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A novel photoreaction of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne

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

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Abstract

Photolysis of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne **1** in benzene provides novel intramolecular photoproducts **4** and **5** via silacyclopropene intermediate **2** and the cyclization product **6**. Vinyltrimethylsilanes **4** and **5** react with β,β-dimethylacryloyl chloride in the presence of aluminum chloride to give the same products **9** and **10** and for the case of **6**, treatment with β,β-dimethylacryloyl chloride gave **14**. Compound **5** can be converted into **4** in the Friedel–Crafts acylation condition. Reactions of **9**, **10**, and **14** with stannic chloride did not give the expected Nazarov cyclization products **16**–**18**, but **9** afforded reduction product **15**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1-*o*-Hydroxyphenyl-2-(pentamethyldisilanyl)ethyne; Silacyclopropene; Intramolecular photoreaction

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1. Introduction

Photolysis of alkynyl-substituted disilanes affords a convenient route to the highly strained silacyclopropenes [1–3] which react with unsaturated functional groups 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 [4]. Although the chemical properties of silacyclopropenes have been extensively investigated [5–9], relatively few examples have been reported on the intramolecular photoreactions of the system. Recently, I reported on the photo-induced intramolecular reactions of 1-*o*-alkoxyphenyl-2-(pentamethyldisilanyl)ethynes [10–14] and 1-*o*-alkoxymethylphenyl-2-(pentamethyldisilanyl)ethynes [15] affording novel intramolecular photoproducts via silacyclopropene intermediate. Along with the studies on the reactions of silacyclopropenes formed from the photolysis of various phenylethynylpentamethyldisilane systems [16,17], I have undertaken the photoreaction of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne **1** since novel photoproducts from the intramolecular reaction of *ortho*-substituted hydroxy group with the silacyclopropene ring are expected and I describe, in this paper, a detailed photochemical study of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne **1** and reactions of novel photoproducts **4**–**6** with β,β-dimethylacryloyl chloride in the presence of aluminum chloride.

2. Experimental

2.1. General methods

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

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(230–400 mesh ASTM). Benzene was distilled from CaH_2 before use. Et_3N 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-o-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne **1***

To a de-aerated solution of 2-iodophenol (0.5 g, 2.27 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 pentamethyldisilanylethyne (0.45 ml, 2.5 mmol) at room temperature. The reaction mixture was heated at 40°C for 2 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 (40:1, v/v) as an eluent gave **1** (0.49 g, 88% yield) as a colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.22 (9H, s), 0.35 (6H, s), 5.93 (1H, s), 6.89 (1H, td, $J = 7.9, 0.7$ Hz), 6.99 (1H, dd, $J = 7.9, 0.7$ Hz), 7.27 (1H, td, $J = 7.8, 1.6$ Hz), 7.38 (1H, dd, $J = 7.8, 1.6$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C -2.55, -2.10, 101.4, 102.0, 110.3, 114.9, 120.6, 130.9, 131.9, 157.4 ppm; UV (CH_2Cl_2) λ_{max} 306, 297, 258, 252 nm; FT-IR (NaCl) 3509.4, 2953.7, 2143.6, 1483.9, 1246.7, 835.2 cm^{-1}; MS (70 eV) *m/z* 248 (M^+); HRMS (M^+) calcd for $C_{13}H_{20}OSi_2$ 248.1053, found 248.1056.

*2.3. Irradiation of 1-o-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne **1** in benzene*

