

Photoreactions of (2-Alkoxyethylphenyl)pentamethyldisilanes

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Photolysis of (2-hydroxymethylphenyl)pentamethyldisilane **1** in methanol provides a novel intramolecular photoproduct **4** via silene intermediate **2** but the photoreaction of (2-acetoxymethyl- or allyloxymethylphenyl)pentamethyldisilanes **5** or **10** in methanol affords unexpected photoproducts **8** or **13**, respectively, instead of expected intramolecular photoproducts.

Key Words : (2-Hydroxymethylphenyl)pentamethyldisilane, (2-Acetoxymethylphenyl)pentamethyldisilane, (2-Allyloxymethylphenyl)pentamethyldisilane, Silene

Introduction

It is well known that the photolysis of the benzenoid aryl disilanes affords the silenes, arising from the 1,3-trimethylsilyl shift to an *ortho* carbon atom in the aryl ring as a major photoproduct since the first report on the photolysis of phenylpentamethyldisilane and (*p*-tolyl)pentamethyldisilane in forming the silene intermediates by Ishikawa *et al.*¹ in 1975. The reaction of silenes thus formed with various trapping agents, such as alcohols,²⁻¹¹ carbonyl compounds,¹²⁻¹⁵ alkenes,¹⁶⁻²⁴ and alkynes²⁵ gives the addition products but in the absence of such trapping agents, dimerization products of silene intermediates were obtained.^{26,27} Although the photoreactions of aryl disilanes have been extensively studied, relatively little is known about the photochemical behavior of *ortho*-substituted aryl disilanes. Recently, I have found that the photolysis of *ortho*-substituted 1-aryl-2-(pentamethyldisilanyl)ethynes afforded novel intramolecular photoproducts via silacyclopentene or 1-silaallene intermediates.²⁸ Very recently, the author reported on the photo-induced intramolecular reaction of (2-substituted-phenyl)pentamethyldisilanes 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 in the photoexcited state to the C₆ position of benzene ring.²⁹ To learn more about the photoreactions of *ortho*-substituted aryl disilanes, I have now investigated the photoreactions of (2-alkoxyethylphenyl)pentamethyldisilanes since novel photoproducts from the intramolecular reaction of *ortho*-substituted group with the silene intermediate are expected. In this article, I would like to report the detailed photochemical study of (2-alkoxyethylphenyl)pentamethyldisilanes.

Experimental Section

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 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).

Materials. (2-Hydroxymethylphenyl)pentamethyldisilane **1**³⁰ and *o*-allyloxymethyl-iodobenzene **9**³¹ were prepared as reported in the literature. Tetrahydrofuran was refluxed over sodium benzophenone and distilled under nitrogen. Methanol (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.

Synthesis of (2-acetoxymethylphenyl)pentamethyldisilane 5. Triethylamine (0.44 mL, 3.15 mmol) was added to a solution of (2-hydroxymethylphenyl)pentamethyldisilane **1** (0.5 g, 2.1 mmol) in diethyl ether (30 mL) at 0 °C under nitrogen atmosphere. Acetyl chloride (0.3 mL, 4.2 mmol) was added dropwise to the resulting solution and the mixture was stirred at 0 °C for 1 h. 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 (MgSO₄). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10/1, v/v) as an eluent gave **5** (0.54 g, 92% yield) as a colorless oil; ¹H NMR (CDCl₃, 600 MHz) δ_H 0.12 (9H, s), 0.44 (6H, s), 2.14 (3H, s), 5.16 (2H, s), 7.33 (1H, td, *J* = 7.5, 1.5 Hz), 7.39 (1H,

td, $J = 7.5, 1.5$ Hz), 7.43 (1H, dd, $J = 7.5, 1.5$ Hz), 7.52 (1H, dd, $J = 7.5, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ -2.28, -1.98, 21.0, 66.9, 127.5, 128.9, 129.0, 134.9, 138.7, 140.9, 170.8; UV (CH_2Cl_2) λ_{max} 236 nm; FT-IR (NaCl) 3057.3, 2951.6, 1740.9, 1436.9, 1247.9, 1028.5, 834.5 cm^{-1} ; MS (70 eV) m/z 280 (M^+); HRMS (M^+) calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}_2$ 280.1315, found 280.1362.

