nm UV lamp in methanol under the identical reaction condition as the photolysis of **1** to obtain, as expected, **8**, **11**, and **12** in 3, 20, and 41% yields, respectively, along with some other products of unknown structure.

The structures of these photoproducts, **2**, **8**, **11**, **12**, and **13**, were determined by various physical methods, such as ^{1}H NMR, ^{13}C NMR, UV, FT-IR, and high resolution mass spectrometry. The molecular ion peaks (M^-) of **11** and **12** indicate that the photoproducts are formed by the addition of one methanol molecule to **9**. The structure of photoisomer **11** could be distinguished from that of **12** on the basis of the ^{1}H NMR spectra of the isomer pair. The –OH peaks in ^{1}H NMR



Scheme 1



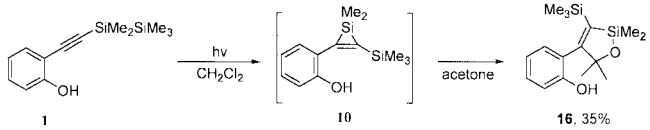
Scheme 2

spectra of **11** and **12**, appearing at δ 5.29 and 7.60, respectively, indicate intramolecular hydrogen bonding between the hydroxy group and the methoxy group in **12**, but not for **11**. The vinyl protons in **11** show *trans* coupling constant (J = 12.9 Hz), whereas those in **12** show *cis* coupling constant (J = 7.1 Hz). In the case of **13**, the vinyl protons in the ^{1}H NMR spectrum of **13** also show *trans* coupling constant (J = 19.3 Hz). Compound **8** gives an ^{1}H NMR spectrum typical of a compound with three hydrogens substituted on a double bond at δ 5.36, 5.76, and 6.98. Each proton has a chemical shift and a coupling constant different from those of each of the other protons.

Indeed, research has established that the photochemical reactions of phenylethynylpentamethyldisilane in the presence of methanol were reported to give mainly photoaddition products like **14** or **15** through the silacyclopropene intermediates.[7-9,12-14,16,17] But, Shim *et al.*[20] found that the photolysis of 1-(*p*-nitrophenyl)-4-pentamethyldisilanyl-1,3-butadiyne in methanol gives 1-(*p*-nitrophenyl)-1,3-butadiyne through C-Si bond cleavage from transient (zwitterion species), which formed from the intramolecular electron transfer from disilanyl to the nitro group. In the case of the photolysis of **1** in methanol, the formation of the photoproducts **8**, **11**, and **12** can also be explained by the reduction or methanol addition reaction of the reaction intermediate **9**, which was probably formed through C-Si bond cleavage in the photoexcited state of **1**. The formation of the photoproducts **2** and **13** is explained *via* the silacyclopropene intermediate **10**. From these results, a plausible photoreaction mechanism as shown in Scheme 1, is proposed. The photolysis of **1** has been found to proceed simultaneously by two different routes, one of which, leads to the production of **9**. The other comprises the formation of the silacyclopropene intermediate **10**. Compound **9** affords the reduction product **8** and two methanol addition products **11** and **12**. The photoproduct **2** formed from the liberation of dimethylsilylene in **10** gives the reduction product **13**.

In conclusion, the photolysis of **1** afforded the two reaction intermediates **9** and **10** and the various photoproducts **2**, **8**, and **13**, and the methanol addition photoproducts **11** and **12** formed from this reaction intermediate **9** were obtained, but the other expected methanol addition photoproducts **14** and **15** formed from the reaction of silacyclopropene intermediate and methanol were not obtained in the methanol solvent system. The other expected 1-sila-1,2-propadiene intermediate was also not formed in this photolysis.

Photoreaction of 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne 1 with Acetone. To trap the reaction intermediates formed from the photolysis of **1**, I used acetone as a trapping agent in the various solvent conditions. Irradiation of **1** with acetone in deaerated benzene, initially, yielded **2**, **3**, and **5** in 25, 15, and 10% yields, respectively, but the expected acetone photoaddition product was not obtained. When a methylene chloride solution of **1** in the presence of acetone was irradiated instead of benzene solution, site specific and regioselective 1 : 1 photoadduct **16** was formed as the only product, in 35% yield, along with other photoproducts of unknown structure.



