

PHOTOCHEMISTRY OF 1-(*o*-SUBSTITUTED-PHENYL)-2-PENTAMETHYLDISILANYL ETHYNES

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(Received 2 April 1999; accepted 7 May 1999)

Abstract—Irradiation of 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne **2a** in methanol yields two 1:1 photoaddition products **3** and **4** via silacyclopropene intermediate. Photolysis of **2a** with acetone in deaerated methylene chloride yields site specific and regioselective 1:1 adducts **6** and **7** via silacyclopropene and 1-sila-1,2-propadiene intermediate, respectively. Photolysis of **2a** and 1-(*o*-(3',3'-dimethyl-2'-propenyloxy)phenyl)-2-pentamethyldisilanylethyne **2b** in benzene provides novel stereoselective intramolecular cyclization products **10** and **11**, respectively. Irradiation of 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanyl ethyne **2c** in benzene yields the photo-Fries rearrangement products **18** and **19** and a photoproduct **17** via silacyclopropene intermediate. Photolysis of 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyl disilanylethyne **2d** in benzene provides a novel intramolecular cycloaddition product **25** and 1-(*o*-methoxycarbonylmethoxyphenyl)-2-trimethylsilylethyne **26** via silacyclopropene intermediate.

INTRODUCTION

Photolysis of alkynyl-substituted disilanes affords a convenient route to the highly strained silacyclopropenes.¹ These silacyclopropenes react readily with methanol or acetone in the presence of methanol or acetone as trapping agents.²⁻⁵ Silacyclopropenes also react with unsaturated functional groups such as aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzynes, terminal 1,3-dienes, and conjugated imines to give five-membered cyclic organosilicon products in which C=O, C=C, C≡C or C=N bonds are inserted into the Si-C bond of the silacyclopropene ring.⁶ Although the chemical properties of silacyclopropenes have been extensively investigated⁷⁻¹¹, relatively few examples have been reported on the intramolecular photoreactions of the system. In order to check whether the C=C or C=O bonds in the ortho substituents insert intramolecularly into Si-C bond of the silacyclopropene ring, we have recently synthesized **2a**~**2d** which have allyloxy^{12,13}, 3,3-dimethyl-2-propenyloxy¹³, acetoxy¹⁴, or methoxycarbonylmethoxy¹⁵ group, respectively, as ortho substituents in phenylethynylpentamethyldisilane¹⁶⁻¹⁸ and reported a photochemical reaction of these compounds. In this paper, we describe a detailed photochemical study of 1-(*o*-substituted-phenyl)-2-pentamethyldisilanyl ethynes.

MATERIALS AND METHOD

Materials. 2-Iodophenol, allyl chloride, sodium hydride, bis(triphenylphosphine)palladium dichloride, copper(I) iodide,

acetyl chloride, 1-chloro-3-methyl-2-butene, methyl bromoacetate were purchased from Aldrich Chemical Co. and used without further purification. Methylene chloride was dried with P₂O₅ followed by fractional distillation prior to use. Acetone was dried with K₂CO₃ followed by fractional distillation immediately prior to use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents were used for HPLC and UV absorption spectra.

Instruments. 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. 2D NMR spectra were recorded in CDCl₃ solutions on a Varian Unity-500 spectrometer. UV absorption spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Mass spectra were determined at 70eV 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. Rayonet Photochemical Reactor was used for the photoreaction.

Synthesis of *o*-(3,3-dimethyl-2-propenyloxy)iodobenzene **1b.** A solution of 2-iodophenol(3 g, 13.6 mmol) in N, N-dimethyl formamide(20 mL) was added to a solution of NaH(0.36 g, 14.9 mmol) in DMF(40 mL) at room temperature under nitrogen atmosphere. 1-chloro-3-methyl-2-butene(1.6 mL, 13.6 mmol) was added dropwise to the resulting solution and the mixture was stirred at room temperature for 2 h. Water(30 mL) was added to the solution and was extracted with ethyl acetate(3 × 30mL).

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The combined ethyl acetate solution was washed with water (20 mL), brine (20 mL) and dried (MgSO_4), and concentrated in vacuo to give the crude product.

Flash column chromatography (10% ethyl acetate/*n*-hexane) gave the *o*-(3,3-dimethyl-2-propenyloxy)iodobenzene **1b** (3.91 g, 99% yield).

