Photoreactions of 2-(Pentamethyldisilanyloxy)phenylpentamethyldisilane

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Photolysis of 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane **1** in methanol provides five photo-products **3, 4, 5, 6,** and **7.** Compounds **3** and **4** were probably formed from the methanol addition reactions of silene intermediate **2** and the formation of **5, 6,** and **7** can best be explained by the nucleophilic attack of methanol to silicon atom in pentamethyldisilanyloxy or pentamethyldisilanyl group of the photoexcited state of **1.** Irradiation of **1** in *n*-hexane gives a photoproduct **6** *via* silyl radical intermediate **8** and a novel intramolecular cyclization photoproduct **11** *via* silene **9** and silyl radical intermediate **10.** Irradiation of **1** in deaerated methylene chloride in the presence of acetone affords a novel photoproduct **11** and phenol **7** but the expected photoproducts from the reaction of the silene intermediate with acetone were not obtained.

Key Words : 2-(Pentamethyldisilanyloxy)phenylpentamethyldisilane, Silene

Introduction

Silenes that contain the Si=C moiety are highly reactive intermediates which formed from the thermal and photo-chemical reactions of the various organosilicon compounds.[1-7] One of the silene formation reactions is the photolysis of the aryldisilane compounds which is originated from the first report on the photolysis of phenylpentamethyldisilane and (*p*-tolyl)pentamethyldisilane in forming the silene inter-mediates by Ishikawa *et al.*[8] in 1975. It is well known that the photolysis of substituted phenylpentamethyldisilanes[9] has four reaction pathways, as shown in Scheme 1: (path a) formation of a silene compound and a trimethylsilane, (path b) formation of a silatriene compound arising from 1,3-shift of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon bond to the C₆ position of ben-zene ring, (path c) formation of a trimethylsilyl compound *via* elimination of a silylene, (path d) formation of a direct solvolysis compound accompanied by the formation of

trimethylalkoxysilane and trimethylsilane.

All silenes thus formed react with various trapping agents, such as alcohols,[10-17] carbonyl compounds,[18-21] alkenes.[22-29] and alkynes[30] to give the addition products and in the absence of such trapping agents, dimerization products of silene intermediates were obtained.[31,32] The photolysis of the aromatic compounds having two pentamethyldisilanyl groups, such as 1,2-, 1,3-, 1,4-bis(pentamethyldisilanyl)-benzenes.[33] 1,4-, 1,5-bis(pentamethyldisilanyl)naphthal-enes[34] also affords the silene intermediates but in the case of 4,4'-bis(pentamethyldisilanyl)biphenyl,[35] the photoproducts from the silene intermediate were not obtained.

In connection with the photoreactions of aryldisilanes, the author very recently reported on the photoinduced intra-molecular reaction of (2-substituted-phenyl)pentamethyl-disilanes. as an *ortho*-substituted aryldisilanes affording a novel intramolecular photoproduct *via* silene intermediate arising from 1,3-migration of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon bond.[36,37] However, relatively little is known about the photolysis of the compounds having the two pentamethyldisilanyl groups at carbon and oxygen atoms. To learn about the photo-reactions of these compounds, I have now investigated the photoreactions of 2-(pentamethyldisilanyloxy)phenylpenta-methyldisilane **1** since novel photoproducts from the intra-molecular reaction between two *ortho*-pentamethyldisilanyl groups are expected. In this article, I would like to report the detailed photochemical study of 2-(pentamethyldisilanyl-oxy)phenylpentamethyldisilane **1.**

Experimental

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 spectro-meters with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent CDCl₃. UV
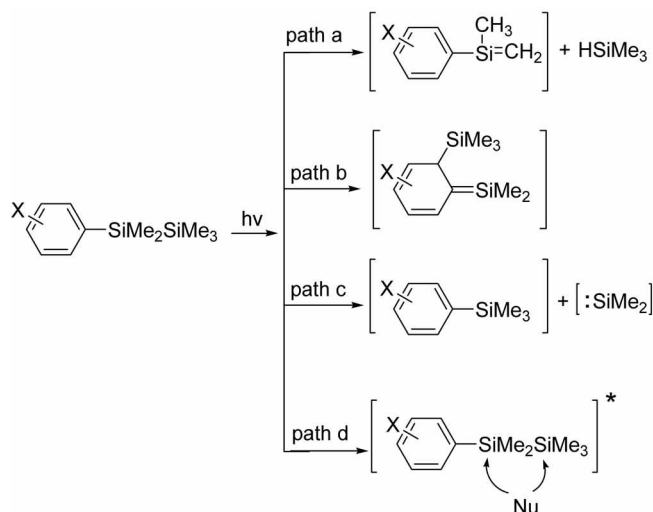
Scheme 1

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 (230-400 mesh ASTM).

