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Photolysis of Organopolysilanes. Photochemical Behavior of Branched Polysilanes

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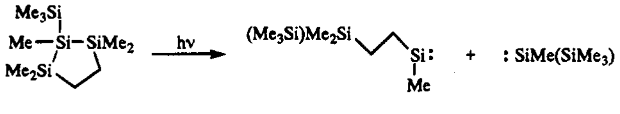
The highly branched permethylpolysilanes, 2-(trimethylsilyl)nonamethyltetrasilane, 2,2-bis(trimethylsilyl)octamethyltetrasilane (**1b**), 2,3-bis(trimethylsilyl)octamethyltetrasilane, and 2,2,3,3-tetrakis(trimethylsilyl)hexamethyltetrasilane (**1d**), and branched polysilaalkanes, 1,2-bis[tris(trimethylsilyl)silyl]ethane, 1,3-bis[tris(trimethylsilyl)silyl]propane, and 1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclopentane were prepared, and their photochemical behavior was investigated in the presence or absence of 2,3-dimethylbutadiene in pentane. Irradiation of the branched permethylated polysilanes with a low-pressure mercury lamp produced two different types of silylenes, while the branched polysilaalkanes gave a single silylene. In the photolysis of **1b** and **1d**, hydrosilanes arising from homolytic scission of an Si—Si bond followed by the hydrogen abstraction of the resulting silyl radicals were obtained.

Introduction

The photochemical behavior of linear and cyclic peralkyl-substituted oligosilanes and polysilane high molecular weight polymers has been investigated in detail.[1] The photolysis of these compounds undergoes skeletal contraction with two different routes. One involves extrusion of silylene species, while the other comprises homolytic scission of a silicon—silicon bond. The photochemical formation of silylenes is remarkably common for cyclic and linear polysilane oligomers and offers a convenient method to produce various types of silylenes.[2] Although the photolysis of polysilane high molecular weight polymers also produces silylenes, homolytic scission of silicon—silicon bonds in the polymer backbone is involved to a large extent.[3]

It is of considerable interest to us to investigate the photochemical behavior of branched polysilanes and branched polysilaalkanes consisting of various kinds of silicon skeletons. Previously, we have reported that the photolysis of methyltris(trimethylsilyl)silane in cyclohexane gave methyl(trimethylsilyl)silylene,[4] while 1,1,2,3,3-pentamethyl-2-(trimethylsilyl)-1,2,3-trisilacyclopentane produced two different types of the silylene, methyl(trimethylsilyl)silylene and a silylene arising from an intramolecular 1,2-trimethylsilyl shift, which were trapped by diethylmethylsilane.[5]

$$(Me_3Si)_3SiMe \xrightarrow{h\nu} Me_3SiSiMe_3 \; + \; :SiMe(SiMe_3)$$



In the photolysis of poly(dialkylsilanes), Miller and Michl have reported the formation of the silylene derived from chain scission involving a 1,2-alkyl shift in the polymer backbone, in addition to well-known photochemical formation of the silylene and homolytic scission of an Si—Si bond.[6] Davidson et al. have published a preliminary account of the photochemistry of branched polysilanes.[7] They found that dimethylsilylene is extruded via a 1,2-methyl shift in the photolysis of both 2,3-bis(trimethylsilyl)octamethyltetrasilane and 2,2-diethylhexamethyltrisilane as a minor pathway.

In this paper, we report the photolysis of four highly branched polysilanes and three branched polysilaalkanes in the presence or absence of 2,3-dimethylbutadiene as a trapping agent.

Results and Discussion

Synthesis. The starting compound, 2-(trimethylsilyl)nonamethyltetrasilane (**1a**), was obtained by the reaction of 2-lithio-2-(trimethylsilyl)octamethyltetrasilane, prepared from treatment of 2,2-bis(trimethylsilyl)octamethyltetrasilane (**1b**) with methyllithium in THF, with methyl iodide in 38% yield (Scheme 1). Compound **1b** was synthesized by the reaction of tris(trimethylsilyl)silyllithium with chloropentamethyldisilane in 86% yield. 2,3-Bis(trimethylsilyl)octamethyltetrasilane (**1c**)[8] and 2,2,3,3-tetrakis(trimethylsilyl)tetrasilane (**1d**)[9] were prepared by the method reported previously.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1994.

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[8] Ishikawa, M.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845.

