

Silicon-carbon unsaturated compounds

XXXII *. Photolysis of tolyl- and xylylpentamethyldisilanes

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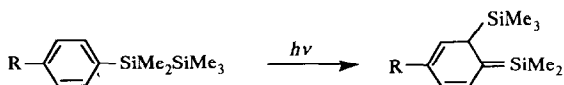
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Abstract

The photolysis of *ortho*- and *meta*-tolylpentamethyldisilane (**1** and **2**) and 2,5- and 2,6-xylylpentamethyldisilane (**3** and **4**) in the presence of isobutene and acetone as trapping agents has been studied. All reactions investigated, with the single exception of compound **4**, afforded the 1:1 adducts derived from the silene as a result of a 1,3-silyl shift to the aryl ring with the trapping agents. The photolysis of **1** and **3** in the presence of isobutene or acetone afforded a single adduct, but **2** gave 5,6-bis(silyl)-substituted toluene and 3,4-bis(silyl)-substituted toluene, respectively. Irradiation of **4** in the presence of isobutene afforded no volatile products, while in the presence of methanol it gave methoxypentamethyldisilane and *m*-xylene.

Introduction

In 1975, we found that irradiation with a low-pressure mercury lamp of a solution of pentamethylphenyldisilane in benzene produced a silene arising from a 1,3-shift of a trimethylsilyl group to an *ortho* carbon atom of the phenyl ring [1]. Further studies in this laboratory showed that this remarkable photochemical formation of a silene is a general phenomenon for various benzenoid aromatic disilanes [2]. Recently, we have reported the photochemical behaviour of 1,2-, 1,3- and 1,4-bis(pentamethyldisilanyl)benzene in the presence of isobutene [3]. However, only little interest has been shown in the photolysis of ring-substituted aromatic benzenoid disilanes, although the photolysis of *p*-substituted phenyldisilanes has been investigated [4–7].



* For Part XXXI, see ref. 10

In this paper we wish to report the synthesis and photochemical behaviour of *o*- and *m*-tolylpentamethyldisilane and 2,5- and 2,6-xylylpentamethyldisilane.

Results and discussion

o- And *m*-tolylpentamethyldisilane (**1**) and (**2**) were synthesized by the reaction of Grignard reagents prepared in 31 and 73% yields, respectively from *o*- and *m*-bromotoluene and magnesium in THF with chloropentamethyldisilane. 2,5-Xylylpentamethyldisilane (**3**) was synthesized by the reaction of the Grignard reagent prepared in 45% yield from 1-bromo-2,5-dimethylbenzene with chloropentamethyldisilane. Similarly, 2,6-xylylpentamethyldisilane (**4**) was synthesized by the lithium reagent prepared in 26% yield from 1-bromo-2,6-dimethylbenzene and *n*-butyllithium which chloropentamethyldisilane.

The structures of compounds **1–4** were confirmed by IR, mass, and ^1H and ^{13}C NMR spectroscopic analysis, as well as by elemental analysis.

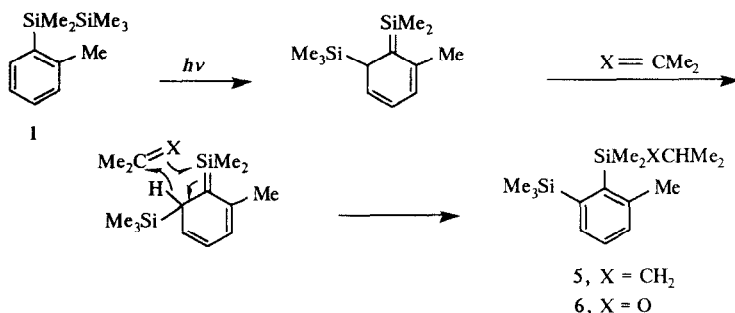
Photolysis of *o*-tolylpentamethyldisilane (**1**)

When a benzene solution of **1** in the presence of a large excess of isobutene was photolyzed with a low-pressure mercury lamp bearing a Vycor filter at ambient temperature for 3 h, 2-(isobutyldimethylsilyl)-3-(trimethylsilyl)toluene (**5**) was obtained in 66% yield, in addition to 15% of the unreacted starting compound **1** (Scheme 1).

The product **5** whose structure was confirmed by IR, mass, and ^1H and ^{13}C NMR spectrometric analysis, as well as by elemental analysis, could readily be separated in a pure form by preparative GLC.

