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Silicon–carbon unsaturated compounds

XL *. Photolysis of 1,4-bis(2-phenyltetramethyldisilanyl)benzene

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Abstract

The photolysis of 1,4-bis(2-phenyltetramethyldisilanyl)benzene (**1**) in the presence of isobutene in benzene gave 4-(isobutyldimethylsilyl)-1-(2-phenyltetramethyldisilanyl)-3-(dimethylphenylsilyl)benzene, 2-(isobutyldimethylsilyl)-1-{dimethyl[4-(2-phenyltetramethyldisilanyl)phenyl]silyl}benzene, and 1,4-bis(isobutyldimethylsilyl)-2,5-bis(dimethylphenylsilyl)benzene in 49, 4 and 12% yields, respectively, along with small amounts of 1-(2-phenyltetramethyldisilanyl)-4-(dimethylphenylsilyl)benzene (**5a**), 4-dimethylsilyl-1-(2-phenyltetramethyldisilanyl)benzene (**6**), dimethylphenylsilane (**7**) and dimethyldiphenylsilane (**8a**). Irradiation of **1** in the absence of isobutene afforded **5a** (2% yield), **6** (less than 1% yield), **7** (2% yield) and **8a** (3% yield). Similar irradiation of **1** in deuteriobenzene produced a mixture of **5a** and 4-[(pentadeuteriophenyl)dimethylsilyl]-1-(2-phenyltetramethyldisilanyl)benzene, in addition to **6**, **7** and (pentadeutertiophenyl)dimethylphenylsilane.

Introduction

The photolysis of benzenoid aromatic disilanes produces the silene (rearranged silene) arising from a 1,3-silyl shift to an ortho carbon atom of the benzenoid aromatic ring [1–3]. The silene thus formed reacts with various trapping agents [2]. In the absence of the trapping agent, the silenes undergo polymerization to give nonvolatile products. In some cases, the formation of another type of a silene which is formed from homolytic scission of a silicon–silicon bond, followed by disproportionation of the resulting silyl radicals has been observed [4]. This type of silene (nonrearranged silene) is produced only in low yield when aryldisilanes are photolyzed. However, the photolysis of the polymeric system involving a disilanylenephenylene group proceeds mainly to give the nonrearranged silene [5].

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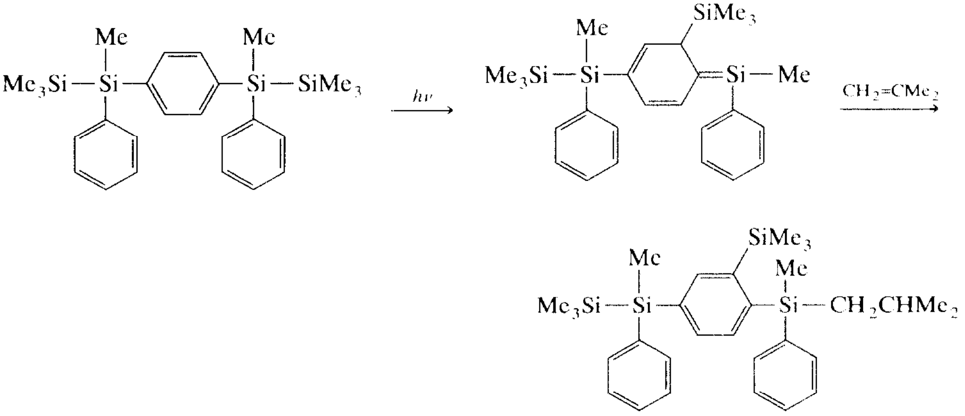
We have recently found that irradiation of 1,4-bis(1-phenyltetramethyldisilanyl)benzene in the presence of isobutene in benzene gives 4-(isobutylmethylphenylsilyl)-1-(1-phenyltetramethyldisilanyl)-3-(trimethylsilyl)benzene produced from the ene reaction of the rearranged silene arising from the 1,3-shift of a trimethylsilyl group to the phenylene ring, but not the phenyl ring, with isobutene in high yield [6]. In this photolysis, no products derived from the nonrearranged silene can be detected in the reaction mixture. As part of an investigation concerning the photochemistry of disilanes with two different π-electron systems [4,7], we have examined the photochemical behavior of 1,4-bis(2-phenyltetramethyldisilanyl)benzene.

