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Silicon–carbon unsaturated compounds

XLIV*. Photochemical behavior of permethylated *p*-(disilanylene)phenylene oligomers

Mitsuo Ishikawa, Koki Watanabe, Hiromu Sakamoto and Atsutaka Kunai

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724 (Japan)

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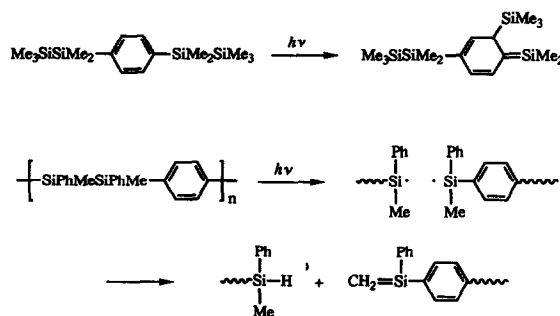
Abstract

The *p*-(disilanylene)phenylene oligomers, $\text{Me}_3\text{Si}(\text{Me}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiMe}_2)_n\text{SiMe}_3$ with $n = 2-4$ (2, 3, and 4) were prepared and their photochemical behavior was investigated in a benzene solution. Photolysis of 2 in the presence of isobutene afforded 1-isobutyldimethylsilyl-4-pentamethyldisilanyl-2-(dimethyl[4-(pentamethyldisilanyl)phenyl]silyl)benzene and its isomer in 58% and 5% yields, in addition to 4-dimethylsilyl-1-(pentamethyldisilanyl)benzene (6a) (1% yield) and 4-dimethylphenylsilyl-1-(pentamethyldisilanyl)benzene (7a) (2% yield). Irradiation of 2 in the absence of isobutene gave 6a and 7a in 2% and 5% yields. Irradiation of 3 in the presence of isobutene afforded 1-isobutyldimethylsilyl-2-dimethyl[4-(pentamethyldisilanyl)phenyl]silyl-4-[2-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilanyl]benzene (8) and 4-dimethyl[2-isobutyldimethylsilyl-5-(pentamethyldisilanyl)phenyl]silyl-1-[2-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilanyl]benzene (9) in 4% and 2% yields, along with small amounts of 6a and 7a. Similar irradiation of 3 in the absence of isobutene produced 6a, 7a, and 4-pentamethyldisilanyl-1-[2-[4-(dimethylphenylsilyl)phenyl]tetramethyldisilanyl]benzene (10) in 1%, 1%, and 2% yields. The photolysis of 4 under the same conditions gave 6a, 7a, 10, and 2-[4-(dimethylsilyl)phenyl]-1-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilane (11) in 1%, 11%, 11%, and 1% yields.

1. Introduction

In 1975, we found that the photolysis of pentamethylphenyldisilane gives a silene arising from a concerted 1,3-silyl shift to an *ortho* carbon atom of the phenyl ring [1]. A trace amount of the other silene (non-rearranged silene) formed from homolytic scission of a silicon–silicon bond, followed by disproportionation of the resulting silyl radicals is also produced in this photolysis. Indeed, many types of aryldisilanes undergo photolysis to give the silenes derived from a 1,3-silyl shift to the aryl ring (rearranged silene), but the silenes originating from homolytic scission of a silicon–silicon bond are produced only in low yields [2,3]. Some aryldisilanes produce no silenes derived from homolytic scission of a silicon–silicon bond. For example, the photolysis of 1,4-bis(pentamethyldisilanyl)benzene af-

fords only the rearranged silene resulting from a 1,3-trimethylsilyl shift from one of two pentamethyldisilanyl groups to the phenylene ring. No products arising



from homolytic scission of the silicon–silicon bond can be detected by either GLC analysis or spectrometric analysis [4]. In contrast to the photolysis of aryldisilanes, *p*-(disilanylene)phenylene polymers results in homolytic scission of a silicon–silicon bond in the polymer backbone as a main route [3a].

Correspondence to: Dr. M. Ishikawa.

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It is of interest to investigate the photochemical behavior of the *p*-(disilanylene)phenylene oligomers, and to find a correlation between the mode of reaction (concerted 1,3-silyl shift and homolytic scission of a silicon-silicon bond) and the degree of a repeating disilanylene-phenylene unit in the molecule.

