

Photoreaction of 1-(*o*-Acetoxyphenyl)-2-pentamethyldisilanyl Ethyne

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Irradiation of 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanyl ethyne **2** in benzene yields the photo-Fries rearrangement products **5** and **6** and a photoproduct **4** via silacyclopropene intermediate.

Introduction

Photolysis of alkynyl-substituted disilanes affords a convenient route to the highly strained silacyclopropenes¹ which react with unsaturated functional groups to give five-membered cyclic organosilicon products.²

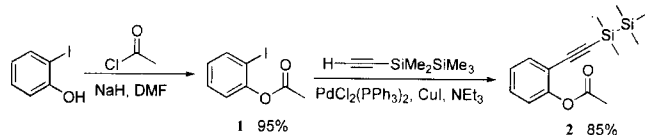
Although the chemical properties of silacyclopropenes have been extensively investigated,³ relatively a few examples have been reported on the intramolecular photoreactions of the system.⁴ In order to check whether or not the C=O bond in the ortho substituent inserts intramolecularly into Si-C bond of the silacyclopropene ring, we have recently synthesized 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanyl ethyne **2** which has the acetoxy group as ortho substituent to phenylethynylpentamethyldisilane and investigated the photolysis of **2** in benzene to obtain the photo-Fries rearrangement products **5** and **6** instead of the expected intramolecular cyclization product **7** or **8**.

Results and Discussion

The starting 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanyl ethyne **2** was prepared by the reaction of *o*-acetoxyiodobenzene **1** with ethynyl pentamethyldisilane⁵ in the presence of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in triethylamine at 40 °C (Scheme 1).

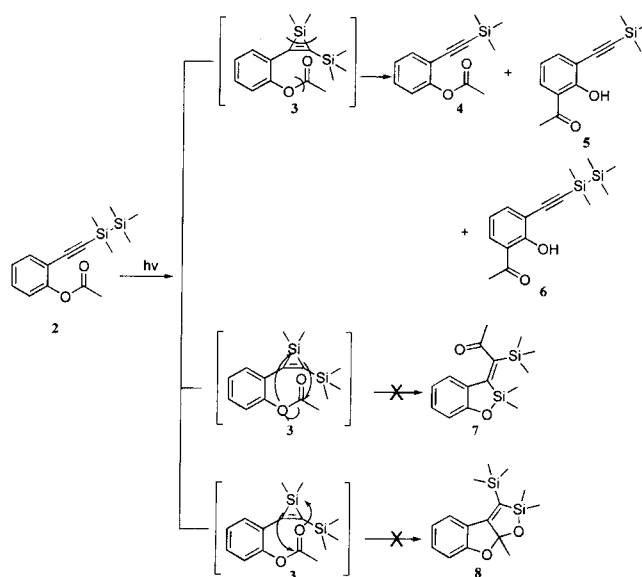
Irradiation of **2** in benzene affords two photo-Fries rearrangement products **5** and **6** and a photoproduct **4** along with some decomposition products of unknown structure but neither the expected reaction of the C=O bond in *o*-acetoxy group with Si-C bond of silacyclopropene intermediate **3** to give the compound **8** nor the photoproduct **7** via the intramolecular oxygen-silicon bond formation is observed in this photoreaction (Scheme 2).

The structures of these photoproducts **4**, **5**, and **6** are determined by various physical methods such as ¹H NMR, ¹³C NMR, 2D NMR (¹H-¹H, ¹H-¹³C COSY, HMBC, NOESY), UV, FT-IR, and mass spectrometry. The UV absorption



Scheme 1

spectra of these photoproducts **5** and **6** are similar to each other and the absorption maxima were red-shifted compared to that of **2**. The UV absorption spectrum of the photoproduct **4** is similar to that of **2** indicating that the chromophore of **2** and **4** are the same. Mass spectra of **5** and **6** show the molecular ion peaks (*M*⁺) indicating that the photoproduct **5** is formed by ejection of dimethylsilylene and the photo-Fries rearrangement and the photoproduct **6** is formed by the photo-Fries rearrangement from **2**. FT-IR spectra of **4**, **5**, and **6** show the typical ethynyl absorption at 2163.5, 2165.0, and 2166.3 cm⁻¹, respectively. The carbonyl groups in **5** and **6** appearing at 1642.5 and 1643.9 cm⁻¹, respectively, are substantially shifted in comparison to that of **2** appearing at 1770.1 cm⁻¹. This shift is a result of the intramolecular hydrogen bonding between the carbonyl group at C(6) and the hydroxyl group at C(1). The ¹H and ¹³C NMR spectra of **4** are very similar to those of **2** except that the photoproduct **4** has the trimethylsilylethynyl group instead of the pentamethyldisilanylethynyl group. The ¹H-¹H and ¹H-¹³C correlation spectroscopy (COSY) spectra of **5** and **6** were studied to identify the protons directly attached to the individual carbons. From the correlated peaks in **5** and **6**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Tables 1 and 2. In order to locate the qua-