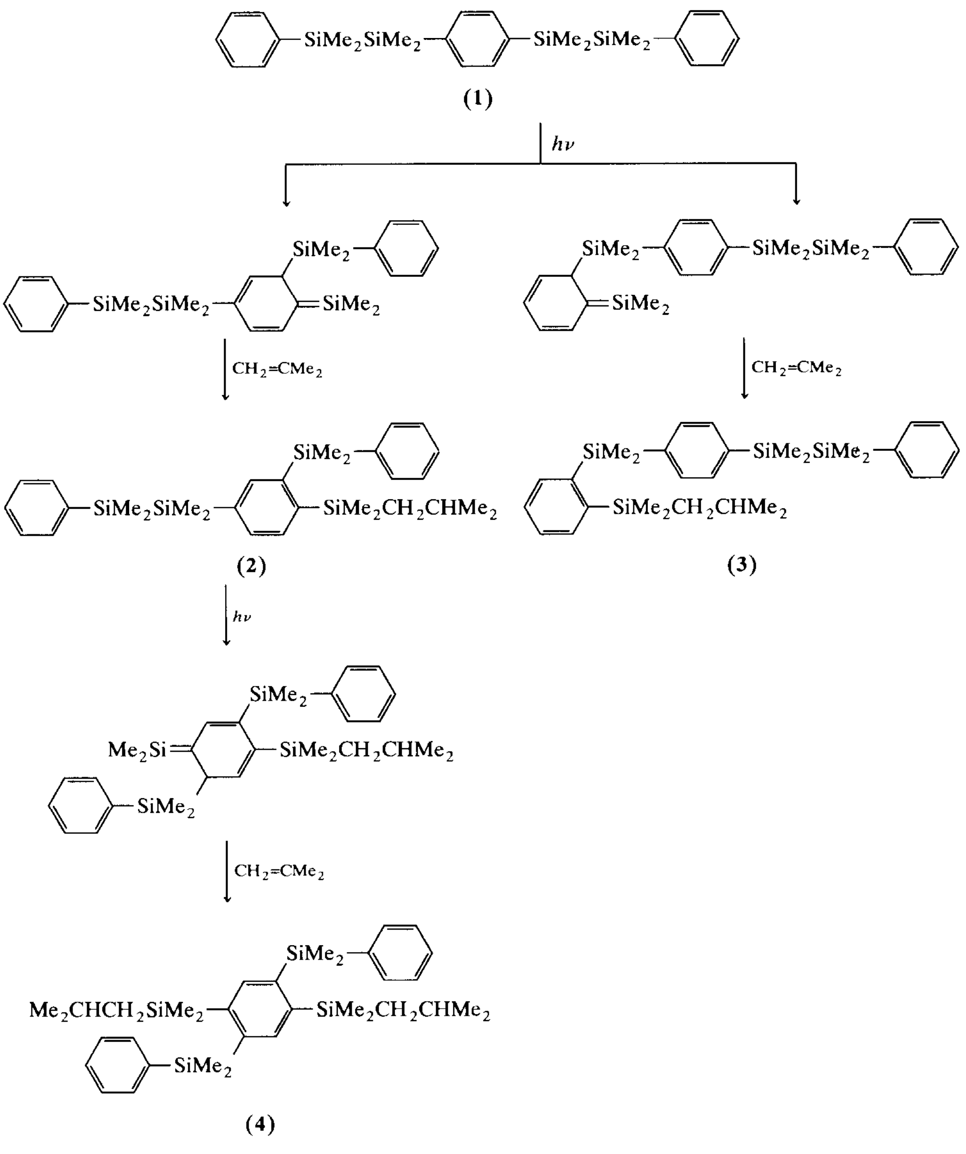


Results and discussion

1,4-Bis(2-phenyltetramethyldisilanyl)benzene (**1**) was prepared by the reaction of 1-chloro-2-phenyltetramethyldisilane with the di-Grignard reagent prepared from *p*-dibromobenzene and magnesium in THF.