Materials. Tetrahydrofuran was refluxed over sodium benzophenone and distilled under nitrogen. Methanol (HPLC grade) and n-hexane(HPLC grade) were distilled from CaH_2 before use. Methylene chloride (HPLC grade) was dried with P_2O_5 followed by fractional distillation prior to use. Acetone was dried with K_2CO_3 followed by fractional distillation immediately prior to 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.

Synthesis of 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane 1. Triethylamine (0.76 mL, 5.45 mmol) was added to a solution of 2-iodophenol (1 g, 4.54 mmol) in tetrahydrofuran (30 mL) at room temperature under nitrogen atmosphere. Chloropentamethyldisilane (1.05 mL, 5.45 mmol) was added dropwisely to the resulting solution and the mixture was refluxed for 3 h. The reaction mixture was filtered with celite, and concentrated *in vacuo*. To this reaction residue, THF (30 mL) was added. This resulting reaction solution was added to Mg (0.33 g, 13.6 mmol) at room temperature under nitrogen atmosphere. Chloropentamethyldisilane (1.05 mL, 5.45 mmol) was added dropwisely to the resulting solution and the mixture was refluxed for 0.5 h. The reaction mixture was filtered with celite, and concentrated *in vacuo*. Water (30 mL) was added to the solution and extracted with ethyl acetate (3 × 15 mL). The combined ethyl acetate solution was washed with water (20 mL), brine (20 mL) and dried ($MgSO_4$). The solvent was evaporated *in vacuo* to give the crude product. Flash column chromatography with n-hexane/ethyl acetate (100/1, v/v) as an eluent gave **1** (1.16 g, 72% yield) as a colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.043 (9H, s), 0.095 (9H, s), 0.32 (6H, s), 0.42 (6H, s), 6.69 (1H, d, J = 8.1 Hz), 6.90 (1H, td, J = 7.2, 0.6 Hz), 7.21 (1H, td, J = 7.8, 1.8 Hz), 7.30 (1H, dd, J = 7.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −3.13, −1.41, −1.38, 0.68, 116.1, 120.5, 129.1, 130.1, 135.7, 161.2; UV (CH_2Cl_2) λ_{max} 287, 281 nm; FT-IR (NaCl) 3062.4, 2951.0, 2894.5, 1583.8, 1467.5, 1247.4, 832.7 cm^{-1}; MS (70 eV) m/z 354 (M$^+$); MS m/z (%) 354 (M$^+$, 0.1), 281 (33), 193 (100), 133 (78), 74 (98); HRMS (M$^+$) calcd for $C_{16}H_{34}OSi_4$

354.1687, found 354.1632.

Irradiation of 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane 1 in methanol. A solution (5 × 10^{-4} M) of 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane 1 (177 mg) in methanol (1 L) was deaerated by nitrogen purging for 1 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 50 min, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts **3**, **4**, **5**, **6**, and **7** were isolated in (11.5 mg, 6% yield), (15.4 mg, 8% yield), (10.9 mg, 7% yield), (40.9 mg, 29% yield), and (11.8 mg, 25% yield), respectively, in addition to 6% (10.6 mg) of the starting material **1** by column chromatography with n-hexane/ethyl acetate (60/1, v/v) as an eluent followed by normal phase HPLC using n-hexane/ethyl acetate (20/1, v/v) as an eluent.