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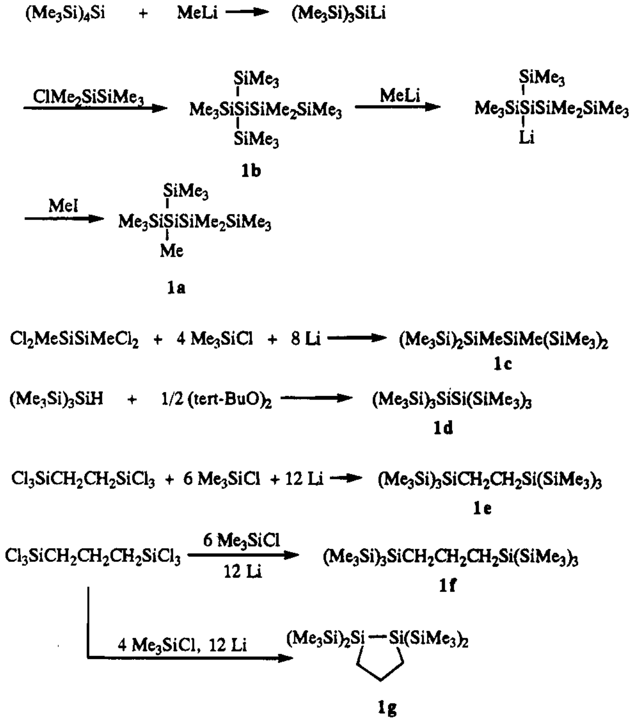
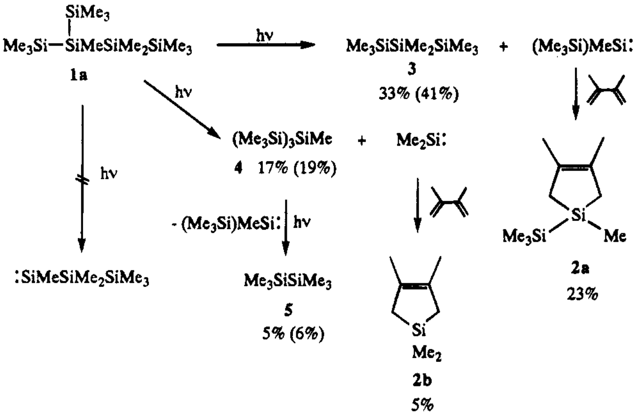
Scheme 1



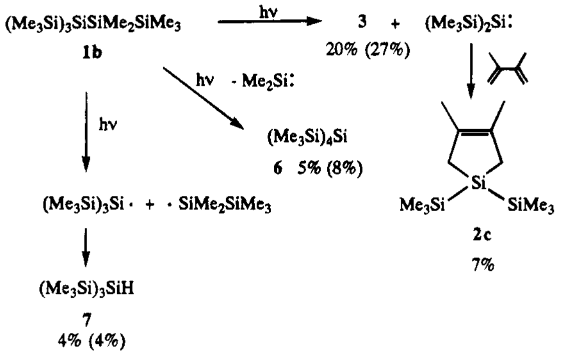
Scheme 2



1,2-Bis[tris(trimethylsilyl)silyl]ethane (**1e**) was synthesized by the lithium condensation reaction of 1,2-bis(trichlorosilyl)ethane with chlorotrimethylsilane in 25% yield, while a mixture of 1,3-bis[tris(trimethylsilyl)-silyl]propane (**1f**) and 1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclopentane (**1g**) was obtained in a ratio of 2:1, by similar condensation of 1,3-bis(trichlorosilyl)-propane with chlorotrimethylsilane.

Photolysis. Irradiation of a pentane solution of **1a** with a low-pressure mercury lamp (254 nm) in the presence of 2,3-dimethylbutadiene gave 1,3,4-trimethyl-1-(trimethylsilyl)-1-silacyclopent-3-ene (**2a**), 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (**2b**), octamethyltrisilane (**3**), methyltris(trimethylsilyl)silane (**4**), and hexamethyldisilane (**5**) in 23%, 5%, 33%, 17%, and 5% yields, respectively, when 74% of the starting compound **1a** was photolyzed (Scheme 2). All products **2a**, **2b**, and **3**–**5** were isolated by preparative GLC, and all spectral data for **2b** and **3**–**5** were identical with those of the authentic samples. Compound **2a** was characterized by spectrometric analysis as well as by elemental analysis (see Experimental Section).

Scheme 3



The formation of **2a** and **3** clearly indicates that the photolysis of **1a** produces methyl(trimethylsilyl)silylene, while products **2b** and **4** show the production of dimethylsilylene. For the formation of hexamethyldisilane **5**, one might consider the possibility that methyl-(pentamethyldisilanyl)silylene would be produced; however, no product derived from addition of this silylene to 2,3-dimethylbutadiene was detected by GC–mass spectrometric analysis of the reaction mixture. Accordingly, it seems likely that compound **5** is produced as a secondary photoproduct. In fact, as we and Davidson et al. reported previously, irradiation of **4** readily affords **5** and methyl(trimethylsilyl)silylene.[4,7]

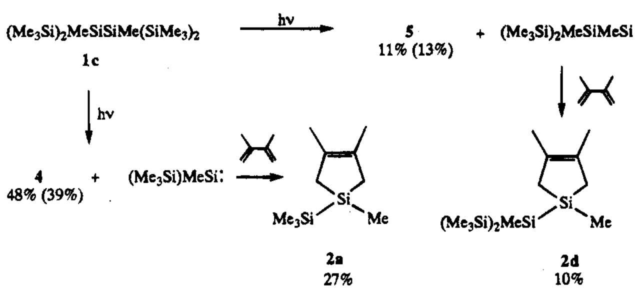
When **1a** was photolyzed in the absence of a trapping agent under the same conditions, products **3**–**5** were obtained in 41%, 19%, and 6% yields, respectively. GC–mass spectrometric analysis of the resulting photolysis mixture showed the absence of products having an Si—H bond, indicating that no homolytic scission of an Si—Si bond occurred. No volatile products which might be derived from silylenes were detected in the reaction mixture.

A similar photolysis of **1b** in the presence of 2,3-dimethylbutadiene afforded **3**, 3,4-dimethyl-1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene (**2c**), tetrakis(trimethylsilyl)silane (**6**), and tris(trimethylsilyl)silane (**7**) in 20%, 7%, 5%, and 4% yields, together with 26% of unchanged starting compound **1b** (Scheme 3). The formation of **2c** and **3** suggests extrusion of bis(trimethylsilyl)silylene. Compound **6** indicates the production of dimethylsilylene, although a product arising from addition of this silylene into a trapping agent could not be detected in the reaction mixture. This may be due to a low concentration of dimethylsilylene.

