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Silicon–Carbon Unsaturated Compounds. 33. Regiochemistry in the Photochemical Formation of Silenes from 1,2,2,2-Tetramethyl-, 1,1,2,2-Tetramethyl-, and 2-Ethyl-1,2,2-trimethylphenylvinyldisilane

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The photolysis of phenylvinyldisilanes has been studied. Irradiation of 1,2,2,2-tetramethylphenylvinyldisilane (1) in the presence of acetone gave two products, 1-[(isopropenyloxy)methylphenylsilyl]-2-(trimethylsilyl)ethane and 1-(isopropoxymethylvinylsilyl)-2-(trimethylsilyl)benzene, which were produced from the reaction of two different silenes derived from a 1,3-silyl shift to the vinyl group and also to the phenyl group with acetone in 56 and 5% yield, respectively. Similar irradiation of 1 in the presence of 2,3-dimethylbutadiene afforded *trans*-1-[methyl(2,3-dimethyl-2-butenyl)phenylsilyl]-2-(trimethylsilyl)ethene, 1-[methyl(3-methyl-2-methylene-3-butenyl)phenylsilyl]-2-(trimethylsilyl)ethane, and 1-[methyl(2,3-dimethyl-3-butenyl)vinylsilyl]-2-(trimethylsilyl)benzene, in 9, 31, and 28% yields. The photolysis of 2-ethyl-1,2,2-trimethylphenylvinyldisilane (9) in the presence of methanol produced 2-(ethyldimethylsilyl)-1-(methoxymethylphenylsilyl)ethane in 94% yield. Irradiation of 9 in the presence of acetone gave 2-(ethyldimethylsilyl)-1-[(isopropenyloxy)methylphenylsilyl]ethane in 67% yield, in addition to a small amount of 2-(ethyldimethylsilyl)-1-(isopropoxymethylvinylsilyl)benzene. Irradiation of 9 in the presence of 2,3-dimethylbutadiene gave *trans*-2-(ethyldimethylsilyl)-1-[methyl(2,3-dimethyl-2-butenyl)phenylsilyl]ethene, 2-(ethyldimethylsilyl)-1-[methyl(3-methyl-2-methylene-3-butenyl)phenylsilyl]ethane, and (*E*)-2-[(ethyldimethylsilyl)methyl]-1,4,5-trimethyl-1-phenyl-1-silacyclo-4-hexene in 5, 57, and 20% yields. Irradiation of 1,1,2,2-tetramethylphenylvinyldisilane (16) in the presence of acetone produced 1-[(isopropenyloxy)dimethylsily]-2-(dimethylphenylsilyl)ethane, (isopropenyloxy)dimethylphenylsilane, and dimethylphenylsilane, while in the presence of 2,3-dimethylbutadiene 16 gave *trans*-1-[dimethyl(2,3-dimethyl-2-butenyl)silyl]-2-(dimethylphenylsilyl)ethene and 1-[dimethyl(3-methyl-2-methylene-3-butenyl)silyl]-2-(dimethylphenylsilyl)ethane in 20 and 42% yields.

Introduction

The photolysis of π-electron system-substituted disilanes offers a convenient method to synthesize many types of silenes. In fact, irradiation of aryl-, alkenyl-, and alkynyldisilanes with a low-pressure mercury lamp affords the respective silenes that are formed from a 1,3-silyl shift to the π-electron system.[1] The photolysis of disilanes having two different types of the π-electron systems, dihydropyranyl-substituted phenyldisilanes, produces mainly two types of silenes; one involves a 1,3-silyl shift to the dihydropyranyl ring, while the other comprises a 1,3-silyl shift to the phenyl ring. The ratio of the products formed from two different silenes depends highly on the trapping agent used. For example, the photolysis of 1-(3,4-dihydro-2*H*-6-pyranyl)-1,2,2,2-tetramethylphenyldisilane in the presence of methanol gives products derived from the reaction of both silenes with methanol, while in the presence of isobutene as a quenching agent the dihydropyranylphenyldisilane gives an adduct, which is produced by the reaction of the silene arising from a 1,3-silyl shift to the phenyl ring with isobutene,[2] as a single product.

We have reported previously that the photolysis of phenylvinyldisilanes in the presence of methanol gave the only adduct that is formed from the reaction of the silene arising from a 1,3-silyl shift to a vinyl moiety with methanol.[3]

It is of interest to us to investigate the photolysis of these systems in the presence of various trapping agents, because the formation of two different types of the silenes might be observed. We report here the photolysis of 1,2,2,2-tetramethyl-, 1,1,2,2-tetramethyl-, and 2-ethyl-1,2,2-trimethylphenylvinyldisilane in the presence of methanol, acetone, and 2,3-dimethylbutadiene.

