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Photolysis of Organopolysilanes. Photochemical Behavior of 2,2-Diphenylethenyl-Substituted Disilanes

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The photochemical behavior of (2,2-diphenylethenyl)pentamethyldisilane (**1a**), 1-(2,2-diphenylethenyl)-1-phenyltetramethyldisilane (**1b**), and 1-(2,2-diphenylethenyl)-2-phenyltetramethyldisilane (**1c**) has been studied. Irradiation of **1a** with a low-pressure mercury lamp afforded 1,1-diphenyl-2-(trimethylsilyl)ethene (**2a**), 1,1-dimethyl-3-phenyl-1-silaindene (**3a**), and 1,1-dimethyl-3-phenyl-2-(trimethylsilyl)-1-silaindene. Irradiation of **1b** afforded **2a**, 1-methyl-1,3-diphenyl-1-silaindene, 1-methyl-1,3-diphenyl-2-(trimethylsilyl)-1-silaindan, and 1-methyl-1,3-diphenyl-5-(trimethylsilyl)-1-silaindene, while **1c** afforded **3a**, 2-(dimethylphenylsilyl)-1,1-diphenylethene, 1,1-dimethyl-2-(dimethylphenylsilyl)-3-phenyl-1-silaindene, and dimethylphenylsilane. A possible mechanism leading to the observed products is described.

Introduction

We have demonstrated that the photolysis of π-electron system-substituted polysilanes results in a 1,2- and 1,3-silyl shift to unsaturated carbon–carbon units such as vinyl,[1,2] phenyl,[3,4] and ethynyl[5,6] groups. The reaction course leading to final products, however, highly depends on the structure of the polysilanes and also the substituents attached to the silicon atoms. For example, the photolysis of (*E*)-(2-phenylethenyl)pentamethyldisilane affords 1,1-dimethyl-2-(trimethylsilyl)-1-silaindan and 1,1-dimethyl-3-phenyl-2-(trimethylsilyl)-1-silacyclopropane derived from a 1,2-silyl shift as the main products,[7] while (*E*)-2-(2-phenylethenyl)-2-(trimethylsilyl)hexamethyltrisilane affords (*E*)-2-phenyl-1-(trimethylsilyl)ethene and (*Z*)-2-phenyl-1-(trimethylsilyl)ethene arising from extrusion of bis(trimethylsilyl)silylene.[8] 2-(2,2-Diphenylethenyl)-2-phenylhexamethyltrisilane, however, undergoes homolytic scission of an Si–Si bond, along with extrusion of a silylene.

In order to learn more about the photochemical behavior of arylethenyl-substituted polysilanes, we have investigated the photolysis of (2,2-diphenylethenyl)pentamethyldisilane (**1a**), 1-(2,2-diphenylethenyl)-1-phenyltetramethyldisilane (**1b**), and 1-(2,2-diphenylethenyl)-2-phenyltetramethyldisilane (**1c**).

Results and Discussion

Like the photolysis of 2-(2,2-diphenylethenyl)-2-phenylhexamethyltrisilane reported previously,[7] irradiation of (2,2-diphenylethenyl)pentamethyldisilane (**1a**) with a low-pressure mercury lamp in hexane for 12 h afforded a silylene-extrusion product, 1,1-diphenyl-2-(trimethylsilyl)ethene (**2a**), a product from scission of an Si–Si bond, 1,1-dimethyl-3-phenyl-1-silaindene (**3a**), and an isomerization product derived from a 1,2-silyl shift, 1,1-dimethyl-3-phenyl-2-(trimethylsilyl)-1-silaindene (**4a**) in 18%, 32%, and 3% yields, respectively, together with 35% of the starting compound **1a** (see Table I). Addition of piperylene led to a small decrease in the yield of **3a** (25%).

Trapping reactions of **1a** with 2,3-dimethylbutadiene, methanol, and diethylmethylsilane were carried out to trap reactive intermediates. Although the formation of **2a** clearly indicated that the photolysis of **1a** produced dimethylsilylene, silylene species could not be trapped in the presence of 2,3-dimethylbutadiene, but products **2a** and **3a** were obtained in 11% and 32% yields, respectively, together with a trace of **4a**. Similarly, the photolysis of **1a** in the presence of methanol afforded **2a** and **3a** in 6% and 19% yields, respectively, together with a trace of **4a**. Again, no silylene adduct was detected in the reaction mixture. However, when diethylmethylsilane was used as a trapping agent, a silylene adduct, 1,1-diethyl-1,2,2-trimethyldisilane (**5**) was obtained in 6% yield, along with **2a** (17%), **3a** (25%), and **4a** (trace).

Interestingly, the photolysis of 1-(2,2-diphenylethenyl)-1-phenyltetramethyldisilane (**1b**) gave products quite different from those of **1a**. Thus, irradiation of **1b** produced 1-methyl-1,3-diphenyl-2-(trimethylsilyl)-1-silaindan (**6b**) and 1-methyl-1,3-diphenyl-5-(trimethylsilyl)-1-silaindene (**7b**) in 9% and 5% yields, respectively, in addition to **2a** (13%), 1,3-diphenyl-1-methyl-1-silaindene (**3b**) (24%), and 14% of the starting compound **1b**. The photolysis of **1b** in the presence of piperylene obviously led to suppression of the products, silaindenes **3b** (13%) and **7b** (0.3%), and silaindan **6b** (5%).