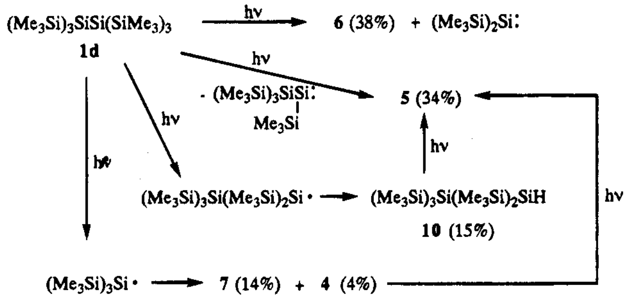
In contrast to the photolysis of **1a**, in which no product derived from homolytic scission of an Si—Si bond was detected, **1b** afforded product **7** which is probably formed from homolytic scission of an Si(2)—Si(3) bond, followed by hydrogen abstraction of the resulting silyl radical. Pentamethyldisilane which would be produced from the pentamethyldisilanyl radical, however, could not be detected by GLC analysis because of overlapping with the solvent pentane.

We found that the photolysis of **1c** produced methyl-(trimethylsilyl)silylene and methyl[methylbis(trimethylsilyl)silyl]silylene. Thus, irradiation of **1c** in the presence of 2,3-dimethylbutadiene gave silacyclopentene **2a** and 1,3,4-trimethyl-1-[methylbis(trimethylsilyl)silyl]-1-silacyclopent-3-ene (**2d**) in 27% and 10% yields, respectively, along with a 48% yield of **4** and an 11% yield of **5**, when 52% of the starting compound **1c** was photolyzed (Scheme 4).

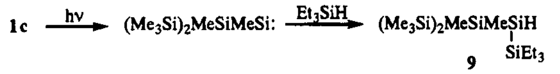
Scheme 4



Scheme 5



Davidson and his co-workers have recently reported the photolysis of **1c** in the presence of triethylsilane.[7] They found that methyl(trimethylsilyl)silylene is trapped by triethylsilane as a main product, in addition to small amounts of adducts arising from insertion of bis(trimethylsilyl)silylene and dimethylsilylene into an Si—H bond. However, no product derived from methyl[methylbis(trimethylsilyl)silyl]silylene has been reported. In order to check whether or not this silylene inserts into an Si—H bond in triethylsilane, we carried out the photolysis of **1c** in the presence of triethylsilane. Thus, irradiation of a pentane solution of **1c** in the presence of a 10-fold excess of triethylsilane afforded **4** and 1,1,1-triethyl-2,3,3,3-tetramethyltrisilane (**8**) in 90% and 43% yields, when 93% of the starting compound **1c** was consumed. However, when 76% of **1c** was photolyzed in this reaction, indeed, an insertion product, 4,4,4-triethyl-1,1,1,2,3-pentamethyl-2-(trimethylsilyl)tetrasilane (**9**) was obtained in 7% yield, in addition to



$$\mathbf{1c} \xrightarrow{h\nu} (Me_3Si)_2MeSiMeSi\!: \xrightarrow{Et_3SiH} (Me_3Si)_2MeSiMe\underset{SiEt_3}{\underset{|}{Si}}H$$

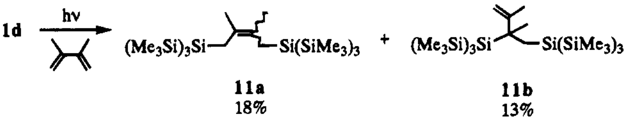
9

a 73% yield of **4** and a 53% yield of **8**. Presumably, product **9** is photoactive and undergoes further photolysis, leading to the formation of degradation products such as compound **8** during prolonged irradiation.

When the photolysis of **1b** and **1c** was carried out in the absence of a trapping agent, all of the silylenes generated underwent polymerization to give nonvolatile products, and products arising from chain contraction such as **3**–**7** were obtained. The yields of these compounds are shown in parentheses in the schemes.

When **1d** was photolyzed in the absence of 2,3-dimethylbutadiene in pentane for 20 h, hexamethyldisilane **5** and tetrakis(trimethylsilyl)silane (**6**) were obtained in 34% and 38% yields, respectively (Scheme 5). The formation of **5** and **6** indicates that the photolysis of **1d** produces (trimethylsilyl)[tris(trimethylsilyl)silyl]silylene and bis(trimethylsilyl)silylene. In this photolysis, methyltris(trimethylsilyl)silane (**4**), tris(trimethylsilyl)silane (**7**), 1,1,1-trimethyl-2,2,3,3-tetrakis(trimethylsilyl)trisilane (**10**) were obtained in 4%, 14%, and 15% yields, respectively. The formation of **7** and **10** can be best understood by assuming the tris(trimethylsilyl)silyl radical and pentakis(trimethylsilyl)disilanyl radical arising from the homolytic scission of the Si(2)—Si(3) bond and Si(1)—Si(2) bond, respectively. The pathway leading to compound **4** is still unknown. It might involve a 1,3-methyl shift from the Si(1) position to the Si(3) atom in **1d**, giving dimethyl-1,1-bis(trimethylsilyl)silene or abstraction of a methyl group from any available sources by the tris(trimethylsilyl)silyl radical, although evidence for the formation of the silene or abstraction of the methyl group by the tris(trimethylsilyl)silyl radical has not yet been obtained.