Results and Discussion

First we reinvestigated the photolysis of 1,2,2,2-tetramethylphenylvinyldisilane (1) in the presence of methanol in detail. Thus, irradiation of 1 with a low-pressure mercury lamp in the presence of a large excess of methanol in hexane afforded 1-(methoxymethylphenylsilyl)-2-(trimethylsilyl)ethane (3), which was produced from the addition of methanol to the silene (2a) arising from a 1,3-trimethylsilyl shift to the vinyl group in 94% yield, when 92% of 1 was photolyzed, as reported previously. Similar photolysis of 1 in the presence of acetone, however, gave 1-[(isopropenyloxy)methylphenylsilyl]-2-(trimethylsilyl)ethane (4) and 1-(isopropoxymethylvinylsilyl)-2-(trimethylsilyl)benzene (5) in 60 and 5% yields.

The product 4 is probably formed by the ene reaction of the silene 2a with acetone (Scheme I). The reaction of the silene with carbonyl compounds normally gives olefins and cyclosiloxanes.[1,4] The silene 2a, however, reacted with acetone to give only product 4 derived from the ene reaction. Such ene reactions have been reported previously.[4-6] The formation of 5 can best be explained in terms of the ene reaction of the silene (2b) arising from a 1,3-silyl shift to a phenyl group with acetone. Indeed, it is well-known that this type of compound can be always

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[1] Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* 1981, *19*, 51.

[2] Takaki, K.; Sakamoto, H.; Nishimura, Y.; Sugihara, Y.; Ishikawa, M. *Organometallics* 1991, *10*, 888.

[3] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* 1978, *149*, 37.

[4] Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons Ltd.: New York, 1989; Chapter 17.

[5] Wiberg, N.; Wagner, G. *Chem. Ber.* 1986, *119*, 1467.

[6] Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* 1982, *104*, 6830.

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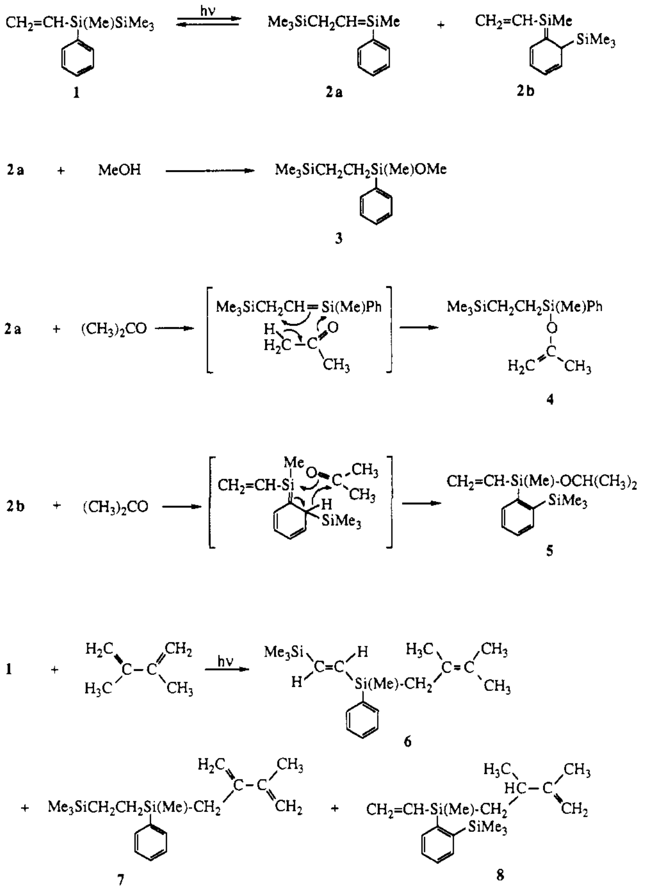
Scheme I



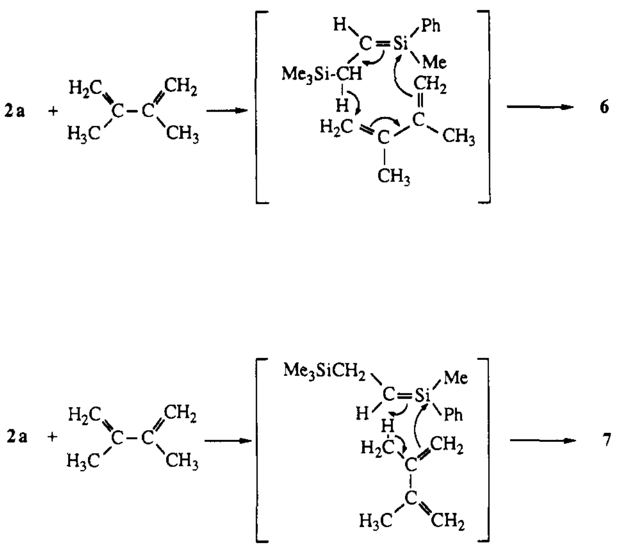
produced in the photolysis of benzenoid aromatic disilanes in the presence of ketones.[1]

