

Photoreactions of (2-substituted-phenyl)pentamethyldisilanes

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Abstract

Photolysis of (2-allyloxyphenyl)pentamethyldisilane **2a** in benzene provides a novel intramolecular photoproduct **5** via silatriene intermediate **3** in addition to **6** and **7** but the photoreaction of [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b** in benzene affords **6** and **12** instead of a expected intramolecular photoproduct.

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1. Introduction

Since the first reports on the unusual electronic spectra of aryl- and vinyl-substituted polysilanes by Sakurai and Kumada [1], Gilman et al. [2], and Hague and Prince [3] in 1964, the electronic properties [4–25] and photoreactions [26–45] of arylidisilanes have been extensively investigated. The photoreactions of phenyldisilanes in the presence of alcohols involve four types of reaction [46]: (a) formation of a silaethene [26], (b) formation of a silatriene via 1,3-silyl migration [27–40], (c) elimination of a silylene [27,43], and (d) nucleophilic cleavage of a Si–Si bond in the photoexcited state [44]. Although the photoreactions of arylidisilanes have been extensively studied, relatively little is known about the excited state behavior of *ortho*-substituted arylidisilanes.

Recently, I have found that the photolysis of *ortho*-substituted 1-aryl-2-(pentamethyldisilanyl)ethynes afforded novel intramolecular photoproducts via silacyclopene or 1-silaallene intermediates [47–58].

In connection with my ongoing studies for the utility of silacycloprenes, 1-silaallenes, silaethenes, and silatrienes as reaction intermediates in organic synthe-

sis of silicon-containing heterocyclic compounds, I was interested in the generation of silatriene intermediate through the photolysis of *ortho*-substituted arylidisilanes. And, I would like to report the photoreactions of (2-allyloxyphenyl)pentamethyldisilane **2a** and [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b**, since novel photoproducts from the intramolecular reaction of *ortho*-substituted group with the silatriene intermediate, which is formed from the radical scission of a silicon–silicon bond followed by migration of the resulting trimethylsilyl radical to the C₆ position of the benzene ring, are expected and I describe, in this paper, a detailed photochemical study of (2-substituted-phenyl)pentamethyldisilanes **2a** and **2b**.

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

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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).

2.2. Materials

o-Allyloxyiodobenzene **1a** [53] and *o*-(3,3-dimethyl-2-propenyloxy)iodo-benzene **1b** [54] were prepared as reported in the literature. Tetrahydrofuran used in the preparation of **2a** and **2b** was refluxed over sodium benzophenone and distilled under nitrogen. Benzene (HPLC grade) was distilled from CaH₂ before use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents were used for HPLC and UV absorption spectra.

2.3. Synthesis of (2-allyloxyphenyl)pentamethyldisilane **2a**

A solution of *o*-allyloxyiodobenzene (0.5 g, 1.92 mmol) in tetrahydrofuran (5 ml) was added to a solution of magnesium (60.8 mg, 2.5 mmol) in THF (15 ml) at room temperature under nitrogen atmosphere. Chloropentamethyldisilane (0.38 g, 2.31 mmol) was added dropwise to the resulting solution and the mixture was refluxed for 1.5 h. The reaction solution was filtered through Celite and then hydrolyzed with water (20 ml). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 15 ml). The organic layer and the extracts were combined, washed with water (20 ml), brine (20 ml) and dried (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (40/1, v/v) as an eluent gave **2a** (0.42 g, 83% yield) as a colorless oil; ¹H NMR (CDCl₃, 600 MHz) δ_H 0.12 (9H, s), 0.41 (6H, s), 4.61 (2H, dt, *J* = 5.5, 1.5 Hz), 5.34 (1H, dq, *J* = 11, 1.5 Hz), 5.44 (1H, dq, *J* = 17, 1.5 Hz), 6.14 (1H, m), 6.86 (1H, dd, *J* = 7.5, 1.5 Hz), 7.01 (1H, td, *J* = 7.5, 1.5 Hz), 7.36 (1H, td, *J* = 7.5, 1.5 Hz), 7.43 (1H, dd, *J* = 7.5, 1.5 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ_C -3.16, -1.40, 68.9, 110.3, 117.9, 120.9, 127.8, 130.4, 133.9, 135.4, 163.1; UV (CH₂Cl₂) λ_{max} 287, 280 nm; FT-IR (NaCl) 3063.7, 2950.8, 2894.2, 1586.1, 1437.2, 1245.6, 833.7 cm⁻¹; MS (70 eV) *m/z* 264 (M⁺); HRMS (M⁺) calcd for C₁₄H₂₄OSi₂ 264.1366, found 264.1378.