When a benzene solution of **1** in the presence of a 93-fold excess of isobutene was photolyzed with a low-pressure mercury lamp bearing a Vycor filter (254 nm) at ambient temperature for 30 min, four products, 4-(isobutyldimethylsilyl)-1-(2-phenyltetramethyldisilanyl)-3-(dimethylphenylsilyl)benzene (**2**), 2-(isobutyldimethylsilyl)-1-{dimethyl[4-(2-phenyltetramethyldisilanyl)phenyl]silyl}benzene (**3**), 1,4-bis(isobutyldimethylsilyl)-2,5-bis(dimethylphenylsilyl)benzene (**4**) and an isomer of **4** were obtained in 49, 4, 12 and 5% yields, respectively, in addition to 15% of the starting compound **1** (Scheme 1). In the photolysis of **1**, four other products detected by GLC were produced in less than 1% yield. The GC-mass spectrometric analysis of these products indicates that two of them have a parent ion peak at *m/e* 404, corresponding to the calculated molecular weight of 1-(2-phenyltetramethyldisilanyl)-4-(dimethylphenylsilyl)benzene (**5a**), while parent ions of the others are calculated to be *m/e* 328 and 136, corresponding to the molecular weight of 4-(dimethylsilyl)-1-(2-phenyltetramethyldisilanyl)benzene (**6**) and dimethylphenylsilane (**7**), respectively.

The formation of **2** and **3** may be understood in terms of the reaction of two types of the rearranged silenes with isobutene. One of the silenes is probably produced from a 1,3-dimethylphenylsilyl shift to the phenylene ring, while the



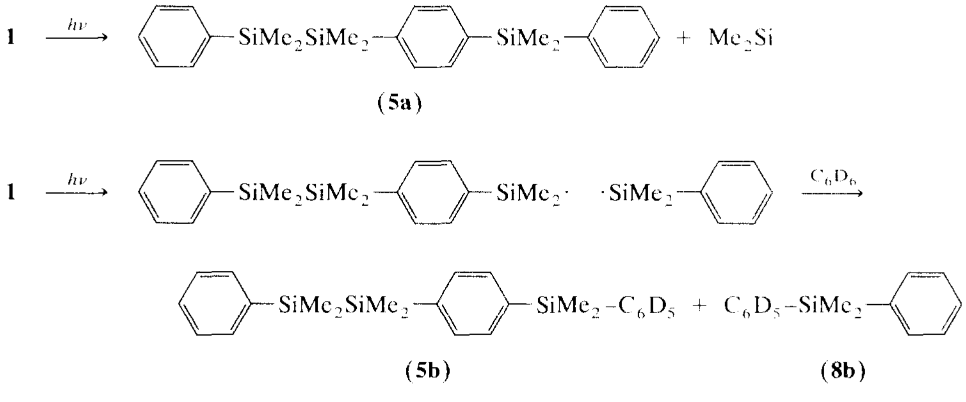
Scheme 1.

other involves a 1,3-shift of a dimethyl [4-(2-phenyltetramethyldisilanyl)phenyl]silyl group to an *ortho* carbon atom of the terminal phenyl ring. Compound **4** is not a primary photoproduct, but a secondary product. In fact, compound **4** cannot be detected in the reaction mixture in the early stages of the photolysis. For example, in the photolysis of **1** in the presence of isobutene, when 39% of **1** was photolyzed, products **2** and **3** were produced in 30 and 11% yields, respectively, in addition to trace amounts of **5a** and **6**. No compound **4** was detected in the photolysis mixture by either GLC or spectrometric analysis. That compound **4** was produced photochemically from **2** was confirmed by the fact that the photolysis of **2** under the same conditions gave compound **4**. Thus, the photolysis of **2** which was isolated in a pure form in the presence of isobutene gave **4** in 9% yield, along with 30% of the unchanged compound **2**. Careful analysis of the reaction mixture indicated that the isomer of **4** could not be detected. Therefore, the isomer of **4** would be produced photochemically from compound **3**, although the structure of this compound could not be verified at present. The structures of compound **2**, **3** and **4** were confirmed by spectrometric analysis, as well as by elemental analysis.