De-aerated solution (5×10^{-4} M) of **1** (124 mg) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 1 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **3**, **4**, **5**, and **6** were isolated in 23.7 mg (25% yield), 43 mg (35% yield), 18 mg (15% yield), and 25 mg (20% yield), 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. **3**: colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.29 (9H, s), 5.86 (1H, s), 6.85 (1H, td, $J = 7.5, 0.9$ Hz), 6.95 (1H, d, $J = 8.1$ Hz), 7.25 (1H, td, $J = 7.6, 1.6$ Hz), 7.35 ppm (1H, dd, $J = 7.6, 1.6$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 0.35, 99.4, 102.7, 109.9, 114.9, 120.6, 131.0, 132.0, 157.5 ppm; UV (CH_2Cl_2) λ_{max} 304, 296, 257, 245 nm; FT-IR (NaCl) 3510.9, 2961.8, 2145.3, 1576.7, 1484.4, 1251.2, 847.7 cm^{-1}; MS (70 eV) *m/z* 190 (M^+); HRMS (M^+) calcd for $C_{11}H_{14}OSi$ 190.0814, found 190.0818. **4**: colorless oil; UV (CH_2Cl_2) λ_{max} 312, 281, 272, 228 nm; FT-IR (NaCl) 2955.7, 1600.6, 1538.4, 1273.7, 859.2 cm^{-1}; MS (70 eV) *m/z* 248 (M^+); HRMS (M^+) calcd for $C_{13}H_{20}OSi_2$ 248.1053, found 248.1057. **5**: colorless oil; UV (CH_2Cl_2) λ_{max} 282 nm; FT-IR (NaCl) 3067.6, 2953.7, 1598.1, 1486.1, 1279.5, 1255.8, 830.0 cm^{-1}; MS (70 eV) *m/z* 248 (M^+); HRMS (M^+) calcd for $C_{13}H_{20}OSi_2$ 248.1053, found 248.1078. **6**: colorless oil; UV (CH_2Cl_2) λ_{max} 290, 283, 259 nm; FT-IR (NaCl) 2953.5, 1469.9, 1442.0, 1250.8, 834.4 cm^{-1}; MS (70 eV) *m/z* 248 (M^+); HRMS (M^+) calcd for $C_{13}H_{20}OSi_2$ 248.1053, found 248.1065.

*2.4. Reaction of **4**or **5** with β,β-dimethylacryloyl chloride in the presence of aluminum chloride*

In a dry, two-necked flask equipped with a nitrogen inlet and rubber septum were placed dry dichloromethane (3 ml) and anhydrous aluminum chloride (23.1 mg, 0.17 mmol). The slurry was cooled to −78°C, and β,β-dimethylacryloyl chloride (19.3 μl, 0.17 mmol) was added via syringe followed by **4** or **5** (43 mg, 0.17 mmol). The solution turned slightly yellow during 1 h before being poured into 3 M hydrochloric acid (1 ml). After being stirred vigorously for 15 min, the reaction mixture was diluted with ether, and the layer were separated. The organic phase was washed with water (5 ml), a saturated solution of sodium bicarbonate (5 ml), and brine (5 ml). The resulting solution was concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane:ethyl acetate (10:1, v/v) as eluents gave **9** (20 mg, 35% yield) and **10** (21.7 mg, 62% yield). **9**: colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.18 (9H, s), 0.37 (6H, s), 2.01 (3H, d, $J = 0.8$ Hz), 2.18 (3H, d, $J = 0.8$ Hz), 6.71 (1H, m), 6.88 (1H, d, $J = 8.4$ Hz), 7.46 (1H, s), 7.74 (1H, d, $J = 2.2$ Hz), 7.79 ppm (1H, dd, $J = 8.4, 2.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C -0.24, 2.40, 21.5, 28.3, 119.7, 121.6, 124.7, 130.7, 132.2, 132.5, 138.5, 151.2, 155.6, 158.0, 190.6 ppm; UV (CH_2Cl_2) λ_{max} 274 nm; FT-IR (NaCl) 2955.9, 1660.2, 1599.4, 1257.7, 834.8 cm^{-1}; MS (70 eV) *m/z* 330 (M^+); HRMS (M^+) calcd for $C_{18}H_{26}O_2Si_2$ 330.1471, found 330.1479. **10**: colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.01 (3H, s), 2.27 (3H, s), 6.45 (1H, s), 6.91 (1H, t, $J = 7.6$ Hz), 6.97 (1H, d, $J = 8.1$ Hz), 7.08 (1H, d, $J = 16.2$ Hz), 7.26 (1H, td, $J = 7.6, 1.3$ Hz), 7.51 (1H, dd, $J = 7.6, 1.3$ Hz), 8.01 ppm (1H, d, $J = 16.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 21.7, 28.4, 117.1, 120.8, 122.5, 123.7, 128.9, 129.6, 131.9, 139.6, 156.7, 157.2, 192.8 ppm; UV (CH_2Cl_2) λ_{max} 330, 293 nm; FT-IR (NaCl) 3286.4, 2954.1, 1617.6, 1455.2, 1247.6 cm^{-1}; MS (70 eV) *m/z* 202 (M^+); HRMS (M^+) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0914.