2.4. Synthesis of [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b**

A solution of *o*-(3,3-dimethyl-2-propenyloxy)iodobenzene **1b** (0.5 g, 1.74 mmol) in tetrahydrofuran (5 ml) was added to a solution of magnesium (55.9 mg, 2.3 mmol) in THF (15 ml) at room temperature under nitrogen atmosphere. Chloropentamethyldisilane (0.34 g, 2.09 mmol) was added dropwise to the resulting solution and the mixture was refluxed for 1.5 h. The reaction solution was filtered through Celite and then hydrolyzed with water (20 ml). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 15 ml). The organic layer and the extracts were combined, washed with water (20 ml), brine (20 ml) and dried (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (40/1, v/v) as an eluent gave **2b** (0.40 g, 79% yield) as a colorless oil; ¹H NMR (CDCl₃, 600 MHz) δ_H 0.058 (9H, s), 0.34 (6H, s), 1.76 (3H, s), 1.82 (3H, s), 4.54 (2H, d, *J* = 6.5 Hz), 5.51 (1H, m), 6.82 (1H, dd, *J* = 7.5, 1.5 Hz), 6.96 (1H, td, *J* = 7.5, 1.5 Hz), 7.32 (1H, td, *J* = 7.5, 1.5 Hz), 7.37 (1H, dd, *J* = 7.5, 1.5 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ_C -3.29, -1.55, 18.4, 25.9, 64.5, 109.9, 120.4, 120.5, 127.8, 130.3, 135.3, 137.1, 163.4; UV (CH₂Cl₂) λ_{max} 288, 281 nm; FT-IR (NaCl) 3063.4, 2949.9, 1585.0, 1436.9, 1245.1, 833.1, 777.0 cm⁻¹; MS (70 eV) *m/z* 292 (M⁺); HRMS (M⁺) calcd for C₁₆H₂₈OSi₂ 292.1679, found 292.1639.

2.5. Irradiation of (2-allyloxyphenyl)pentamethyldisilane **2a** in benzene

A solution (5 × 10⁻⁴ M) of (2-allyloxyphenyl)pentamethyldisilane **2a** (132 mg) 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 photoproducts **5**, **6**, and **7** were isolated in 33.5 mg (31% yield), 4.4 mg (3% yield), and 4.3 mg (4% yield) as colorless oils, respectively, in addition to 18% (23.8 mg) of the starting compound **2a** by column chromatography with *n*-hexane/ethyl acetate (20/1, v/v) as an eluent. **5**; UV (CH₂Cl₂) λ_{max} 300, 288 nm; FT-IR (NaCl) 3057.6, 2951.2, 2895.4, 1420.3, 1244.8, 1040.8, 832.8 cm⁻¹; MS (70 eV) *m/z* 264 (M⁺); HRMS (M⁺) calcd for C₁₄H₂₄OSi₂ 264.1366, found 264.1361. **6**; ¹H NMR (CDCl₃, 600 MHz) δ_H 0.059 (9H, s), 0.11 (9H, s), 0.33 (6H, s), 0.43 (6H, s), 6.70 (1H, dd, *J* = 7.5, 1.5 Hz), 6.92 (1H, td, *J* = 7.5, 1.5 Hz), 7.22 (1H, td, *J* = 7.5, 1.5 Hz), 7.32 (1H, dd, *J* = 7.5, 1.5 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ_C -3.10, -1.41, -1.39, 0.67, 116.1, 120.5, 129.1, 130.0, 135.7, 161.2; UV (CH₂Cl₂) λ_{max} 287, 281 nm; FT-IR (NaCl) 3076.6, 2951.5, 2894.2, 1583.9, 1467.7, 1247.0, 833.2, 795.9 cm⁻¹; MS (70 eV) *m/z* 354 (M⁺); HRMS (M⁺) calcd for C₁₆H₃₄OSi₄ 354.1687,