We carried out the reactions of **1b** in the presence of 2,3-dimethylbutadiene, methyl alcohol, *tert*-butyl alcohol, and diethylmethylsilane. When *tert*-butyl alcohol and diethylmethylsilane were used as the trapping agents, the respective silylene adducts *tert*-butoxymethylphenylsilane (**8**) and 1,1-diethyl-1,2-dimethyl-2-phenylsilane (**9**) were obtained in 4% and 3% yields, indicating that **2a** is formed by extrusion of methylphenylsilylene from **1b**.

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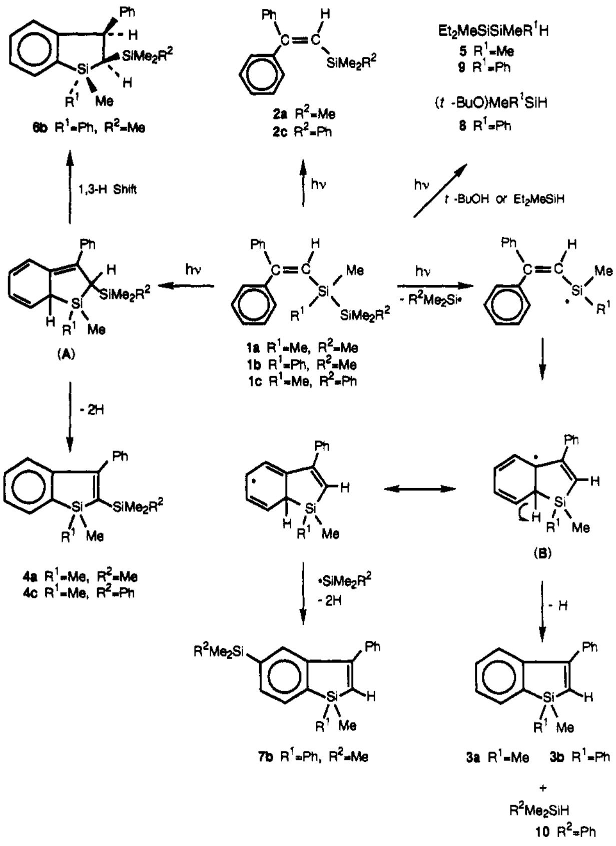
Table I. Photolysis of Disilanes at 254 nm in Hexane

disilane	additive	time (h)	product [yield (%)]					
1a	none	12	**1a** [35]	**2a** [18]	**3a** [32]	**4a** [3]		
1a	piperylene	11	**1a** [14]	**2a** [14]	**3a** [25]	**4a** [2]		
1a	DMB[a]	18	**1a** [18]	**2a** [11]	**3a** [32]	**4a** [tr]		
1a	MeOH	19	**1a** [19]	**2a** [6]	**3a** [19]	**4a** [tr]		
1a	Et_2MeSiH	8	**1a** [19]	**2a** [17]	**3a** [25]	**4a** [tr]	**5** [6]	
1b	none	12	**1b** [14]	**2a** [13]	**3b** [24]	**6b** [9]	**7b** [5]	
1b	piperylene	6	**1b** [1]	**2a** [12]	**3b** [13]	**6b** [5]	**7b** [0.3]	
1b	DMB	7	**1b** [12]	**2a** [23]	**3b** [22]	**6b** [2]	**7b** [2]	
1b	MeOH	12	**1b** [23]	**2a** [7]	**3b** [18]	**6b** [2]	**7b** [4]	
1b	*t*-BuOH	10	**1b** [1]	**2a** [12]	**3b** [21]	**6b** [10]	**7b** [tr]	**8** [4]
1b	Et_2MeSiH	8	**1b** [1]	**2a** [13]	**3b** [21]	**6b** [5]	**7b** [4]	**9** [3]
1c	none	9	**1c** [8]	**2c** [10]	**3a** [15]	**4c** [3]	**10** [3]	
1c	piperylene	6	**1c** [9]	**2c** [12]	**3a** [12]	**4c** [2]	**10** [1]	
1c	DMB	7	**1c** [9]	**2c** [13]	**3a** [18]	**4c** [3]	**10** [1]	
1c	MeOH	9	**1c** [14]	**2c** [7]	**3a** [13]	**4c** [3]	**10** [3]	
1c	Et_2MeSiH	5	**1c** [13]	**2c** [14]	**3a** [15]	**4c** [2]	**10** [1]	**5** [3]

[a] 2,3-Dimethylbutadiene.

Scheme I



The photolysis of 1-(2,2-diphenylethenyl)-2-phenyltetramethyldisilane (**1c**) in hexane afforded the products similar to those of **1a**, 2-(dimethylphenylsilyl)-1,1-diphenylethene (**2c**) (10%), **3a** (15%), and 1,1-dimethyl-2-(dimethylphenylsilyl)-3-phenyl-1-silaindene (**4c**) (3%). Dimethylphenylsilane (**10**) was also detected in 3% yield. The formation of both **3a** and **10** clearly indicates that the homolytic scission of an Si–Si bond is certainly involved in the present photolysis. Similar photolysis of **1c** in the presence of diethylmethylsilane afforded **5** in 3% yield, but no silylene adduct was trapped in the presence of dimethylbutadiene and methanol as a trapping agent. When **1c** was photolyzed in the presence of piperylene, the yields of **3a** and **10** decreased slightly.