1b: Colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 1.76(3H, s), 1.81(3H, s), 4.60(2H, d, $J=6.4$ Hz, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2$), 5.53(1H, t, $J=6.4$ Hz, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2$), 6.71(1H, td, $J=7.5, 1.2$ Hz, ArH), 6.84(1H, dd, $J=7.5, 1.2$ Hz, ArH), 7.29(1H, td, $J=7.5, 1.2$ Hz, ArH), 7.79(1H, dd, $J=7.5, 1.2$ Hz, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.84, 26.24, 66.70, 87.39, 113.11, 119.96, 122.87, 129.77, 138.31, 139.90, 157.88; UV (CH_2Cl_2) λ_{max} 279, 287 nm; FT-IR (NaCl) 3026.7, 2972.9, 1581.7, 1275.6, 747.4 cm^{-1} ; MS (70 eV) m/z 288(M^+).

Synthesis of 1-(o-(3',3'-dimethyl-2'-propenyloxy)phenyl)-2-pentamethyldisilanylethyne 2b. To a deaerated solution of *o*-(3,3-dimethyl-2-propenyloxy)iodobenzene **1b** (1.5 g, 5.2 mmol), bis(triphenylphosphine)palladium dichloride (36 mg, 0.052 mmol) and copper(I) iodide (10 mg, 0.052 mmol) in anhydrous triethylamine (30 mL) were added dropwise pentamethyldisilanylethyne (0.89 g, 5.7 mmol) at room temperature. The reaction mixture was heated at 40°C for 1.5 h. To this solution saturated ammonium chloride solution (20 mL) was added and the reaction mixture was extracted with ethyl acetate (3 \times 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 5% ethyl acetate/*n*-hexane as eluents gave **2b** (1.46 g, 89% yield).

2b: Colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 0.16(9H, s), 0.26(6H, s), 1.72(3H, s), 1.77(3H, s), 4.56(2H, d, $J=6.6$ Hz), 5.50(1H, t, $J=6.6$ Hz), 6.85(2H, m), 7.23(1H, td, $J=7.9, 1.8$ Hz), 7.40(1H, dd, $J=7.9, 1.8$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 3.11, -2.70, 18.15, 25.64, 65.60, 97.29, 103.53, 112.50, 112.39, 120.03, 120.30, 129.63, 133.95, 137.43, 160.03; UV (CH_2Cl_2) λ_{max} 307, 299, 261 nm; FT-IR (NaCl) 2952.2, 2151.8, 1488.0, 1246.9, 749.1 cm^{-1} ; MS (70 eV) m/z 316(M^+); HRMS (M^+) calcd for $\text{C}_{18}\text{H}_{28}\text{OSi}_2$ 316.1679, found 316.1654.

Synthesis of o-(methoxycarbonylmethoxy)iodobenzene 1d. Methyl bromoacetate (1.03 mL, 11 mmol) was added dropwise to a solution of 2-iodophenol (2 g, 9.09 mmol) and potassium carbonate (3.77 g, 27 mmol) in *N,N*-dimethyl formamide (20 mL) at 120°C under nitrogen atmosphere and the mixture was stirred at 120°C for 3 h. Water (30 mL) was added to the solution and was extracted with ethyl acetate (3 \times 30 mL). The combined ethyl acetate solution was washed with water (20 mL), brine (20 mL) and dried (MgSO_4), and concentrated in vacuo to give the crude product. Flash column chromatography (15% ethyl acetate/*n*-hexane) gave the *o*-(methoxycarbonylmethoxy)iodobenzene **1d** (2.60 g, 98% yield).

1d: Colorless oil; ^1H NMR (CDCl_3 , 200 MHz) δ 3.79(3H, s), 4.68(2H, s), 6.73(2H, m), 7.25(2H, m), 7.78(1H, dd, $J=7.6, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 50 MHz) δ 52.3, 66.3, 86.5, 112.4, 123.6, 129.4, 139.9, 156.7, 168.8; UV (CH_2Cl_2) λ_{max} 284, 277, 233 nm; FT-IR (NaCl) 3061.9, 2952.4, 1760.0, 1582.2, 1284.5, 1206.5 cm^{-1} ; MS (70 eV) m/z 292(M^+).

Synthesis of 1-(o-methoxycarbonylmethoxyphenyl)-2-pen-

tamethyl disilanylethyne 2d. To a deaerated solution of *o*-(methoxycarbonylmethoxy)iodobenzene **1d** (1 g, 3.42 mmol), bis(triphenylphosphine)palladium dichloride (24 mg, 0.0342 mmol) and copper(I) iodide (6.5 mg, 0.0342 mmol) in anhydrous triethylamine (30 mL) were added dropwise pentamethyldisilanylethyne (0.59 g, 3.76 mmol) at room temperature. The reaction mixture was heated at 40°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 \times 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 15% ethyl acetate/*n*-hexane as eluents gave **2d** (0.96 g, 88% yield).