*2.5. Reaction of **6** with β,β-dimethylacryloyl chloride in the presence of aluminum chloride*

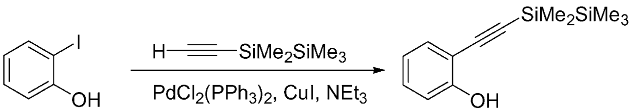
In a dry, two-necked flask equipped with a nitrogen inlet and rubber septum were placed dry dichloromethane (3 ml) and anhydrous aluminum chloride (13.4 mg, 0.1 mmol). The slurry was cooled to −78°C, and β,β-dimethylacryloyl chloride (11.2 μl, 0.1 mmol) was added via syringe followed by **6** (25 mg, 0.1 mmol). The solution turned slightly yellow during 1 h before being poured into 3 M hydrochloric acid (1 ml). After being stirred vigorously for 15 min, the reaction mixture was diluted with ether, and the layer were separated. The organic phase was washed with water (5 ml), a saturated solution of sodium bicarbonate (5 ml), and brine (5 ml). The resulting solution was concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane:ethyl acetate (40:1, v/v) as eluents gave **14** (18.7 mg, 93% yield). **14**: colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.01 (3H, d, $J = 0.9$ Hz), 2.34 (3H, d, $J = 0.9$ Hz), 6.87 (1H, m), 7.31 (1H, td, $J = 7.4$, 1.2 Hz), 7.47 (1H, td, $J = 8.4$, 1.2 Hz), 7.5 (1H, d, $J = 0.8$ Hz), 7.6 (1H, dd, $J = 8.4$, 0.5 Hz), 7.71 ppm (1H, d, $J = 7.9$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 21.8, 28.7, 112.2, 112.8, 120.3, 123.5, 124.1, 127.8, 128.1, 154.8, 155.9, 159.8, 181.2 ppm; UV (CH_2Cl_2) λ_{max} 316 nm; FT-IR (NaCl) 3118.5, 2974.8, 1658.3, 1289.3, 1165.1 cm^{-1}; MS (70 eV) *m/z* 200 (M^+); HRMS (M^+) calcd for $C_{13}H_{12}O_2$ 200.0837, found 200.0835.

2.6. Reaction of 9 with stannic chloride

To a solution of **9** (20 mg, 0.06 mmol) in dry dichloromethane (2 ml) was added stannic chloride (21.3 μl, 0.18 mmol), and the solution was heated to reflux for 3 days. The solution was poured onto 1.5 M hydrochloric acid (1 ml) and diluted with ethyl acetate (2 ml). The organic layer was washed with water (3 ml), a saturated solution of sodium bicarbonate (3 ml), and brine (3 ml) before dried. The resulting solution was concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane:ethyl acetate (10:1, v/v) as eluents gave **15** (10.9 mg, 70% yield). **15**: colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 0.37 (6H, s), 2.00 (3H, d, $J = 0.9$ Hz), 2.18 (3H, d, $J = 0.9$ Hz), 5.98 (1H, d, $J = 14.3$ Hz), 6.71 (1H, m), 6.89 (1H, d, $J = 8.4$ Hz), 7.30 (1H, d, $J = 14.3$ Hz), 7.73 (1H, d, $J = 2.2$ Hz), 7.78 ppm (1H, dd, $J = 8.4$, 2.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C 1.87, 21.5, 28.3, 119.7, 121.5, 124.3, 124.4, 130.4, 131.8, 132.5, 145.4, 155.9, 157.8, 190.7 ppm; UV (CH_2Cl_2) λ_{max} 260 nm; FT-IR (NaCl) 2961.9, 1659.5, 1602.9, 1259.6, 796.9 cm^{-1}; MS (70 eV) *m/z* 258 (M^+); HRMS (M^+) calcd for $C_{15}H_{18}O_2Si$ 258.1076, found 258.1071.

3. Results and discussion

The starting 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl) ethyne **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 (Scheme 1).