Synthesis of (2-allyloxymethylphenyl)pentamethyldisilane 10. A solution of *o*-allyloxymethyl-iodobenzene **9** (0.5 g, 1.82 mmol) in THF (20 mL) was treated with *n*-BuLi (0.8 mL, 2.0 mmol) at -78 °C followed by chloropentamethyldisilane (0.53 mL, 2.74 mmol). The reaction mixture was warmed to room temperature and stirred for 3 h. After evaporation of solvent, the reaction mixture was extracted with ethyl acetate (3×20 mL), washed with water (3×20 mL), and dried with MgSO_4 , and concentrated in vacuo to give the crude product. Flash column chromatography using *n*-hexane : ethyl acetate (30 : 1, v/v) as an eluent gave **10** (0.36 g, 71% yield) as a colorless oil; ^1H NMR (CDCl_3 , 600 MHz) δ 0.22 (9H, s), 0.54 (6H, s), 4.22 (2H, dt, $J = 5.5, 1.5$ Hz), 4.67 (2H, s), 5.35 (1H, dq, $J = 11, 1.5$ Hz), 5.47 (1H, dq, $J = 17, 1.5$ Hz), 6.12 (1H, m), 7.37 (1H, td, $J = 7.5, 1.5$ Hz), 7.47 (1H, td, $J = 7.5, 1.5$ Hz), 7.60 (2H, m); ^{13}C NMR (CDCl_3 , 150 MHz) δ -2.26, -1.79, 71.48, 72.61, 117.0, 126.8, 127.9, 128.7, 134.6, 134.8, 137.3, 143.6; UV (CH_2Cl_2) λ_{max} 235 nm; FT-IR (NaCl) 3056.5, 2949.7, 2892.5, 1647.4, 1435.6, 1245.7, 1087.9, 833.9, 799.5 cm^{-1} ; MS (70 eV) m/z 278 (M^+); HRMS (M^+) calcd for $\text{C}_{15}\text{H}_{26}\text{OSi}_2$ 278.1522, found 278.1528.

Irradiation of (2-hydroxymethylphenyl)pentamethyldisilane 1 in methanol. A solution (5×10^{-4} M) of (2-hydroxymethylphenyl)pentamethyldisilane **1** (119 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 254 nm lamps. After irradiation for 1.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproduct **4** was isolated in 38.9 mg (33% yield) in addition to 9% (10.7 mg) of the starting compound **1** by column chromatography with *n*-hexane/ethyl acetate (10/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (5/1, v/v) as an eluent. **4**; UV (CH_2Cl_2) λ_{max} 268, 230 nm; FT-IR (NaCl) 3057.4, 2953.2, 1462.1, 1251.9, 1064.8, 837.1 cm^{-1} ; MS (70 eV) m/z 236 (M^+); HRMS (M^+) calcd for $\text{C}_{12}\text{H}_{20}\text{OSi}_2$ 236.1053, found 236.1072.

Irradiation of (2-acetoxymethylphenyl)pentamethyldisilane 5 in methanol. A solution (5×10^{-4} M) of (2-acetoxymethylphenyl)pentamethyldisilane **5** (140 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 254 nm lamps. After irradiation for 3 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproduct **8** was isolated in 18.9 mg (15% yield) as colorless oil, in addition to 12% (16.8 mg) of the starting material **5** by column chromatography with *n*-hexane/ethyl acetate (30/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl

acetate (20/1, v/v) as an eluent. **8**; UV (CH_2Cl_2) λ_{max} 283, 275 nm; FT-IR (NaCl) 3055.9, 2955.8, 1588.4, 1561.2, 1467.9, 1249.0, 1088.3, 837.9 cm^{-1} ; MS (70 eV) m/z 252 (M^+); HRMS (M^+) calcd for $\text{C}_{13}\text{H}_{24}\text{OSi}_2$ 252.1366, found 252.1301.