3: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.11 (9H, s), 0.24 (9H, s), 0.36 (6H, s), 0.41 (6H, s), 3.53 (3H, s), 6.72 (1H, d, J = 7.8 Hz), 7.42 (1H, dd, J = 7.8, 1.8 Hz), 7.61 (1H, d, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −2.36, −1.73, −0.66, 0.43, 51.1, 116.1, 120.5, 130.9, 136.6, 140.9, 162.2; UV (CH_2Cl_2) λ_{max} 285, 279 nm; FT-IR (NaCl) 3061.9, 2954.9, 2896.2, 1586.5, 1468.8, 1269.2, 1090.8, 795.7 cm^{-1}; MS (70 eV) m/z 384 (M$^+$); MS m/z (%) 384 (M$^+$, 0.1), 316 (100), 282 (74), 229 (53), 195 (38), 132 (15), 73 (51); HRMS (M$^+$) calcd for $C_{17}H_{36}O_2Si_4$ 384.1792, found 384.1772.

4: FT-IR (NaCl) 3030.2, 2954.0, 2896.9, 2826.7, 1607.7, 1247.0, 1202.5, 1098.2, 835.9 cm^{-1}; MS (70 eV) m/z 386 (M$^+$); MS m/z (%) 386 (M$^+$, 16), 369 (10), 329 (23), 311 (100), 254 (80), 238 (12), 148 (20); HRMS (M$^+$) calcd for $C_{17}H_{38}O_2Si_4$ 386.1949, found 386.1923.

5: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.096 (9H, s), 0.36 (6H, s), 0.41 (6H, s), 3.51 (3H, s), 6.73 (1H, d, J = 8.1 Hz), 6.95 (1H, td, J = 7.2, 0.9 Hz), 7.27 (1H, td, J = 7.8, 1.8 Hz), 7.46 (1H, dd, J = 7.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −1.92, −1.51, 0.32, 50.8, 116.4, 120.4, 127.4, 130.9, 135.5, 160.9; UV (CH_2Cl_2) λ_{max} 284, 278 nm; FT-IR (NaCl) 3062.4, 2954.6, 2896.4, 1586.9, 1469.3, 1248.5, 833.7, 795.5 cm^{-1}; MS (70 eV) m/z 312 (M$^+$); MS m/z (%) 312 (M$^+$, 0.2), 283 (65), 268 (23), 205 (48), 149 (55), 131 (15), 73(100); HRMS (M$^+$) calcd for $C_{14}H_{28}O_2Si_3$ 312.1397, found 312.1390.

6: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 0.088 (9H, s), 0.32 (6H, d, J = 3.9 Hz), 0.41 (6H, s), 4.41 (1H, septet, J = 3.9 Hz), 6.74 (1H, d, J = 8.1 Hz), 6.93 (1H, td, J = 7.2, 0.9 Hz), 7.26 (1H, td, J = 7.8, 1.8 Hz), 7.39 (1H, dd, J = 7.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C −3.65, −1.75, 0.60, 116.9, 120.9, 127.8, 131.0, 136.0, 161.5; UV (CH_2Cl_2) λ_{max} 285, 279 nm; FT-IR (NaCl) 3063.2, 2953.7, 2896.2, 2119.4 (Si-H stretching band), 1585.9, 1468.3, 1247.1, 917.6, 889.5, 834.3 cm^{-1}; MS (70 eV) m/z 282 (M$^+$); MS m/z (%) 282 (M$^+$, 7), 281 (28), 268 (40), 212 (100), 197 (28), 74 (13); HRMS (M$^+$) calcd for $C_{13}H_{26}OSi_3$ 282.1291, found 282.1231.

Irradiation of 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane 1 in n-hexane. A solution (5 × 10^{-4} M) of 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane 1 (177 mg) in n-hexane (1 L) was deaerated by
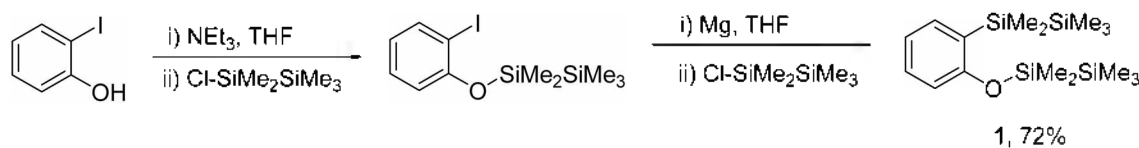
Scheme 2

nitrogen purging for 1 h and irradiated in a Rayonet photo-chemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 10 min, the resulting photo-reaction mixture was concentrated *in vacuo*. The photo-products **6** and **11** were isolated in (36.7 mg, 26% yield) and (17.7 mg, 17% yield), respectively, in addition to 19% (33.6 mg) of the starting material **1** by column chromatography with *n*-hexane/ethyl acetate (100/1. v/v) as an eluent follow-ed by normal phase HPLC using *n*-hexane/ethyl acetate (40/1, v/v) as an eluent.