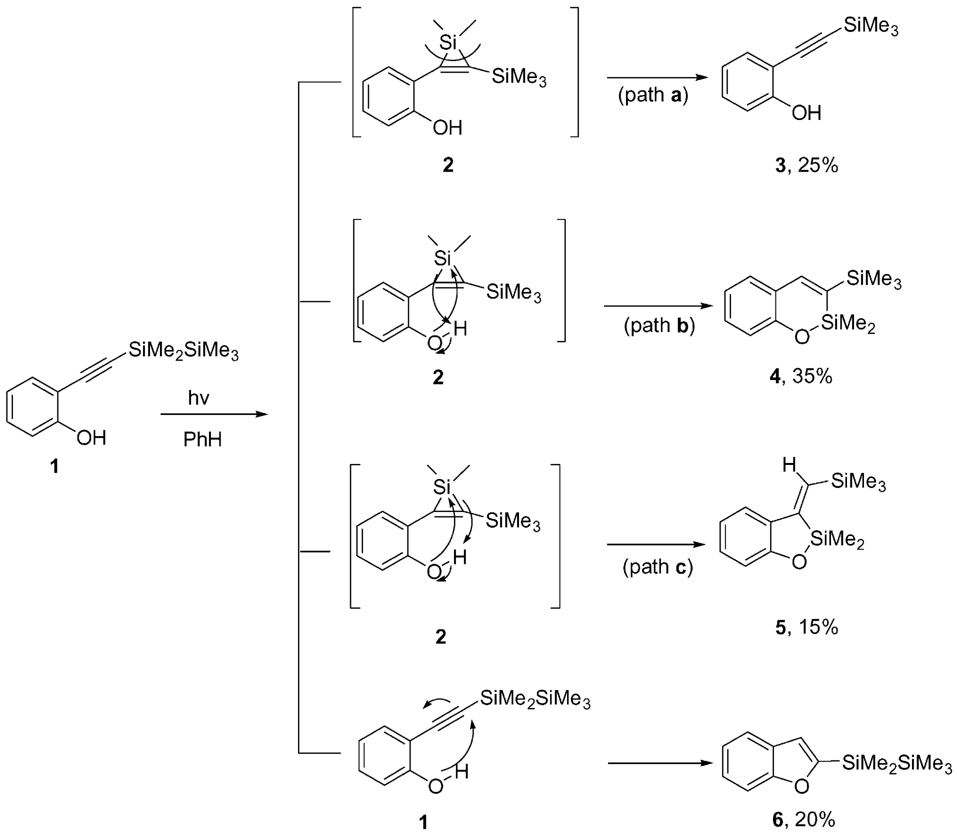


1, 88%

Scheme 1.

Irradiation of **1** in de-aerated benzene with 300 nm UV light provided novel cycloaddition products **4** (35% yield), **5** (15% yield), and the cyclization product **6** (20% yield) in addition to **3** (25% yield) along with some products of unknown structure as shown in Scheme 2. The formation of photoproducts **4** and **5** can be rationalized in terms of the initial formation of silacyclopropene intermediate **2** upon irradiation followed by the concerted intramolecular cycloaddition reaction (path b and path c, respectively) between the hydroxy group in *ortho*-substituent and Si–C bond of silacyclopropene formed. The formation of photoproduct **6** can be explained in terms of the intramolecular cyclization reaction between the hydroxy group in *ortho*-substituent and the carbon–carbon triple bond of pentamethyldisilanylethynyl group. Liberation of dimethylsilylene species from the silacyclopropene intermediate **2** (path a) resulted in the formation of **3**.