Scheme 2

Table 1. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) data for photoproduct **5** in CDCl_3^a

Posit ion	δ_{C} (ppm)	M^b	δ_{H} (ppm)	I^c	M^d	$J_{\text{H-H}}$ (Hz)	NOESY
1	163.21	s					
2	113.51	s					
3	140.25	d	7.62	1H	dd	7.8 ($J_{3\text{H-4H}}$), 1.6 ($J_{3\text{H-5H}}$)	4H ^e
4	118.46	d	6.85	1H	dd	8.0 ($J_{4\text{H-5H}}$), 7.8 ($J_{4\text{H-3H}}$)	3H ^e , 5H ^e
5	130.97	d	7.71	1H	dd	8.0 ($J_{5\text{H-4H}}$), 1.6 ($J_{5\text{H-3H}}$)	4H ^e
6	119.49	s					
7	204.37	s					
8	26.71	q	2.63	3H	s		
OH			12.84	1H	s		
1'	99.33	s					
2'	100.15	s					
3'	-0.02	q	0.27	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 Important correlations by NOESY spectrum.

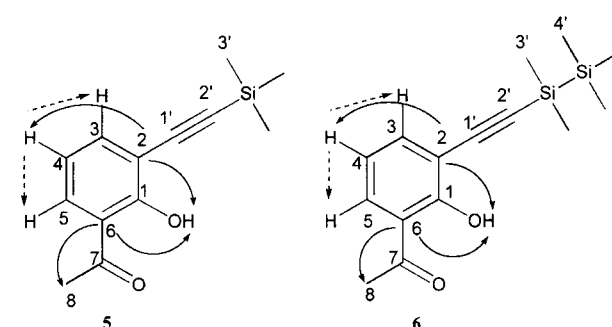
Table 2. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) data for photoproduct **6** in CDCl_3^a

Posit ion	δ_{C} (ppm)	M^b	δ_{H} (ppm)	I^c	M^d	$J_{\text{H-H}}$ (Hz)	NOESY
1	163.43	s					
2	113.34	s					
3	140.19	d	7.63	1H	dd	7.6 ($J_{3\text{H-4H}}$), 1.6 ($J_{3\text{H-5H}}$)	4H ^e
4	118.45	d	6.86	1H	dd	8.0 ($J_{4\text{H-5H}}$), 7.6 ($J_{4\text{H-3H}}$)	3H ^e , 5H ^e
5	131.11	d	7.72	1H	dd	8.0 ($J_{5\text{H-4H}}$), 1.6 ($J_{5\text{H-3H}}$)	4H ^e
6	119.55	s					
7	204.34	s					
8	26.73	q	2.64	3H	s		
OH			12.79	1H	s		
1'	98.18	s					
2'	99.67	s					
3'	2.37	q	0.32	6H	s		
4'	1.78	q	0.16	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 Important correlations by NOESY spectrum.

ternary carbons, the HMBC spectrum was taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(4) and -OH and the quaternary carbons C(2) in **5** and **6** showed the connectivity of the carbon C(2) to the carbons C(1) and C(3). In the same manner, the connectivity of the carbon C(6) to the carbons C(7) and C(1) was established. The 3D-structure of **5** and **6** was determined by a nuclear overhauser and exchange spectroscopy (NOESY) spectrum. In particular, the presence of the cross-peaks between a proton of C(4) and the protons of C(3) and C(5) showed the close proximity of a proton of C(4) to the protons of C(3) and C(5), indicating that these protons are located on the same side of the molecule.