11: UV (CH$_2$Cl$_2$) λ_{max} 285, 279 nm; FT-IR (NaCl) 3061.6, 2955.4. 2926.6. 1586.5. 1468.8. 1247.7. 833.5, 793.4 cm^{-1}: MS (70 eV) *m/z* 208 (M$^-$); MS m/z (%) 208 (M$^+$. 1), 193 (40), 150 (30), 132 (28). 118 (20). 91 (18). 73 (100); HRMS (M$^+$) calcd for C$_{10}$H$_{16}$OSi$_2$ 208.0740, found 208.0710.

Irradiation of 2-(pentamethyldisilanyloxy)phenyl-pentamethyldisilane 1 in methylene chloride in the presence of acetone. A solution (5 × 10^{-4} M) of 2-(penta-methyldisilanyloxy)phenylpentamethyldisilane **1** (177 mg) and acetone (10 mL) in methylene chloride (1 L) was

deaerated by nitrogen purging for 1 h, and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 10 min. the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts **7** and **11** were isolated in (14.6 mg, 31% yield) and (21.8 mg, 21% yield). respectively, in addition to 17% (30.1 mg) of the starting material **1** by column chromatography with *n*-hexane/ethyl acetate (60/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (20/1, v/v) as an eluent.

Results and Discussion

The starting 2-(pentamethyldisilanyloxy)phenylpenta-methyldisilane **1** was prepared by the reaction of chloro-pentamethyldisilane with 2-(pentamethyldisilanyloxy)phen-ylmagnesium iodide in tetrahydrofuran (Scheme 2).

Photoreaction of 2-(pentamethyldisilanyloxy)phenyl-pentamethyl disilane 1 in methanol. Irradiation of **1** in deaerated methanol with 300 nm UV light afforded five
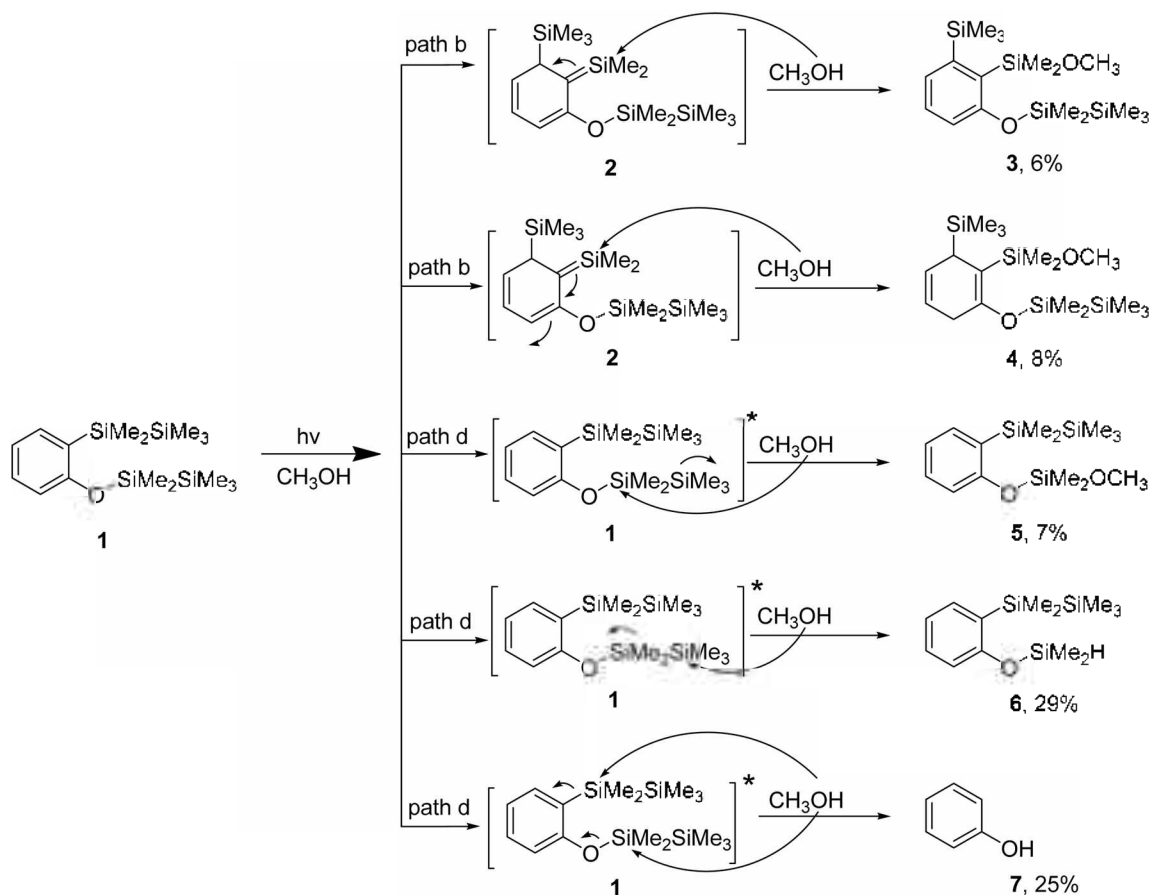
Scheme 3