The structure of this photoproduct **16** was determined by various physical methods, such as ^{1}H NMR, ^{13}C NMR, UV, FT-IR, and high resolution mass spectrometry. Mass spectra of **16** show the molecular ion (M^+) peaks, indicating that the photoproduct is formed by the addition of one acetone molecule to **1**. The ^{13}C NMR spectrum of photoadduct **16** 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.[7-9,12,16,17] The formation of photoproduct **16** is best understood by assuming the intermediacy of silacyclopropene **10**. Insertion of acetone into the silicon-carbon bond in **10** generates a five membered ring compound **16**.

In conclusion, the photolysis of **1** afforded the reaction intermediate, silacyclopropene, which is trapped with acetone to give the photoaddition product **16** in the methylene chloride solvent system not in the benzene solvent system. The other expected reaction intermediate, 1-sila-1,2-propadiene, of this photoreaction was not detected.

Experimental Section

General methods. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 or Bruker AC-200 spectrometer 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 a 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. A Lichrosorb SI-60 column was used for preparative analyses. Methylene chloride was dried with P_2O_5 followed by fractional distillation before

use. Acetone was dried with K_2CO_3 followed by fractional distillation immediately before use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia Company Inc., Fairfield. Ohio) were used for HPLC and UV absorption spectra. Photolysis was performed in a Rayonet photochemical reactor, model RPR-208. equipped with RUL 300 nm lamps.

Irradiation of 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne 1 in a concentrated benzene solution. A solution (3×10^{-3} M) of **1** (744 mg, 3 mmol) in benzene (1 L) was deaerated by nitrogen purging for 1 h and irradiated. After irradiation for 2.5 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoadducts **2**. **3**. **4**, **5**. and **7** were isolated in 103 mg (0.5 mmol, 18%). 186 mg (0.7 mmol. 25%), 74 mg (0.3 mmol, 10%), 97 mg (0.4 mmol, 13%), and 198 mg (0.4 mmol. 13%), respectively, by column chromatography with *n*-hexane/ethyl acetate (500/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (500/1. v/v) as an eluent.

7: ^{1}H NMR ($CDCl_3$, 600 MHz) δ-0.11 (3H, s), 0.24 (9H. s). 0.32 (3H, s). 0.41 (9H, s). 0.46 (3H, s). 0.54 (3H, s). 1.48 (1H, d. J = 13.2 Hz), 2.28 (1H, d, J = 13.2 Hz), 6.76 (1H, td. J = 7.8, 1.1 Hz). 6.77 (1H. dd, J = 7.4. 1.3 Hz), 6.85 (1H, dd. J = 7.8, 1.3 Hz), 6.90 (1H, td. J = 7.8, 1.1 Hz), 7.13 (1H, dd. J = 7.5, 0.8 Hz). 7.14 (1H. td. J = 7.8, 1.3 Hz). 7.20 (1H. td. J = 7.8. 1.3 Hz), 7.63 (1H. dd. J = 7.8, 0.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ-1.60, -1.53. 0.35. 0.86, 1.64, 1.96. 27.6, 101.3. 112.2. 120.3, 120.4. 120.5, 125.2, 125.7. 128.8, 129.2, 131.4, 134.9, 137.2, 155.7, 165.7: UV (CH_2Cl_2) λ_{max} 317. 282, 266 nm: FT-IR (NaCl) 3077. 2955, 1480. 1255, 836. 798 cm^{-1}; MS (70 eV) m/z 496 (M^+). HRMS (M^+) calcd for $C_{26}H_{40}O_2Si_4$ 496.2105, found 496.2123.