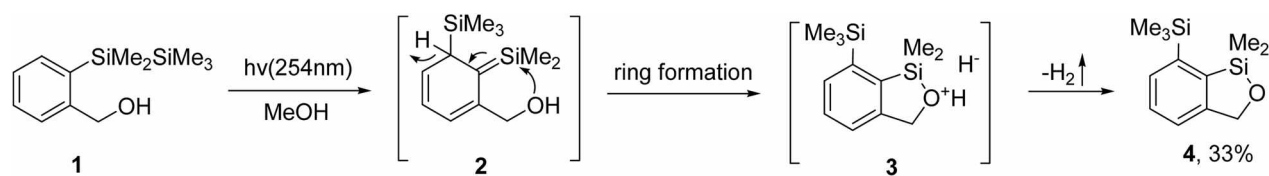
Irradiation of (2-allyloxymethylphenyl)pentamethyldisilane 10 in methanol. A solution (5×10^{-4} M) of (2-allyloxymethylphenyl)pentamethyldisilane **10** (139 mg) in methanol (1 L) was deaerated by nitrogen purging for 1 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 2 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproduct **13** was isolated in 17 mg (23% yield) as colorless oil, in addition to 10% (13.9 mg) of the starting material **10** by column chromatography with *n*-hexane/ethyl acetate (50/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (30/1, v/v) as an eluent. **13**; ^1H NMR (CDCl_3 , 600 MHz) δ 4.09 (2H, dt, $J = 5.5, 1.5$ Hz), 4.59 (2H, s), 5.27 (1H, dq, $J = 11, 1.5$ Hz), 5.38 (1H, dq, $J = 17, 1.5$ Hz), 6.03 (1H, m), 7.41 (5H, m); ^{13}C NMR (CDCl_3 , 150 MHz) δ 70.9, 71.9, 116.8, 127.4, 127.5, 128.2, 134.6, 138.2; UV (CH_2Cl_2) λ_{max} 259, 253 nm; FT-IR (NaCl) 3085.2, 3030.9, 2855.9, 1496.0, 1453.7, 1090.2, 1073.2 cm^{-1} ; MS (70 eV) m/z 148 (M^+); HRMS (M^+) calcd for $\text{C}_{10}\text{H}_{12}\text{O}$ 148.0888, found 148.0812.

Results and Discussion

Photoreaction of (2-hydroxymethylphenyl)pentamethyldisilane 1. To investigate whether or not the hydroxymethyl group as *ortho* substituent in **1** reacts intramolecularly with silene moiety in **2**, the photolysis of **1** was performed.

Irradiation of **1** in deaerated methanol with 254 nm UV light afforded a novel intramolecular photoproduct **4** (33% yield) along with some decomposition products of unknown structure as shown in Scheme 1, when 91% of **1** was photolyzed. The formation of a novel 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 photoexcited state of **1** to the C_6 position of benzene ring (Scheme 1). The intramolecular reaction to form a five-membered ring in this silene **2** resulted in the formation of the compound **3** accompanied by a hydrogen gas elimination to give the compound **4**. In relation to the formation of the compound **3** from the compound **2**, it has been reported that the photolysis of 1,2-bis(pentamethyldisilanyl)benzene¹⁸ and *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane³² in the presence of isobutene afforded photoproducts *via* the ene reaction of the photochemically generated rearranged silene intermediates with isobutene. In these cases, the elimination of the hydride from the silene intermediate like **2** was proposed in the ene reaction. In contrast to the photoreaction of **1** in methanol, no product was detected in the photolysis of **1** in deaerated benzene.