compounds **3** (6% yield), **4** (8% yield), **5** (7% yield), **6** (29% yield), and **7** (25% yield) along with some decomposition products of unknown structure as shown in Scheme 3, when 94% of **1** was photolyzed. The formation of a photoproduct **3** or a non-aromatic photoproduct **4** can best be explained in terms of the initial formation of silene intermediate **2** arising from 1,3-migration of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon bond in the pentamethyldisilanyl group of the photoexcited state of **1** to the C_6 position of benzene ring (path b, Scheme 3). The intermolecular reaction of silene **2** and methanol resulted in the formation of the compounds **3** and **4**. Compounds **5** and **6** were probably formed from the nucleophilic attack at α or β silicon atom of pentamethyldisilanyloxy group in the photoexcited state of **1** by methanol. The formation of phenol **7** was explained by two α silicon atom attacks of both pentamethyldisilanyl groups in the photoexcited state of **1** by methanol (path d, Scheme 3). The structures of the photoproducts **3**, **5**, **6**, and **7** were determined by various physical methods, such as ^{1}H NMR, ^{13}C NMR, UV, FT-IR, and high resolution mass spectrometry. The photoproducts **3** and **5** can be distinguished by the proton resonances in the phenyl region and the number of alkylsilyl groups. The ^{1}H NMR spectrum of **3** shows the 1,2,3-trisubstituted benzene structure and four alkylsilyl groups, but **5** shows the 1,2-disubstituted benzene structure and three alkylsilyl groups. The ^{1}H NMR and IR absorption spectra of **6** show a septet resonance at δ4.41 and a characteristic absorption at 2119.4 cm^{-1}, respectively, due to a Si-H proton and a Si-H stretching mode in the dimethylsilyl group of **6**. The structure of the photoproduct **4** was 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, and 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** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **4**, I have been able to identify the pairs of carbons and directly bonded
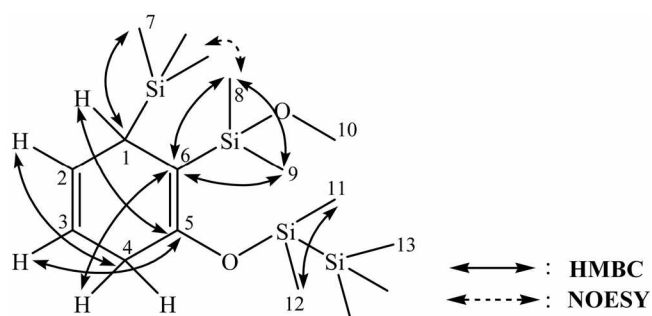

Figure 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **4**.