The ^1H NMR spectrum of the phenyl region for **5** clearly indicates that this compound has a 1,2,3-trisubstituted benzene structure. The proton resonance at δ 7.11 ppm shows double doublets due to *ortho* and *meta* coupling ($J = 7$ and 2 Hz), and the proton at 7.19 ppm reveals a triplet signal owing to coupling with two different *ortho* protons ($J = 7$ Hz), while the proton at 7.51 ppm shows *ortho* and *meta* coupling ($J = 7$ and 2 Hz). These results are wholly consistent with the structure proposed for **5**.

The formation of **5** can be understood in terms of the ene reaction of the photochemically generated silene with isobutene, as reported previously [1–4,8]. In



Scheme 1.

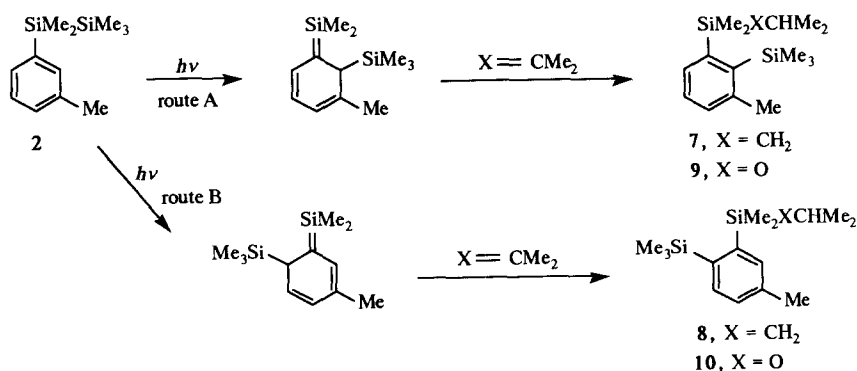
this photolysis, a trace amount (less than 5%) of an unidentified product was detected by GLC. Unfortunately, we could not isolate this compound, but the GC-mass spectrometric analysis of this product showed a parent ion peak at 278, corresponding to the calculated molecular weight of $C_{16}H_{30}Si_2$.

Similar irradiation of a benzene solution of **1** in the presence of acetone as a trapping agent produced 2-(isopropoxydimethylsilyl)-3-(trimethylsilyl)toluene (**6**) in 57% yield, in addition to trace amounts of other products (less than 5% combined yield), when 81% of the starting compound **1** was photolyzed. The product **6** was separated from the reaction mixture by preparative GLC and its structure was verified by IR, mass, 1H and ^{13}C NMR, and by elemental analysis. The 1H NMR spectrum of **6** clearly indicated a 1,2,3-trisubstituted benzene structure analogous to compound **5**.

In the photolysis of 1,2-bis(pentamethyldisilanyl)benzene reported recently, 1,2,3-trisubstituted benzene was initially formed from the silene and isobutene was readily converted into its isomers by photochemical valence isomerization [3]. However, such isomerization was not observed in the photolysis of **1**. Furthermore, the photolysis of compound **5** in benzene under the same conditions afforded no isomerization product.

Photolysis of *m*-tolylidisilane (**2**)

Irradiation of a benzene solution of **2** in the presence of isobutene with a low-pressure mercury lamp afforded two products, 5-(isobutyldimethylsilyl)-6-(trimethylsilyl)toluene (**7**) and 3-(isobutyldimethylsilyl)-4-(trimethylsilyl)toluene (**8**) in 44 and 14% yields, respectively, in addition to 16% of the starting compound **2** (Scheme 2). In this photolysis, trace amounts of two other products which could not be isolated were detected by GLC (less than 5% combined yield). The GC-mass spectrometric analysis of these products indicated a parent ion peak at 278, corresponding to the molecular weight calculated for **7**. The structures of **7** and **8** were confirmed by IR, mass, and 1H and ^{13}C NMR spectroscopic analysis and also by elemental analysis. The 1H NMR spectrum of **7** indicates that the proton resonance at δ 7.10 ppm shows double doublets due to *ortho* and *meta* coupling ($J = 7$ and 2 Hz), and the proton at 7.20 ppm shows triplets due to *ortho* coupling ($J = 7$ Hz) with two different protons, and as expected, the proton at 7.50 ppm



Scheme 2.

reveals double doublets attributed to *ortho* and *meta* coupling ($J = 7$ and 2 Hz). These results suggest that the product **7** must have a 1,2,3-trisubstituted benzene structure. On the other hand, the ^1H NMR spectrum of **8** clearly indicates a 1,2,4-trisubstituted benzene structure. The proton at 7.11 ppm shows broad doublets owing to *ortho* and *meta* coupling ($J = 8$ and ~ 0 Hz), and the proton at 7.44 ppm reveals a broad singlet due to meta coupling ($J = \sim 0$ Hz), while the proton at 7.56 ppm shows a doublet ($J = 8$ Hz).