We carried out NOE-FID difference experiments at 270 MHz, to confirm the structure of **3**. Thus, saturation of the dimethylsilyl protons of an isobutyldimethylsilyl group caused a strong positive NOE of methylene and methine protons of an isobutyl group and dimethylsilyl protons at δ 0.64 ppm, as well as phenylene ring protons. Irradiation of the tetramethyldisilanylene protons at δ 0.34 ppm produced a positive NOE of protons on phenyl and phenylene rings. These results are wholly consistent with the structure proposed for **3**.

In order to learn more about the mechanism for the formation of minor products, **5a**, **6** and **7a**, we carried out the photolysis of **1** in the absence of a trapping agent. In general, the rearranged silenes in the absence of a trapping agent produced photochemically from benzenoid aromatic disilanes undergo polymerization to give nonvolatile substances. Thus, when the photolysis of **1** was carried out in the absence of isobutene in benzene, no compounds **2**–**4** were detected in the photolysis mixture, but **5a** (2% yield), **6** (less than 1% yield), **7** (2% yield), and **8a** (3% yield) were produced, in addition to an isomer of **5a** (less than 1%) and 14% of the starting compound **1**. Interestingly, similar photolysis of **1** in deuteriobenzene afforded a mixture of **5a** and 4-[(pentadeuteriophenyl)dimethylsilyl]-1-(2-phenyltetramethyldisilanyl)benzene (**5b**) (3% combined yield), together with **6** (less than 1% yield), **7** (2% yield) and (pentadeuteriophenyl)dimethylphenylsilane (**8b**) (1% yield). The ratio of **5a**/**5b** was calculated to be 3:2 by mass spectrometric analysis.

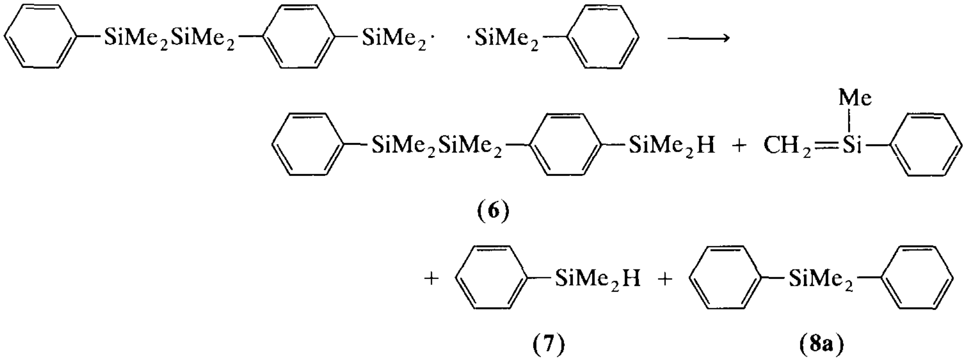
Compound **5a** is probably formed by extrusion of dimethylsilylene [2,3] from the starting compound **1**, although evidence for the formation of this silylene could not be obtained. In contrast to this, compounds **5b** and **8b** may be understood in terms of homolytic scission of a silicon–silicon bond in the starting compound **1**, followed



Scheme 2.

by homolytic aromatic substitution of the resulting silyl radicals onto deuteriobenzene (Scheme 2). Compound **6** can be explained by homolytic scission of a silicon–silicon bond of **1**, followed by disproportionation of the resulting silyl radicals. Although the product derived from a nonrearranged silene, 1-methyl-1-phenylsilene could not be detected, such disproportionation of the silyl radicals is well known [4,7,8].

The structures of **5a** and **6** were confirmed by comparison with mass fragmentation patterns and retention time in GLC of authentic samples obtained from an independent synthesis (see Experimental section). Similarly, compounds **7** and **8a** were identified by comparison with mass fragmentation patterns and also the GLC retention time of authentic samples. Compounds **5b** and **8b** were identified by mass spectrometric analysis.