protons as shown in Table 1. In order to determine the location of the quaternary carbons, the HMBC spectrum of **4** was taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(7) and the carbon C(1), the proton of C(1) and the carbon C(7) in **4** showed the connectivity of the carbon C(1) to the trimethylsilyl group in **4**. In the same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C(8) and C(9) and the quaternary carbon C(6) in **4** showed the connectivity of the carbon C(6) to the methoxydimethylsilyl group in **4**. The two methyl protons of carbon C(8) and carbon C(9) located on a silicon atom adjacent to a stereocenter (carbon 1) in **4** are diastereotopic, and they not only have different chemical shifts (0.19 and 0.23 ppm, respectively, in ^{1}H NMR) but they also show the presence of the cross-peaks due to the vicinal coupling between the protons of C(8) and the carbon C(9) in HMBC spectrum of **4**. In the same way, the carbon C(11) and carbon C(12) in **4** are diastereotopic, and have different ^{1}H and ^{13}C chemical shifts. The 3D-structure of **4** 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(8) in **4** showed the close proximity of the protons of C(7) to the protons of C(8) indicating that these protons are located on the same side of the molecule. Thus,

Table 1. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), and HMBC data for photoproduct **4** in CDCl$_3$[a]

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	$J_{H\text{-}H}$ (Hz)	HMBC[e]
1	32.7	d	2.48	1H	m		H7
2	130.2	d	5.84	1H	ddt	9.3 ($J_{2H\text{-}3H}$), 5.1 ($J_{2H\text{-}1H}$), 2.2 ($J_{2H\text{-}4H}$)	H4
3	119.5	d	5.53	1H	dt	9.3 ($J_{3H\text{-}2H}$), 3.6 ($J_{3H\text{-}4H}$)	H1
4	33.2	t	2.73	2H	m		H2
5	153.7	s					H1, H3, H4
6	121.3	s					H4, H8, H9
7	−1.97	q	0.004	3H	s		H1
8	−1.00	q	0.19	3H	s		
9	−0.48	q	0.23	3H	s		H8
10	50.2	q	3.40	3H	s		
11	0.96	q	0.29	3H	s		H12
12	1.57	q	0.30	3H	s		
13	−1.72	q	0.112	3H	s		

[a]All these assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{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.

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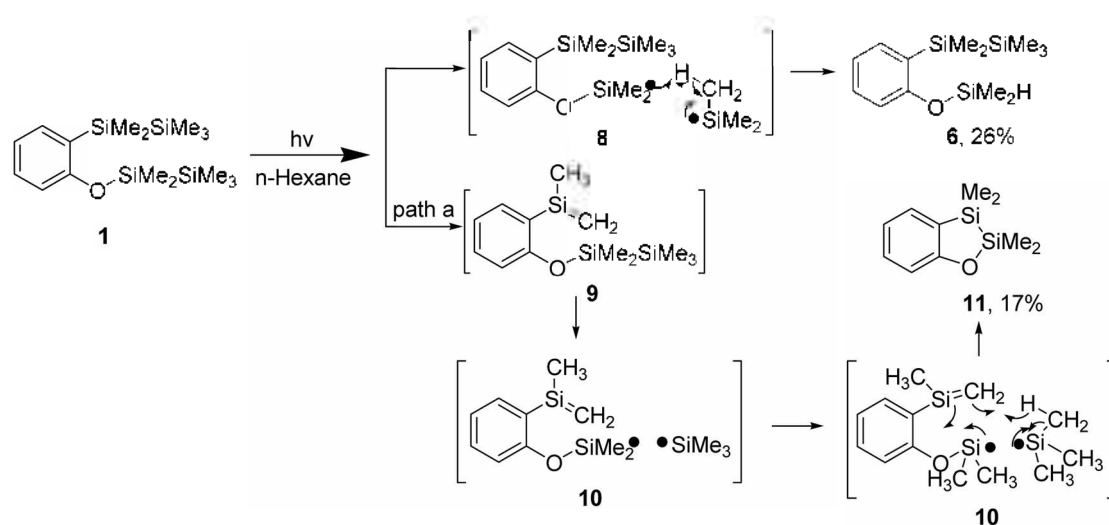
Scheme 4

the skeletal structure of **4** was unambiguously established as shown in Figure 1.