found 354.1679. **7**; ^1H NMR (CDCl_3 , 600 MHz) δ_{H} 0.096 (9H, s), 0.38 (6H, s), 3.44 (2H, dt, $J=6$, 1.5 Hz), 5.17 (1H, s), 5.23 (1H, dq, $J=11.5$, 1.5 Hz), 5.26 (1H, m), 6.05 (1H, m), 6.93 (1H, t, $J=7.5$ Hz), 7.13 (1H, dd, $J=7.5$, 1.5 Hz), 7.28 (1H, dd, $J=7.5$, 1.5 Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ_{C} -3.30, -1.58, 36.2, 117.2, 121.0, 123.2, 126.1, 131.6, 134.2, 136.5, 159.4; UV (CH_2Cl_2) λ_{max} 286, 280 nm; FT-IR (NaCl) 3536.9, 3050.3, 2948.8, 2893.5, 1574.6, 1423.3, 1242.4, 833.9 cm^{-1} ; MS (70 eV) m/z 264 (M^+); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{24}\text{OSi}_2$ 264.1366, found 264.1336.

2.6. Irradiation of [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b** in benzene

A solution (5×10^{-4} M) of [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b** (146 mg) 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 photoproducts **6** and **12** were isolated in 8.5 mg (6% yield) and 10.5 mg (9% yield) as colorless oils, in addition to 20% (29.2 mg) of the starting material **2b** by column chromatography with *n*-hexane as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (20/1, v/v) as an eluent. **12**; ^1H NMR (CDCl_3 , 600 MHz) δ_{H} 0.063 (9H, s), 0.35 (6H, s), 1.80 (3H, s), 1.82 (3H, s), 3.35 (2H, d, $J=7$ Hz), 5.28 (1H, s), 5.31 (1H, m), 6.87 (1H, t, $J=7.5$ Hz), 7.10 (1H, dd, $J=7.5$, 1.5 Hz), 7.22 (1H, dd, $J=7.5$, 1.5 Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ_{C} -3.31, -1.62, 18.1, 25.9, 39.0, 115.9, 120.6, 121.8, 127.7, 131.0, 133.6, 135.8, 159.4; UV (CH_2Cl_2) λ_{max} 288, 279 nm; FT-IR (NaCl) 3465.4, 3054.1, 2951.7, 1594.8, 1422.2, 1244.9, 834.1 cm^{-1} ; MS (70 eV) m/z 292 (M^+); HRMS (M^+) calcd for $\text{C}_{16}\text{H}_{28}\text{OSi}_2$ 292.1679, found 292.1672.

3. Results and discussion

The starting (2-allyloxyphenyl)pentamethyldisilane **2a** or [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b** were prepared by the reaction of pentamethyldisilanyl chloride with 2-allyloxyphenyl magnesium iodide

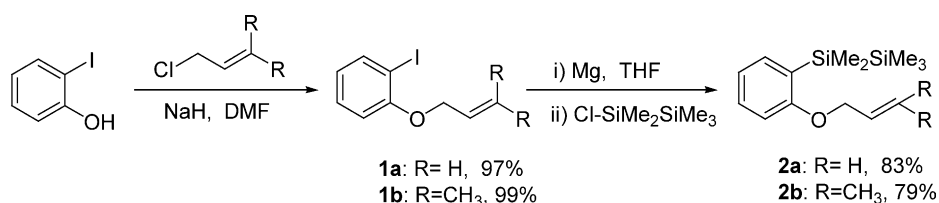
or 2-(3,3-dimethyl-2-propenyloxy)phenylmagnesium iodide in tetrahydrofuran (Scheme 1).