Interestingly, irradiation of 1 in the presence of 2,3-dimethylbutadiene yielded three products, *trans*-1-[methyl(2,3-dimethyl-2-butenyl)phenylsilyl]-2-(trimethylsilyl)ethene (**6**), 1-[methyl(3-methyl-2-methylene-3-butenyl)phenylsilyl]-2-(trimethylsilyl)ethane (**7**), and 1-[methyl(2,3-dimethyl-3-butenyl)vinylsilyl]-2-(trimethylsilyl)benzene (**8**) in 9, 31, and 28% yields. The products **6** and **7** are probably formed by two types of the ene reaction of the silene **2a** with 2,3-dimethylbutadiene, respectively. The formation of compound **6** involves a hydrogen shift from a methylene group of the silene **2a** to a butadiene molecule, while **7** comprises the hydrogen shift from a methyl group of the butadiene to **2a** (Scheme II). However, for compound **8**, again the formation of the silene **2b** must be considered.

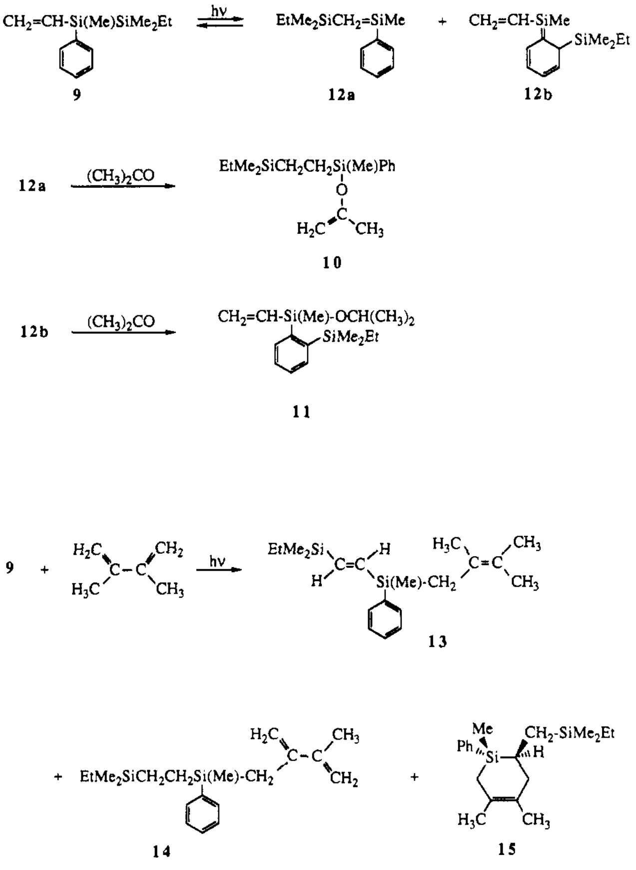
The fact that the photolysis of **1** in the presence of methanol gives the product **3** in 94% yield but in the presence of acetone and 2,3-dimethylbutadiene the adducts formed from both silenes, **2a** and **2b**, are produced indicates the existence of the equilibrium between the starting compound **1** and the silenes **2a** and **2b** or between two different silenes, **2a** and **2b**. Since the backward reaction of the silene produced photochemically from acylpolysilanes to the starting compound has been observed by Brook et al.,[7] it seems likely that the equilibrium between the starting compound **1** and both silanes **2a** and **2b** exists in the present system.

The photolysis of 2-ethyl-1,2,2-trimethylphenylvinyldisilane (**9**) in the presence of methanol gave 2-(ethyldimethylsilyl)-1-(methoxymethylphenylsilyl)ethane in 94% yield, when 70% of **9** was photolyzed. Similar irradiation of compound **9** in the presence of acetone produced 2-(ethyldimethylsilyl)-1-[(isopropenyloxy)methylphenylsilyl]ethane (**10**) in 67% yield, in addition to a small amount of 2-(ethyldimethylsilyl)-1-(isopropoxymethylvinylsilyl)benzene (**11**) (5% yield) (Scheme III). Again, the formation of **10** may be explained by the ene reaction of the silene (**12a**) formed from a 1,3-silyl shift to the vinyl group with acetone, while compound **11** can be understood by the reaction of the silene (**12b**) generated from a 1,3-silyl shift to the phenyl ring with acetone.