The structures of these photoproducts **4–6** were determined by various physical methods such as ^{1}H NMR, ^{13}C NMR, 2D NMR (^{1}H–^{1}H, ^{1}H–^{13}C COSY, HMBC, NOESY), UV, FT-IR, and high-resolution mass spectrometry. The ^{1}H–^{1}H and ^{1}H–^{13}C correlation spectroscopy (COSY) spectra of **4–6** were studied to identify the protons directly attached to the individual carbons. From the correlated peaks in **4–6**, I have been able to identify the pairs of carbons and directly bonded protons as shown in Tables 1–3. In order to locate the quaternary carbons, the HMBC spectra of **4–6** were taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(9), C(10) and C(7), C(9), respectively, and the quaternary carbon C(8) in **4** and **6** showed the connectivity of the carbon C(8) to the trimethylsilyl, dimethylsilyl group and dimethylsilyl group, respectively, and the carbon C(7). In the same manner, the connectivity of the carbon C(7) to the carbon C(8) and the benzene ring in **4** and **6** was established. The presence of the cross-peaks due to the vicinal coupling between a proton of C(8) and the quaternary carbon C(6), the protons of C(9) and the quarternary carbon C(8) in **5** showed the connectivity of the carbon C(8) to the carbon C(7) and trimethylsilyl group. In the same manner, the connectivity of the carbon C(7) to the benzene ring in **5** was established. The 3D structures of **4–6** were determined by a nuclear overhauser and exchange spectroscopy (NOESY) spectrum. In particular, the presence of the cross-peaks between a proton of C(1) and a proton of C(7) in **4** and **6** showed the close proximity of a proton of C(1) to a proton of C(7), indicating that these protons are located on the same



Scheme 2.

side of the molecule. In the same manner, the presence of the cross-peaks between a proton of C(1) and a proton of C(8), the protons of trimethylsilyl group and the protons of dimethylsilyl group in **5** showed the close proximity of a proton of C(1) to a proton of C(8), the protons of C(9) to the protons of C(10). Thus, the skeletal structures of **4–6** were established as shown in Fig. 1.

To investigate the chemical properties of **4–6** obtained by photolysis of **1**, I attempted to synthesize the cyclopentenone annulation product **8** by reaction of vinyltrimethylsilane **4** with β,β-dimethylacryloyl chloride in the presence of aluminum chloride via the Friedel–Crafts acylation followed by the Nazarov reaction as shown in Scheme 3. Indeed, it is well known that the cyclopentenone annulation products were obtained by the Friedel–Crafts acylation of vinyltrimethylsilanes with acryloyl chloride in the presence of aluminum chloride and subsequent Nazarov cyclization with Lewis acid catalysis [18,19].

Table 1
^{1}H 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]	$J_{H–H}$ (Hz)	HMBC[e]
1	131.2	d	7.12	1H	dt	7.4 ($J_{1H–2H}$), 1.3 ($J_{1H–3H,4H}$)	H3, H7
2	120.8	d	6.92	1H	t	7.4 ($J_{2H–1H,3H}$)	H4
3	130.0	d	7.17	1H	td	8.1 ($J_{3H–2H,4H}$), 1.5 ($J_{3H–1H}$)	H1
4	119.5	d	6.88	1H	d	8.1 ($J_{4H–3H}$)	H2
5	154.1	s					H1, H4, H7
6	125.1	s					H2, H4, H7
7	151.5	d	7.43	1H	s		H1
8	137.2	s					H9, H10
9	−0.19	q	0.20	9H	s		
10	2.26	q	0.37	6H	s		

[a] All these assignments were confirmed by ^{1}H–^{1}H and ^{1}H–^{13}C COSY, NOESY, and 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 **5** in $CDCl_3$[a]

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	J_{H-H} (Hz)	HMBC[e]
1	129.2	d	7.01	1H	d	7.3 (J_{1H-2H})	H3, H8
2	120.1	d	6.86	1H	t	7.4 ($J_{2H-1H,3H}$)	H4
3	128.1	d	7.05	1H	td	7.4 ($J_{3H-2H,4H}$), 1.5 (J_{3H-1H})	H1
4	118.4	d	6.61	1H	d	8.1 (J_{4H-3H})	H2
5	152.7	s					H1, H3
6	133.7	s					H2, H4, H8
7	144.5	s					H8
8	152.4	d	7.54	1H	s		H1, H9
9	0.55	q	0.21	9H	s		
10	2.20	q	0.11	6H	s		