3.1. Photoreactions of (2-allyloxyphenyl)pentamethyldisilane **2a**

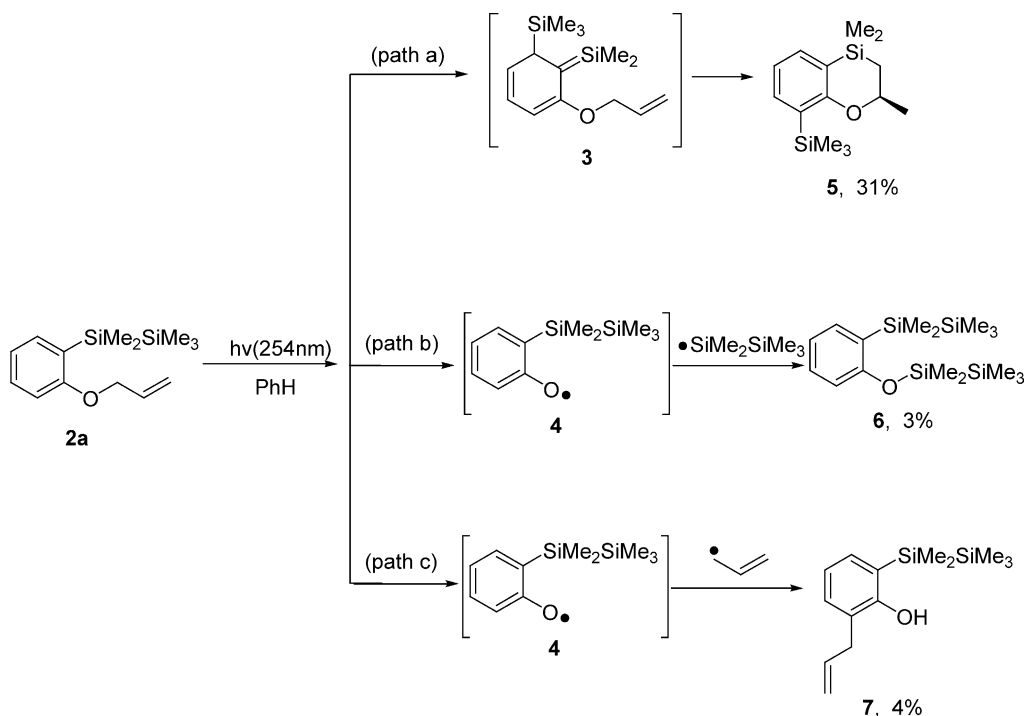
To investigate whether or not the allyloxy group as *ortho* substituent in **2a** reacts intramolecularly with silatriene moiety in **3**, the photolysis of **2a** was performed.

Irradiation of **2a** in deaerated benzene with 254 nm UV light afforded a novel intramolecular photoproduct **5** (31% yield) in addition to **6** and **7** (3 and 4% yield, respectively) along with some decomposition products of unknown structure as shown in Scheme 2, when 82% of **2a** was photolyzed. The formation of a novel photoproduct **5** can best be explained in terms of the initial formation of silatriene intermediate **3** arising from 1,3-migration of trimethylsilyl radical, which is formed via homolytic cleavage of silicon-silicon bond in the photoexcited state of **2a** to the C_6 position of benzene ring (Scheme 3). The intramolecular reaction to form a oxirane ring in this silatriene **3** resulted in the formation of the compound **8** accompanied by a 1,4-trimethylsilyl shift and aromatization to give the compound **5**. Indeed, it is well known that the silatriene intermediate like **3** can be produced in the photolysis of arylsilylanes [27–40]. For example, Kira et al. [46] found that the photolysis of 4-(trifluoromethyl)phenylpentamethyldisilane in the presence of alcohol gives rise to four types of reaction via silaethene, silatriene, and silylene intermediates and the yield of the photoproducts via silatriene intermediate increases with increasing the electron-donating ability of the substituent and with decreasing the polarity of the solvent. No product derived from the intramolecular reaction of other possible intermediates except silatriene intermediate **3** with *ortho*-substituted allyloxy group in **2a** was detected in the photolysis of **2a**.