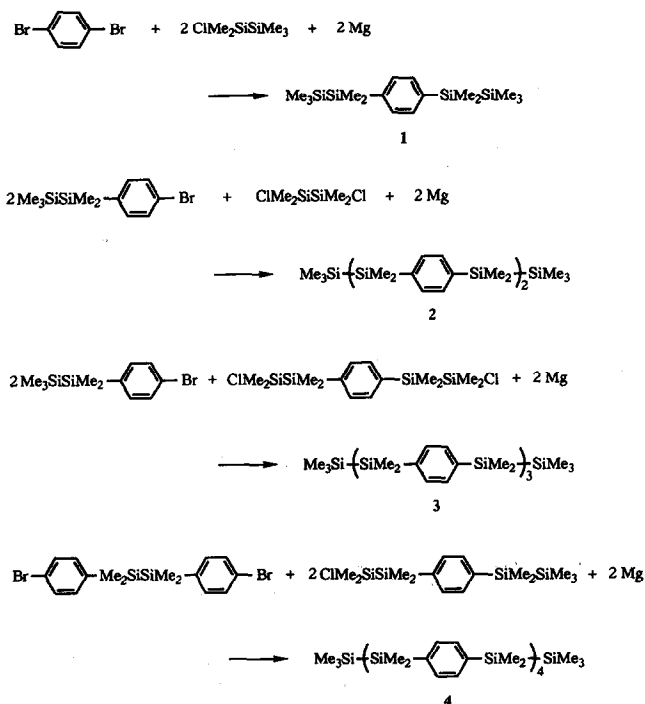
2. Results and discussion

2.1. Synthesis of *p*-(disilanylene)phenylene oligomers

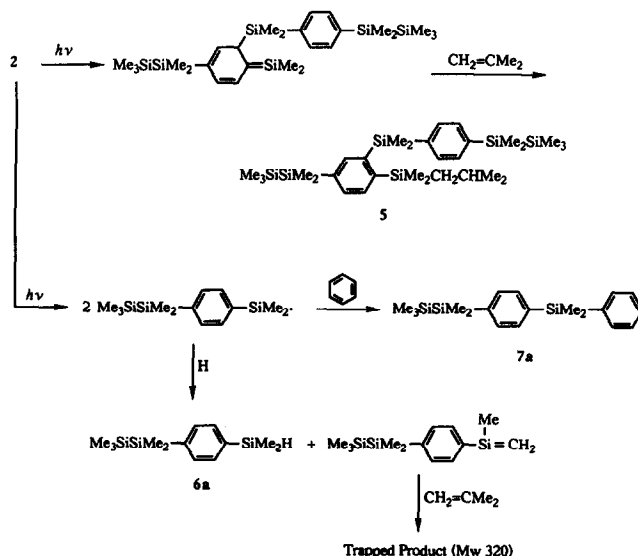
The starting *p*-(disilanylene)phenylene oligomers, 1,4-bis(pentamethyldisilanyl)benzene (**1**), 1,2-bis[4-(pentamethyldisilanyl)phenyl]tetramethyldisilane (**2**), 1,4-bis[2-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilanyl]benzene (**3**), and 1,2-bis[4-[2-(4-pentamethyldisilanyl)phenyl]tetramethyldisilanyl]phenyl]tetramethyldisilane (**4**) were prepared by the reaction of Grignard reagents with the corresponding chloro- and dichloro-disilane derivatives as shown in Scheme 1.

2.2. Photolysis of *p*-(disilanylene)phenylene oligomers, 2-4

As reported previously [4], the photolysis of 1,4-bis(pentamethyldisilanyl)benzene (**1**) in the presence of isobutene in benzene gave two products, 1-isobutyldimethylsilyl-4-pentamethyldisilanyl-2-(trimethylsilyl)benzene and 1,1-dimethyl-6-[1,1-dimethyl-2-(trimethylsilyl)ethyl]-3-(pentamethyldisilanyl)silolepin as main

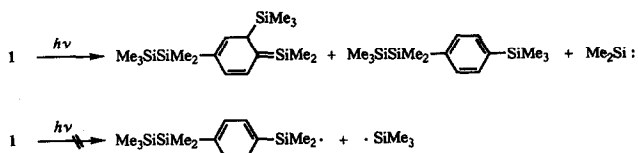


Scheme 1.



Scheme 2.

products; they were produced by reaction of the silene arising from a 1,3-trimethylsilyl shift to the phenylene ring with isobutene in 72% and 14% yields, when 96% of **1** was photolyzed. Although a trace amount (less than 3% yield) of a product produced by the extrusion of dimethylsilylene was detected by GC-mass spectrometric analysis, no products originating from homolytic scission of a silicon-silicon bond were observed in the photolysis mixture. In contrast to **1**, the photolysis of compound **2** involves both the formation of the rear-ranged silene and silyl radicals arising from homolytic scission of a silicon-silicon bond.



Thus, irradiation of compound **2** under the same conditions afforded 1-isobutyldimethylsilyl-4-pentamethyldisilanyl-2-(dimethyl[4-(pentamethyldisilanyl)phenyl]silyl)benzene (**5**) and its isomer [**5**] in 58% and 5% yields, along with two products, 4-dimethylsilyl-1-(pentamethyldisilanyl)benzene (**6a**) (1% yield) and 4-dimethylphenylsilyl-1-(pentamethyldisilanyl)benzene (**7a**) (2% yield), when 76% of **2** was photolyzed (Scheme 2). All attempts to isolate the isomer of **5** were unsuccessful, but GC-mass spectrometric analysis of this compound showed a parent ion at m/e 586, corresponding to a calculated molecular weight of $\text{C}_{30}\text{H}_{58}\text{Si}_6$.

GLC analysis of the mixture showed that a product whose molecular weight was determined to be 320 was also produced in 2% yield. Unfortunately, this product could not be isolated, but the molecular weight of the

observed product corresponds to that of an adduct which is produced from the reaction of 1-methyl-1-[4-(pentamethyldisilanyl)phenyl]silene arising from homolytic scission of an internal silicon-silicon bond of **2**, followed by disproportionation of the resulting silyl radicals with isobutene. The fact that the silene is produced from homolytic scission of a silicon-silicon bond, followed by disproportionation of the resulting silyl radicals is well known [3].

The structure of **5** was confirmed by mass, IR, and ^1H and ^{13}C NMR spectrometric analysis. Furthermore, saturation of the resonance at δ 0.21 ppm of dimethylsilyl protons at the C-1 position of **5** performed in NOE-FID difference experiments at 270 MHz produced a positive NOE of a proton (7.65 ppm) at the C-6 position on the 1,2,4-tri-substituted phenyl ring, methyl protons (0.67 ppm) on the silicon atom at the C-2 position of this ring, and two protons (7.42 ppm) on the 1,4-substituted phenyl ring, as well as isobutyl protons. Irradiation of dimethylsilyl protons (0.28 ppm) of the disilanyl group at the C-4 position of the 1,2,4-tri-substituted phenyl ring caused a positive NOE of two protons (7.45 and 7.74 ppm) at the C-5 and C-3 positions on this ring. These results are consistent with the structure proposed for **5**. Compounds **6a** and **7a** were identified by comparison of retention time on gas chromatography and mass fragmentation pattern with those of the authentic samples obtained from independent synthesis.

Compound **5** is probably formed by the ene reaction of the silene arising from a photochemical 1,3-shift of a dimethyl[4-(pentamethyldisilanyl)phenyl]silyl group in the starting compound **2** with isobutene. The products **6a** and **7a** may be explained in terms of homolytic scission of the internal silicon-silicon bond of **2**. Hydrogen abstraction of the resulting silyl radical affords the product **6a**, while homolytic aromatic substitution [5] onto benzene used as a solvent produces compound **7a**. No product derived from homolytic scission of a terminal silicon-silicon bond in compound **2** was detected by GC-mass spectrometric analysis.