2d: Colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 0.14(9H, s), 0.26(6H, s), 3.77(3H, s), 4.69(2H, s), 6.77(1H, dd, $J=8.3, 0.9$ Hz), 6.92(1H, td, $J=7.6, 0.9$ Hz), 7.21(1H, td, $J=7.6, 0.9$ Hz), 7.41(1H, dd, $J=7.6, 1.7$ Hz); ^{13}C NMR (CDCl_3 , 50 MHz) δ -3.07, -2.60, 52.1, 66.4, 98.2, 102.7, 113.4, 113.9, 121.7, 129.5, 134.1, 158.7, 169.2; UV (CH_2Cl_2) λ_{max} 303, 294, 261 nm; FT-IR (NaCl) 3074.7, 2953.5, 2152.1, 1764.8, 1596.3, 1245.9 cm^{-1} ; MS (70 eV) m/z 320 (M^+); HRMS (M^+) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{Si}_2$ 320.1264, found 320.1333.

Irradiation of 1-(o-allyloxyphenyl)-2-pentamethyldisilanylethyne 2a in benzene. Deaerated solution (5×10^{-4} M) of 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne **2a** (144 mg) in benzene (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 photoadduct **10** was isolated in 36 mg (25% yield), by column chromatography with *n*-hexane/ethyl acetate (60/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (60/1, v/v) as an eluent.

10: Colorless oil; ^1H NMR (CDCl_3 , 500 MHz) δ 0.20(3H, s), 0.21(3H, s), 0.22(3H, s), 0.54(6H, s), 3.41(2H, dt, $J=4.9, 2.0$ Hz), 5.08(1H, dq, $J=17.6, 2.0$ Hz), 5.15(1H, dq, $J=10.3, 2.0$ Hz), 6.01(1H, m), 6.82(1H, td, $J=7.8, 1.5$ Hz), 6.88(1H, dd, $J=7.8, 1.5$ Hz), 7.14(1H, td, $J=7.8, 1.5$ Hz), 7.59(1H, dd, $J=7.8, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 0.48, 0.50, 0.51, 1.17, 38.34, 115.27, 116.40, 119.83, 127.59, 129.36, 130.58, 135.66, 147.41, 153.01, 160.0; UV (CH_2Cl_2) λ_{max} 324, 280, 273 nm; FT-IR (NaCl) 2956.8, 1594.9, 1252.3, 751.7 cm^{-1} ; MS (70 eV) m/z 288(M^+); HRMS (M^+) calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}_2$ 288.1366, found 288.1367.

Irradiation of 1-(3',3'-dimethyl-2'-propenyloxyphenyl)-2-pentamethyl disilanylethyne 2b in benzene. Deaerated solution (5×10^{-4} M) of 1-(3',3'-dimethyl-2'-propenyloxyphenyl)-2-pentamethyl-disilanylethyne **2b** (158 mg) in benzene (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 photoadduct **11** was isolated in 28 mg (18% yield), by column chromatography with *n*-hexane/ethyl acetate (60/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (60/1, v/v) as an eluent.

11: Colorless oil; ^1H NMR (CDCl_3 , 300 MHz) δ 0.20(9H, s), 0.51(6H, s), 1.68(3H, d, $J=0.9$ Hz), 1.75(3H, d, $J=1.5$ Hz),

3.30(2H, d, $J=4.2$ Hz), 5.07(1H, m), 6.82(1H, td, $J=7.9, 1.5$ Hz), 6.87(1H, dd, $J=7.9, 1.5$ Hz), 7.13(1H, td, $J=7.9, 1.5$ Hz), 7.52(1H, dd, $J=7.9, 1.5$ Hz); ^{13}C NMR(CDCl_3 , 75 MHz) δ 0.29, 1.00, 18.18, 25.56, 33.84, 115.25, 119.87, 123.35, 128.06, 129.14, 131.01, 133.33, 145.70, 156.54, 160.14; UV(CH_2Cl_2) λ_{max} 323, 280, 273 nm; FT-IR (NaCl) 2964.1, 1595.1, 1251.4, 751.5 cm^{-1} ; MS (70 eV) m/z 316(M^+); HRMS (M^+) calcd for $\text{C}_{18}\text{H}_{28}\text{OSi}_2$ 316.1679, found 316.1679.

Irradiation of 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanylethyne 2d in benzene. Deaerated solution (5×10^{-4} M) of 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanylethyne **2d** (160 mg) in benzene (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 **25** and **26** were isolated in 24 mg, 15% yield and 31 mg, 24% yield, respectively, by column chromatography with *n*-hexane/ethyl acetate (60/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (60/1, v/v) as an eluent.