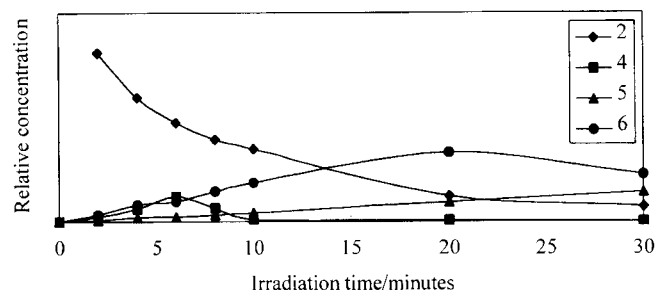
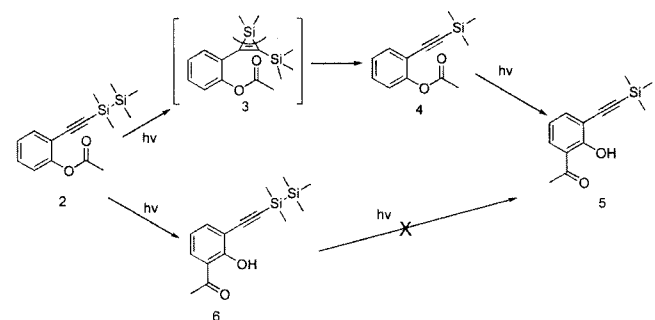
Thus, the skeletal structure of **5** and **6** was established as

**Figure 1.** Important correlations observed in HMBC and NOESY spectra of photoproducts **5** and **6**. \rightarrow : HMBC correlation, \dashrightarrow : NOESY correlation.

shown in Figure 1.

As shown in Figure 2, the photoproduct **4** is initially formed and prolonged irradiation of the solution results in the formation of the photoproduct **5** indicating that **4** is the primary and **5** is the secondary photoproduct. Photolysis of pure **4** in deaerated benzene results in the formation of **5**, strongly supporting the mechanism. The photoproduct **6** is formed by the photo-Fries rearrangement from the compound **2**. After the irradiation of the pure **6** in deaerated benzene for 4 hours, HPLC analysis showed some product of unknown structure instead of the photoproduct **5**. It is thought that this material was probably formed from the reaction of the silacyclopene intermediate derived from **6** and ortho substituted hydroxy group in photoproduct **6**. Further studies are in progress to elucidate this compound from the photoreaction of 1-(*o*-hydroxyphenyl)-2-pentamethylid-isilanyl ethyne.

From these results, we propose a plausible photoreaction mechanism as shown in Scheme 3. The silacyclopene

**Figure 2.** Kinetics of the photoreaction of (**2**).**Scheme 3**

intermediate formed from the excited state of **2** ejects dimethylsilylene to give the primary photoproduct **4**, and the prolonged irradiation of **4** gives the secondary photoproduct **5** by the photo-Fries rearrangement. The photoproduct **6** is directly formed from **2** by the photo-Fries rearrangement.

Experimental Section

General Methods. 2D NMR spectra of (**5**) and (**6**) were recorded in CDCl₃ solutions on a Varian Unity-500 spectrometer. 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 chromatography (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. Methylene chloride was dried with P₂O₅ followed by fractional distillation prior to use. Acetone was dried with K₂CO₃ and followed by fractional distillation immediately prior to use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia) were used for HPLC and UV absorption spectra.

Synthesis of *o*-acetoxyiodobenzene **1.** 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. Acetyl chloride (1.45 mL, 20.4 mmol) was added dropwise to the resulting solution and the mixture was stirred at room temperature for 2 hrs. Water (30 mL) was added to this resulting solution and the reaction mixture was extracted with ethyl acetate (3×30 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. Purification by flash column chromatography eluting with 10% ethyl acetate/*n*-hexane gave the *o*-acetoxyiodobenzene (3.4 g, 95 % yield).

Colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 2.35 (3H, s), 6.96 (1H, td, *J* = 7.6, 1.5 Hz), 7.09 (1H, dd, *J* = 7.9, 1.5 Hz), 7.34 (1H, td, *J* = 7.6, 1.5 Hz), 7.81 (1H, dd, *J* = 7.9, 1.5 Hz); ¹³C NMR (CDCl₃, 50 MHz) δ_C 21.1, 90.5, 122.9, 127.5, 129.3, 139.3, 151.1, 168.4; UV (CH₂Cl₂) λ_{max} 260, 232 nm; FT-IR (NaCl) 3073.5, 1771.9, 1465.1, 1190.9, 1018.4 cm⁻¹; MS (70 eV) *m/z* (relative intensity) 262 (M⁺, 90), 220 (100), 203 (11), 191 (55), 127 (48), 93 (57).