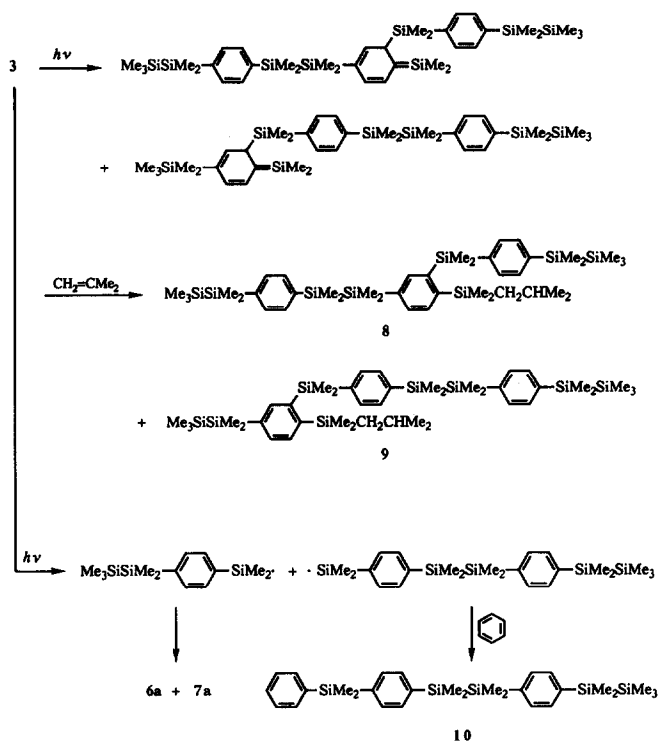
In order to obtain more information about the photochemical reaction of **2**, we carried out the photolysis of **2** in the absence of isobutene. In the absence of a trapping agent, the rearranged silenes formed from a concerted 1,3-silyl shift to the phenylene ring undergo polymerization to give non-volatile substances. In contrast to the rearranged silenes, silyl radicals arising from homolytic scission of a silicon-silicon bond are transformed into volatile products such as hydrosilanes. Consequently, the product analysis for the volatile photolysis mixture is simplified. Thus, the photolysis of **2** in benzene afforded products **6a** and **7a** in 2% and 5% yields, along with the product formed by

extrusion of dimethylsilylene from the starting compound **2** ($472\text{ (M}^+)$, less than 1% yield). In addition, several products with shorter retention times than that of the starting compound **2** were detected by GLC analysis, but the yields of these products were calculated to be less than 0.5%. Interestingly, the similar reaction of **2** in hexadeuteriobenzene produced a mixture composed of **6a** and 4-deuteriodimethylsilyl-1-(pentamethyldisilanyl)benzene (**6b**) (3% combined yield), and 4-dimethyl(pentadeuteriophenyl)silyl-1-(pentamethyldisilanyl)benzene (**7b**) (3% yield). The ratio of **6a** and **6b** was calculated to be 4:1 by mass spectrometric analysis, indicating that compound **6** is mainly produced from disproportionation of dimethyl[4-(pentamethyldisilanyl)phenyl]silyl radicals (see Scheme 2). These results clearly indicate that homolytic scission of an internal silicon-silicon bond occurs for the photolysis of **2**, although this route is a minor one.

The photolysis of compound **3** in the presence of isobutene afforded rearranged addition products, analogous to compound **5** in low yields. GLC analysis of the reaction mixture showed that 1-isobutyldimethylsilyl-2-dimethyl[4-(pentamethyldisilanyl)phenyl]silyl-4-{2-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilanyl}benzene (**8**) and 4-dimethyl[2-isobutyldimethylsilyl-5-(pentamethyldisilanyl)phenyl]silyl-1-{2-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilanyl}benzene (**9**) were produced in 4% and 2% yields, respectively, along with compounds **6a** (less than 1% yield), **7a** (1% yield), 4-pentamethyldisilanyl-1-{2-[4-(dimethylphenylsilyl)-phenyl]tetramethyldisilanyl}benzene (**10**) (1% yield), and 17% of the starting compound **3** (Scheme 3). Such low yields of the rearranged addition products **8** and **9** may be ascribed to the steric effect of a large substituent on the six-membered ring of the silene. GLC analysis of the reaction mixture revealed that several unidentified products which were calculated to be less than 0.5% yields were detected.

The photolysis of **3** in the presence of methanol afforded no clear-cut results. Silene-methanol adducts could not be isolated, since GLC and LC analysis of the reaction mixture showed only broad peaks on the chromatograms.

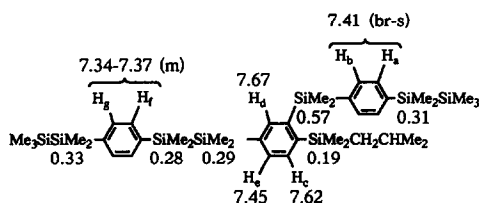
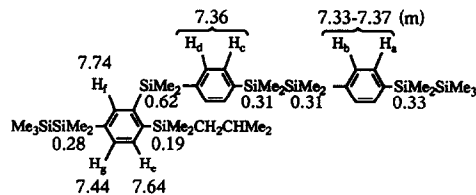
The products **8** and **9** were isolated by MPLC, and their structures were verified by spectroscopic analysis, as well as high resolution mass spectrometric analysis. ^1H NMR chemical shifts that were the basis of identification for compounds **8** and **9** are shown in Figs. 1 and 2, respectively. As expected for **8**, saturation of dimethylsilyl protons at 0.19 ppm caused the enhancement of a proton (H_c) at 7.62 ppm and isobutyl protons, while irradiation of tetramethyldisilanylene protons at 0.28 and 0.29 ppm resulted in a strong enhancement of



Scheme 3.

protons (H_e , H_d and H_f) at 7.45, 7.67 and 7.34–7.37 ppm. Similar irradiation of dimethylsilyl protons at 0.57 ppm led to a positive NOE of protons (H_b and H_d) at 7.41 and 7.67 ppm.