Scheme I illustrates a possible mechanistic interpretation of the observed reaction course. Extrusion of dimethylsilylene from **1a** and **1c** and that of methylphenylsilylene from **1b** afford **2a** and **2c**, respectively. The formation of **4a**, **6b**, and **4c** in the photolysis of **1a**–**1c** may be best explained in terms of a 1,2-silyl shift to the α-position of the olefin unit leading to the dihydrosilole intermediate A.[9] Elimination of a hydrogen molecule from intermediate A results in the formation of the 2-silylsilaindenes **4a** and **4c**, while a 1,3-shift of a hydrogen atom at the bridgehead affords the silaindan **6b**.

The formation of **3a**, **3b**, and **7b** can be understood by homolytic scission of an Si–Si bond of **1a**–**1c**. Homolytic aromatic substitution of the resulting silyl radical onto the *ortho* position of the phenyl ring gives rise to intermediate B. Elimination of a hydrogen atom from B affords another type of silaindene, **3a** and **3b**, while coupling with the trimethylsilyl radical and then aromatization lead to the formation of the 5-silylsilaindene **7b**. The isolation of dimethylphenylsilane (**10**) in the photolysis of **1b** is consistent with these assumptions. The fact that the presence of piperylene decreases the yields of the products derived from radical species, **3a** from the photolysis of **1a**, **3b** and **7b** from **1b**, and **3a** and **10** from **1c**, indicates that these products may be produced from excited triplet states of **1a**–**1c**. The lower quenching efficiency of piperylene to the present excited triplet species is probably due to the shorter lifetime of the excited states of these molecules, as compared with those produced from trisilane derivatives.[8]

In order to clarify the effect of piperylene, the initial stages of the reaction for **1c** in the absence or presence of piperylene were monitored by GLC. The results showed that **1c** decreases with a constant rate, while **3a** and **2c** increase linearly with increasing irradiation time. In the absence of piperylene, yields of products on the basis of **1c** consumed were calculated to be 47% for **3a** and 20% for **2c** when 17% of **1c** was photolyzed. Similar photolysis of **1c** in the presence of piperylene, however, gave **3a** and **2c** in 28% and 19% yields, respectively, when 15% of **1c** was photolyzed. Irradiation of **1b** in the absence of piperylene produced **3b** and **2a** in 39% and 23% yields at 19% conversion of **1b**, while in the presence of piperylene, **1b** afforded **3b** and **2a** in 31% and 20% yields, respectively. These results indicate that, in the initial stages of the reaction, the formation of **3a** and **3b** arising from homolytic

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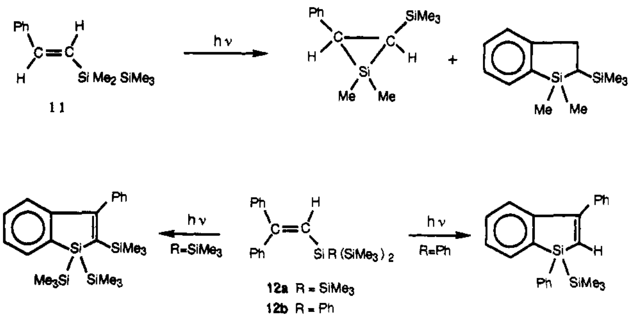
[9] One of the referees suggested the possibility that intermediate A is formed by a radical recombination reaction, analogous to the formation of **7b**. However, compounds arising from intermediate A were obtained only in low yields. Therefore, we could not clarify the mechanism for the formation of intermediate A.

Scheme II



scission of an Si–Si bond of **1c** and **1b** is suppressed with the presence of piperylene, though the effect is small.[10]

As reported previously, the photolysis of (*E*)-(2-phenylethenyl)pentamethyldisilane (**11**) gives a silacyclopropane via a 1,2-trimethylsilyl shift.[7] However, the photolysis of trisilanes **12a** and **12b** having the bulky diphenylethenyl group produces no silacyclopropanes (Scheme II).[8] This may be ascribed to steric hindrance.

We have also found that the photolysis of the 2-trimethylsilyl derivative **12a** undergoes a 1,2-silyl shift to give a 2-silylsilaindene, while 2-phenyl derivative **12b** results in Si–Si bond scission giving silaindene with loss of a trimethylsilyl group (Scheme II).[8] In the reaction of disilanes **1a**–**1c**, a 1,2-silyl shift and scission of an Si–Si bond occur competitively, together with extrusion of silylene. Interestingly, the photolysis of disilane **1b** that has a phenyl group on an α-silicon atom produced 2-silylsilaindan **6b** as the result of a 1,2-silyl shift, as in the photolysis of less hindered disilane **11** that afforded a similar silaindan.[7] In addition, **1b** produced a 5-silylsilaindene **7b** arising from scission of an Si–Si bond. Introduction of a phenyl group on an α-silicon atom of diphenylethenylpolysilanes certainly affects the photodegradation pathway, but unfortunately, at present, we have no precise data for discussing the reason of such unusual phenomena.

The structures of all products isolated were verified by spectroscopic analysis, as well as by elemental analysis. ^{1}H NMR spectra of the starting materials **1a**–**1c** and photochemical products **2a** and **2c** show a singlet resonance due to an isolated olefin proton at δ 6.30, 6.54, 6.25, 6.31, and 6.47 ppm, respectively, along with resonances due to phenyl and methylsilyl protons.