[a] All these assignments were confirmed by ^{1}H–^{1}H and ^{1}H–^{13}C COSY, NOESY, and 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 3
^{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	120.9	d	7.56	1H	d	7.4 (J_{1H-2H})	H3
2	122.4	d	7.19	1H	t	7.4 ($J_{2H-1H,3H}$)	H4
3	124.2	d	7.25	1H	t	7.4 ($J_{3H-2H,4H}$)	H1
4	111.4	d	7.49	1H	d	7.4 (J_{4H-3H})	H2
5	158.5	s					H1, H3, H7
6	126.3	s					H2, H4, H7
7	116.4	d	6.92	1H	s		H1
8	163.9	s					H7, H9
9	−4.44	q	0.39	6H	s		
10	−2.12	q	0.14	9H	s		

[a] All these assignments were confirmed by ^{1}H–^{1}H and ^{1}H–^{13}C COSY, NOESY, and HMBC spectra.
[b] Multiplicities were determined by DEPT spectrum.
[c] Integrated intensity.
[d] Multiplicities.
[e] Protons correlated to carbon resonances in ^{13}C column.

Reaction of **4** or **5** with 1 equiv. each of β,β-dimethylacryloyl chloride and aluminum chloride in anhydrous dichloromethane at −78°C for 1 h afforded the same products **9** and **10** in 35 and 62% yield, respectively (Scheme 4). The formation of **9** was explained by the Friedel–Crafts acylation of the benzene ring of **4** with β,β-dimethylacryloyl chloride. Also, the trimethylsilyl group of **4** was recognized to powerfully activate and direct the Friedel–Crafts

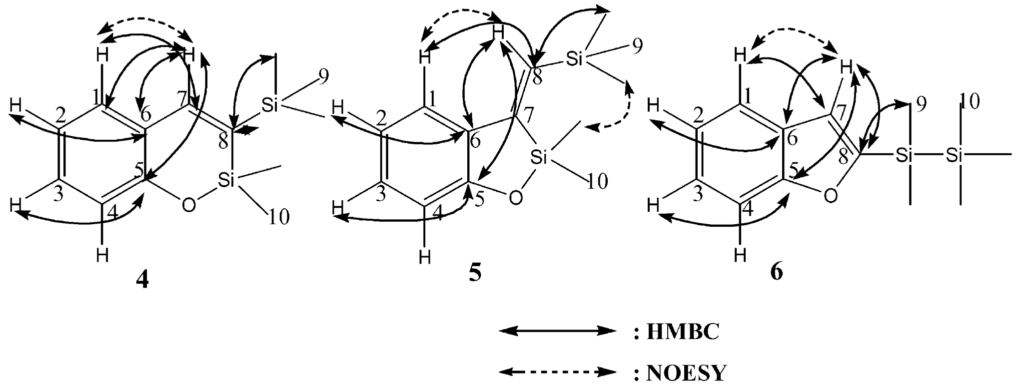
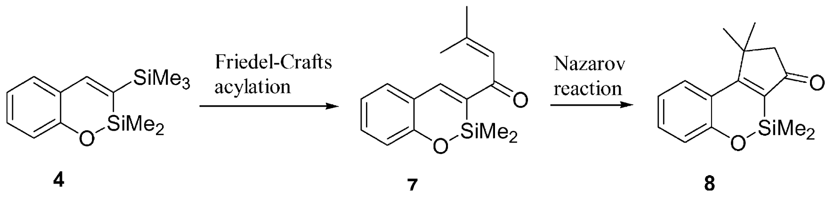
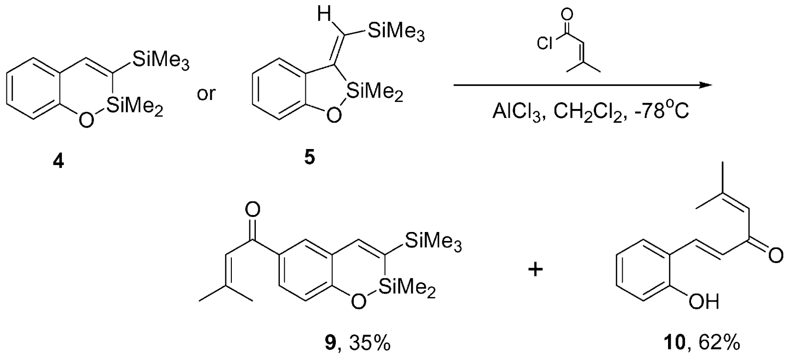


Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproducts **4**–**6**.