Irradiation of 1-(*o*-hydroxyphenyl)-2-pentamethyldisilanylethyne 1 in methanol. A solution (5×10^{-4} M) of 1-(*o*-hydoxyphenyl)-2-pentamethyl-disilanylethyne (124 mg. 0.5 mmol) in methanol (1 L) was deaerated by nitrogen purging for 1 h and irradiated. After irradiation for 1 h. the resulting photoreaction mixture was concentrated *in vacuo*. The photoadducts **2**. **8**. **11**. **12**. and **13** were isolated in 9mg (0.05 mmol. 9%). 18 mg (0.15 mmol, 29%). 5 mg (0.03 mmol, 6%), 7 mg (0.05 mmol. 9%) and 7 mg (0.04 mmol. 7%). respectively, by column chromatography with *n*-hexane/ethyl acetate (8/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (2/1. v/v) as an eluent.

8: ^{1}H NMR ($CDCl_3$, 300 MHz) δ5.17 (1H. s). 5.36 (1H. dd. J = 11.3, 1.2 Hz), 5.76 (1H, dd. J = 17.9. 1.2 Hz), 6.82 (1H, d, J = 8.1 Hz). 6.92 (1H. t, J = 7.5 Hz). 6.98 (1H. dd, J = 17.9. 11.3 Hz), 7.15 (1H. td. J = 7.5. 1.5 Hz). 7.41 (1H, dd. J = 7.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ116.2. 121.3. 127.7, 129.5, 131.9, 134.3, 139.8, 153.3: UV (CH_2Cl_2) λ_{max} 299. 247 nm: FT-IR (NaCl) 3397, 2926. 1605. 1454, 1247. 751 cm^{-1}; MS (70 eV) m/z 120 (M^+); HRMS (M^-) calcd for C_8H_8O 120.0575. found 120.0569.

11: ^{1}H NMR ($CDCl_3$, 300 MHz) δ3.73 (3H, s), 5.29 (1H. s). 5.93 (1H. d, J = 12.9 Hz). 6.79 (1H. dd, J = 8.1, 1.2 Hz). 6.88 (1H, td. J = 7.5. 1.2 Hz), 7.07 (1H. td. J = 7.5. 1.5 Hz). 7.09 (1H. d, J = 12.9 Hz). 7.21 (1H. dd. J = 7.5, 1.8 Hz); ^{13}C NMR ($CDCl_3$. 75 MHz) δ 56.8. 106.7, 117.8. 120.5. 121.9, 126.0, 131.4. 143.8, 159.7; UV (CH_2Cl_2) λ_{max} 289, 281, 257 nm: FT-IR (NaCl) 3649. 3065. 2955. 1442. 1251 cm^{-1}; MS (70 eV) m/z 150 (M^+); HRMS (M^-) calcd for $C_9H_{10}O_2$ 150.0681, found 150.0679.

12: ^{1}H NMR ($CDCl_3$, 300 MHz) δ3.87 (3H, s). 5.42 (1H. d. J = 7.1 Hz). 6.08 (1H, d. J = 7.1 Hz). 6.87 (1H, td, J = 7.4, 1.0 Hz), 6.94 (1H, d. J = 8.1 Hz). 7.13 (1H. dd, J = 7.6, 1.2 Hz). 7.18 (1H. td. J = 7.6. 1.5 Hz), 7.60 (1H, s); ^{13}C NMR ($CDCl_3$. 75 MHz) δ 61.0. 105.7. 118.1. 120.5. 121.9, 129.2, 131.3, 143.7, 154.1: UV (CH_2Cl_2) λ_{max} 255 nm: FT-IR (NaCl) 3341, 2955, 1486. 1252 cm^{-1}: MS (70 eV) m/z 150 (M^-): HRMS (M^-) calcd for $C_9H_{10}O_2$ 150.0681, found 150.0676.