The ^{13}C NMR spectrum of silaindene **3a** shows a signal at δ −4.00 ppm due to methylsilyl carbons, together with eight resonances with high intensities at δ 123–132 ppm and four resonances with low intensities at δ 140–161 ppm, assigned to aromatic ring carbons with and without hydrogen, respectively. The ^{1}H NMR spectrum of **3a** reveals two singlet resonances at δ 0.38 and 6.17 ppm in the ratio 6:1, due to dimethylsilyl protons and an olefin proton, respectively, along with multiplet resonances that collapse to five groups centered at δ 7.22 (dd, 1 H), 7.30 (m, 1 H), 7.39 (m, 2 H), 7.45 (m, 4 H), and 7.60 (dd, 1 H) ppm, attributed to aromatic ring protons. These results clearly indicate that the molecule has a silaindene ring bearing phenyl and dimethylsilyl groups. The location of the substituents on the silaindene ring was established by NOE-FID difference experiments at 270 MHz. Irradiation of the dimethylsilyl protons at δ 0.38 ppm resulted in a strong enhancement of the signal at δ 6.17 ppm, attributed to the proton at C(2) in the silaindene ring, as well as the signal at δ 7.60 ppm, attributed to the proton at the C(7) position. Saturation of the olefin proton at δ 6.17 ppm caused a positive NOE of the dimethylsilyl protons at δ 0.38 ppm, together with partial enhancement of the signals appearing at δ 7.45 ppm, attributed to aromatic ring protons including two *o*-protons of the C-phenyl group, but no enhancement was observed for the signals at δ 7.22 (C(4)–H) and 7.60 (C(7)–H) ppm.

For **3b**, irradiation of methylsilyl protons at δ 0.70 ppm leads to strong enhancement of signals at δ 6.27 (s, C(2)–H) and 7.62 (dd, C(7)–H) ppm. Saturation of the olefin proton at 6.27 ppm caused a positive NOE of the methylsilyl protons at δ 0.70 ppm, together with partial enhancement of signals appearing at δ 7.46–7.52 ppm, attributed to ring protons including *o*-protons in the phenyl groups, but the signal at δ 7.62 ppm (C(7)–H) was not affected.

The ^{13}C NMR spectrum of **4a** shows two resonances at δ −2.93 ($SiMe_2$) and 0.72 ($SiMe_3$) ppm and five resonances at δ 141–167 ppm (ring C), in addition to seven resonances at δ 123–131 ppm (ring HC). The ^{1}H NMR spectrum of **4a** reveals two singlet resonances at δ −0.10 (9 H, $SiMe_3$) and 0.42 (6 H, $SiMe_2$) ppm and multiplet resonances that collapse to four groups centered at δ 6.82 (dd, 1 H), 7.21 (m, 4 H), 7.38 (m, 3 H), and 7.59 (dd, 1 H) ppm. Saturation of the dimethylsilyl protons at 0.42 ppm caused a positive NOE of the trimethylsilyl protons at δ −0.10 ppm, as well as of the proton of the C(7) position at δ 7.59 ppm. Irradiation of the trimethylsilyl protons at δ −0.10 ppm resulted in a strong enhancement of the signal at δ 0.42 ppm (ring $SiMe_2$), together with partial enhancement of the signal appearing at δ 7.21 ppm. No enhancement was found for the proton at δ 6.82 ppm (C(4)–H) in these NOE-FID experiments.

For **4c**, saturation of ring dimethylsilyl protons at δ 0.25 ppm resulted in a positive NOE of the proton signals at δ 7.58 (dd, C(7)–H) and 0.11 (s, C(2)–$SiMe_2$) ppm, as well as signals appearing at δ 7.37–7.42 ppm (SiPh), while irradiation of the other dimethylsilyl protons at δ 0.11 ppm caused enhancement of signals appearing at δ 7.07–7.11 (CPh) and 7.37–7.42 ppm (SiPh).

The ^{13}C NMR spectrum of **6b** reveals four resonances at δ −2.10 (SiMe), 0.22 ($SiMe_3$), 23.7 (C(3)), and 54.2 (C(2)) ppm, together with ten signals at δ 126–135 ppm (ring HC) and four signals at δ 138–158 ppm (ring C). The ^{1}H NMR spectrum of **6b** reveals two singlet resonances at δ −0.33 (9 H, $SiMe_3$) and 0.81 (3 H, SiMe) ppm and two doublet resonances (J = 8.6 Hz) centered at δ 1.25 (C(3)–H) and 4.90 (C(2)–H) ppm, as well as multiplet resonances at δ 7.06–7.56 ppm (14 H, ring H). Saturation of the trimethylsilyl protons at δ −0.33 ppm results in a strong enhancement of the proton signals at δ 0.81 (ring SiMe) and 4.90 (C(2)–H) ppm and signals appearing at δ 7.06–7.09 (CPh *ortho* H) ppm but not the signal at δ 1.25 ppm (C(3)–H), while irradiation of the ring methylsilyl protons at δ 0.81 ppm caused a positive NOE of the trimethylsilyl protons at δ −0.33 ppm and protons appearing at δ 7.50–7.56 ppm (C(7)–H and SiPh *ortho* H), indicating that **6b** has an *r*-1-methyl-*c*-2-(trimethylsilyl)-*c*-3-phenyl configuration.

^{1}H NMR chemical shifts that are the basis of identification of the 5-silylsilaindene **7b** are shown in Figure 1. As expected, an ^{1}H–^{1}H COSY experiment at 400 MHz clearly reveals the interaction between protons, H_b–H_c,

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[10] We could not find out the effect of piperylene on the yields of **4c** and **6b**, as well as **7b**, because of the low yields of these products in the initial stages of the reaction.