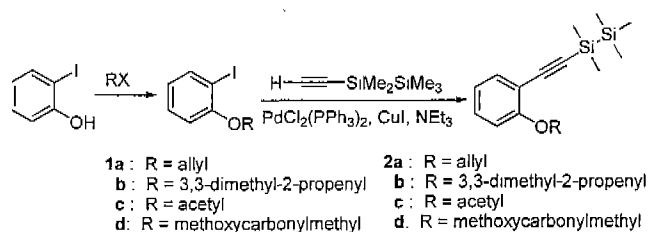
25: Colorless oil; UV(CH_2Cl_2) λ_{max} 313, 262, 230 nm; FT-IR (NaCl) 2955.1, 1575.9, 1476.9, 1269.6 cm^{-1} ; MS (70 eV) m/z 320 (M^+); HRMS (M^+) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{Si}_2$ 320.1264, found 320.1280.

26: Colorless oil; ^1H NMR(CDCl_3 , 300 MHz) δ 0.24(9H, s), 3.78(3H, s), 4.69(2H, s), 6.76(1H, dd, $J=8.3, 0.9$ Hz), 6.92(1H, td, $J=7.7, 0.8$ Hz), 7.21(1H, td, $J=7.7, 0.8$ Hz), 7.42(1H, dd, $J=7.7, 1.7$ Hz); ^{13}C NMR(CDCl_3 , 50 MHz) δ 0.05, 52.1, 66.4, 99.2, 100.6, 113.4, 113.5, 121.8, 129.8, 134.2, 158.8, 169.1; UV(CH_2Cl_2) λ_{max} 302, 293, 260, 248 nm; FT-IR (NaCl) 3073.6, 2957.2, 2158.8, 1764.4, 1596.9, 1250.4 cm^{-1} ; MS (70 eV) m/z 262 (M^+); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Si}$ 262.1025, found 262.1033.

Oxygen effect on the photoreaction of 2a with acetone. The relative quantum yields of the photoreactions of **2a** (0.8 mmol dm^{-3}) with acetone (20 mmol dm^{-3}) to give photoadducts **6** and **7** were measured in the presence of oxygen (bubbled with dry oxygen) and compared with those obtained in the deaerated condition (degassed by N_2 bubbling). The 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps was shone for 5 min. The quantitative analyses were carried out by HPLC using the following conditions: column Lichrosorb Si 60 (25 \times 1.0 cm, mean particle size 7 μm , E. Merck); eluents, hexane-ethyl acetate (60:1, v/v).

RESULTS AND DISCUSSION

The starting 1-(*o*-substituted-phenyl)-2-pentamethyldisilanylethyne — 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne **2a**, 1-(*o*-(3', 3'-dimethyl-2'-propenyloxy)phenyl)-2-pentamethyl-disilanylethyne **2b**, 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanylethyne **2c**, 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanylethyne **2d**, were prepared by the reaction of *o*-allyloxyiodobenzene **1a**, *o*-(3,3-dimethyl-2-propenyloxy)iodobenzene **1b**, *o*-acetoxyiodo-ben-

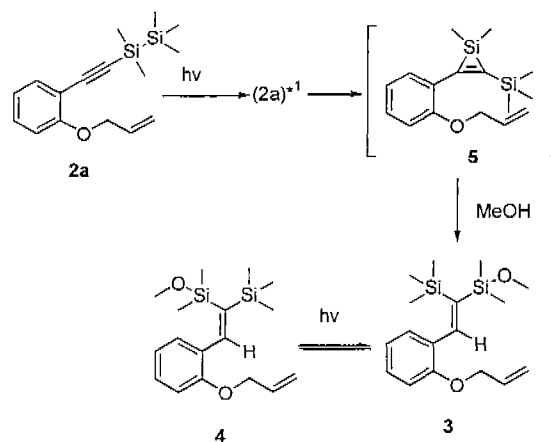


Scheme 1.

zene **1c**, *o*-(methoxycarbonylmethoxy)iodobenzene **1d**, respectively, with ethynylpentamethyldisilane in the presence of bis(triphenylphosphine)palladiumdichloride and copper(I) iodide in triethylamine (Scheme 1).

Photoreaction of 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne 2a with methanol

First we examined the photolysis of 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne **2a** in the presence of a quenching agent, methanol. Irradiation of **2a** in methanol affords two 1:1 photoaddition products **3** and **4** in 25 and 9% yields, respectively, but neither the photoproduct from the reaction of the C=C bond in *o*-allyloxy group with Si-C bond of silacyclopentene intermediate **5** nor the photoproduct via [3, 3] sigmatropic rearrangement of allyl group in **2a** is observed in this photoreaction (Scheme 2).