Photoreaction of 2-(pentamethyldisilanyloxy)phenyl-pentamethyl disilane 1 in *n*-hexane. Irradiation of **1** in deaerated n-hexane with 300 nm UV light afforded a novel intramolecular photoproduct **11** (17% yield) in addition to **6** (26% yield) along with some decomposition products of unknown structure as shown in Scheme 4, when 81% of **1** was photolyzed. The formation of a novel photoproduct **11** can best be explained in terms of the initial formation of silene intermediate **9** *via* the elimination of trimethylsilane (path a) and then the homolytic cleavage of silicon-silicon bond of pentamethyldisilanyloxy group in the photoexcited state of **9** to form a silyl radical intermediate **10** (Scheme 4). The intramolecular reaction to form silicon-silicon bond in **10** *via* the elimination of dimethylsilene resulted in the formation of the compound **11**. The photoproduct **6** in *n*-hexane solvent was probably formed through silyl radical intermediate **8** which is formed *via* homolytic cleavage of silicon-silicon bond of pentamethyldisilanyloxy group in the photoexcited state of **1** (Scheme 4). The hydrogen abstraction of a silyl radical intermediate **8** in *n*-hexane solvent cage accompanied by the elimination of dimethylsilene gave the compound **6**. The structure of the photoproduct **11** was
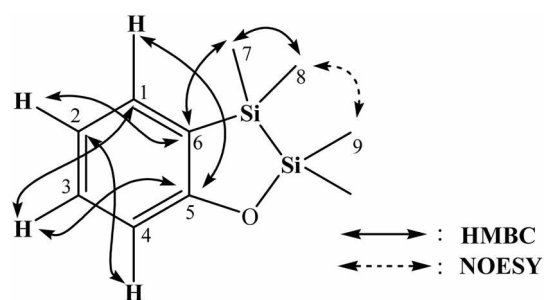

Figure 2. Important correlations observed in HMBC and NOESY spectra of photoproduct **11**.

also 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, and NOESY), UV, FT-IR, and high resolution mass spectrometry. The ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy (COSY) spectra of **11** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **11**, I have been able to identify the pairs of carbons and directly bonded protons as shown in Table 2. From the HMBC spectrum of **11**, the structure skeleton of **11** was determined. The connectivity of the carbon C(6) to the dimethylsilyl group in **11** was established

Table 2. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), and HMBC data for photoproduct **11** in CDCl$_3$[a]

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	J_{H-H} (Hz)	HMBC[e]
1	135.7	d	7.56	1H	dd	7.2 (J_{1H-2H}), 1.8 (J_{1H-3H})	H3
2	129.0	d	6.93	1H	t	7.2 ($J_{2H-1H, 3H}$)	H4
3	120.5	d	7.25	1H	td	7.8 ($J_{3H-2H, 4H}$) 1.8 (J_{3H-1H})	H1
4	116.2	d	6.72	1H	d	8.1 (J_{4H-3H})	H2
5	160.8	s					H1, H3
6	130.7	s					H2, H7
7	1.93	q	0.37	3H	s		H8
8	0.61	q	0.42	3H	s		H7
9	−1.60	q	0.099	3H	s		