Scheme 3.

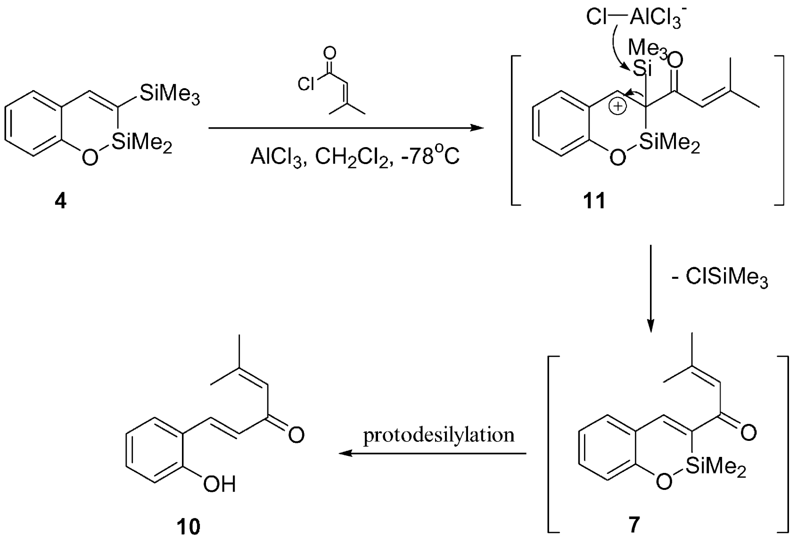


Scheme 4.

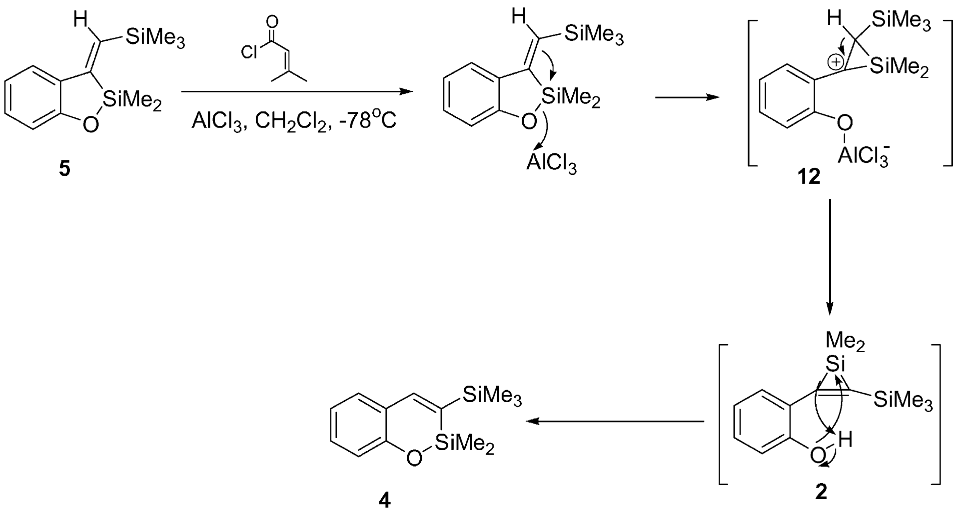
acylation of a vinyltrimethylsilane part in **4**, resulting in the acylium ion becoming bonded directly to the silicon-bearing carbon with subsequent loss of the trimethylsilyl group by the attack of chloride ion and then, **10** was obtained by the $AlCl_3$-catalyzed protodesilylation from the expected reaction product **7** (Scheme 5).

To explain the result that the same products **9** and **10** were obtained by the Friedel–Crafts acylation of **4** or **5** with β,β-dimethylacryloyl chloride, a possible mechanism for the ring expansion of **5** to **4** was proposed in Scheme 6. Flow of pi electrons from the carbon–carbon double bond to silicon atom in 5-membered ring of **5**, leaving a positive charge in the silacyclopropane ring, resulted in the formation of intermediate **12**, which undergo the elimination of H^+ to give **2**, which cyclized to **4** (path b) (Scheme 6).