In the photolysis of **2**, two different silenes, regio-isomers, should be produced; one involves a 1,3-trimethylsilyl shift to the C-2 position of the benzene ring (route A) and the other a 1,3-trimethylsilyl shift to the C-6 position (route B). In fact, the formation of **7** can be explained by the ene reaction of the silene formed according to route A with isobutene, while compound **8** is the product derived from route B. Interestingly, the abundant product is a result of the silene being formed by the migration of the silyl group to the more hindered C-2 position, rather than to the less hindered C-6 position. Presumably, the silyl group migrates to the more electron rich carbon atom.

Similar irradiation of **2** in the presence of acetone produced 5-(isopropoxydimethylsilyl)-6-(trimethylsilyl)toluene (**9**) and 3-(isopropoxydimethylsilyl)-4-(trimethylsilyl)toluene (**10**) in 45 and 19% yields, respectively, when 85% of **2** was photolyzed. In this reaction, trace amounts of other products which have a parent ion peak at 280, corresponding to the molecular weight of compound **9** or **10** were observed by GC-mass spectrometric analysis (less than 5% combined yield). Products **9** and **10** were identified by IR, mass, and ^1H and ^{13}C NMR spectrometric analysis, and also by elemental analysis. All spectral data obtained for **9** and **10** were wholly consistent with the proposed structure.

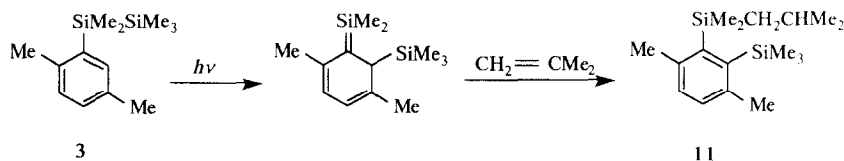
Photolysis of 2,5-xylylpentamethyldisilane (**3**)

When a benzene solution of **3** in the presence of isobutene was photolyzed with a low-pressure mercury lamp, 3,6-dimethyl-1-(isobutyldimethylsilyl)-2-(trimethylsilyl)-benzene (**11**) was obtained in 50% yield, in addition to 18% of the starting compound **3**, as shown in Scheme 3.

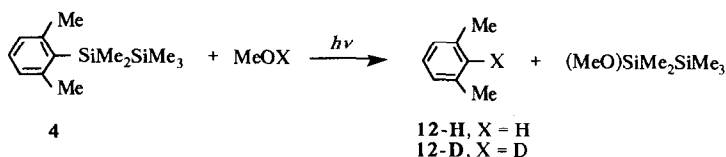
The structure of **11** was verified by IR, mass, and ^1H and ^{13}C NMR spectroscopic analysis, as well as by elemental analysis. Compound **11** is photochemically stable. Spectrometric analysis detected no photochemical valence isomers in the photolysis mixture.

Photolysis of 2,6-xylylpentamethyldisilane (**4**)

When a benzene solution of **4** was photolyzed in the presence of isobutene under the same conditions for 20 h, no volatile products were detected, when 62% of the starting compound **4** was consumed. Nonvolatile substances were obtained after distillation of the reaction mixture. The introduction of substituents on *ortho*



Scheme 3.



Scheme 4.

carbons would prevent the photochemical silyl shift to these carbons. Compound **4** would have been transformed into nonvolatile products by processes which are still unknown. The photolysis of **4** in the presence of methanol, however, afforded an unexpected product. Thus, irradiation of a benzene solution of **4** in the presence of a large excess of methanol for 1.5 h gave methoxypentamethyldisilane and *m*-xylene (**12-H**) in 35 and 32% yields, respectively, in addition to 14% of the unchanged compound **4** (Scheme 4).