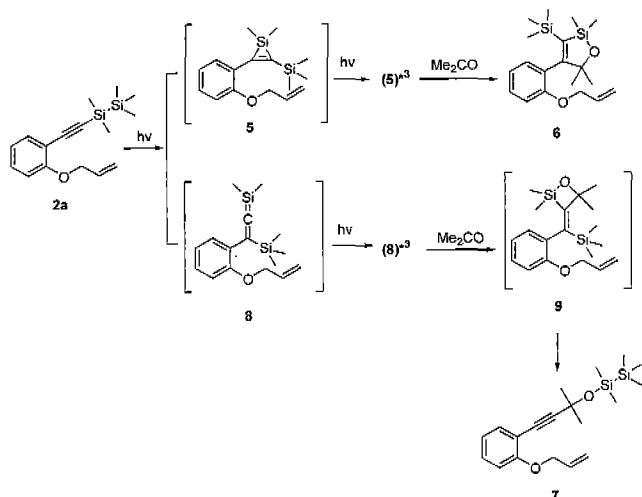


Scheme 2.

The formation of photoproduct **3** can be explained by the methanol addition to a silacyclopentene intermediate **5** which is formed from the singlet excited state of **2a** and geometrical C=C bond photoisomerization of **3** yields **4** upon irradiation of **3**.

Photoreaction of 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne 2a with acetone

When a deaerated methylene chloride solution of **2a** in the



Scheme 3.

presence of acetone as a quenching agent was irradiated at room temperature with RUL 300 nm lamps, site specific and regioselective 1:1 photoadducts **6** and **7** were obtained in 23 and 6% yields, respectively, but the photoproduct from the reaction of the ortho substituent, allyl group, in **2a** and Si-C bond of the silacyclopropene intermediate **5** formed from the photolysis of **2a** was not observed (Scheme 3). A few other photoproducts of unknown structure were observed in trace amounts as byproducts in the reaction.

The oxygen effects on the photoreaction of **2a** with acetone are summarized in Table 1. The quantum yields of photoproducts decreased to 29-35% in aerated solution indicating that the photoadducts are produced *via* triplet excited states.

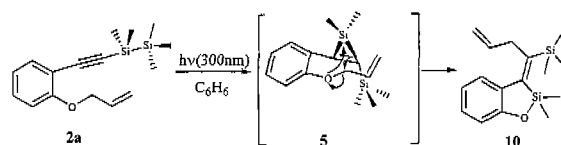
The photolysis of **2a** seems to proceed in two different routes simultaneously. The main route involves the production of silacyclopropene **5**, and the minor route involves the formation of a new type of intermediate, 1-sila-1,2-propadiene **8** (Scheme 3) as observed in the photoreaction of phenylethynylpentamethyldisilane with acetone.⁴ Insertion of acetone into the silicon-carbon bond in the triplet excited state of silacyclopropene **5** generates five membered ring compound **6**. The cycloaddition of acetone to the triplet excited state of 1-sila-1,2-propadiene intermediate **8** to afford silaoxetane **9** followed by migration of trimethylsilyl group to dimethylsilyl position gives the photoproduct **7**.

Photolysis of 1-(o-allyloxyphenyl)-2-pentamethyldisilanylethyne 2a in benzene

Table 1. Oxygen effects on the photoreaction of **2a** with acetone

Photoproducts	Φ aerated*
	Φ deaerated
6	0.29
7	0.35

*Relative quantum yields with respect to deaerated solutions.



Scheme 4.

Irradiation of 1-(*o*-allyloxyphenyl)-2-pentamethyldisilanylethyne **2a** with 300 nm UV light in the absence of a trapping agent afforded a novel stereoselective cyclization product **10** in 25% yield along with some decomposition products of unknown structure (Scheme 4). The UV absorption spectrum of **2a** turned into that of photoproduct **10** gradually with the irradiation time. As the absorbance at around 306 and 298 nm decreased, the intensity of absorption at around 324 and 280 nm increased (Fig. 1).

The results indicate the initial formation of silacyclopropene intermediate **5** upon irradiation followed by the intramolecular oxygen-silicon bond formation to give the product **10** with *Z* configuration as the sole photoproduct. The stereoselective cycloaddition reaction leading to *Z* configuration indicates concerted addition of allyloxy group to silacyclopropene formed.

The structure of the photoproduct **10** was determined by various physical methods including ¹H-¹H and ¹H-¹³C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY) (Fig. 2).