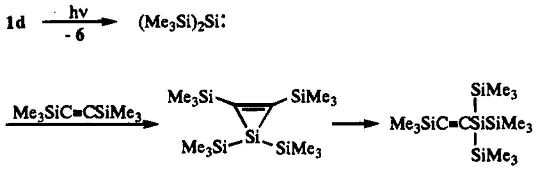
In contrast to the photolysis of **1a**–**1c** in the presence of 2,3-dimethylbutadiene, the photolysis of **1d** under the same conditions gave a complex reaction mixture. Two products identified as 2,3-dimethyl-1,4-bis[tris(trimethylsilyl)silyl]but-2-ene (**11a**) and 2,3-dimethyl-1,2-bis[tris(trimethylsilyl)silyl]but-3-ene (**11b**) were obtained in 18% and 13% yields. In this photolysis, many other products were formed, but only in low yields. Even though silylene adducts were formed, the yields would be less than 5%. All attempts to isolate products **11a** and **11b** were unsuccessful. In all cases, a mixture of **11a** and **11b** was obtained. Therefore, structures of **11a** and **11b** were confirmed by spectrometric analysis of the mixture. The ^1H NMR spectrum for **11a** clearly indicates the presence of a single isomer. It shows three singlets at 0.20, 1.33, and 2.16 ppm, due to Me_3Si, MeC, and CH_2 protons. The formation of **11a** and **11b** may be explained in terms of the reaction of photoexcited **1d** with 2,3-dimethylbutadiene and/or addition of the tris(trimethylsilyl)silyl radical to the butadiene.



11a 18%

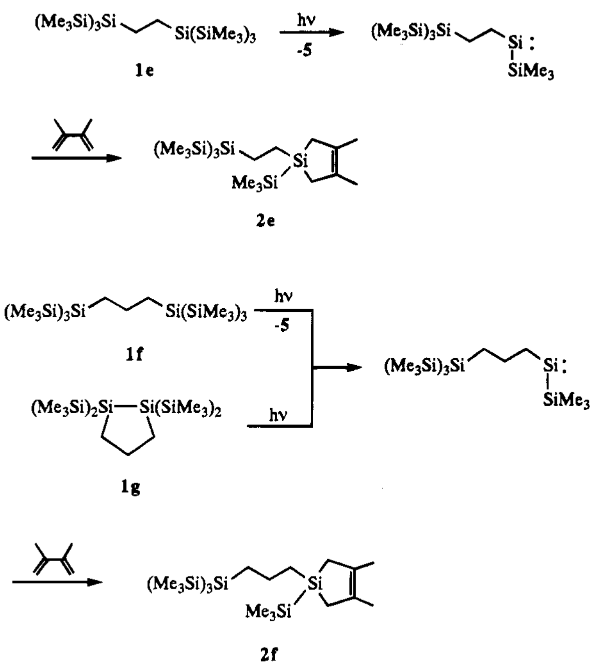
11b 13%

In order to get more information about the photochemical formation of silylenes from **1d**, we carried out the photolysis of **1d** using bis(trimethylsilyl)acetylene as a trapping agent. Thus, when **1d** was photolyzed in the presence of an excess of bis(trimethylsilyl)acetylene in pentane, (trimethylsilyl)[tris(trimethylsilyl)silyl]acetylene (**12**) was obtained in 14% yield along with **4**–**7** and **10** in 7%, 57%, 33%, 17%, and 21% yields, respectively. Compound **12** can be explained by the addition of bis(trimethylsilyl)silylene across the carbon—carbon triple bond of bis(trimethylsilyl)acetylene, leading to the formation of tetrakis(trimethylsilyl)silacyclopropene, followed by isomerization of the resulting silacyclopropane. Similar isomerization of silacyclopropenes to the [(trimethylsilyl)ethynyl]polysilanes has been reported



12 14%

Scheme 6



previously.[10] In this photolysis, no products arising from (trimethylsilyl)[tris(trimethylsilyl)silyl]silylene were detected by either GLC analysis or spectroscopic analysis. Therefore, it seems likely that some other processes such as photodegradation of **4** and **10** are also involved for the formation of compound **5**. In fact, compound **10** was found to be photolabile under the conditions used. Thus, irradiation of the reaction mixture obtained from the photolysis of **1d** which involves compound **10** for 10 h resulted in complete decomposition of **10**.

The photolysis of **1e**–**1g** proceeded smoothly to give a single silylene. Thus, irradiation of **1e** and **1f** with a low-pressure mercury lamp in the absence of a trapping agent in a pentane solution produced hexamethyldisilane **5** as the sole volatile product, while **1g** afforded no volatile products. In all cases, no other products were detected in the reaction mixture by GLC analysis. Irradiation of **1e** in the presence of 2,3-dimethylbutadiene gave **5** and 3,4-dimethyl-1-(trimethylsilyl)-1-{2-[tris(trimethylsilyl)silyl]ethyl}-1-silacyclopent-3-ene (**2e**) in 51% and 20% yields (Scheme 6). Similarly, irradiation of **1f** in the presence of 2,3-dimethylbutadiene gave **5** and 3,4-dimethyl-1-{3-[tris(trimethylsilyl)silyl]propyl}-1-silacyclopent-3-ene (**2f**) in 23% and 15% yields. The structures of adducts **2e** and **2f** were confirmed by spectrometric analysis as well as by elemental analysis. The formation of **2e** and **2f** can be best understood by addition of (trimethylsilyl){2-[tris(trimethylsilyl)silyl]ethyl}silylene and (trimethylsilyl){3-[tris(trimethylsilyl)silyl]propyl}silylene to 2,3-dimethylbutadiene.