(6)

(7)

(8a)

In conclusion, the photolysis of **1** produces two types of rearranged silenes arising from a 1,3-silyl shift to the phenylene ring (main route) and to the phenyl ring (minor route). Homolytic scission of a silicon–silicon bond in compound **1** also occurs slightly.

Experimental

General procedures

All reactions were carried out under an atmosphere of dry argon. Mass spectra were measured on a Shimadzu Model GCMS-QP1000 instrument. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-infrared spectrometer. ^{1}H and ^{13}C NMR spectra were determined with a JEOL Model EX-270 spectrometer using deuteriochloroform as a solvent. Yields of the photoproducts were determined on the basis of the starting compound used by GLC, using tetradecane, pentadecane and undecane as internal standards.

Benzene used as a solvent was dried over lithium aluminium hydride and distilled before use. Tetrahydrofuran (THF) was dried over sodium-benzophenone ketyl. 1-Chloro-2-phenyltetramethyldisilane was prepared as reported previously [9].

Preparation of 1,4-bis(2-phenyltetramethyldisilanyl)benzene (1)

In a 300-mL four-necked flask fitted with a stirrer, reflux condenser and dropping funnel was placed 3.4 g (0.14 mol) of magnesium in 100 mL of THF. To this was added a mixture of 23.31 g (0.14 mol) of 1-chloro-2-phenyltetramethyldisilane and 16.5 g (0.07 mol) of *p*-dibromobenzene in 50 mL of THF at room temperature over a period of 2 h. The reaction mixture was heated to reflux for 6 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water and dried over magnesium sulfate. The solvents were distilled off under reduced pressure (4 mmHg). The residue was recrystallized from 100 mL of ethanol to give 13.08 g of **1** (40% yield): m.p. 113–115°C. UV (in cyclohexane): λ_{max} (ϵ) 253 nm (60, 500). MS: *m/e* 462 (M^+). IR (KBr): 1427, 1400, 1378, 1247, 1127, 1104 cm^{-1}. ^{1}H NMR: δ 0.32 (s, 12H, Me_2Si); 0.33 (s, 12H, Me_2Si); 7.27–7.39 (m, 14H, aromatic ring protons). ^{13}C NMR: δ −4.06 (Me_2Si), −3.92 (Me_2Si), 127.7, 128.4, 133.1, 133.9, 139.0 (aromatic ring carbons). Anal. Found: C, 67.35; H, 8.23. $C_{26}H_{38}Si_4$ calc.: C, 67.46; H, 8.27%.

*Photolysis of **1** in the presence of isobutene*

A mixture of 0.2322 g (0.502 mmol) of **1**, 2.6 g (46.5 mmol) of isobutene and 0.0200 g (0.13 mmol) of pentadecane as an internal standard in 25 mL of benzene was photolyzed upon irradiation of a low-pressure mercury lamp bearing a Vycor filter for 35 min. The mixture was analyzed by GLC as being 4-(isobutyldimethylsilyl)-3-(phenyldimethylsilyl)-1-(2-phenyltetramethyldisilanyl)benzene (**2**) (49% yield), 2-(isobutyldimethylsilyl)-1-{dimethyl[4-(2-phenyltetramethyldisilanyl)phenyl]silyl}-benzene (**3**) (4% yield), 1,4-bis(isobutyldimethylsilyl)-2,5-bis(phenyldimethylsilyl)-benzene (**4**) (12% yield) and an isomer of **4** (5% yield, *m/e* 559 ($M^+ -$ Me)), in addition to 15% of the starting compound **1**, **5a** (less than 1% yield, *m/e* 404 (M^+)), **6** (less than 1% yield, *m/e* 328 (M^+)) and **7** (2% yield, *m/e* 136 (M^+)). The products **2**, **3** and **4** were isolated by medium-pressure liquid chromatography.