In this photolysis, there was no evidence of a product being formed from the reaction of the silene involving a 1,3-shift of a trimethylsilyl group. Similar photolysis of **4** in the presence of methanol-*d*₁ produced methoxypentamethyldisilane and monodeuterioxylylene (**12-D**).

Methoxypentamethyldisilane and *m*-xylene are probably formed by the direct reaction of photoexcited **4** with methanol, such as is observed in the protodesilylation reaction. In this reaction, nucleophilic assistance of a methoxy group onto the silicon atom attached to the aryl ring would be important.

Experimental

All reaction were carried out under an atmosphere of dry argon. Ultraviolet spectra were recorded on a Hitachi U-3210 spectrometer. Infrared spectra were determined on thin liquid films using a Perkin–Elmer 1600 FT-infrared spectrometer. ¹H NMR spectra for compound **1–4** were determined by a JEOL Model PMX-60 SI spectrometer. ¹H and ²H MNR spectra for **12-D** were determined on a JEOL Model EX-270 spectrometer. ¹H and ¹³C MNR spectra for other compounds were determined on a JEOL Model JNM-FX-90A spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000. Gas chromatographic analyses were carried out using a Hitachi 263-30 gas chromatography (10% SE-30 silicone on Uniport HP). Gas chromatographic separations were carried out using a column packed with 30% SE-30 silicone on Chromosorb P.

The yields of products were determined by GLC using an internal standard on the basis of the unrecovered starting disilanes.

1-Chloropentamethyldisilane was prepared as reported previously [8]. Bromobenzene derivatives were used as received. Benzene was dried over lithium aluminium hydride and distilled before use.

Preparation of *o*-tolylpentamethyldisilane (**1**)

2.4 g (0.10 mol) of magnesium and 60 mL of THF were placed in a 200 mL three-necked flask fitted with a condenser, stirrer, and dropping funnel. A mixture of 17.1 g (0.10 mol) of *o*-bromotoluene and 16.9 g (0.10 mol) of 1-chloropentamethyldisilane in 50 mL of THF was added, at room temperature over a period of 2 h. The mixture was heated to reflux for 1 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The

organic layer and the extracts were combined and dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 6.8 g (31% yield) of colourless liquid. B.p. 118.5–120 °C/14 mmHg. MS: m/e 222 (M^+). UV (in cyclohexane): $\lambda_{\max}$ (ϵ) 233 nm (11,500). IR: 3057, 3003, 2951, 2894, 1444, 1400, 1246, 1126, 1076 cm^{-1} . ^1H NMR (δ in CCl_4): 0.08 (s, 9H, Me_3Si); 0.38 (s, 6H, Me_2Si); 2.35 (s, 3H, Me); 6.78–7.35 (m, 4H, aromatic ring protons). ^{13}C NMR (δ in CDCl_3): –2.47 (Me_3Si); –1.64 (Me_2Si); 23.56 (Me); 124.9, 128.7, 129.5, 134.5, 137.8, 143.4 (aromatic ring carbons). Anal. Found: C, 64.72; H, 9.88. $\text{C}_{12}\text{H}_{22}\text{Si}_2$ calcd.: C, 64.78; H, 9.97%.

Preparation of m-tolylpentamethyldisilane (2)

2.4 g (0.10 mol) of magnesium and 60 mL of THF were placed in a 200 mL three-necked flask. A mixture of 17.2 g (0.10 mol) of *m*-bromotoluene and 16.8 g (0.10 mol) of 1-chloropentamethyldisilane in 50 mL of THF was added at room temperature over a period of 2.3 h. The mixture was heated to reflux for 1 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over magnesium sulfate. The solvent was evaporated and the residue was distilled under reduced pressure to give 16.3 g (73% yield) of colourless liquid. B.p. 110–112 °C/13 mmHg. MS: m/e 222 (M^+). UV (in cyclohexane): $\lambda_{\max}$ (ϵ) 232 nm (10,600). IR: 3044, 3018, 2998, 2893, 1475, 1439, 1398, 1245, 1113 cm^{-1} . ^1H NMR (δ in CCl_4): 0.07 (s, 9H, Me_3Si); 0.31 (s, 6H, Me_2Si); 2.29 (s, 3H, Me); 6.80–7.20 (m, 4H, aromatic ring protons). ^{13}C NMR (δ in CDCl_3): –3.93 (Me_3Si); –2.23 (Me_2Si); 21.52 (Me); 127.6, 129.1, 130.8, 134.4, 136.9, 139.6 (aromatic ring carbons). Anal. Found: C, 64.48; H, 9.84. $\text{C}_{12}\text{H}_{22}\text{Si}_2$ calcd.: C, 64.78; H, 9.97%.