Interestingly, the photolysis of **1g** under the same conditions gave product **2f** in 61% yield, as the sole volatile product. Product **2f** in this photolysis is probably produced by addition of (trimethylsilyl){3-[tris(trimethylsilyl)silyl]propyl}silylene derived from a 1,2-trimethylsilyl shift from one silicon to the other in the disilacyclopentane ring, followed by scission of the Si—Si bond to 2,3-dimethylbutadiene. Presumably, the formation of a cyclic silylene arising from elimination of hexamethyldisilane from **1g** is thermodynamically less favorable than that of the ring-opened silylene. In the photolysis of **1e**–**1g**, no products originating from homolytic scission of an Si—Si bond were detected in the volatile products.

In conclusion, the photolysis of highly branched polysilanes **1a**–**1d** produced simultaneously at least two different silylenes as main photochemical pathways. A similar reaction of branched polysilaalkanes **1e**–**1g**, however, afforded a single silylene. In the photolysis of **1b** and **1d**, the formation of the silyl radical is also involved to some extent.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of purified argon. Pentane and THF were dried over lithium aluminum hydride and distilled just before use. NMR spectra were recorded on a JEOL Model PMX-60 spectrometer, a JEOL Model FX-90A spectrometer, and a JEOL Model EX-270 spectrometer at ambient temperature. Mass spectra were measured on a Shimadzu QP-1000 spectrometer. Yields of all photoproducts were determined by GLC analysis using a hydrocarbon as an internal standard on the basis of the starting polysilanes photolyzed. Compounds **1c**[8] and **1d**[9] were prepared as reported in the literature.

Preparation of 1a. To a solution of 10.2 g (27.0 mmol) of compound **1b** (see below) in 100 mL of THF was added dropwise 20 mL (30.0 mmol) of a 1.5 M methyllithium–ether solution at 0 °C over a period of 30 min. The resulting mixture was allowed to warm to room temperature and stirred for 10 h. To this was added 2 mL (36.0 mmol) of methyl iodide at 0 °C, and then the mixture was heated to reflux for 2 h. The mixture was hydrolyzed with water, and the organic layer was separated. The aqueous layer was extracted twice with ether. The combined organic layer and the extracts were washed with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure and a fraction boiling at 120–140 °C (18 mmHg) was collected as a 6:4 mixture of **1a** and methyltris(trimethylsilyl)silane (5.1 g, 38% yield for **1a**). Compound **1a** was isolated by preparative GLC: MS *m/z* 320 (M^+); ^{1}H NMR (δ in CCl_4) 0.10 (br s, 9H, Me_2Si and MeSi), 0.15 (s, 18H, Me_3Si), 0.16 (s, 9H, Me_3Si); ^{13}C NMR (δ in $CDCl_3$) −12.1, −3.8, −1.1, 0.7; UV (in THF) λ_{max} 203 nm (ϵ 25 900), 226 nm (ϵ 13 000). Anal. Calcd for $C_{12}H_{36}Si_5$: C, 44.92; H, 11.31. Found: C, 44.85; H, 11.30.

Preparation of 1b. A solution of 31.3 mmol of [tris(trimethylsilyl)silyl]lithium prepared from 10.0 g (31.3 mmol) of tetrakis(trimethylsilyl)silane and 20.9 mL of a 1.5 M methyllithium–ether solution in 50 mL of THF was added to an ice-cooled 20-mL etheral solution of 5.2 g (31.3 mmol) of chloropentamethyldisilane. The mixture was allowed to warm at room temperature, stirred for 10 h, and then hydrolyzed with water. After the usual workup, as above, the residue was distilled under reduced pressure to give 10.2 g (86% yield) of **1b** (bp 140 °C/1 mmHg). All spectra data obtained in **1b** were identical with those reported in the literature.[9]

Preparation of 1,2-Bis(trichlorosilyl)ethane. A mixture of 124.3 g (0.77 mol) of trichlorovinylsilane, 109.5 g (0.81 mol) of trichlorosilane, and 0.05 mL of a 10% $H_2PtCl_6 \cdot 6H_2O$–isopropyl alcohol solution was stirred at room temperature for 10 h. The resulting mixture was distilled under reduced pressure to give 225.4 g (99% yield) of 1,2-bis(trichlorosilyl)ethane[11] (bp 105 °C/20 mmHg).

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(11) Schmidbaur, H.; Doerzbach, C. *Z. Naturforsch., B: Chem. Sci.* **1987**, *42*, 1088.

Preparation of 1e. A mixture of 225.4 g (0.759 mol) of 1,2-bis(trichlorosilyl)ethane, 642.0 g (5.92 mol) of chlorotrimethylsilane, and 93.8 g (13.6 mol) of lithium in 200 mL of THF was stirred vigorously at room temperature for 5 h. Excess lithium and lithium chloride were filtered off, and the filtrate was hydrolyzed with water. After the usual workup, as above, the residue was sublimed under reduced pressure to give 98.9 g (25% yield) of **1e** (bp 150−180 °C/1 mmHg): mp 191.0−191.5 °C; MS *m/z* 522 (M^+); ^1H NMR (δ in CCl_4) 0.17 (s, 54H, Me_3Si), 0.91 (s, 4H, CH_2); ^{13}C NMR (δ in $CDCl_3$) 1.3, 7.4; UV (in THF) λ_{max} 194 nm (ϵ 55 200). Anal. Calcd for $C_{20}H_{58}Si_8$: C, 45.90; H, 11.17. Found: C, 45.77; H, 11.13.