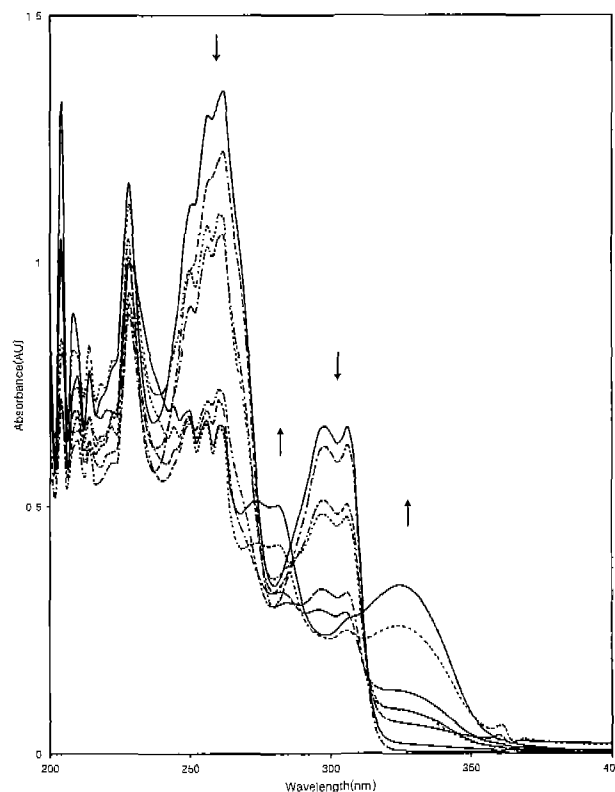


Figure 1. UV absorption change of **2a** on irradiation in benzene at 0, 10, 20, 30, 40, 50, 120, 180 sec.

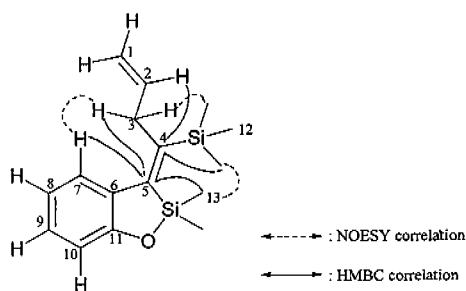


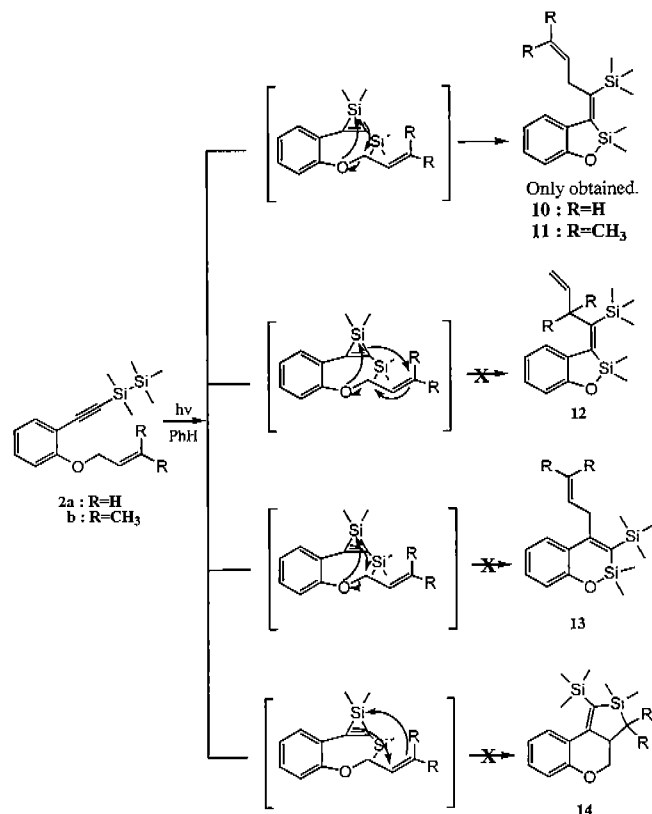
Figure 2. Important correlations observed in HMBC and NOESY spectra of photoproduct **10**.

*Photolysis of 1-(*o*-(3', 3'-dimethyl-2'-propenyloxy)phenyl)-2-pentamethyldisilanylethyne **2b** in benzene*

To investigate the regio and stereochemistry of the above photoinduced intramolecular cyclization reaction, we synthesized 1-(*o*-(3', 3'-dimethyl-2'-propenyloxy)phenyl)-2-pentamethyldisilanylethyne **2b**. When a benzene solution of **2b** was irradiated at room temperature with 300 nm UV light under a purified nitrogen atmosphere, **11** was only obtained in 18% yield but the other possible photoproducts **12**, **13**, and **14** were not observed (Scheme 5).