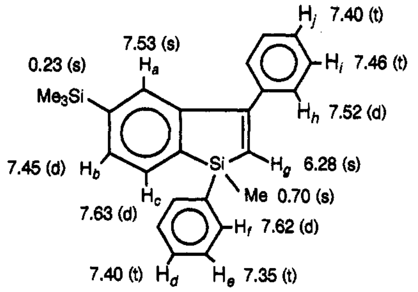

Figure 1. ^{1}H NMR chemical shifts of **7b**.

H_d–H_e, H_e–H_f, H_h–H_i, and H_i–H_j. Furthermore, saturation of trimethylsilyl protons at δ 0.23 ppm caused a positive NOE of the protons H_a and H_b, while irradiation of ring methylsilyl protons at δ 0.70 ppm results in enhancement of the signals due to H_c, H_f, and H_g. Irradiation of H_g shows enhancement for H_f and H_h. Moreover, the ^{13}C NMR spectrum of **7b** reveals two resonances at δ −5.84 (SiMe) and −1.20 ($SiMe_3$) ppm, together with ten signals at 128–135 ppm (ring HC) and four signals at 134–163 ppm (ring C). All of the above results are wholly consistent with the structures proposed for **3a**, **3b**, **4a**, **4c**, **6b**, and **7b**.

Experimental Section

General Information. All reactions were carried out under an atmosphere of purified inert gas. Tetrahydrofuran (THF) and ether were dried over sodium metal in the presence of a small amount of benzophenone and distilled just before use. Hexane and benzene were dried over lithium aluminum hydride and distilled before use. The yields of the photochemical products were determined with Hitachi 263-30 and Shimadzu GC-6A gas chromatographs on OV-17 and SE-30 as the stationary phases using pentadecane as an internal standard. ^{1}H NMR and ^{13}C NMR spectra were measured with JEOL JNM-EX-270 and Bruker AM-X-400 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600-FT-IR spectrophotometer. Mass spectra were recorded on a Shimadzu Model GCMS QP-1000 spectrometer.

Preparation of 1a. Into a 200-mL four-necked round bottom flask equipped with a reflux condenser, dropping funnel, and stirrer was placed a solution of 14.56 g (87 mmol) of chloropentamethyldisilane[11] in 10 mL of THF. To this solution was added dropwise the Grignard reagent prepared from 2-bromo-1,1-diphenylethylene (95 mmol) and magnesium (95 mmol) in 50 mL of THF. The mixture was stirred at room temperature overnight and then poured into ice-water. Products were extracted with ether, and the ethereal solution was dried over magnesium sulfate. The solvent was evaporated, and the residue was distilled in vacuo to give 10.60 g of a distillate. The distillate was chromatographed on silica gel with hexane, and the main fraction was distilled again to give 10.24 g (38% yield) of (2,2-diphenylethenyl)pentamethyldisilane (**1a**): bp 107 °C/5 mmHg; ^{1}H NMR ($CDCl_3$) δ −0.11 (s, 6 H, $SiMe_2$), 0.53 (s, 9 H, $SiMe_3$), 6.30 (s, 1 H, olefin proton), 7.19–7.36 (m, 10 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −2.87 ($SiMe_2$), −1.94 ($SiMe_3$), 127.2 (C=*C*HSi), 127.3, 127.4, 127.9, 128.0, 128.7, 129.8 (phenyl ring carbons), 142.7, 143.6 (phenyl *ipso*-carbons), 156.8 (Ph_2*C*=C); IR 1244 (ν_{Si-C}), 1563 ($\nu_{C=C}$) cm^{-1}; UV (THF) λ_{max} 209.7, 236.1, 273.9; MS *m/e* 310 (M^+). Anal. Calcd for $C_{19}H_{26}Si_2$: C, 73.48; H, 8.44. Found: C, 73.30; H, 8.40.

Preparation of 1b. Into a 200-mL four-necked round bottom flask equipped with a reflux condenser, dropping funnel, and stirrer was placed a solution of 15.99 g (70 mmol) of 1-chloro-1-phenyltetramethyldisilane[12] in 10 mL of THF. To this solution was added dropwise the Grignard solution prepared from 2-bromo-1,1-diphenylethylene (73 mmol) and magnesium (80 mmol) in 50 mL of THF. The mixture was stirred at room temperature overnight, refluxed for 24 h, and then poured into ice-water. Products were extracted with ether, and the ethereal solution was dried over magnesium sulfate. The solvent was evaporated, and the residue was distilled in vacuo to give 21.2 g of a distillate. The distillate was chromatographed on silica gel with hexane, and the main fraction was distilled again to give 19.4 g (74% yield) of 1-(2,2-diphenylethenyl)-1-phenyltetramethyldisilane (**1b**): bp 159 °C/3 mmHg; ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 3 H, SiPh*Me*), 0.05 (s, 9 H, $SiMe_3$), 6.54 (s, 1 H, olefin proton), 7.13–7.48 (m, 15 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −5.21 (SiPh*Me*), −1.80 ($SiMe_3$), 125.8 (C=CHSi), 127.4, 127.6, 127.7, 127.9, 128.0, 128.16, 128.25, 129.8, 134.1 (phenyl ring carbons), 139.2, 142.4, 143.8 (phenyl *ipso*-carbons), 158.3 (Ph_2*C*=C); IR 1560 ($\nu_{C=C}$), 1245 (ν_{Si-C}) cm^{-1}; UV (THF) λ_{max} 207.9, 237.9, 272.7; MS *m/e* 372 (M^+). Anal. Calcd for $C_{24}H_{28}Si_2$: C, 77.35; H, 7.57. Found: C, 77.33; H, 7.44.