Preparation of 1,3-Bis(trichlorosilyl)propane. A mixture of 41.4 g (0.23 mol) of allyltrichlorosilane, 48.1 g (0.36 mol) of trichlorosilane, and 0.02 mL of a 10% $H_2PtCl_6{\cdot}6H_2O$−isopropyl alcohol solution was stirred at 30 °C for 10 h. The resulting mixture was distilled under reduced pressure to give 42.9 g (63% yield) of 1,3-bis(trichlorosilyl)propane[11] (bp 110 °C/28 mmHg).

Preparation of 1f and 1g. A mixture fo 42.9 g (0.144 mol) of 1,3-bis(trichlorosilyl)propane, 121.9 g (1.12 mol) of chlorotrimethylsilane, and 17.8 g (2.53 mol) of lithium in 200 mL of THF was stirred vigorously at room temperature for 5 h. Excess lithium and lithium chloride were filtered off, and the filtrate was hydrolyzed with water. After the usual workup, as above, the residue was distilled under reduced pressure to give 9.1 g of a 2:1 mixture of **1f** and **1g** (bp 120−143 °C/0.7 mmHg). Products **1f** and **1g** were isolated by preparative GLC. For **1f**: MS *m/z* 436 (M^+); ^1H NMR (δ in $CDCl_3$) 0.18 (s, 57H, Me_3Si), 0.65−1.05 (m, 4H, CH_2Si), 1.36−1.55 (m, 2H, CH_2C); ^{13}C NMR (δ in $CDCl_3$) 1.2, 14.1, 26.9; UV (in THF) λ_{max} 192 nm (ϵ 87 400). Anal. Calcd for $C_{21}H_{60}Si_8$: C, 46.94; H, 11.25. Found: C, 46.69; H, 11.22. For **1g**: mp 53.5 °C; MS *m/z* 390 (M^+); ^1H NMR (δ in $CDCl_3$) 0.19 (s, 36H, Me_3Si), 0.88 (t, 4H, J = 6.8 Hz, CH_2), 1.77 (quintet, 2H, J = 6.8 Hz, CH_2); ^{13}C NMR (δ in $CDCl_3$) 1.6, 11.5, 27.9; UV (in THF) λ_{max} 204 nm (ϵ 45 700). Anal. Calcd for $C_{15}H_{39}Si_6$: C, 46.08; H, 10.83. Found: C, 45.88; H, 10.76.

Photolysis of 1a in the Presence of 2,3-Dimethylbutadiene. Into a 25-mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a mixture of 486.3 mg (1.29 mmol) of **1a**, 258 mg (3.15 mmol) of 2,3-dimethylbutadiene, and 9.6 mg (0.036 mmol) of nonadecane as an internal standard. The mixture was photolyzed for 60 h at room temperature. At this stage, 74% of the starting compound **1a** was consumed. The resulting mixture was analyzed by GLC as being **2a** (23%), **2b** (5%), **3** (33%), **4** (17%), and **5** (5%). All products were isolated by preparative GLC. All spectral data obtained for **2b**,[12] **3**,[13] **4**,[13] and **5**[14] were identical with those of authentic samples prepared as reported in the literature. For **2a**: MS *m/z* 198 (M^+); ^1H NMR (δ in C_6D_6) 0.06 (s, 9H, Me_3Si), 0.11 (s, 3H, MeSi), 1.31 (br d, 2H, J = 11.7 Hz, CH_2), 1.48 (br d, 2H, J = 11.7 Hz, CH_2), 1.67 (br s, 6H, MeC); ^{13}C NMR (δ in C_6D_6) −4.2, −1.9, 19.4, 24.5, 130.9. Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 60.30; H, 11.04.

Photolysis of 1b in the Presence of 2,3-Dimethylbutadiene. A mixture of 100.8 mg (0.315 mmol) of **1b**, 1.06 g (12.9 mmol) of 2,3-dimethylbutadiene, and 25.6 mg (0.0826 mmol) of docosane as an internal standard in 25 mL of pentane was irradiated for 9 h. The resulting mixture was analyzed by GLC as being **1b** (26%), **2c** (7%), **3** (20%), **6** (5%), and **7** (4%). All products were isolated by preparative GLC. All spectral data obtained for **3**,[13] **6**,[15] and **7**[16] were identical with those of authentic samples prepared as reported in the literature. For **2c**: MS *m/z* 256 (M^+); ^1H NMR (δ in C_6D_6) 0.22 (s, 18H, Me_3Si), 1.71 (br s, 4H, CH_2), 1.78 (br s, 6H, MeC); ^{13}C NMR (δ in C_6D_6) −1.0, 19.3, 21.0, a signal of olefin carbon atoms is overlapping with signals of C_6D_6. Exact MS Calcd for $C_{12}H_{28}Si_3$: 256.1497. Found: 256.1477.