The structure of the photoproduct **4** was determined by various physical methods, such as ^1H NMR, ^{13}C NMR, 2D



NMR (^1H - ^1H , ^1H - ^{13}C COSY, HMBC, and NOESY), UV, FT-IR, and high resolution mass spectrometry. The ^1H - ^1H and ^1H - ^{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 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 C(8) and the quaternary carbon C(1) in **4** showed the connectivity of the carbon C(1) to the dimethylsilyl group in **4**. In the same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C(9) and the quaternary carbon C(2) in **4** showed the connectivity of the carbon C(2) to the trimethylsilyl group in **4**. In the same manner, the connectivity of the carbon C(7) to the benzene ring in **4** was established. 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(8) and the protons of C(9) in **4** showed the close proximity of the protons of C(8) to the protons of C(9) indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **4** was unambiguously established as shown in Figure 1.

Photoreaction of (2-acetoxymethylphenyl)pentamethyldisilane 5. To investigate the reactivity of acetoxymethyl group instead of hydroxymethyl group as *ortho* substituent to phenylpentamethyldisilane, the photolysis of **5** was carried out.

Irradiation of **5** in deaerated methanol with 254 nm UV light afforded a photoproduct **8** (15% yield) along with some decomposition products of unknown structure as shown in Scheme 2, when 88% of **5** was photolyzed but the expected

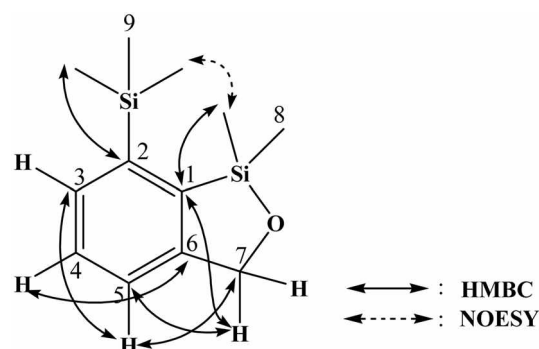


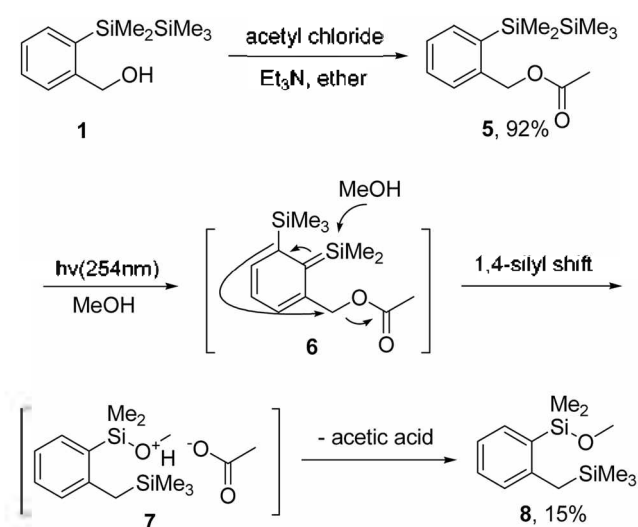
Figure 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **4**.

intramolecular photoproduct like **4** was not obtained. This result indicates that the intermolecular reaction of methanol solvent with silene moiety in reaction intermediate, **6** is much faster than the intramolecular reaction of *ortho*-substituted acetoxymethyl group with silene moiety in **6** to give the cycloaddition photoproduct. But the photolysis of (2-hydroxymethylphenyl)pentamethyldisilane **1** having a hydroxymethyl group as the *ortho*-substituted group gave the intramolecular photoproduct **4**, indicating that the hydroxymethyl group is much more reactive than the acetoxymethyl group in the intramolecular reaction. The photoproduct **8** was probably formed through silene intermediate **6** arising from 1,3-migration of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon bond in the photoexcited state of **5** to the C₆ position of benzene ring. The intermolecular reaction of methanol to silicon atom in silene moiety of intermediate **6** accompanied by an aromatization and 1,4-trimethylsilyl shift give the compound **7**, and it is thought that the photoproduct **8** was