For compound **9**, saturation of dimethylsilyl protons at 0.19 ppm resulted in a strong enhancement of a proton (H_e) at 7.64 ppm as well as isobutyl protons, while saturation of dimethylsilyl protons at 0.28 ppm led to the enhancement of protons (H_g and H_f) at 7.44 and 7.74 ppm. Irradiation of dimethylsilyl protons at 0.62 ppm caused a positive NOE of a proton (H_f) at 7.74 ppm. Similar irradiation of tetramethyldisilanyl protons at 0.31 ppm resulted in a positive enhancement of protons (H_c and H_b) at 7.36 and 7.33–7.37 ppm. These results are wholly consistent with the structures proposed for **8** and **9**. Compound **10** was identified by comparison of its retention time on GLC and its mass

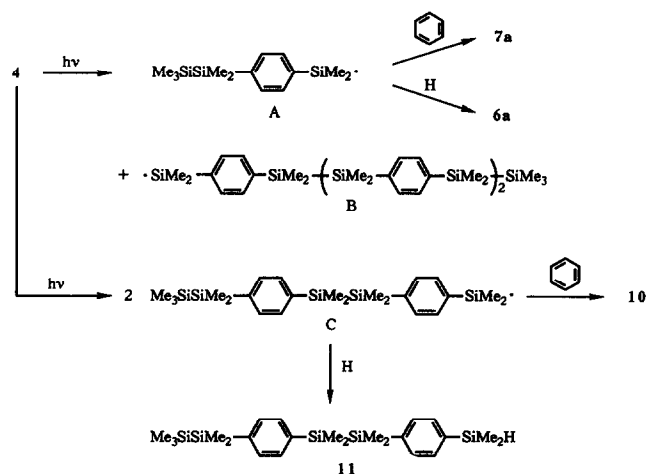
Fig. 1. Selected ^1H NMR chemical shifts of **8**.Fig. 2. Selected ^1H NMR chemical shifts of **9**.

fragmentation pattern with those of the authentic sample isolated from the photolysis of **4**.

The photolysis of **3** in the absence of isobutene afforded compounds **6a**, **7a**, and **10** in 1%, 1%, and 2% yields, respectively, in addition to 12% of the starting compound **3**.

All attempts to elute compound **4** and its isobutene adducts on a GLC column as detectable peaks were unsuccessful, because of their low volatility. Therefore, we carried out the photolysis of **4** in the absence of a trapping agent. In contrast to the photolysis of **2** and **3** in which the products derived from homolytic scission of silicon-silicon bonds were produced only in trace amounts, compound **4** yielded the products originating from silyl radicals **A** and **C** shown in Scheme 4 in appreciable amounts. Thus, the photolysis of **4** in the absence of a trapping agent gave **6a**, **7a**, **10**, and 2-[4-(dimethylsilyl)phenyl]-1-[4-(pentamethyldisilanyl)phenyl]tetramethyldisilane (**11**) in 1%, 11%, 11%, and 1% yields, respectively, when 76% of **4** was photolyzed.

Products derived from radical **B** could not be detected in the reaction mixture by GLC and LC analysis. Compounds **7a** and **10** were isolated by preparative GLC and identified by spectrometric analysis, as well as by elemental analysis. Again, no product originating from homolytic scission of a terminal silicon-silicon bond was detected in the reaction mixture. The struc-



Scheme 4.

ture of **11** was confirmed by comparison of its mass spectral fragmentation and the retention time on GLC with those of the authentic sample prepared by an independent synthesis.

In conclusion, the photolysis of **1** affords no products arising from homolytic scission of a silicon-silicon bond. Compounds **2** and **3** undergo photolysis to give rearranged silenes as a main route, although the silenes can be trapped only in low yields, and homolytic scission of a silicon-silicon bond occurs as a minor route. The photolysis of **4**, however, gives appreciable amounts of the products derived from silyl radicals, indicating that the degree of homolytic scission of a silicon-silicon bond increases with increase in the repeating disilanylenephenylene unit.

3. Experimental details

3.1. General procedure

All photolyses were carried out under an atmosphere of dry argon. Infrared spectra were determined with a Perkin-Elmer 1600 FT-infrared spectrometer. Gas chromatographic separations were carried out using a column packed with 30% silicone SE-30 on Chromosorb P. ^1H and ^{13}C NMR spectra were measured on a JEOL Model EX-270 spectrometer. Mass spectra were determined with a Shimadzu Model GCMS-QP 1000.

Tetrahydrofuran and benzene used as a solvent were dried over lithium aluminum hydride and distilled just before use.

3.2. Preparation of **2**

In a 300-ml three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed 2.0 g (84 mmol) of magnesium and 70 ml of dry THF. To this was added a mixture of 21.3 g (74 mmol) of (4-bromophenyl)pentamethyldisilane, and 5.2 g (28 mmol) of 1,2-dichlorotetramethyldisilane in 40 ml of THF at room temperature over a period of 2 h. The mixture was heated under reflux for 30 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with benzene. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were distilled off under reduced pressure to give crude crystals. The crude crystals were recrystallized from a mixed solvent consisting of ethanol and hexane (10:1) to give 9.4 g (63% yield) of **2**; m.p. 162–163°C. MS: m/e 530 (M^+). IR: 1400, 1378, 1247, 1128 cm^{-1} . UV (cyclohexane): λ_{max} (ϵ) 253 nm (35,800). ^1H NMR (CDCl_3): δ 0.07 (s, 18H, Me_3Si); 0.33 (s, 24H, Me_2Si); 7.30–7.39 (m, 8H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.11 (Me_2Si);

-3.97 (Me_2Si); -2.27 (Me_3Si); 132.9, 133.1, 138.9, 139.7 (phenyl ring carbons). Anal. Found: C, 58.65; H, 9.42. $\text{C}_{26}\text{H}_{50}\text{Si}_6$ calc.: C, 58.78; H, 9.48%.