One might consider the possibility that the photoproduct **5** could be produced by a stepwise process involving the formation of the compound **10** arising from the recombination of trimethylsilyl radical, which is formed via homolytic cleavage of silicon-silicon bond in the photoexcited state of **2a** and phenoxy radical, which is formed via homolytic cleavage of oxygen-carbon bond in *ortho*-substituted allyloxy group in **2a**, followed by the ring formation and 1,5-trimethylsilyl shift to the C_3 position of benzene ring (Scheme 4). However, the formation of the compound **10** and 1,5-trimethylsilyl shift in the formation of the compound **5** from the compound **11** as



Scheme 1.

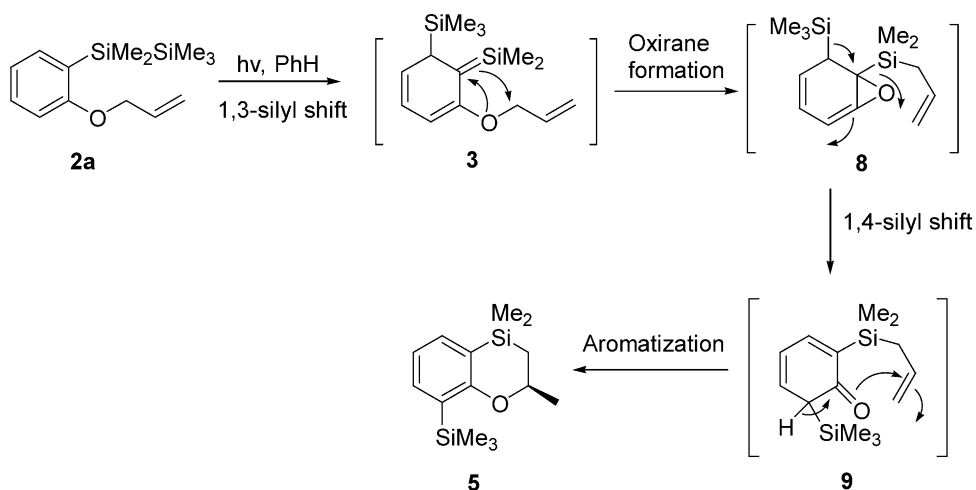


Scheme 2.

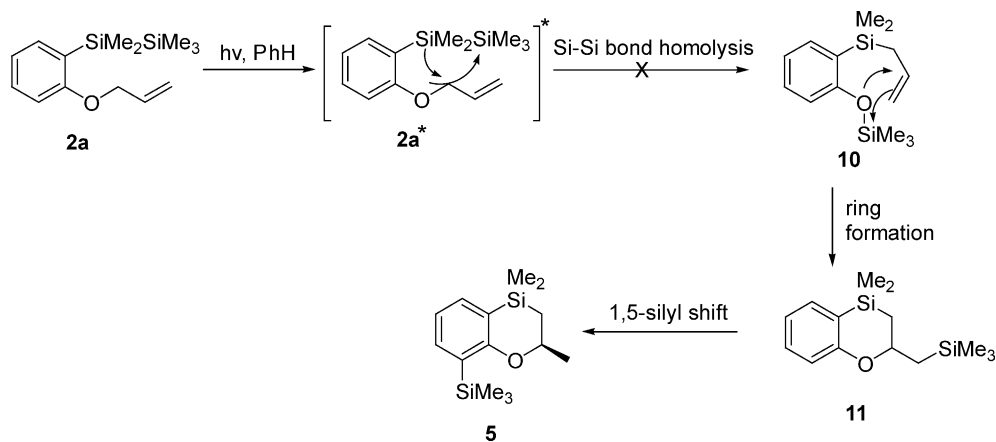
shown in Scheme 4 are not reasonable and the compounds **10** and **11** were not detected in the photolysis mixture by either spectrometric analysis or TLC analysis. Compound **6** was probably formed from the recombination of the radical **4**, which is formed by the homolysis of oxygen-carbon bond in allyloxy group in the photoexcited state of **2a** and pentamethyldisilanyl radical, which is formed by the homolysis of silicon-carbon bond in the photoexcited state of **2a** and compound **7** was probably formed from 1,3-migration of allyl radical, which is formed via homolytic cleavage of oxygen-carbon bond to the C₃ position of

benzene ring although I could not obtain any evidence for the formation of radical **4**, pentamethyldisilanyl radical, and allyl radical in the photolysis of **2a** in benzene.