[a]All these assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{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.
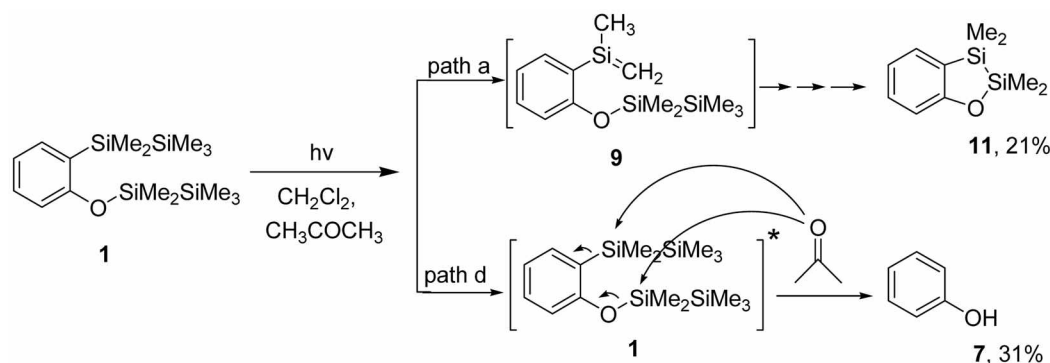
Scheme 5
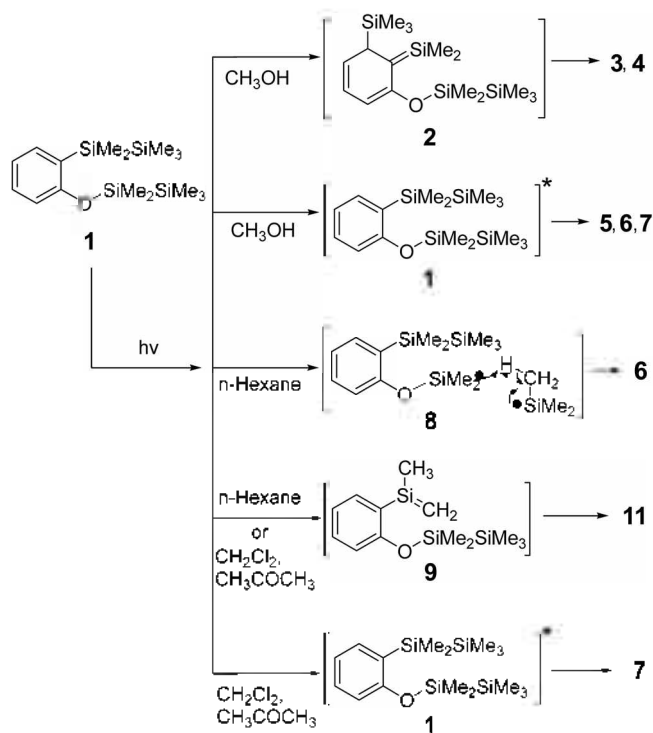
Scheme 6

by the presence of the cross-peaks due to the vicinal coupling between the protons of C(2) and C(7) and the quaternary carbon C(6) in **11**. And, the ^1H and ^{13}C chemical shift differences between two methyl groups which are connected at the same silicon atom in the 5-membered ring of **11** were explained by the presence of the cross-peaks due to the vicinal coupling between the protons of C(8) and the carbon C(7), the protons of C(7) and the carbon C(8) in the HMBC spectrum of **11**. From the presence of the cross-peaks between the protons of C(7),C(8) and the protons of C(9) which is showed in a nuclear overhauser and exchange spectroscopy (NOESY) of **11**, it was determined that these protons are located on the same side of the molecule. Thus, the skeletal structure of **11** was unambiguously established as shown in Figure 2.

Photoreaction of 2-(pentamethyldisilanyloxy)phenyl-pentamethyl disilane 1 in methylene chloride in the presence of acetone. Irradiation of **1** in deaerated methylene

chloride in the presence of acetone with 300 nm UV light afforded a novel intramolecular photoproduct **11** (21% yield) in addition to phenol **7** (31% yield) along with some decomposition products of unknown structure as shown in Scheme 5, when 83% of **1** was photolyzed but the expected photoproducts from the reaction of the silene intermediate with acetone were not obtained. The formation of **11** was explained by the same mechanism as in *n*-hexane solvent (path a) and the formation of phenol **7** was also explained by the acetone attack to two α silicon atoms of two pentamethyldisilanyl groups in the photoexcited state of **1**(path d).

In conclusion, the photolysis of **1** in methanol provided five compounds **3**, **4**, **5**, **6**, and **7**. The formation of **3** and a non-aromatic photoproduct **4** can be rationalized in terms of the methanol addition reactions of silene intermediate **2** and compounds **5** and **6** were probably formed through the α or β silicon atom attack of methanol to pentamethyldisilanyl-oxy group in photoexcited state of **1**. Irradiation of **1** in *n*-hexane gave the photoproduct **6** and a novel intramolecular cyclization photoproduct **11**. The formation of **6** in *n*-hexane solvent was probably explained by the hydrogen abstraction of silyl radical intermediate **8** in *n*-hexane solvent cage. It is thought that the cyclization photoproduct **11** was probably formed *via* silene intermediate **9** and silyl radical intermediate **10**. Irradiation of **1** in deaerated methylene chloride in the presence of acetone afforded phenol **7** and a novel photoproduct **11** but the expected photoproducts from the reaction of the silene intermediate with acetone were not obtained (Scheme 6).

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