Preparation of 2,5-xylylpentamethyldisilane (3)

0.71 g (0.029 mol) of magnesium and 5 mL of THF were placed in a 100 mL three-necked flask. A mixture of 5.69 g (0.030 mol) of 1-bromo-2,5-dimethylbenzene and 4.86 g (0.029 mol) of 1-chloropentamethyldisilane dissolved in 10 mL of THF was added at room temperature over a period of 20 min. The mixture was heated to reflux for 1 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over magnesium sulfate. The solvent was evaporated and the residue was distilled under reduced pressure to give 3.09 g (45% yield). B.p. 82–83 °C/2 mmHg. MS: m/e 236 (M^+). UV (in cyclohexane): $\lambda_{\max}$ (ϵ) 234 nm (10,200). IR: 3004, 2950, 2922, 2894, 1482, 1446, 1402, 1382, 1284, 1246, 1144 cm^{-1} . ^1H NMR (δ in CCl_4): 0.10 (s, 9H, Me_3Si); 0.39 (s, 6H, Me_2Si); 2.30 (s, 3H, Me); 2.37 (s, 3H, Me); 7.00–7.29 (m, 3H, aromatic ring protons). ^{13}C NMR (δ in CDCl_3): –2.42 (Me_2Si); –1.55 (Me_3Si); 31.04 (Me); 22.99 (Me); 129.4 (two carbons); 133.8, 135.2, 137.4, 140.2 (aromatic ring carbons). Anal. Found: C, 66.02; H, 10.23. $\text{C}_{13}\text{H}_{24}\text{Si}_2$ calcd.: C, 66.02; H, 10.23%.

Preparation of 2,6-xylylpentamethyldisilane (4)

19.0 g (0.10 mol) of 1-bromo-2,6-dimethylbenzene and 50 mL of ether were placed in a 300 mL three-necked flask. 69 mL of a 1.6 *M* hexane solution of *n*-butyllithium was added over a period of 1.5 h. The mixture was stirred for 1 h at room temperature. Then, 20 mL of THF was added to the mixture and 18.0 g (0.11 mol) of 1-chloropentamethyldisilane was added over a period of 0.5 h. This mixture

was allowed to stand overnight and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over magnesium sulfate. The solvent was evaporated and the residue was distilled under reduced pressure to give 6.34 g (26% yield). B.p. 83–85 °C/3 mmHg. MS: m/e 236 (M^+). UV (in cyclohexane): $\lambda_{\max}$ (ϵ) 240 nm (10,000). IR: 3051, 2950, 2893, 1448, 1398, 1376, 1246, 1128, 1054, 1026 cm^{-1} . ^1H NMR (δ in CCl_4): 0.13 (s, 9H, Me_3Si); 0.49 (s, 6H, Me_2Si); 2.34 (s, 6H, Me); 6.54–7.04 (m, 3H, aromatic ring protons). ^{13}C NMR (δ in CDCl_3): –2.47 (Me_3Si); –1.28 (Me_2Si); 25.26 (Me); 127.9, 128.4, 136.2, 144.1 (aromatic ring carbons). Anal. Found: C, 66.01; H, 10.01. $\text{C}_{13}\text{H}_{24}\text{Si}_2$ calcd.: C, 66.02; H, 10.23%.