3.3. Preparation of **3**

In a 300-ml three-necked flask was placed 1.01 g (42 mmol) of magnesium and 50 ml of THF. To this was added a mixture of 7.33 g (19 mmol) of 1,4-bis(2-chlorotetramethyldisilanyl)benzene, and 12.51 g (44 mmol) of (4-bromophenyl)pentamethyldisilane in 30 ml of THF at room temperature over a period of 2 h. The mixture was heated under reflux for 3 days and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with benzene. The organic layer and extracts were combined and washed with water, and then dried over calcium chloride. The solvents were evaporated and the resulting crystals were recrystallized from hexane to give 6.7 g (48% yield) of **3**; m.p. 205–206°C. MS: m/e 720 (M^+). IR: 1378, 1247, 1128, 831 cm^{-1} . UV (THF): λ_{max} (ϵ) 255 nm (58,600). ^1H NMR (CDCl_3): δ 0.07 (s, 18H, Me_3Si); 0.324 (s, 24H, Me_2Si); 0.326 (s, 12H, Me_2Si); 7.29 (br s, 4H, phenyl ring protons); 7.32–7.40 (m, 8H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.10, -4.00, -3.97 (Me_2Si); -2.23 (Me_3Si); 132.96, 133.06, 133.12, 138.9, 139.1, 139.7 (phenyl ring carbons). Anal. Found: C, 59.78; H, 9.19. $\text{C}_{36}\text{H}_{66}\text{Si}_8$ calc.: C, 59.75; H, 9.19%.

3.4. Preparation of **4**

To 0.37 g (15 mmol) of magnesium and 10 ml of THF was added a mixture of 3.0 g (7 mmol) of 1,2-bis(4-bromophenyl)tetramethyldisilane and 6.3 g (18 mmol) of 1-(2-chlorotetramethyldisilanyl)-4-(pentamethyldisilanyl)benzene in 90 ml of THF at room temperature over a period of 1 h. The mixture was heated under reflux for 2 days and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined and washed with water, and then dried over calcium chloride. The solvents were evaporated under reduced pressure to give crude crystals. The crystals were recrystallized from a mixed solvent consisting of hexane and benzene (5:4) to give 2.3 g (35% yield) of **4**; m.p. 204–225°C. MS: m/e 914 (M^+). UV (THF): λ_{max} (ϵ) 256 nm (66,400). IR: 1400, 1378, 1247, 1128, 831 cm^{-1} . ^1H NMR (CDCl_3): δ 0.06 (s, 18H, Me_3Si); 0.311 (s, 24H, Me_2Si); 0.315 (s, 24H, Me_2Si); 7.29–7.38 (m, 16H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.08 (Me_2Si), -3.93 (three Me_2Si); -2.21 (Me_3Si); 133.0, 133.15 (two carbons); 133.19, 139.0, 139.2 (two carbons); 139.8 (phenyl ring carbons). Anal. Found: C, 60.29; H, 8.98. $\text{C}_{46}\text{H}_{82}\text{Si}_{10}$ calc.: C, 60.32; H, 9.02%.

3.5. Preparation of (4-bromophenyl)dimethylsilane

In a 300-ml three-necked flask fitted with a stirrer, condenser, and dropping funnel was placed 22.5 g (0.104 mol) of *p*-dibromobenzene in 200 ml of ether. The flask was cooled to -70°C and then 65 ml (0.104 mol) of a butyllithium/hexane solution was added dropwise to the flask at -45°C to -70° . After addition of butyllithium, the mixture was stirred at -40°C for 1 h. The resulting lithium reagent was added to 26.3 g (0.278 mol) of chlorodimethylsilane over a period of 25 min. Lithium salts were filtered off and the solvent was evaporated. The residue was distilled under reduced pressure to give 20.2 g (90% yield) of (4-bromophenyl)dimethylsilane; b.p. $93\text{--}95^{\circ}\text{C}$ (11 mmHg). MS: m/e 214 (M^+). IR: 2122 (Si-H), 1251, 1107, 1067, 1012 cm^{-1} . ^1H NMR (CDCl_3): δ 0.34 (d, 6H, $J = 3.6$ Hz, Me_2Si); 4.37–4.67 (m, 1H, $J = 3.6$ Hz, HSi); 7.37–7.51 (m, 4H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -3.86 (Me_2Si); 124.0, 131.0, 135.6, 136.2 (phenyl ring carbons). Anal. Found: C, 44.55; H, 5.14. $\text{C}_8\text{H}_{11}\text{SiBr}$ calc.: C, 44.66; H, 5.15%.

3.6. Preparation of (4-bromophenyl)pentamethyldisilane

To a *p*-bromophenyllithium solution prepared from 116 ml (0.186 mol) of butyllithium and 43.7 g (0.185 mol) of *p*-dibromobenzene in 200 ml of ether at -40°C to -60°C was added 20.3 g (0.122 mol) of chloropentamethyldisilane. The mixture was stirred at room temperature for 1 h and hydrolyzed with water. The organic layer was separated and washed with water, and then dried over magnesium sulphate. The solvents were evaporated and the residue was distilled under reduced pressure to give 33.3 g (95% yield) of (4-bromophenyl)pentamethyldisilane; b.p. $138\text{--}142^{\circ}\text{C}$ (15 mmHg). MS: m/e 286 (M^+). IR: 1480, 1375, 1302, 1246, 1102, 1066, 1011 cm^{-1} . ^1H NMR (CDCl_3): δ 0.05 (s, 9H, Me_3Si); 0.33 (s, 6H, Me_2Si); 7.29–7.49 (m, 4H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.11 (Me_2Si); -2.35 (Me_3Si); 123.1, 130.9, 135.3, 138.5 (phenyl ring carbons). Anal. Found: C, 45.87; H, 6.66. $\text{C}_{11}\text{H}_{19}\text{Si}_2\text{Br}$ calc.: C, 45.98; H, 6.66%.