Table 1. ^1H 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	$J_{\text{H-C}}$ (Hz)	HMBC ^e
1	140.5	s					H3, H7, H8
2	145.4	s					H4, H9
3	133.3	d	7.56	1H	d	7.5 ($J_{\text{H1-C3}}$)	H5
4	128.8	d	7.38	1H	t	7.5 ($J_{\text{H1-C4}}$), 7.5 ($J_{\text{H1-C5}}$)	H5
5	122.5	d	7.23	1H	d	7.5 ($J_{\text{H1-C5}}$)	H3, H7
6	150.0	s					H4, H7
7	71.2	t	5.15	2H	s		H5
8	2.11	q	0.50	3H	s		
9	0.52	q	0.33	3H	s		

^aAll these assignments were confirmed by ^1H - ^1H and ^1H - ^{13}C COSY and NOESY, HMBC spectra. ^bMultiplicities were determined by DEPT spectrum. ^cIntegrated intensity. ^dMultiplicities. ^eProtons correlated to carbon resonances in ^{13}C column.



Scheme 2

obtained by the elimination of acetic acid from the intermediate **7** (Scheme 2). The photoreaction of **5** in deaerated benzene with 254 nm UV light did not give any photoproduct.

The structure of the photoproduct **8** was also determined by various physical methods, such as ^1H NMR, ^{13}C NMR, 2D NMR (^1H - ^1H , ^1H - ^{13}C COSY, HMBC, and NOESY), UV, FT-IR, and high resolution mass spectrometry. The ^1H - ^1H and ^1H - ^{13}C correlation spectroscopy (COSY) spectra of **8** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **8**, I have been able to identify the pairs of carbons and directly bonded protons as shown in Table 2. In order to determine the location of the quaternary carbons, the HMBC spectrum of **8** was taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(4), C(8), C(10) and the quaternary carbon C(6) in **8** showed the connectivity of the carbon C(6) to the dimethylsilyl group in **8**. And, the presence of the cross-peaks due to the vicinal coupling between the protons of C(4) and C(9) and the carbon C(8) in **8** showed the connectivity of the carbon C(8) to the benzene ring and the trimethylsilyl group in **8**. In the

same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C(8) and the carbon C(9) in **8** also showed the connectivity of the carbon C(8) to the trimethylsilyl group in **8**. The 3D-structure of **8** was determined by a nuclear overhauser and exchange spectroscopy (NOESY). In particular, the presence of the cross-peak between the protons of C(9) and the protons of C(10) in **8** showed the close proximity of the protons of C(9) to the protons of C(10) indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **8** was unambiguously established as shown in Figure 2.

Photoreaction of (2-allyloxymethylphenyl)pentamethyldisilane 10. To investigate the reactivity of allyloxymethyl group instead of hydroxymethyl group as *ortho* substituent to phenylpentamethyldisilane, the photolysis of **10** was carried out.

Irradiation of **10** in deaerated methanol with 254 nm UV light afforded a photoproduct **13** (23% yield) along with some decomposition products of unknown structure as shown in Scheme 3, when 90% of **10** was photolyzed but the expected intramolecular photoproduct like **4** was not obtained. In relation to the formation of the photoproduct **13**, Ishikawa and Sakamoto³³ reported the photolysis of 2,6-xylyl)pentamethyldisilane in the presence of methanol afforded an unexpected products, *m*-xylene and methoxy-pentamethyldisilane by the nucleophilic assistance of a methoxy group onto the silicon atom attached to the aryl