Photolysis of 1 in the presence of isobutene

A solution of 0.916 g (4.12 mmol) of **1**, 6.25 g (111.6 mmol) of isobutene, and 0.240 g (0.773 mmol) of docosane as an internal standard in 110 mL of benzene was placed in a 120 mL reaction vessel, fitted with a 10W low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated at room temperature for 3 h with a slow stream of argon bubbling through the mixture. The reaction mixture was analyzed by GLC as being 2-(isobutyldimethylsilyl)-3-(trimethylsilyl)toluene (**5**) (66% yield) and the starting compound **1** (15% yield). Pure **5** was isolated by preparative GLC. Compound **5**: MS: m/e 278 (M^+). IR: 1462, 1435, 1410, 1380, 1364, 1327, 1250, 1216, 1144, 1089, 1053, 1036 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.36 (s, 9H, Me_3Si); 0.44 (s, 6H, Me_2Si); 0.91 (d, $J = 6$ Hz, 8H, CH_2 and Me_2C); 1.60–1.96 (m, 1H, HC); 2.49 (s, 3H, Ar-Me); 7.11 (dd, $J_{\text{ortho}} = 7$ Hz, $J_{\text{meta}} = 2$ Hz, 1H, Ar-H); 7.19 (t, $J_{\text{ortho}} = 7$ Hz, 1H, Ar-H); 7.51 (dd, $J_{\text{ortho}} = 7$ Hz, $J_{\text{meta}} = 2$ Hz, 1H, Ar-H). ^{13}C NMR (δ in CDCl_3): 3.22 (Me_2Si); 3.33 (Me_3Si); 25.10, 25.26, 26.29, 28.51 (CH_2CHMe_2 and Ar-Me); 127.1, 130.7, 133.2, 144.2, 145.5, 147.0 (aromatic ring carbons). Anal. Found: C, 68.86; H, 10.85. $\text{C}_{16}\text{H}_{30}\text{Si}_2$ calcd.: C, 68.98; H, 10.85 %.

Photolysis of 1 in the presence of acetone

A solution of 0.882 g (3.97 mmol) of **1**, 1.87 g (32.2 mmol) of acetone, and 0.450 g (1.45 mmol) of docosane as an internal standard in 115 mL of benzene was placed in a 120 mL reaction vessel. The mixture was irradiated with a low-pressure mercury lamp for 10 h. The reaction mixture was analyzed by GLC as being **6** (57% yield) and the starting compound **1** (19% yield). After the solvent was evaporated off, the residue was distilled under reduced pressure (1 mmHg) to give volatile products. Pure **6** was isolated by preparative GLC. Compound **6**: MS: m/e 280 (M^+); IR 1454, 1436, 1410, 1384, 1368, 1253, 1172, 1147, 1119, 1059 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.36 (s, 9H, Me_3Si); 0.47 (s, 6H, Me_2Si); 1.26 (d, $J = 6$ Hz, 6H, Me_2C); 2.49 (s, 3H, Ar-Me); 4.19 (septet, $J = 6$ Hz, 1H, CH); 7.11 dd, $J_{\text{ortho}} = 7$ Hz, $J_{\text{meta}} = 2$ Hz, 1H, Ar-H); 7.24 (t, $J_{\text{ortho}} = 7$ Hz, 1H, Ar-H); 7.54 (dd, $J_{\text{ortho}} = 7$ Hz, $J_{\text{meta}} = 2$ Hz, 1H, Ar-H). ^{13}C NMR (δ in CDCl_3): 1.76 (Me_2Si); 3.22 (Me_3Si); 24.45 (Ar-Me); 25.53 (Me_2C); 65.35 (O-C); 127.9, 130.9, 132.9, 142.8, 143.6, 147.5 (aromatic ring carbons). Anal. Found: C, 64.19; H, 9.97. $\text{C}_{15}\text{H}_{28}\text{Si}_2\text{O}$ calcd.: C, 64.22; H, 10.06%.

Photolysis of 2 in the presence of isobutene

A solution of 0.737 g (3.32 mmol) of **2**, 6.12 g (109.3 mmol) of isobutene, and 0.0121 g (0.039 mmol) of docosane as an internal standard in 110 mL of benzene