Photolysis of 1c in the Presence of 2,3-Dimethylbutadiene. A mixture of 296.6 mg (0.785 mmol) of **1c**, 640 mg (7.80 mmol) of 2,3-dimethylbutadiene, and 35.3 mg (0.114 mmol) of docosane as an internal standard in 25 mL of pentane was irradiated for 60 h. The resulting mixture was analyzed by GLC as being **1c** (48%), **2a** (27%), **2d** (10%), **4** (48%), and **5** (11%). GLC retention time and the mass spectrum for **5** were identical with those of an authentic sample. Products **2a**, **2d**, and **4** were isolated by preparative GLC. All spectral data obtained for **2a** and **4** were identical with those of authentic samples. For **2d**: MS *m/z* 314 (M^+); ^1H NMR (δ in C_6D_6) 0.05 (s, 3H, MeSi), 0.10 (s, 18H, Me_3Si), 0.02 (s, 3H, MeSi), 1.34 (br d, 2H, J = 10.8 Hz, CH_2), 1.50 (br d, 2H, J = 10.8 Hz, CH_2), 1.70 (br s, 6H, MeC); ^{13}C NMR (δ in C_6D_6) −13.2, −1.3, 0.4, 19.4, 26.6, 131.0. Anal. Calcd for $C_{14}H_{34}Si_4$: C, 53.42; H, 10.89. Found: C, 53.15; H, 10.85.

Photolysis of 1c in the Presence of Triethylsilane. A 25-mL pentane solution of 487.4 mg (1.29 mmol) of **1c** and 2.0 mL (10 equiv) of triethylsilane was irradiated for 2 h. At this stage, 93% of the starting compound **1c** was photolyzed. The resulting mixture was analyzed by GLC using 28.7 mg (0.113 mmol) of octadecane as an internal standard as being **4** (90%) and **8** (43%). Compounds **4** and **8** were isolated by preparative GLC. All spectral data obtained for **4** were identical with those of an authentic sample. For **8**: MS *m/z* 232 (M^+); ^1H NMR (δ in C_6D_6) 0.25 (s, 9H, Me_3Si), 0.26 (d, 3H, J = 5.28 Hz, MeSi), 0.72 (q, 6H, J = 8.25 Hz, CH_2CH_3), 1.07 (t, 9H, J = 7.59 Hz, CH_3CH_2), 3.53 (q, 1H, J = 5.28 Hz, HSi); ^{13}C NMR (δ in C_6D_6) −11.9, −0.2, 4.9, 8.6; IR ν_{Si-H} 2070 cm^{-1}. Exact MS Calcd for $C_{10}H_{28}Si_3$: 232.1497. Found: 232.1491.

Preparation of Compound 9. A 25-mL pentane solution of 514 mg (1.36 mmol) of **1c** and 2.0 mL of triethylsilane was irradiated for 20 min. The resulting mixture was analyzed by GLC using 14.7 mg (0.0742 mmol) of tetradecane as an internal standard as being **1c** (24%), **4** (73%), **8** (53%), and **9** (7% yield). Compound **9** could not be isolated in a pure form but was separated from the reaction mixture as a 6:4 mixture with **1c** by preparative GLC. For **9**: MS *m/z* 348 (M^+); ^1H NMR (δ in C_6D_6) 0.28 (s, 9H, Me_3Si), 0.29 (s, 3H, MeSi), 0.31 (s, 9H, Me_3Si), 0.36 (d, 3H, J = 5.28 Hz, MeSiH), 0.79 (q, 6H, J = 7.92 Hz, CH_2CH_3), 1.09 (t, 9H, J = 7.92 Hz, CH_3CH_2), 3.79 (q, 1H, J = 5.28 Hz, HSi); ^{13}C NMR (δ in C_6D_6) −11.0, −8.9, 0.0, 0.6, 5.0, 8.7; IR ν_{Si-H} 2060 cm^{-1}. Exact MS Calcd for $C_{14}H_{40}Si_5$: 348.1974. Found: 348.1890.

Photolysis of 1d in the Presence of 2,3-Dimethylbutadiene. A mixture of 364.0 mg (0.737 mmol) of **1d**, 72.5 mg (0.884 mmol) of 2,3-dimethylbutadiene, and 15.5 mg (0.061 mmol) of octadecane as an internal standard in 25 mL of pentane was irradiated for 10 h. At this stage, 88% of the starting compound **1d** was consumed. The resulting mixture was analyzed by GLC as being **11a** (18%) and **11b** (13%). After the solvent was evaporated, the residue was chromatographed on a silica gel column eluting with hexane to give a mixture of **11a** and **11b** in a ratio of 3:1. For **11a**: MS *m/z* 576 (M^+); ^1H NMR (δ in $CDCl_3$) 0.20 (s, 54H, Me_3Si), 1.33 (s, 4H, CH_2), 2.16 (s, 6H, MeC). Exact MS Calcd for $C_{24}H_{64}Si_8$: 576.3160. Found: 576.3153 (as a mixture of **11a** and **11b**). For **11b**: MS *m/z* 576 (M^+); ^1H NMR (δ in $CDCl_3$) 0.20 (s, 54H, Me_3Si), 1.33 (s, 5H, Me and CH_2), 1.83 (br s, 3H, MeC=), 5.96 (br s, 2H, H_2C=); ^{13}C NMR (δ in $CDCl_3$) 2.8 (6Me_3Si), 23.5, 25.0, 32.8, 35.0, 110.1, 150.7.