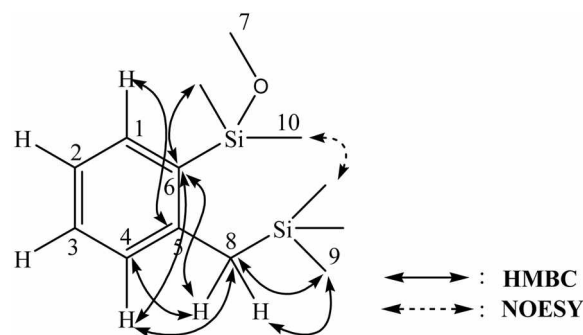
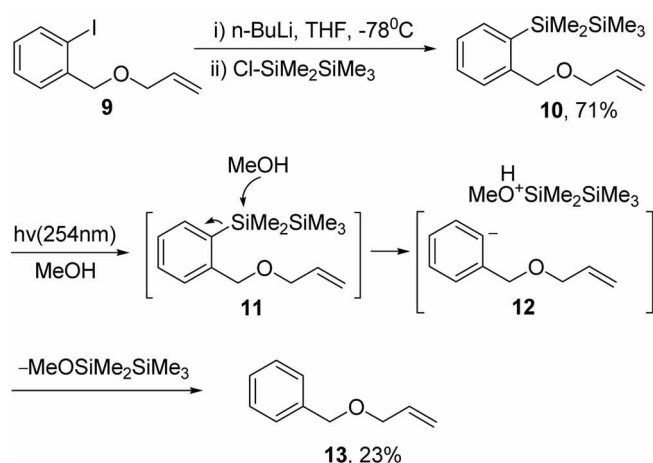


Figure 2. Important correlations observed in HMBC and NOESY spectra of photoproduct **8**.

Table 2. ^1H NMR (600 MHz), ^{13}C NMR (150 MHz), and HMBC data for photoproduct **8** in CDCl_3 ^a

Position	δ_{C} (ppm)	M^b	δ_{H} (ppm)	I^c	M^d	$J_{\text{H/C}}$ (Hz)	HMBC ^e
1	134.9	d	7.48	1H	dd	7.5 ($J_{\text{H1-2H}}$), 1.5 ($J_{\text{H1-3H}}$)	H3
2	123.4	d	7.10	1H	td	7.5 ($J_{\text{2H-1H}}$, $J_{\text{2H-3H}}$), 1.5 ($J_{\text{2H-4H}}$)	H4
3	129.4	d	7.28	1H	td	7.5 ($J_{\text{3H-2H}}$, $J_{\text{3H-4H}}$) 1.5 ($J_{\text{3H-1H}}$)	H1
4	128.4	d	7.08	1H	d	7.5 ($J_{\text{4H-3H}}$)	H2, H8
5	146.9	s					H1, H3
6	134.7	s					H4, H8, H10
7	50.3	q	3.46	3H	s		
8	26.25	t	2.38	2H	s		H4, H9
9	-1.01	q	0.05	3H	s		H8
10	-0.57	q	0.43	3H	s		

^aAll these assignments were confirmed by ^1H - ^1H and ^1H - ^{13}C COSY and NOESY, HMBC spectra. ^bMultiplicities were determined by DEPT spectrum. ^cIntegrated intensity. ^dMultiplicities. ^eProtons correlated to carbon resonances in ^{13}C column.



Scheme 3

ring. The formation of the photoproduct **13** was most likely explained by a mechanism involving a nucleophilic attack of methanol at silicon atom of the pentamethyldisilane moiety in **11** to form a ion complex, **12**, which proceeds to the photoproduct **13** by the elimination of methoxypentamethyldisilane. In the case of the allyloxy group as *ortho* substituent to phenylpentamethyldisilane, a novel intramolecular photoproduct *via* silene intermediate was obtained in deaerated benzene solvent²⁹ but the photoreaction of **10** having the allyloxymethyl group as *ortho* substituent to phenylpentamethyldisilane did not provide a novel intramolecular photoproduct in deaerated benzene or methanol solvent. The photoreaction of **10** in deaerated benzene with 254 nm UV light did not give any photoproduct.

In conclusion, the photolysis of **1** in methanol provided a novel intramolecular photoproduct **4** *via* silene intermediate **2** but the methanol addition photoproduct was not obtained. Irradiation of **5** in methanol gave a intermolecular addition photoproduct **8** of a methanol to silene moiety *via* silene intermediate **6** but the expected intramolecular photoproduct like **4** was not obtained. The photolysis of **10** in methanol provided an unexpected photoproduct **13** instead of a expected intramolecular photoproduct. No photoproduct from the photoreactions of **1**, **5**, or **10** in benzene was obtained.

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