was placed in a 120 mL reaction vessel. The mixture was irradiated for 1.5 h. The reaction mixture was analyzed by GLC as being **7** (44% yield), **8** (14% yield), and the starting compound **2** (16% yield). After the solvent was evaporated off, the residue was distilled under pressure. Product **7** and **8** were isolated from the mixture by preparative GLC. For **7**: MS: m/e 278 (M^+). IR: 1460, 1435, 1410, 1380, 1364, 1251, 1215, 1144, 1088, 1035 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.38 (s, 6H, Me_2Si); 0.43 (s, 9H, Me_3Si); 0.89 (d, $J = 6.8$ Hz, 2H, CH_2); 0.93 (d, $J = 6.6$ Hz, 6H, Me_2C); 1.57–2.06 (m, 1H, CH); 2.50 (s, 3H, Ar-Me); 7.10 (dd, $J_{ortho} = 7$ Hz, $J_{meta} = 2$ Hz, 1H, Ar-H); 7.20 (t, $J_{ortho} = 7$ Hz, 1H, Ar-H); 7.50 (dd, $J_{ortho} = 7$ Hz, $J_{meta} = 2$ Hz, 1H, Ar-H). ^{13}C NMR (δ in CDCl_3): 2.41 (Me_3Si); 3.92 (Me_2Si); 25.12, 25.32, 26.39, 28.88 (CH_2CHMe_2 and Ar-Me); 127.2, 130.7, 133.4, 144.3, 145.3, 147.0 (aromatic ring carbons). Anal. Found: C, 68.90; H, 10.85. $\text{C}_{16}\text{H}_{30}\text{Si}_2$ calcd.: C, 68.98; H, 10.85%. For **8**: MS: m/e 278 (M^+). IR: 1459, 1364, 1328, 1248, 1149, 1108, 1089, 1048 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.34 (s, 9H, Me_3Si); 0.38 (s, 6H, Me_2Si); 0.81 (d, $J = 6.8$ Hz, 2H, CH_2); 0.90 (d, $J = 6.4$ Hz, 6H, Me_2C); 1.56–2.00 (m, 1H, HC); 2.33 (s, 3H, Ar-Me); 7.11 (br d, $J_{ortho} = 8$ Hz, $J_{meta} = \sim 0$ Hz, 1H, Ar-H); 7.44 (br s, $J_{meta} = \sim 0$ Hz, 1H, Ar-H); 7.56 (d, $J_{ortho} = 8$ Hz, 1H, Ar-H). ^{13}C NMR (δ in CDCl_3): 1.05 (Me_2Si); 2.24 (Me_3Si); 21.47, 25.21, 26.35, 28.08 (CH_2CHMe_2 and Ar-Me); 128.4, 135.6, 136.4, 147.0, 142.3, 145.9 (aromatic ring carbons). Anal. Found: C, 68.81; H, 10.80. $\text{C}_{16}\text{H}_{30}\text{Si}_2$ calcd.: C, 68.98; H, 10.85%.

Photolysis of 2 in the presence of acetone

A mixture of 0.830 g (3.74 mmol) of **2**, 2.00 g (34.5 mmol) of acetone, and 0.307 g (0.990 mmol) of docosane as an internal standard in 115 mL of benzene was placed in a 120 mL reaction vessel. The mixture was irradiated with a low-pressure mercury lamp for 12 h. The reaction mixture was analyzed by GLC as being **9** (45% yield), **10** (19% yield), and the starting compound **2** (15% yield). After the solvent was evaporated off, the residue was distilled under reduced pressure (1 mmHg) to give volatile products. Pure **9** and **10** were obtained by GLC. Compound **9**: MS: m/e 280 (M^+). IR: 1463, 1453, 1436, 1381, 1368, 1252, 1172, 1146, 1122, 1019 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.43 (s, 6H, Me_2Si); 0.45 (s, 9H, Me_3Si); 1.19 (d, $J = 6$ Hz, 6H, Me_2C); 2.50 (s, 3H, Ar-Me); 4.10 (septet, $J = 6$ Hz, 1H, CH); 7.12 (dd, $J_{ortho} = 7$ Hz, $J_{meta} = 2$ Hz, 1H, Ar-H); 7.22 (t, $J_{ortho} = 7$ Hz, 1H, Ar-H); 7.51 (dd, $J_{ortho} = 7$ Hz, $J_{meta} = 2$ Hz, 1H, Ar-H). ^{13}C NMR (δ in CDCl_3): 2.35 (Me_3Si); 3.76 (Me_2Si); 25.51 (ar-Me); 25.70 (Me_2C); 65.52 (O-C); 127.1, 131.2, 132.6, 144.2, 145.6, 145.7 (aromatic ring carbons). Anal. Found: C, 64.20, H, 10.04. $\text{C}_{15}\text{H}_{28}\text{Si}_2\text{O}$ calcd.: C, 64.22; H, 10.06%. For **10**: MS: m/e 280 (M^+). IR: 1452, 1381, 1368, 1251, 1172, 1149, 1117, 1017 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.34 (s, 9H, Me_3Si); 0.39 (s, 6H, Me_2Si); 1.20 (d, $J = 6$ Hz, 6H, Me_2C); 2.32 (s, 3H, Ar-Me); 4.11 (septet, $J = 6$ Hz, 1H, CH); 7.14 (br d, $J_{ortho} = 7$ Hz, $J_{meta} = \sim 0$ Hz, 1H, Ar-H); 7.43 (br s, $J_{meta} = \sim 0$ Hz, 1H, Ar-H); 7.56 (d, $J_{ortho} = 7$ Hz, 1H, Ar-H). ^{13}C NMR (δ in CDCl_3): 1.27 (Me_2Si); 1.70 (Me_3Si); 21.42 (ar-Me); 25.70 (Me_2C); 65.52 (O-C); 128.9, 135.2, 235.6, 136.9, 142.7, 144.8 (aromatic ring carbons). Anal. Found: C, 64.18; H, 10.01. $\text{C}_{15}\text{H}_{28}\text{Si}_2\text{O}$ calcd.: C, 64.22; H, 10.06%.