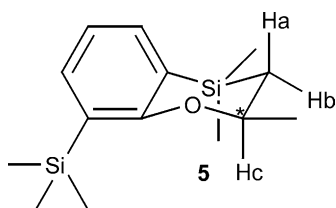
The structure of the photoproduct **5** was determined by various physical methods, such as ¹H NMR, ¹³C NMR, UV, FT-IR, and high resolution mass spectrometry. The two methylene protons (Ha and Hb) located on a carbon adjacent to a stereocenter in **5** is diastereotopic, and they not only have different chemical shifts (3.30 and 2.80 ppm, respectively, in ¹H NMR) but they also show splitting interactions (²J_{Ha-Hb,gem} = 15.0 Hz, ³J_{Ha-Hc,vic} = 8.5 Hz,



Scheme 3.



$^3J_{\text{Hb-Hc,vic}} = 7.5 \text{ Hz}$). The splitting patterns for the protons (Ha and Hb) in **5** appear as two doublet of doublets (dd).



The structure of the photoproduct **5** was also determined by various spectroscopic methods including ^1H - ^1H and ^1H - ^{13}C correlation spectroscopy (COSY), HMBC, nuclear overhauser and exchange spectroscopy (NOESY) (Table 1). The ^1H - ^1H and ^1H - ^{13}C correlation spectroscopy (COSY) spectra of **5** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **5**, I 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

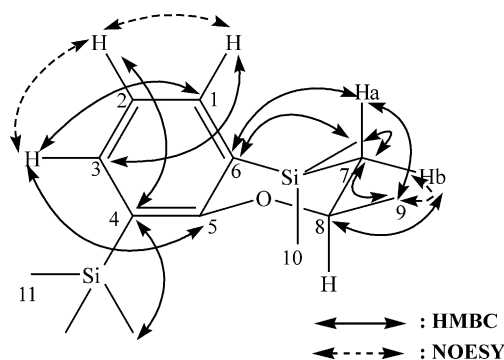


Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **5**.

HMBC spectrum of **5** was taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(7) and C(10) and the quaternary carbon C(6) in **5** showed the connectivity of the carbon C(6) to the dimethylsilyl group in **5**. In the same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C(2) and C(11)

Table 1
 ^1H 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}	$J_{\text{H-H}}$ (Hz)	HMBC ^e
1	125.4	d	7.16	1H	dd	7.0 ($J_{1\text{H}-2\text{H}}$), 1.0 ($J_{1\text{H}-3\text{H}}$)	H3
2	118.9	d	6.84	1H	t	7.0 ($J_{2\text{H}-1\text{H}}$), 7.0 ($J_{2\text{H}-3\text{H}}$)	
3	133.3	d	7.16	1H	dd	7.0 ($J_{3\text{H}-2\text{H}}$), 1.0 ($J_{3\text{H}-1\text{H}}$)	H1
4	120.0	s					H2, H11
5	164.7	s					H1, H3
6	125.7	s					H2, H10, H7a, H7b
7a	37.3	t	3.30	1H	dd	15.0 ($J_{7\text{aH}-7\text{bH}}$), 8.5 ($J_{7\text{aH}-8\text{H}}$)	H8, H9, H10
7b	37.3	t	2.80	1H	dd	15.0 ($J_{7\text{bH}-7\text{aH}}$), 7.5 ($J_{7\text{bH}-8\text{H}}$)	H8, H9, H10
8	78.7	d	4.88	1H	m		H7a, H7b
9	22.2	q	1.46	3H	d	6.5 ($J_{9\text{H}-8\text{H}}$)	H7a, H7b
10	-3.79	q	0.35	3H	s		
11	-1.71	q	0.10	3H	s		