3.7. Preparation of 1,2-bis(4-bromophenyl)tetramethyldisilane

To a *p*-bromophenyllithium solution prepared from 60 ml (0.096 mol) of butyllithium and 21.8 g (0.093 mol) of *p*-dibromobenzene in 150 ml of ether at -40°C to -60°C was added 7.1 g (0.038 mol) of 1,2-dichlorotetramethyldisilane. The mixture was stirred at room temperature for 1 h and hydrolyzed with water. The organic layer was separated and washed with water, and then dried over magnesium sulphate. The solvents were evaporated and the residue was recrystallized from ethanol to give 12.41 g (77% yield) of 1,2-bis(4-

bromophenyl)tetramethyldisilane; m.p. $75\text{--}78^{\circ}\text{C}$. MS: m/e 426 (M^+). IR: 1400, 1376, 1249, 1067, 1011 cm^{-1} . ^1H NMR (CDCl_3): δ 0.31 (s, 12H, Me_2Si); 7.19–7.46 (m, 8H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.15 (Me_2Si); 123.4, 130.9, 135.3, 137.4 (phenyl ring carbons). Anal. Found: C, 44.86; H, 4.70. $\text{C}_{16}\text{H}_{20}\text{Si}_2\text{Br}_2$ calc.: C, 44.87; H, 4.71%.

3.8. Preparation of 1-(2-chlorotetramethyldisilanyl)-4-(pentamethyldisilanyl)benzene

A Grignard reagent prepared from 9.9 g (0.035 mol) of (4-bromophenyl)pentamethyldisilane and 0.92 g (0.038 mol) of magnesium in 50 ml of THF was added dropwise to a solution of 15.4 g (0.082 mol) of 1,2-dichlorotetramethyldisilane in 60 ml of THF. The mixture was heated to reflux for 10 h and then the resulting magnesium salts were filtered off. After evaporation of the solvent, the residue was distilled under reduced pressure to give 9.40 g (76% yield) of 1-(2-chlorotetramethyldisilanyl)-4-(pentamethyldisilanyl)benzene; m.p. $60\text{--}63^{\circ}\text{C}$, b.p. $110\text{--}114^{\circ}\text{C}$ (3 mmHg). MS: m/e 358 (M^+). IR: 1399, 1378, 1247, 1129, 1069 cm^{-1} . ^1H NMR (CDCl_3): δ 0.07 (s, 9H, Me_3Si); 0.34 (s, 6H, Me_2Si); 0.452 (s, 6H, Me_2Si); 0.459 (s, 6H, Me_2Si); 7.452 (br s, 4H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.65 , -4.10 (Me_2Si); -2.24 (Me_3Si); 2.16 (Me_2Si); 133.1, 133.3, 136.5, 140.7 (phenyl ring carbons). Anal. Found: C, 50.07; H, 8.62. $\text{C}_{15}\text{H}_{31}\text{Si}_4\text{Cl}$ calc.: C, 50.16; H, 8.70%.

3.9. Preparation of 1,4-bis(2-chlorotetramethyldisilanyl)benzene

A di-Grignard reagent prepared from 44.7 g (0.19 mol) of *p*-dibromobenzene and 9.3 g (0.38 mol) of magnesium in 250 ml of THF was added dropwise to 101.3 g (0.54 mol) of 1,2-dichlorotetramethyldisilane in 60 ml of THF. The mixture was heated under reflux for 10 h. The mixture was filtered off to remove magnesium salts and the filtrate was concentrated. The residue was distilled under reduced pressure to give 37.1 g (52% yield) of the product; m.p. $78\text{--}83^{\circ}\text{C}$, b.p. $139\text{--}142^{\circ}\text{C}$ (2 mmHg). MS: m/e 378 (M^+). IR: 1400, 1378, 1248, 1129, 1053 cm^{-1} . ^1H NMR (CDCl_3): δ 0.457 (s, 12H, Me_2Si); 0.464 (s, 12H, Me_2Si); 7.49 (br d, 4H, $J = 1.0$ Hz, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.67 , 2.16 (Me_2Si); 133.3, 137.7 (phenyl ring carbons). Anal. Found: C, 44.10; H, 7.40. $\text{C}_{14}\text{H}_{28}\text{Si}_4\text{Cl}_2$ calc.: C, 44.29; H, 7.43%.

3.10. Preparation of 6a

To 0.88 g (36.1 mmol) of magnesium and 20 ml of THF was added a mixture of 10.4 g (36.1 mmol) of (4-bromophenyl)pentamethyldisilane and 4.44 g (46.9 mmol) of chlorodimethylsilane in 10 ml of THF at

room temperature over a period of 40 min. The mixture was heated under reflux for 5 days and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and then dried over magnesium sulphate. The solvents were evaporated, and the residue was distilled under reduced pressure to give 5.7 g (60% yield) of **6a**; b.p. 124–125°C (14 mmHg). MS: m/e 266 (M^+). IR: 2120, 1917, 1816, 1400, 1378, 1330, 1247, 1132 cm^{-1} . ^1H NMR (CDCl_3): δ 0.07 (s, 9H, Me_3Si); 0.34 (s, 6H, Me_2Si); 0.36 (d, 6H, $J = 3.6$ Hz, Me_2Si); 4.39–4.47 (m, 1H, $J = 3.6$ Hz, HSi); 7.44–7.53 (m, 4H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.01 (Me_2Si); -3.79 (Me_2Si); -2.17 (Me_3Si); 133.2, 133.3, 137.3, 140.8 (phenyl ring carbons). Anal. Found: C, 58.40; H, 9.75. $\text{C}_{13}\text{H}_{26}\text{Si}_3$ calc.: C, 58.57; H, 9.83%.