Photolysis of 3 in the presence of isobutene

A solution of 0.552 g (2.34 mmol) of **3**, 2.25 g (40.2 mmol) of isobutene, and 0.111 g (0.035 mmol) of docosane as an internal standard in 60 mL of benzene was

placed in a 70 mL reaction vessel. The mixture was photolyzed for 2.5 h. The reaction mixture was analyzed by GLC as being **11** (50% yield) and the starting compound **3** (11% yield). Product **11** was isolated from the mixture by preparative GLC. Compound **11**: MS: m/e 292 (M^+). IR: 1462, 1409, 1379, 1364, 1250, 1214, 1154, 1088, 1035 cm^{-1} . ^1H NMR (δ in CDCl_3): 0.43 (s, 9H, Me_3Si); 0.44 (s, 6H, Me_2Si); 0.94 (d, $J = 6.4$ Hz, 2H, Me_2C); 0.98 (d, $J = 6.8$ Hz 6H, CH_2); 1.58–2.05 (m, 1H, CH); 2.48 (s, 6H, Ar-Me); 6.99 (s, 2H, aromatic ring protons). ^{13}C NMR (δ in CDCl_3): 2.89 (Me_3Si); 3.92 (Me_2Si); 24.02 (CH); 25.32 (Me_2C); 26.24 (two Ar-Me); 28.84 (CH_2); 129 (two carbons); 141.5, 141.6, 147.6, 147.8 (aromatic ring carbons). Anal. Found: C, 69.71; H, 10.06. $\text{C}_{17}\text{H}_{32}\text{Si}_2$ calcd.: C, 69.78; H, 11.02%.

Photolysis of 4 in the presence of isobutene

A solution of 0.416 g (1.76 mmol) of **4**, 4.23 g (45.5 mmol) of isobutene, and 0.168 g (0.542 mmol) of docosane as an internal standard in 60 mL of benzene was placed in a 70 mL reaction vessel. The mixture was photolyzed with a low-pressure mercury lamp for 20 h. GLC analysis of the reaction mixture showed that no volatile products were formed. The starting compound **4** was recovered in 38% yield.

Photolysis of 4 in the presence of methanol

A solution of 0.4785 g (2.03 mmol) of **4**, 0.4266 g (13.3 mmol) of methanol, and 0.1419 g (0.458 mmol) of docosane as an internal standard in 60 mL of benzene was placed in a 70 mL reaction vessel. The mixture was photolyzed with a low-pressure mercury lamp for 1.5 h. The reaction mixture was analyzed by GLC as being methoxypentamethyldisilane (35% yield), **12-H** (32% yield), and the starting compound **4** (14% yield). All spectral data for methoxypentamethyldisilane [9] and *m*-xylene were identical with those of authentic samples.

Photolysis of 4 in the presence of methanol- d_1

A solution of 0.3190 g (1.35 mmol) of **4**, 0.2642 g (8.00 mmol) of methanol- d_1 , and 0.1065 g (0.344 mmol) of docosane as an internal standard in 25 mL of benzene was photolyzed for 1 h. The mixture was analyzed by GLC as being methoxypentamethyldisilane (37% yield) and **12-D** (36% yield), in addition to 16% of the unchanged starting compound **4**. For **12-D**: MS: m/e 107 (M^+). IR: 3026, 2921, 2863, 2242, 1602, 1466, 1376, 1164, 1098, 1037 cm^{-1} . ^1H NMR (δ in CDCl_3): 2.32 (s, 6H, Me-Ar); 6.97 (d, $J = 7.6$ Hz, 2H, C_4 - and C_6 -H); 7.15 (t, $J = 7.6$ Hz, 1H, C_5 -H). ^2H NMR (δ in CDCl_3): 7.06 (C_2 -D).

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