Preparation of 1c. Into a 300-mL four-necked round bottom flask equipped with a reflux condenser, dropping funnel, and stirrer was placed a solution of 19.02 g (83 mmol) of 1-chloro-2-phenyltetramethyldisilane[13] in 20 mL of THF. To this solution was added dropwise the Grignard reagent prepared from 2-bromo-1,1-diphenylethylene (83 mmol) and magnesium (90 mmol) in 50 mL of THF. The mixture was refluxed for 1 h and then poured into ice-water. Products were extracted with ether, and the ethereal solution was dried over magnesium sulfate. The solvent was evaporated, and the residue was distilled in vacuo to give 21.9 g of a distillate. The distillate was chromatographed on silica gel with hexane, and the main fraction was distilled again to give 21.02 g (67% yield) of 1-(2,2-diphenylethenyl)-2-phenyltetramethyldisilane (**1c**): bp 145–150 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ −0.13 (s, 6 H, =CHSi*Me*$_2$), 0.34 (s, 6 H, SiPh*Me*$_2$), 6.25 (s, 1 H, olefin proton), 7.03–7.48 (m, 15 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −3.65 (=CHSi*Me*$_2$), −2.87 (SiPh*Me*$_2$), 127.2 (C=*C*HSi), 127.3, 127.5, 127.7, 127.80, 127.84, 128.0, 128.4, 129.7, 133.9 (phenyl ring carbons), 139.5, 142.4, 143.6 (phenyl *ipso*-carbons), 157.1 (Ph_2*C*=C); IR 1563 ($\nu_{C=C}$), 1245 (ν_{Si-C}) cm^{-1}; UV (THF) λ_{max} 208.9, 235.5, 277.1; MS *m/e* 372 (M^+). Anal. Calcd for $C_{24}H_{28}Si_2$: C, 77.35; H, 7.57. Found: C, 77.23; H, 7.42.

General Procedure for the Photochemical Reaction. A solution of disilane in hexane was irradiated with a 6-W low-pressure mercury lamp under dry argon in either the presence or absence of a quencher. Products **2a**, **3a**, **3b**, **9**, **2c**, and **10** were isolated by medium-pressure liquid chromatography (MPLC) on silica gel, eluting with hexane. Products **4a**, **6b**, **7b**, and **4c** were isolated by gel-permeation chromatography (GPC), eluting with chloroform. Products **5** and **8** were isolated by preparative gas–liquid chromatography (GLC) using SE 30 as the column. Results are summarized in Table I.

Photolysis of 1a. A solution of 1.13 mmol of disilane **1a** in 60 mL of hexane was irradiated for 12 h. Products **2a**[8] and **3a** were isolated by MPLC. Product **4a** was isolated by GPC.

For **2a**:[8] ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9 H, $SiMe_3$), 6.31 (s, 1 H, olefin proton), 7.20–7.36 (m, 10 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −0.05 ($SiMe_3$), 127.2, 127.3, 127.6, 127.9, 128.0, 129.7 (phenyl ring carbons and C=CHSi), 142.6, 143.2 (phenyl *ipso*-carbons), 157.1 (Ph_2*C*=C); IR 1566 ($\nu_{C=C}$), 1247 (ν_{Si-C}) cm^{-1}; MS *m/e* 252 (M^+).

For **3a**: ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 6 H, $SiMe_2$), 6.17 (s, 1 H, olefin proton), 7.20–7.62 (m, 9 H, phenyl and phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ −4.00 ($SiMe_2$), 123.4, 126.7, 127.5, 128.0, 128.2, 129.3, 131.1, 131.9 (phenyl and phenylene ring carbons and silole ring α-carbon), 140.1, 140.3, 148.8, 160.9 (phenyl *ipso*-carbon, silole ring β-carbon, and fused carbons); IR 1534 ($\nu_{C=C}$), 1246 (ν_{Si-C}) cm^{-1}; MS *m/e* 236 (M^+). Anal. Calcd for $C_{16}H_{16}Si$: C, 81.30; H, 6.82. Found: C, 81.30; H, 6.80.

For **4a**: ^{1}H NMR ($CDCl_3$) δ −0.10 (s, 9 H, $SiMe_3$), 0.42 (s, 6 H, $SiMe_2$), 6.80–7.61 (m, 9 H, phenyl and phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ −2.93 ($SiMe_2$), 0.72 ($SiMe_3$), 123.8, 126.8,

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127.0, 128.0, 128.6, 129.4, 131.1 (phenyl and phenylene ring carbons), 140.6, 141.7, 142.2, 151.7, 167.1 (phenyl *ipso*-carbon, silole ring carbons, and fused carbons); IR 1247 (ν_{Si-C}) cm^{-1}; MS *m/e* 308 (M$^+$); exact mass calcd for $C_{19}H_{24}Si_2$ 308.1417, found 308.1413.

Photolysis of 1a in the Presence of Piperylene. A solution of 1.06 mmol of disilane **1a** and 16.9 mmol of piperylene in 60 mL of hexane was irradiated for 11 h.

Photolysis of 1a in the Presence of 2,3-Dimethylbutadiene. A solution of 0.97 mmol of disilane **1a** and 10 mmol of 2,3-dimethylbutadiene in 60 mL of hexane was irradiated for 18 h.