3.11. Preparation of **11**

A solution of 2.3 g (10.5 mmol) of (4-bromophenyl) dimethylsilane and 3.7 g (10.2 mmol) of 1-(2-chlorotetramethyldisilanyl)-4-(pentamethyldisilanyl)benzene in 40 ml of THF was added to 0.23 g (9.4 mmol) of magnesium and 20 ml of THF at room temperature over a period of 1.5 h. After the mixture was heated to reflux for 5 days, 0.1189 g (0.76 mmol) of undecane as an internal standard was added to the mixture. The resulting solution was analyzed by GLC and found to contain **11** (62% yield). Hexane (ca. 20 ml) was added to the mixture and then magnesium salts were filtered off. The filtrate was treated with a short column and the resulting solution was concentrated. Compound **11** was isolated by preparative GLC; m.p. 79–82°C. MS: m/e 458 (M^+). IR: 2114, 1918, 1399, 1378, 1247, 1131 cm^{-1} . ^1H NMR (CDCl_3): δ 0.07 (s, 9H, Me_3Si); 0.329 (s, 6H, Me_2Si); 0.332 (s, 12H, two Me_2Si); 0.35 (d, 6H, $J = 3.6$ Hz, Me_2Si); 4.38–4.46 (m, 1H, $J = 3.6$ Hz, HSi); 7.35–7.48 (m, 8H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.13, -3.98, -3.93, -3.88 (Me_2Si); -2.26 (Me_3Si); 133.0, 133.1, 133.2, 133.3, 137.3, 138.8, 139.7, 140.3 (phenyl ring carbons). Anal. Found: C, 59.98; H, 8.93. $\text{C}_{23}\text{H}_{42}\text{Si}_5$ calc.: C, 60.18; H, 9.22%.

3.12. Photolysis of **2**

A solution of 0.305 g (0.573 mmol) of **2**, 3.75 g (66.8 mmol) of isobutene, and 0.054 g (0.279 mmol) of tetradecane as an internal standard in 55 ml of benzene was photolyzed with a low-pressure mercury lamp bearing a Vycor filter for 40 min. The mixture was analyzed by GLC and found to contain **5** (58% yield), an isomer of **5** (5% yield, m/e 586 (M^+)), **6a** (1% yield), **7a** (2% yield), and 24% of the starting compound **2**. Compound **5** was isolated by medium-pressure liquid chro-

matography. MS: m/e 586 (M^+). IR: 1463, 1403, 1380, 1246, 1131, 1091 cm^{-1} . ^1H NMR (CDCl_3): δ 0.04 (s, 9H, Me_3Si); 0.06 (s, 9H, Me_3Si); 0.21 (s, 6H, Me_2Si); 0.28 (s, 6H, Me_2Si); 0.33 (s, 6H, Me_2Si); 0.667 (s, 6H, Me_2Si); 0.673 (d, 2H, $J = 6.4$ Hz, CH_2); 0.82 (d, 6H, $J = 6.4$ Hz, CH_3); 1.65–1.73 (m, 1H, $J = 6.4$ Hz, CH); 7.42 (br s, 4H, phenyl ring protons); 7.45 (br d, 1H, $J_{\text{ortho}} = 7.3$ Hz, phenyl ring proton); 7.65 (br d, 1H, $J_{\text{ortho}} = 7.3$ Hz, phenyl ring proton); 7.74 (br s, 1H, phenyl ring proton). ^{13}C NMR (CDCl_3): δ -4.10 (two Me_2Si); -2.20 (two Me_3Si); 0.83, 1.05 (Me_2Si); 25.0, 26.3, 27.9 (CH_2CHMe_2); 133.0, 133.2, 133.6, 134.8, 138.3, 140.2, 140.4, 141.9, 142.4, 146.7 (phenyl ring carbons). Anal. Found: C, 61.23; H, 9.94. $\text{C}_{30}\text{H}_{58}\text{Si}_6$ calc.: C, 61.35; H, 9.95%. GC-mass spectrometric analysis of **6a** and **7a** showed that mass fragmentation patterns were identical to those of authentic samples.

3.13. Photolysis of **2** in benzene

A solution of 0.0856 g (0.161 mmol) of **2** and 0.0184 g (0.093 mmol) of tetradecane as an internal standard in 20 ml of benzene was photolyzed for 15 min. The mixture was analyzed by GLC and found to contain **6a** (2% yield), **7a** (5% yield), and 11% of the starting compound **2**.

3.14. Photolysis of **2** in deuteriobenzene

In a 5-ml quartz tube was placed 0.0106 g (0.020 mmol) of **2** and 0.0046 g (0.023 mmol) of tetradecane as an internal standard in 1 ml of deuteriobenzene. The mixture was photolyzed externally with a low-pressure mercury lamp under an argon atmosphere for 15 min. The mixture was analyzed by GC-mass spectrometry and found to contain **6a** and **6b** (3% combined yield, **6a/6b** = 4 : 1), **7b** (3% yield, m/e 347 (M^+)), and 19% of the starting compound **2**.

3.15. Photolysis of **3** in the presence of isobutene in benzene

A solution of 0.0981 g (0.136 mmol) of **3**, 1.39 g (24.8 mmol) of isobutene, and 0.0203 g (0.102 mmol) of tetradecane as an internal standard in 115 ml of benzene was photolyzed for 30 min. The mixture was analyzed by GLC and found to contain **6a** (less than 1% yield), **7a** (1% yield), **8** (4% yield), **9** (2% yield), **10** (1% yield), and 17% of the starting compound **3**. The products **8** and **9** were isolated by preparative MPLC (silica gel, eluted with hexane).

For **8**: MS: m/e 778 (M^+). ^1H NMR (CDCl_3): δ 0.06 (s, 9H, Me_3Si); 0.07 (s, 9H, Me_3Si); 0.19 (s, 6H, Me_2Si); 0.28 (s, 6H, Me_2Si); 0.29 (s, 6H, Me_2Si); 0.31 (s, 6H, Me_2Si); 0.33 (s, 6H, Me_2Si); 0.57 (s, 6H, Me_2Si); 0.65 (d, 2H, $J = 6.3$ Hz, CH_2); 0.82 (d, 6H, $J = 6.3$ Hz, CH_3); 1.60–1.75 (m, 1H, $J = 6.3$ Hz, CH); 7.34–7.41