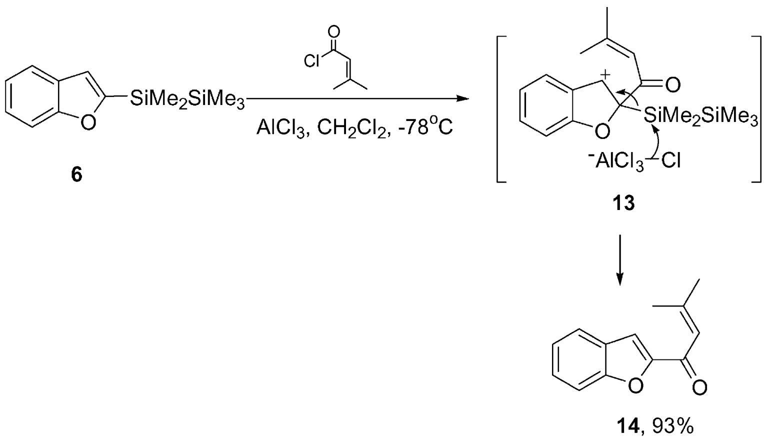
Reaction of **6** with 1 equiv. each of β,β-dimethylacryloyl chloride and aluminum chloride in anhydrous dichloromethane at −78°C for 1 h afforded **14** in 93% yield. The formation of **14** was explained by the attack of the acylium ion to carbon–carbon double bond in **6** followed by the attack of chloride ion to pentamethyldisilanyl group in the reaction intermediate **13** to give **14** (Scheme 7).



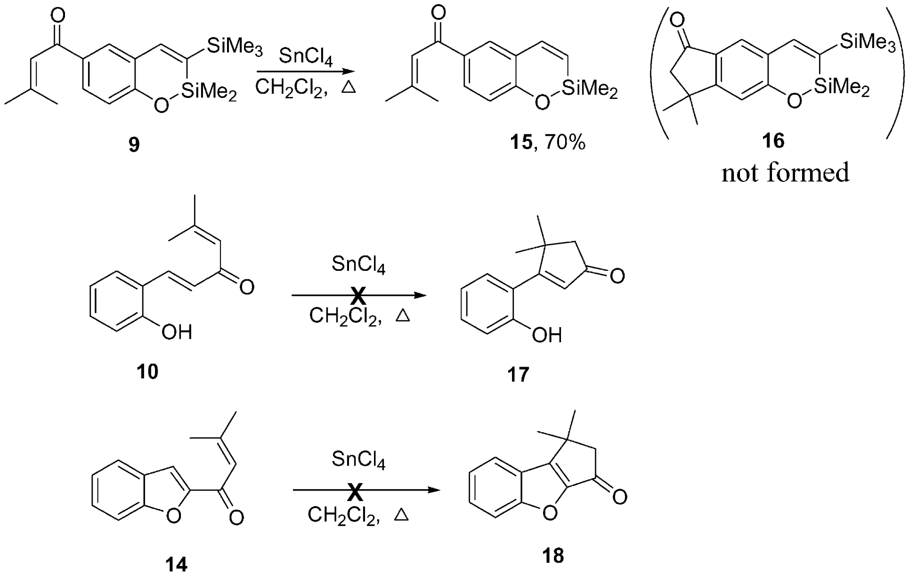
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

Treatment of **9** with stannic chloride in dichloromethane afforded the reduction product **15** in 70% yield as the only reaction product instead of the expected Nazarov annulation product **16**. For the case of **10** and **14**, some decomposition products of unknown structure were obtained but **17** and **18** were not obtained (Scheme 8).

In conclusion, the photo-induced intramolecular reaction of 1-*o*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne **1** in benzene afforded the novel intramolecular photoproducts **4** and **5**, via silacyclopropene intermediate **2**, and the cyclization product **6**. The formation of the photoproducts **4** and **5** was explained by the concerted intramolecular reactions as shown in Scheme 2. Vinyltrimethylsilanes **4** and **5** react with β,β-dimethylacryloyl chloride to give the same products **9** and **10** and for the case of **6**, treatment of β,β-dimethylacryloyl chloride gave **14**. Compound **5** can be converted into **4** in the Friedel–Crafts acylation condition. Reaction of **9** with stannic chloride gave the reduction product **15** instead of the expected Nazarov cyclization products **16**.

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