Photolysis of 1d in the Presence of Bis(trimethylsilyl)acetylene. A mixture of 630.5 mg (1.27 mmol) of **1d**, 1.40 g (8.23 mmol) of bis(trimethylsilyl)acetylene, and 47.7 mg (0.336 mmol) of decane as an internal standard in 25 mL of pentane was irradiated for 15 h. At this stage, 58% of the starting compound **1d** was consumed. The resulting mixture was

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analyzed by GLC as being **4** (7%), **5** (57%), **6** (33%), **7** (17%), **10** (21%), and **12** (14%). Retention times on GLC and the mass spectra of products **4**–**7** and **12** were identical with those of the authentic samples. Compound **10** could not be isolated in a pure form, but was separated from the reaction mixture as a mixture of **1d** in a ratio of 1:1 by preparative GPC eluting with benzene: MS *m/z* 348 ($M^+ - HSiMe_3$); IR ν_{Si-H} 2045 cm^{-1}; ^1H NMR (δ in C_6D_6); 0.36 (s, 27H, Me_3Si), 0.37 (s, 18H, Me_3Si), 2.82 (s, 1H. HSi); ^{13}C NMR (δ in C_6D_6) 3.2 ($2Me_3Si$), 3.4 ($3Me_3Si$); ^{29}Si NMR (δ in C_6D_6) −132.5, −115.6 (HSi, J_{Si-H} = 156.3 Hz), −10.8 ($5SiMe_3$). Exact MS Calcd for $C_{12}H_{36}Si_6$ ($M^+ - HSiMe_3$): 348.1433. Found: 348.1408.

Preparation of 12. In a 50-mL two-necked flask fitted with a dropping funnel was placed a mixture of 3.2 g (11.3 mmol) of chlorotris(trimethylsilyl)silane and 5 mL of THF. To this was added dropwise a solution of [(trimethylsilyl)ethynyl]lithium prepared from 1.8 mL (12.8 mmol) of (trimethylsilyl)acetylene and 7.9 mL (12.8 mmol) of a 1.62 M *n*-butyllithium–hexane solution in 10 mL of hexane. The resulting mixture was stirred at room temperature for 2 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 2.6 g (67% yield) of compound **12** (bp 104 °C/0.8 mmHg): MS *m/z* 170 (M^+); IR $\nu_{C\equiv C}$ 2084 cm^{-1}; ^1H NMR (δ in $CDCl_3$) 0.13 (s, 9H, Me_3Si), 0.19 (s, 27H, Me_3Si); ^{13}C NMR (δ in $CDCl_3$) 0.3, 107.9, 117.7. Anal. Calcd for $C_{14}H_{36}Si_5$: C, 48.76; H, 10.52. Found: C, 48.47; H, 10.40.

Photolysis of 1e in the Presence of 2,3-Dimethylbutadiene. A mixture of 205.9 mg (0.394 mmol) of **1e**, 323 mg (3.94 mmol) of 2,3-dimethylbutadiene, and 17.7 mg (0.0736 mmol) of heptadecane as an internal standard in 25 mL of pentane was irradiated for 15 h. At this stage, 69% of the starting compound **1e** was consumed. The resulting mixture was analyzed by GLC as being **5** (51%) and **2e** (20%). GLC retention time and the mass spectrum of **5** were identical with those of an authentic sample. Product **2e** was isolated by preparative GLC: MS *m/z* 458 (M^+); ^1H NMR (δ in $CDCl_3$) 0.28 (s, 9H, Me_3Si), 0.33 (s, 27H, Me_3Si), 0.90 (s, 4H, CH_2), 1.51 (br d, 2H, *J* = 6.6 Hz, ring CH_2), 1.62 (br d, 2H, *J* = 6.6 Hz, ring CH_2), 1.83 (br s, 6H, MeC); ^{13}C NMR (δ in $CDCl_3$) −1.5, 1.2, 12.2 (2C), 19.1, 22.3, 130.9. Anal. Calcd for $C_{20}H_{50}Si_6$: C, 52.32; H, 10.98. Found: C, 52.27; H, 10.96.

Photolysis of 1f in the Presence of 2,3-Dimethylbutadiene. A mixture of 62.0 mg (0.116 mmol) of **1f**, 97.9 mg (1.19 mmol) of 2,3-dimethylbutadiene, and 18.3 mg (0.0180 mmol) of hexadecane as an internal standard in 25 mL of pentane was irradiated for 55 h. At this stage, 80% of the starting compound **1f** was consumed. The resulting mixture was analyzed GLC as being **5** (23%) and **2f** (15%). GLC retention time and the mass spectrum for compound **5** were identical with those of an authentic sample. Product **2f** was isolated by preparative GLC: MS *m/z* 472 (M^+); ^1H NMR (δ in $CDCl_3$) 0.20 (s, 9H, Me_3Si), 0.27 (s, 27H, Me_3Si), 0.77–1.42 (m, 6H, CH_2), 1.44–1.56 (m, 4H, ring CH_2), 1.77 (br s, 6H, MeC); ^{13}C NMR (δ in $CDCl_3$) −1.5, 1.4, 13.0, 19.2, 19.5, 22.9, 25.3, 131.3. Anal. Calcd for $C_{21}H_{52}Si_6$: C, 53.31; H, 11.08. Found: C, 52.89; H, 11.18.

Photolysis of 1g in the Presence of 2,3-Dimethylbutadiene. A mixture of 232.9 mg (0.597 mmol) of **1g**, 495 mg (6.04 mmol) of 2,3-dimethylbutadiene, and 4.2 mg (0.0247 mmol) of dodecane as an internal standard in 25 mL of pentane was irradiated for 50 min. At this stage, 82% of the starting compound **1g** was consumed. The resulting mixture was analyzed by GLC as being **2f** (61%). Product **2f** was isolated by preparative GLC. All spectral data obtained for **2f** were identical with those of an authentic sample.

Photolysis of **1a**–**g** in the absence of 2,3-dimethylbutadiene was carried out in a manner similar to that above.

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