For **2**: MS: *m/e* 518 (M^+). IR (neat): 1403, 1380, 1246, 1131 cm^{-1}. ^{1}H NMR: δ 0.23 (s, 6H, Me_2Si); 0.33 (s, 6H, Me_2Si); 0.34 (s, 6H, Me_2Si); 0.61 (s, 6H, Me_2Si); 0.69 (d, 2H, CH_2, $J = 6.9$ Hz); 0.86 (d, 6H, Me_2, $J = 6.9$ Hz); 1.6–1.8 (m, 1H, CH); 7.28–7.59 (m, 11H, aromatic ring protons); 7.66 (br d, 1H, aromatic ring proton, $J_{ortho} = 7$ Hz); 7.73 (br d, 1H, aromatic ring proton, $J_{meta} = 1$ Hz). ^{13}C NMR: δ −4.20 (Me_2Si), −3.88 (Me_2Si), 0.78 (Me_2Si), 1.05 (Me_2Si), 25.0, 26.2, 27.9 (CH_2CHMe_2), 127.7 (two carbons), 128.4, 128.8, 133.4, 133.8, 134.2, 134.8, 137.6, 139.0, 140.5, 141.7, 142.2, 146.8, (aromatic ring carbons). Anal. Found: C, 69.35; H, 8.90. $C_{30}H_{46}Si_4$ calc.: C, 69.42; H, 8.93%.

For **3**: MS: *m/e* 518 (M^+). IR (neat): 1427, 1380, 1248, 1130, 1040 cm^{-1}. ^{1}H NMR: δ 0.20 (s, 6H, Me_2Si); 0.34 (s, 12H, two Me_2Si); 0.64 (s, 6H, Me_2Si); 0.69 (d, 2H, CH_2, $J = 6.6$ Hz); 0.84 (d, 6H, Me_2, $J = 6.6$ Hz); 1.70 (nonet, 1H, CH, $J = 6.6$ Hz); 7.29–7.75 (m, 13H, aromatic ring protons). ^{13}C NMR: δ −4.05 (Me_2Si), −3.92 (Me_2Si), 0.90 (Me_2Si), 1.09 (Me_2Si), 25.0, 26.2, 27.9 (CH_2CHMe_2), 127.5, 127.7, 128.0, 128.4, 133.1, 133.5, 133.9, 135.7, 136.6, 139.0, 139.6, 140.4, 143.1, 147.0 (aromatic ring carbons). Exact mass: Found: 518.2656. $C_{30}H_{46}Si_4$ calc.: 518.2678.

For **4**: m.p. 75–76°C (after recrystallized from ethanol). MS: *m/e* 517 ($M^+ -$ CH_2CHMe_2). IR (KBr): 1428, 1258, 1179, 1110, 1086 cm^{-1}. ^{1}H NMR: δ 0.10 (s, 12H, two Me_2Si); 0.56 (d, 4H, CH_2, $J = 6.6$ Hz); 0.61 (s, 12H, two Me_2Si); 0.76 (d, 12H, Me_2, $J = 6.6$ Hz); 1.60 (nonet, 2H, CH, $J = 6.6$ Hz); 7.30–7.47 (m, 10H, aromatic ring protons); 7.89 (s, 2H, aromatic ring proton). ^{13}C NMR: δ 0.67 (Me_2Si), 0.81 (Me_2Si), 24.9, 26.2, 27.7 (CH_2CHMe_2), 127.7, 128.8, 134.3, 140.3, 142.1, 143.6, 145.0 (aromatic ring carbons). Anal. Found: C, 71.00; H, 9.40. $C_{34}H_{54}Si_4$ calc.: C, 71.00; H, 9.46.

Photolysis of 1 in the absence of isobutene

A mixture of 0.2478 g (0.534 mmol) of **1** and 0.0290 g (0.186 mmol) of pentadecane as an internal standard in 20 mL of benzene was photolyzed for 33 min. The mixture was analyzed by GLC as being 1-(2-phenyltetramethyldisilanyl)-4-(dimethylphenylsilyl)benzene (**5a**) (2% yield, m/e 404 (M^+)), 4-(dimethylsilyl)-1-(2-phenyltetramethyldisilanyl)benzene (**6**) (less than 1% yield, m/e 328 (M^+)), dimethylphenylsilane (**7**) (2% yield, m/e 136 (M^+)), and dimethyldiphenylsilane (**8a**) (3% yield, m/e 212 (M^+)), in addition to 14% of the starting compound **1** and an isomer of **5a** (less than 1% yield, m/e 404 (M^+)). GC-mass spectrometric analysis of **5** and **7** indicated that mass fragmentation patterns were consistent with those of authentic samples.