Photolysis of 1a in the Presence of Methanol. A solution of 0.97 mmol of disilane **1a** and 20 mmol of methanol in 60 mL of hexane was irradiated for 19 h.

Photolysis of 1a in the Presence of Diethylmethylsilane. A solution of 1.03 mmol of disilane **1a** and 2.16 mmol of diethylmethylsilane in 60 mL of hexane was irradiated for 8 h. Product **5**[14] was isolated by preparative GLC.

For **5**:[14] ^{1}H NMR (CDCl$_3$) δ 0.05 (s, 3 H, SiEt$_2$*Me*), 0.16 (d, 6 H, SiH*Me*$_2$, $J = 4.6$ Hz), 0.64 (q, 4 H, *CH*$_2$CH$_3$, $J = 7.8$ Hz), 0.98 (t, 6 H, CH$_2$*CH*$_3$, $J = 7.8$ Hz), 3.74 (sept, 1 H, SiH, $J = 4.6$ Hz); ^{13}C NMR (CDCl$_3$) δ −6.29 (SiEt$_2$*Me*), −6.00 (SiHMe$_2$), 5.47 (CH$_2$*CH*$_3$), 8.25 (CH$_2$); IR 2091 (ν_{Si-H}), 1247 (ν_{Si-C}) cm^{-1}; MS *m/e* 160 (M$^+$), 145 (M$^+$ − Me), 131 (M$^+$ − Et).

Photolysis of 1b. A solution of 0.83 mmol of disilane **1b** in 60 mL of hexane was irradiated for 12 h. Product **3b** was isolated by MPLC. Products **6b** and **7b** were isolated by GPC.

For **3b**: ^{1}H NMR (CDCl$_3$) δ 0.70 (s, 3 H, SiMe), 6.27 (s, 1 H, silole ring proton), 7.26–7.64 (m, 14 H, phenyl and phenylene ring protons); ^{13}C NMR (CDCl$_3$) δ −5.86 (SiMe), 123.6, 127.1, 127.7, 128.00, 128.03, 128.2, 129.5, 129.6, 129.8, 132.6, 134.4 (phenyl and phenylene ring carbons and silole α-carbon), 134.3, 138.6, 140.1, 149.3, 162.3 (phenyl *ipso*-carbons, silole β-carbon, and fused carbons); IR 1253 (ν_{Si-C}) cm^{-1}; MS *m/e* 298 (M$^+$). Anal. Calcd for $C_{21}H_{18}Si$: C, 84.51; H, 6.08. Found: C, 84.40; H, 6.08.

For **6b**: ^{1}H NMR (CDCl$_3$) δ −0.33 (s, 9 H, SiMe$_3$), 0.81 (s, 3 H, SiMe), 1.25 (d, 1 H, silolene β-proton, $J = 8.58$ Hz), 4.90 (d, 1 H, silolene α-proton, $J = 8.58$ Hz), 7.06–7.56 (m, 14 H, phenyl and phenylene ring protons); ^{13}C NMR (CDCl$_3$) δ −2.10 (SiMe), 0.22 (SiMe$_3$), 23.7, 54.2 (silolene ring carbons), 126.2, 126.3, 126.5, 127.7, 128.2, 129.2, 129.3, 129.9, 132.2, 134.5 (phenyl and phenylene ring carbons), 138.4, 138.6, 146.6, 158.1 (phenyl *ipso*-carbons and fused carbons); IR 1249 (ν_{Si-C}) cm^{-1}; MS *m/e* 372 (M$^+$); exact mass Calcd for $C_{24}H_{28}Si_2$ 372.1730, found 372.1755.

For **7b**: ^{1}H NMR (CDCl$_3$) δ 0.23 (s, 9 H, SiMe$_3$), 0.70 (s, 3 H, SiMe), 6.28 (s, 1 H, silole ring proton), 7.30–7.65 (m, 13 H, phenyl and phenylene ring protons); ^{13}C NMR (CDCl$_3$) δ −5.84 (SiMe), −1.20 (SiMe$_3$), 127.7, 127.9_8, 128.0_0, 128.0_6, 128.2, 129.5, 129.8, 131.9, 132.1, 134.5 (phenyl and phenylene ring carbons and silole α-carbon), 134.3, 139.3, 140.1, 142.0, 148.2, 162.6 (phenyl *ipso*-carbons, silole β-carbon, and fused carbons); IR 1248 (ν_{Si-C}) cm^{-1}; MS *m/e* 370 (M$^+$); exact mass calcd for $C_{24}H_{26}Si_2$ 370.1572, found 370.1556.

Photolysis of 1b in the Presence of Piperylene. A solution of 0.94 mmol of disilane **1b** and 14.1 mmol of piperylene in 60 mL of hexane was irradiated for 6 h.

Photolysis of 1b in the Presence of 2,3-Dimethylbutadiene. A solution of 0.62 mmol of disilane **1b** and 8.54 mmol of 2,3-dimethylbutadiene in 30 mL of hexane was irradiated for 7 h.

Photolysis of 1b in the Presence of Methanol. A solution of 0.83 mmol of disilane **1b** and 16 mmol of methanol in 60 mL of hexane was irradiated for 12 h.

Photolysis of 1b in the Presence of *tert*-Butyl Alcohol. A solution of 0.62 mmol of disilane **1b** and 11.6 mmol of *tert*-butyl alcohol in 30 mL of hexane was irradiated for 10 h. Product **8**[15] was isolated by preparative GLC.