13: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.24 (9H, s). 5.35 (1H. s), 6.52 (1H, d. J = 19.3 Hz), 6.83 (1H, d. J = 8.0 Hz). 6.98 (1H. t. J = 7.5 Hz), 7.19 (1H. t. J = 8.0 Hz). 7.24 (1H, d, J = 19.3 Hz). 7.51 (1H. dd. J = 7.7. 1.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -0.75, 116.4, 121.4, 126.2. 127.5. 129.4, 131.9. 138.2, 153.1: UV (CH_2Cl_2) λ_{max} 257 nm; FT-IR (NaCl) 3407. 2955. 1600. 1455, 1248, 838 cm^{-1}; MS (70 eV) m/z 192 (M^-): HRMS (M^+) calcd for $C_{11}H_{16}OSi$ 192.0970. found 192.0968.

Synthesis of 1-(*o*-hydroxyphenyl)-2-trimethylsilylethyne 2. To a deaerated solution of 2-iodophenol (0.5 g, 2.27 mmol). bis(triphenylphosphine)palladium dichloride (15 mg. 0.02 mmol) and copper(I) iodide (4 mg. 0.02 mmol) in anhydrous triethylamine (10 mL) was added dropwise trimethylacetylene (0.35 mL, 2.5 mmol) at room temperature. The reaction mixture was heated at 40 °C for 1.5h. 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 (20/1. v/v) as eluents gave **2** 0.4 g (2.1 mmol, 93%).

Synthesis of *o*-hydroxyphenylethyne 9. The reaction solution of 1-(*o*-hydroxyphenyl)-2-trimethylsilylethyne **2** (0.4 g, 2.1 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in benzene (10 mL) was stirred for 7h at reflux temperature. The reaction mixture was acidified with 2 N HCl solution, concentrated *in vacuo*. and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate solution was dried over $MgSO_4$ and evaporated *in vacuo* to give crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10 : 1, v/v) as eluents gave *o*-hydroxyphenylacetylene **9** 0.2 g (1.7 mmol, 81%).

9: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.47 (1H, s). 6.11 (1H, s), 6.89 (1H. td, J = 7.5, 0.9 Hz). 6.98 (1H, dd. J = 8.4. 0.9 Hz). 7.27 (1H. td, J = 7.8, 1.5 Hz), 7.41 (1H, dd. J = 7.8, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 78.9, 84.7, 108.8. 115.4, 120.8, 131.3. 132.7. 157.8: UV (CH_2Cl_2) λ_{max} 300, 292, 247 nm; FT-IR (NaCl) 3503. 3289. 2105, 1573, 1484. 1288 cm^{-1}; MS (70 eV) m/z 118 (M^-): HRMS (M^+) calcd for C_8H_6O 118.0419, found 118.0410.

Irradiation of 1-(*o*-hydroxyphenyl)-2-pentamethyl-

disilanylethyne 1 with acetone. A solution (5×10^{-4} M) of 1-(*o*-hydroxyphenyl)-2-pentamethyl-disilanylethyne **1** (124 mg, 0.5 mmol) and acetone (2.5 mL, 34 mmol) in methylene chloride (1 L) was deaerated by nitrogen purging for 1 h and irradiated. After irradiation for 1 hr, the resulting photoreaction mixture was concentrated *in vacuo*. The photoadduct **16** was isolated in 54 mg (0.17 mmol, 35%) by silica gel column chromatography with *n*-hexane/ethyl acetate (10/1, v/v) as an eluent. The product was purified by normal phase HPLC using *n*-hexane/ethyl acetate (4/1, v/v) as an eluent.

16: ^{1}H NMR ($CDCl_3$, 300 MHz) δ-0.14 (9H, s), 0.34 (3H, s), 0.36 (3H, s), 1.29 (3H, s), 1.39 (3H, s), 4.89 (1H, s), 6.91 (3H, m), 7.21 (1H, td, J = 7.8, 1.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.007, 2.53, 2.62, 29.6, 29.7, 89.0, 115.7, 120.2, 127.6, 129.4, 129.6, 143.1, 152.3, 171.7; UV (CH_2Cl_2) λ_{max} 282, 274 nm; FT-IR (NaCl) 3247, 2923, 1557, 1446, 1249, 864 cm^{-1}; MS (70 eV) m/z 306 (M^+); HRMS (M^-) calcd for $C_{16}H_{26}O_2Si_2$ 306.1471, found 306.1471.

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