Photolysis of 1 in deuteriobenzene

A mixture of 0.0071 g (0.015 mmol) of **1** and 0.0033 g (0.017 mmol) of tetradecane as an internal standard in 0.5 mL of deuteriobenzene was photolyzed for 55 min. The reaction mixture was analyzed by GLC as being **5a** and 4-[(pentadeuteriophenyl)dimethylsilyl]-1-(2-phenyltetramethyldisilanyl)benzene (**5b**) (3% combined yield; the ratio of **5a**/**5b** was calculated to be 3:2), **6** (less than 1% yield), **7** (2% yield), and (pentadeuteriophenyl)dimethylphenylsilane (**8b**) (1% yield), in addition to 13% of the starting compound **1**.

Photolysis of 2 in the presence of isobutene

A mixture of 0.1628 g (0.314 mmol) of **2**, 3.63 g (64.7 mmol) of isobutene and 0.0497 g (0.234 mmol) of pentadecane in 55 mL of benzene was photolyzed for 2 h. The mixture was analyzed by GLC as being **4** (9% yield) and starting compound **2** (30% yield). All spectral data obtained from **4**, which was isolated by preparative GLC, were identical with those of the authentic sample.

Preparation of 5a

To a Grignard reagent prepared from 1.447 g (4.97 mmol) of *p*-bromophenyldimethylphenylsilane and 0.1111 g (4.57 mmol) of magnesium in 10 mL of THF was added 1.183 g (5.17 mmol) of 1-chloro-2-phenyltetramethyldisilane in 5 mL of THF. The reaction mixture was heated to reflux for 43 h. After approx. 20 mL of hexane was added to the mixture, the resulting magnesium salts was filtered off and the filtrate was treated with a short column. Compound **5a** (0.731 g, 40% yield) was isolated by medium-pressure liquid chromatography. MS: m/e 404 (M^+). IR (neat): 1426, 1406, 1379, 1247, 1131, 1112 cm^{-1}. ^1H NMR: δ 0.32 (s, 6H, Me_2Si); 0.34 (s, 6H, Me_2Si); 0.57 (s, 6H, Me_2Si); 7.27–7.56 (m, 14H, ring protons). ^{13}C NMR: δ -3.95, -3.86 and -2.44 (Me_2Si), 127.7, 127.8, 128.4, 129.1, 133.2, 133.4, 133.9, 134.2, 138.2, 138.3, 139.0, 140.0 (ring carbons). Anal. Found: C, 71.19; H, 7.94. $C_{24}H_{32}Si_3$ calc.: C, 71.22; H, 7.97%.

Preparation of 6

To 0.2607 g (1.07 mmol) of magnesium in 1 mL of THF was added a mixture of 2.466 g (11.5 mmol) of *p*-bromophenyldimethylsilane and 2.669 g (11.7 mmol) of

1-chloro-2-phenyltetramethyldisilane dissolved in 15 mL of THF. The mixture was heated to reflux for 17 h. To this was added approx. 20 mL of hexane, and the resulting magnesium salts were filtered off. The filtrate was distilled under reduced pressure to give 1.474 g (42% yield) of **6**: b.p. 103–106°C/0.5 mmHg. MS: m/e 328 (M^+). IR (neat): ν(Si–H) 2119 cm^{-1}. ^{1}H NMR: δ 0.33 (s, 6H, Me_2Si); 0.34_5 (s, 6H, Me_2Si); 0.35_2 (d, 6H, Me_2Si, $J = 3.6$ Hz); 4.43 (sept, 1H, HSi, $J = 3.6$ Hz); 7.29–7.51 (m, 9H, ring protons). ^{13}C NMR: δ −3.95 (Me_2Si), −3.88 (two Me_2Si), 127.7, 128.4, 133.2, 133.3, 133.9, 137.4, 138.9, 140.2 (ring carbons). Anal. Found: C, 65.73; H, 8.58. $C_{18}H_{28}Si_3$ calc.: C, 65.78; H, 8.59%.

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