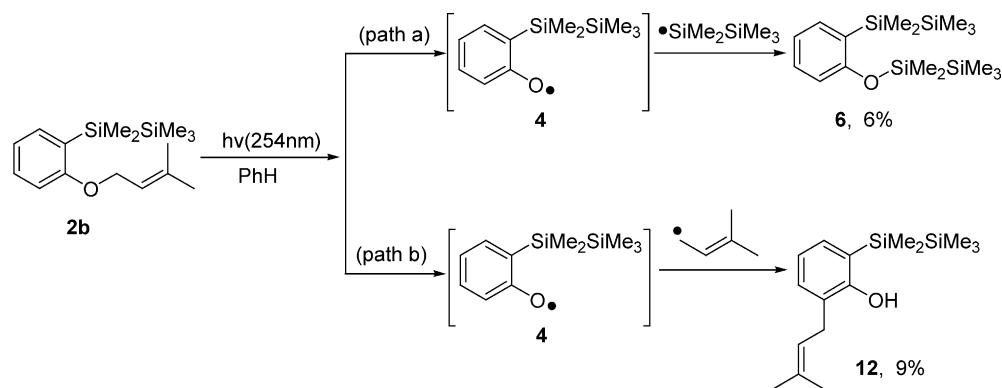
^a All these assignments were confirmed by ^1H - ^1H and ^1H - ^{13}C COSY and NOESY, HMBC spectra.

^b Multiplicities were determined by DEPT spectrum.

^c Integrated intensity.

^d Multiplicities.

^e Protons correlated to carbon resonances in ^{13}C column.



Scheme 5.

and the quaternary carbon C(4) in **5** showed the connectivity of the carbon C(4) to the trimethylsilyl group in **5**. The 3D-structure of **5** was determined by a nuclear overhauser and exchange spectroscopy (NOESY). In particular, the presence of the cross-peak between the protons of C(7) and the protons of C(9) in **5** showed the close proximity of the protons of C(7) to the protons of C(9) indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **5** was unambiguously established as shown in Fig. 1.

To make the proposed mechanism as shown in Scheme 3 reliable and obtain the products formed from the reaction of the proposed reaction intermediates **3**, **8**, or **9** with trapping agents, the photolysis of **2a** in the presence of trapping agents such as water or methanol was carried out but the expected photoproducts formed from the reaction of the proposed intermediates **3**, **8**, or **9** with water or methanol except the photoproducts **5**, **6**, and **7** were not obtained.

3.2. Photoreactions of [2-(3,3-dimethyl-2-propenyloxy)phenyl]pentamethyldisilane **2b**

To investigate the reactivity of 3,3-dimethyl-2-propenyloxy group instead of allyloxy group as *ortho* substituent to phenylpentamethyldisilane, the photolysis of **2b** was carried out.

Irradiation of **2b** in deaerated benzene with 254 nm UV light afforded two photoproduct **6** and **12** (6 and 9% yield, respectively) along with some decomposition products of unknown structure as shown in Scheme 5, when 80% of **2b** was photolyzed but the expected intramolecular photoproduct like **5** was not obtained. Compound **12** was probably formed from 1,3-migration of 3,3-dimethyl-2-propenyl radical, which is formed via homolytic cleavage of oxygen–carbon bond in 3,3-dimethyl-2-propenyloxy group in the photoexcited state of **2b** to the C₃ position of benzene ring. The structure of photoproduct **12** could be distinguished from that of Claisen rearrangement product on the basis of the ¹H NMR spectrum of **12**. The doublet from the benzylic protons of **12** was observed at 3.35 ppm, while Claisen rearrangement product does not have the benzylic protons, indicating that Claisen

rearrangement did not occur in the photolysis of **2a** or **2b** in benzene.

In conclusion, the photolysis of **2a** in benzene provided a novel intramolecular photoproduct **5** in addition to **6** and **7** but the expected water or methanol addition photoproduct via silatriene intermediate **3** were not obtained. Irradiation of **2b** in benzene gave two photoproducts **6** and **12** but the expected intramolecular photoproduct like **5** was not obtained in this case.

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