For **8**:[15] ^{1}H NMR (CDCl$_3$) δ 0.42 (d, 3 H, SiMe, $J = 2.64$ Hz), 1.42 (s, 9 H, CMe$_3$), 5.12 (q, 1 H, SiH, $J = 2.64$ Hz), 7.29–7.57 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −0.38 (SiMe), 31.4 (C*Me*$_3$), 73.1 (*C*Me$_3$), 127.8, 129.6, 133.7 (phenyl ring carbons), 138.0 (phenyl *ipso*-carbon); IR 2117 (ν_{Si-H}), 1252 (ν_{Si-C}), 1043 (ν_{Si-O}) cm^{-1}; MS *m/e* 194 (M$^+$).

Photolysis of 1b in the Presence of Diethylmethylsilane. A solution of 0.94 mmol of disilane **1b** and 19.6 mmol of diethylmethylsilane in 60 mL of hexane was irradiated for 8 h. Product **9**[16] was isolated by MPLC.

For **9**:[16] ^{1}H NMR (CDCl$_3$) δ 0.07 (s, 3 H, SiEt$_2$*Me*), 0.44 (d, 3 H, SiHPh*Me*, $J = 4.6$ Hz), 0.62–0.69 (m, 4 H, Si*CH*$_2$CH$_3$), 0.91–0.98 (m, 6 H, SiCH$_2$*CH*$_3$), 4.27 (q, 1 H, SiH, $J = 4.6$ Hz), 7.26–7.52 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −7.47 (SiEt$_2$*Me*), −6.47 (SiHPh*Me*), 5.16 (SiCH$_2$*CH*$_3$), 8.07 (Si*CH*$_2$CH$_3$), 127.8, 128.5, 134.7 (phenyl ring carbons), 136.3 (phenyl *ipso*-carbon); IR 2092 (ν_{Si-H}), 1248 (ν_{Si-C}) cm^{-1}; MS *m/e* 222 (M$^+$).

Photolysis of 1c. A solution of 0.62 mmol of disilane **1c** in 60 mL of hexane was irradiated for 9 h. Products **3a**, **2c**, and **10**[17] were isolated by MPLC. Product **4c** was isolated by GPC.

For **2c**: ^{1}H NMR (CDCl$_3$) δ 0.08 (s, 6 H, SiMe$_2$), 6.47 (s, 1 H, olefin proton), 7.12–7.51 (m, 15 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −1.54 (SiMe$_2$), 127.3, 127.4, 127.7, 127.76, 127.83, 128.0, 128.7, 129.7, 133.7 (phenyl ring carbons and Ph$_2$C=*C*H), 140.1, 142.3, 143.2 (phenyl *ipso*-carbon), 158.3 (Ph$_2$*C*=CH); IR 1248 (ν_{Si-C}) cm^{-1}; MS *m/e* 314 (M$^+$). Anal. Calcd for $C_{22}H_{22}Si$: C, 84.02; H, 7.05. Found: C, 84.01; H, 6.96.

For **4c**: ^{1}H NMR (CDCl$_3$) δ 0.11 (s, 6 H, SiPh*Me*$_2$), 0.25 (s, 6 H, SiMe$_2$), 6.82–7.59 (m, 14 H, phenyl and phenylene ring protons); ^{13}C NMR (CDCl$_3$) δ −3.02 (SiMe$_2$), −0.90 (SiPh*Me*$_2$), 124.0, 126.95, 127.04, 127.5, 127.9, 128.5, 128.6, 129.4, 131.1, 133.9 (phenyl and phenylene ring carbons), 140.1, 140.5, 140.9, 141.3, 151.4, 168.4 (phenyl *ipso*-carbons, silole ring carbons, and fused carbons); IR 1247 (ν_{Si-C}) cm^{-1}; MS *m/e* 370 (M$^+$). Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.76; H, 7.02.

For **10**:[17] ^{1}H NMR (CDCl$_3$) δ 0.35 (d, 6 H, SiMe, $J = 3.63$ Hz), 4.44 (sept, 1 H, SiH, $J = 3.63$ Hz), 7.34–7.57 (m, 5 H, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −3.83 (SiMe), 127.9, 129.2, 134.0 (phenyl ring carbons), 137.4 (phenyl *ipso*-carbons). MS *m/e* 136 (M$^+$).

Photolysis of 1c in the Presence of Piperylene. A solution of 0.94 mmol of disilane **1c** and 14.8 mmol of piperylene in 60 mL of hexane was irradiated for 6 h.

Photolysis of 1c in the Presence of Diethylmethylsilane. A solution of 0.94 mmol of disilane **1c** and 1.92 g (18.8 mmol) of diethylmethylsilane in 60 mL of hexane was irradiated for 5 h.

Photolysis of 1c in the Presence of 2,3-Dimethylbutadiene. A solution of 0.62 mmol of disilane **1c** and 8.54 mmol of 2,3-dimethylbutadiene in 30 mL of hexane was irradiated for 7 h.

Photolysis of 1c in the Presence of Methanol. A solution of 0.62 mmol of disilane **1c** and 12.5 mmol of methanol in 30 mL of hexane was irradiated for 9 h.

Photolysis of 1c in the Presence of Diethylmethylsilane. A solution of 0.94 mmol of disilane **1c** and 18.8 mmol of diethylmethylsilane in 60 mL of hexane was irradiated for 5 h.

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