*Photolysis of 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanylethyne **2c** in benzene*

In order to check whether or not the C=O bond in the ortho



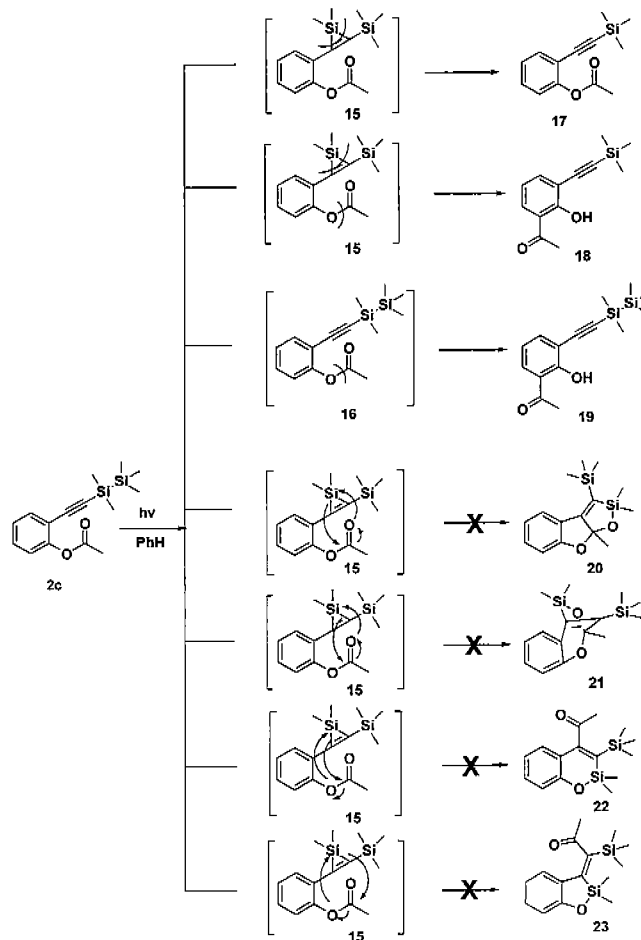
Scheme 5.

substituent inserts intramolecularly into Si-C bond of the sila-cyclopropene ring, we have synthesized 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanylethyne **2c** which has the acetoxy group as ortho substituent to phenylethynylpentamethyldisilane and investigated the photolysis of **2c** in benzene to obtain the photo-Fries rearrangement products **18** and **19** instead of the expected intramolecular cyclization product **20** and **21** (Scheme 6).

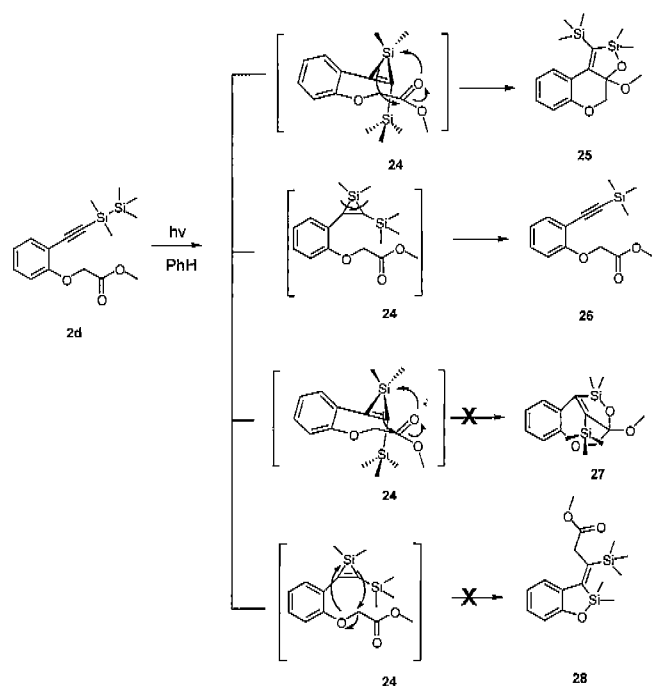
*Photolysis of 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanylethyne **2d***

Intramolecular cycloaddition of C=O group to sila-cyclopropene intermediate will provide a novel reaction path and utility for the synthesis of Si containing heterocycles. We, therefore, synthesized 1-(*o*-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanylethyne **2d** which has a carbonyl group in the ortho position of phenylethynylpentamethyldisilane.

Irradiation of **2d** in deaerated benzene with 300nm UV light provided a novel cycloaddition product **25** (15% yield) and 1-(*o*-methoxycarbonylmethoxyphenyl)-2-trimethylsilyl ethyne **26** (24% yield) along with some decomposition products of unknown structure as shown in Scheme 7 but the other possible photoproducts **27** and **28** were not observed.