(m, 8H, phenyl ring protons); 7.45 (br dd, 1H, $J_{ortho} = 7.6$ Hz, $J_{meta} = 1.3$ Hz, phenyl ring proton); 7.62 (br d, 1H, $J_{ortho} = 7.6$ Hz, phenyl ring proton); 7.67 (br s, 1H, phenyl ring proton). ^{13}C NMR (CDCl_3): δ -4.15, -4.11, -4.04, -3.95 (Me_2Si); -2.26, -2.19 (Me_3Si); 0.78, 0.99 (Me_2Si); 25.0, 26.3, 27.8 (CH_2CHMe_2); 133.0 (two carbons); 133.2, 133.4, 133.6, 134.8, 137.7, 138.9, 139.7, 140.2, 140.3, 141.8, 142.4, 146.8 (phenyl ring carbons). Exact MS: Found (no parent): 763.3713 ($\text{M}^+ - \text{Me}$). $\text{C}_{39}\text{H}_{71}\text{Si}_8$ calc.: 763.3711. Anal. Found (mixture of **8** and **9**): C, 61.59; H, 9.55. $\text{C}_{40}\text{H}_{74}\text{Si}_8$ calc.: C, 61.62; H, 9.57%.

For **9**: MS: m/e 778 (M^+). ^1H NMR (CDCl_3): δ 0.03 (s, 9H, Me_3Si); 0.06 (s, 9H, Me_3Si); 0.19 (s, 6H, Me_2Si); 0.28 (s, 6H, Me_2Si); 0.31 (s, 12H, two Me_2Si); 0.33 (s, 6H, Me_2Si); 0.62 (s, 6H, Me_2Si); 0.67 (d, 2H, $J = 6.6$ Hz, CH_2); 0.82 (d, 6H, $J = 6.6$ Hz, CH_3); 1.62–1.75 (m, 1H, $J = 6.6$ Hz, CH); 7.33–7.37 (m, 8H, phenyl ring protons); 7.44 (br dd, 1H, $J_{ortho} = 7.6$ Hz, $J_{meta} = 1.3$ Hz, phenyl ring proton); 7.64 (br d, 1H, $J_{ortho} = 7.6$ Hz, phenyl ring proton); 7.74 (br s, 1H, phenyl ring proton). ^{13}C NMR (CDCl_3): δ -4.20, -4.11 (Me_2Si); -3.99 (two Me_2Si); -2.24 (two Me_3Si); 0.78, 1.03 (Me_2Si); 25.0, 26.2, 27.8 (CH_2CHMe_2); 133.0 (two carbons); 133.1, 133.2, 133.5, 134.8, 138.2, 138.9, 139.6, 139.7, 140.5, 141.8, 142.3, 146.6 (phenyl ring carbons). Exact MS: Found (no parent): 763.3738 ($\text{M}^+ - \text{Me}$). $\text{C}_{39}\text{H}_{71}\text{Si}_8$ calc.: 763.3711. GC-mass spectrometric analysis of **6a**, **7a** and **10** indicated that mass fragmentation patterns were identical with those of authentic samples.

3.16. Photolysis of **3** in benzene

A solution of 0.0403 g (0.056 mmol) of **3** and 0.0126 g (0.064 mmol) of tetradecane as an internal standard in 60 ml of benzene was photolyzed for 50 min. The mixture was analyzed by GLC and found to contain **6a** (less than 1% yield), **7a** (1% yield), **10** (2% yield), and 12% of the starting compound **3**.

3.17. Photolysis of **4** in benzene

A solution of 0.0100 g (0.011 mmol) of **4** and 0.0041 g (0.021 mmol) of tetradecane as an internal standard in 115 ml of benzene was photolyzed for 17 min. The mixture was analyzed by GLC and found to contain **6a** (1% yield), **7a** (11% yield), **10** (11% yield), **11** (1% yield), and 24% of the starting compound **4** (the yield of **4** recovered was calculated by using analytical GPC).

3.18. Isolation of **7a** and **10**

A mixture of 0.0781 g (0.085 mmol) of **4** and 0.0034 g (0.017 mmol) of tetradecane as internal standard was photolyzed at 60–70°C for 11 min. The mixture was

analyzed by GLC and found to contain **6a** (3% yield), **7a** (6% yield), **10** (6% yield), and **11** (3% yield). Similar photolysis was repeated 15 times because of poor solubility of **4** in benzene, and the resulting photolysis mixtures were collected. The solvent benzene was concentrated, and compounds **7a** and **10** were isolated by preparative GLC.

For **7a**: MS: m/e 342 (M^+). IR: 1426, 1403, 1378, 1247, 1130, 1112 cm^{-1} . ^1H NMR (CDCl_3): δ 0.07 (s, 9H, Me_3Si); 0.32 (s, 6H, Me_2Si); 0.56 (s, 6H, Me_2Si); 7.35–7.56 (m, 9H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.06, -2.44 (Me_2Si); -2.24 (Me_3Si); 127.8, 129.1, 133.1, 133.4, 134.2, 138.0, 138.3, 140.7 (phenyl ring carbons). Anal. Found: C, 66.44; H, 8.78. $\text{C}_{19}\text{H}_{30}\text{Si}_3$ calc.: C, 66.59; H, 8.82%.

For **10**: m.p. 109–111°C. MS: m/e 534 (M^+). IR: 1248, 1130, 1113, 831 cm^{-1} . ^1H NMR (CDCl_3): δ 0.05 (s, 9H, Me_3Si); 0.31 (s, 6H, Me_2Si); 0.32 (s, 12H, two Me_2Si); 0.54 (s, 6H, Me_2Si); 7.33–7.55 (m, 13H, phenyl ring protons). ^{13}C NMR (CDCl_3): δ -4.11, -3.95, -3.92, -2.46 (Me_2Si); -2.24 (Me_3Si); 127.8, 129.1, 133.0, 133.1, 133.2, 133.3, 134.2, 138.1, 138.3, 138.8, 139.7, 140.1 (phenyl ring carbons). Anal. Found: C, 65.03; H, 8.63. $\text{C}_{29}\text{H}_{46}\text{Si}_5$ calc.: C, 65.09; H, 8.66%. GC-mass spectrometric analysis of **6a** and **11** shows that mass fragmentation patterns were identical with those of the authentic samples.

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