Synthesis of 1-(*o*-acetoxyphenyl)-2-pentamethyldisilanyl ethyne **2.** To a deaerated solution of *o*-acetoxyiodobenzene (1 g, 3.8 mmol), bis(triphenylphosphine)palladium dichloride (27 mg, 0.038 mmol) and copper(I) iodide (7.3

mg, 0.038 mmol) in anhydrous triethylamine (30 mL) was added dropwise ethynylpentamethyldisilane (0.66 g, 4.2 mmol) at room temperature. The reaction mixture was heated at 40 °C for 5hrs. 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), evaporated in vacuo to give the crude product. Purification by flash column chromatography with 5% ethyl acetate/*n*-hexane as eluents to give **2** (0.94g, 85% yield).

Colorless oil; ¹H NMR (CDCl₃, 300 MHz) δ_H 0.16 (9H, s), 0.26 (6H, s), 2.32 (3H, s), 7.07 (1H, dd, *J* = 7.9, 1.2 Hz), 7.18 (1H, td, *J* = 7.6, 1.2 Hz), 7.32 (1H, td, *J* = 7.9, 1.5 Hz), 7.50 (1H, dd, *J* = 7.6, 1.5 Hz); ¹³C NMR (CDCl₃, 50 MHz) δ_C 3.2, -2.7, 20.8, 98.8, 101.6, 117.6, 122.3, 125.8, 129.5, 133.5, 151.8, 168.8; UV (CH₂Cl₂) λ_{max} 260 nm; FT-IR (NaCl) 2953.8, 2155.9, 1770.1, 1484.2, 1205.4, 1180.3 cm⁻¹; MS (70 eV) *m/z* (relative intensity) 290 (M⁺, 24), 273 (17), 257 (10), 229 (35), 149 (100), 71 (55); HRMS (M⁺) calcd for C₁₅H₂₂O₂Si₂ 290.1158, found 290.1155.

Irradiation of 1-(*o*-acetoxy phenyl)-2-pentamethyldisilanyl ethyne in benzene. Deaerated solution (5×10⁻⁴ M) of 1-(*o*-acetoxyphenyl)-2-pentamethyl-disilanyl ethyne **2** (145 mg) in benzene (1 L) was irradiated with 254 nm UV light in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 5.5 hrs, the starting material **2** disappeared. The resulting photoreaction mixture was concentrated *in vacuo*. The photoadducts **4**, **5**, and **6** were isolated in (2.3 mg, 2% conversion yield based on **2**), (13.9 mg, 12% conversion yield based on **2**), and (40.6 mg, 28% conversion yield based on **2**), respectively, by column chromatography with *n*-hexane/ethyl acetate (6/1) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (6/1, v/v) as an eluent.

Data for **4**: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.24 (9H, s), 2.32 (3H, s), 7.07 (1H, dd, *J* = 8.1, 1.2 Hz), 7.18 (1H, td, *J* = 7.8, 1.2 Hz), 7.34 (1H, td, *J* = 8.1, 1.5 Hz), 7.50 (1H, dd, *J* = 7.8, 1.5 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ_C 0.26, 20.7, 99.6, 101.7, 117.4, 122.2, 125.9, 129.7, 133.3, 152.1, 168.9; UV (CH₂Cl₂) λ_{max} 259, 248 nm; FT-IR (NaCl) 2953.7, 2163.5, 1773.5, 1457.6, 1205.1, 1180.9 cm⁻¹; MS (70 eV) *m/z* (relative intensity) 232 (M⁺, 33), 190 (11), 175 (34), 119 (10), 84 (78), 49 (100); HRMS (M⁺) calcd for C₁₃H₁₆O₂Si 232.0920, found 232.0936.

Data for **5**: UV (CH₂Cl₂) λ_{max} 348, 260, 239 nm; FT-IR (NaCl) 3397.6, 2960.9, 2165.0, 1642.5, 1433.8, 1251.2 cm⁻¹; MS (70 eV) *m/z* (relative intensity) 232 (M⁺, 28), 217 (45), 199 (40), 175 (12), 167 (22), 149 (80), 73 (61), 57 (100); HRMS (M⁺) calcd for C₁₃H₁₆O₂Si 232.0920, found 232.0913.

Data for **6**: UV (CH₂Cl₂) λ_{max} 347, 260, 239 nm; FT-IR (NaCl) 3448.1, 2958.3, 2166.3, 1643.9, 1434.1, 1253.9 cm⁻¹; MS (70 eV) *m/z* (relative intensity) 290 (M⁺, 30), 273 (19), 257 (6), 233 (13), 217 (19), 149 (100), 73 (12); HRMS (M⁺) calcd for C₁₅H₂₂O₂Si₂ 290.1158, found 290.1150.

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