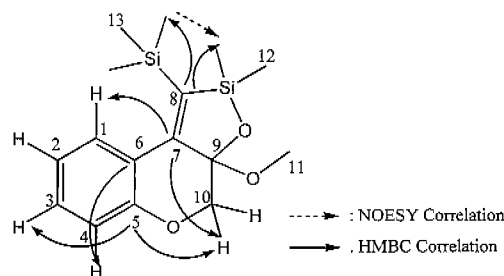


Scheme 6.



Scheme 7.

The formation of photoproduct **25** can be rationalized in terms of the initial formation of silacyclopropene intermediate **24** upon irradiation followed by the concerted intramolecular cycloaddition reaction between the carbonyl group in ortho substituent and Si-C bond of silacyclopropene formed. Liberation of dimethylsilylene species from the silacyclopropene intermediate **24** results in the formation of **26**. The quantum yield of photoproduct **25** decreased to 10% in aerated solution indicating that the triplet excited state is involved in this reaction. Since silacyclopropene intermedi-

Figure 3. Important correlations observed in HMBC and NOESY spectra of photoproduct **25**.

ate is formed from the singlet excited state of **2d**, this process is not quenched by oxygen efficiently indicating that the triplet excited state of **24** is involved in the intramolecular cycloaddition reaction of silacyclopropene ring with carbonyl group in the ortho substituent. This result is the same as the photoinduced intermolecular cycloaddition reaction of 1-aryl-4-(pentamethyldisilanyl)-1,3-butadiynes⁹ and 1,4-bis(pentamethyldisilanyl)-butadiyne¹⁰. The structure of the photoproduct **25** was determined by various physical methods including ¹H-¹H and ¹H-¹³C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY) (Table 2). The 3D structure of **25** was determined by NOESY spectrum. In particular, the presence of the cross-peaks between the protons of C(12) and the protons of C(13) showed the close proximity of the protons of C(12) to the protons of C(13). The quaternary carbons were identified by the cross-peaks in the HMBC spectrum. Vicinal coupling between the protons of C(10) and C(1) and the quaternary carbon C(7) showed the connectivity of the carbon C(7) and the benzene ring and C(9). In the same manner, the connectivity of the carbon C(8) and dimethylsilyl group and trimethylsilyl group was established. The skeletal struc-

Table 2. ¹H NMR(500MHz) and ¹³C NMR(125MHz) data for photoproduct **25** in CDCl₃*

Position	δ_c (ppm)	M †	δ_H (ppm)	I ‡	M §	J_{H-H} (Hz)	NOESY
1	128.49	d	7.44	1H	dd	7.3(J_{1H-2H}), 1.5(J_{1H-3H})	2H
2	119.69	d	6.90	1H	dd	7.3(J_{2H-1H}), 8.8(J_{2H-3H})	1H, 3H
3	130.81	d	7.24		ddd	8.8(J_{3H-2H}), 7.3(J_{3H-4H}), 1.5(J_{3H-1H})	2H, 4H
4	116.82	d	6.89	1H	d	7.3(J_{4H-3H})	3H
5	154.77	s					
6	121.36	s					
7	157.95	s					
8	135.20	s					
9	102.48	s					
10 _a	72.86	t	4.45	1H	d	11.2($J_{10aH-10\beta H}$)	
10 _{β}	72.86	t	3.92	1H	d	11.2($J_{10\beta H-10aH}$)	
11	49.56	q	3.13	3H	s		
12	1.27	q	0.30	3H	s		
12	0.62	q	0.46	3H	s		13H
13	0.91	q	0.25	9H	s		12H

*All these assignments were confirmed by ¹H-¹H and ¹H-¹³C COSY and NOESY, HMBC spectra. †Multiplicities were determined by DEPT spectrum. ‡Integrated intensity. §Multiplicities. ||Important correlations in NOESY spectrum.

ture of **25** was established as shown in Fig. 3.

In summary, photolysis of **2a**, **2b**, and **2d** in benzene provides novel intramolecular cyclization product **10**, **11**, and cycloaddition product **25**, respectively, *via* silacyclopropene intermediate but irradiation of **2c** in benzene yields the photo-Fries rearrangement products **18** and **19**. Irradiation of **2a** in methanol gives 1:1 photoaddition products **3** and **4** *via* silacyclopropene intermediate but the photolysis of **2a** in methylene chloride with acetone provides 1:1 photoaddition products **6** and **7** *via* silacyclopropene intermediate and 1-sila-1,2-propadiene intermediate, respectively.

Acknowledgment—This investigation was supported by the Basic Science Research Institute program, Ministry of Education (BSRI-97-3406), the Korea Advanced Institute of Science and Technology and the University of Suwon.

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