Scheme II



Scheme III



In contrast to the photolysis of **1**, irradiation of compound **9** in the presence of 2,3-dimethylbutadiene afforded three products: *trans*-2-(ethyldimethylsilyl)-1-[methyl(2,3-dimethyl-2-butenyl)phenylsilyl]ethene (**13**), 2-

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[7] Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

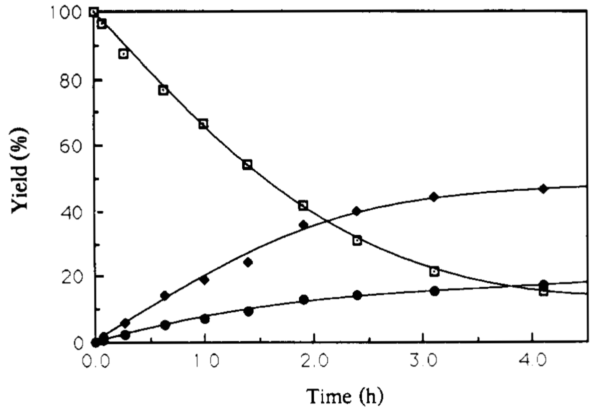
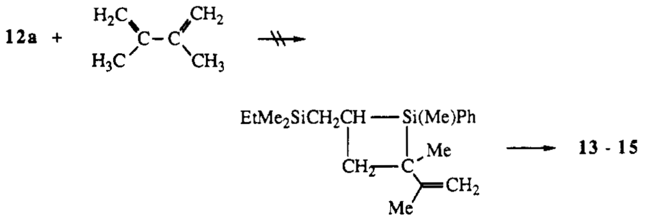


Figure 1. Yields of products vs time for the photolysis of **9** in the presence of 2,3-dimethylbutadiene: (□) compound **9**; (◆) products **13** and **14**; (●) product **15**.

(ethyldimethylsilyl)-1-[methyl(3-methyl-2-methylene-3-butenyl)phenylsilyl]ethane (**14**), and (*E*)-2-[(ethyldimethylsilyl)methyl]-1,4,5-trimethyl-1-phenyl-1-silacyclo-4-hexene (**15**) were obtained in 5, 57, and 20% yields, respectively. No product derived from the reaction of silene **12b** with 2,3-dimethylbutadiene was detected in the photolysis mixture. Compounds **13** and **14** are the products from the ene reaction of silene **12a** and 2,3-dimethylbutadiene, while compound **15** is the [2 + 4] cycloadduct produced from the reaction of **12a** with the trapping agent.

One might consider the possibility that the products **13–15** could be produced by a stepwise process involving the formation of a [2 + 2] cycloadduct such as 2-[(ethyldimethylsilyl)methyl]-1,4-dimethyl-1-phenyl-4-isopropenyl-1-silacyclobutane, followed by photochemical radical scission of the resulting silacyclobutane. However, as can be seen in Figure 1, the observed yields of products plotted against time for the photolysis of **9** in the presence of 2,3-dimethylbutadiene clearly indicate that compounds **13–15** are the primary products, not the secondary ones.



The structures of **10**, **11**, and **13–15** could be confirmed by mass, IR, and ^{1}H and ^{13}C NMR spectrometric analysis, as well as by elemental analysis (see Experimental Section). The *E* geometry of product **15** was established from NOE-FID difference experiments at 270 MHz. Thus, saturation of the resonance of the methylsilyl protons at δ 0.25 ppm produced a positive NOE of silyl-substituted methylene protons at the C_2 position of the silacyclohexenyl ring and one of two hydrogens at the C_6 position, in addition to phenyl protons on the ring silicon atom, but no effect was observed for hydrogen on the C_2 position.

In the reaction of the silene produced from a 1,3-silyl shift to the phenyl group with trapping agents, the steric bulkiness of the substituents on the silicon atom at the C_2 position of the cyclohexadienyl ring seems to be severe for the ene reactions. In the case of **2b** and **12b**, the existence of the vinyl group or ethyl group on the silicon atom at the C_2 position would sterically disturb the ene reaction with the trapping agent, and hence the silenes **2b** and **12b** formed would go back to the starting disilane. Some of the silene would also be converted to nonvolatile substances, as observed in the photolysis of benzenoid aryldisilanes which are transformed into polymeric substances in the absence of the trapping agent. Consequently, the products derived from the silenes **2a** and **12a** are obtained. The silenes arising from a 1,3-silyl shift to the vinyl moiety seem to be more reactive than those produced from a 1,3-silyl shift to the phenyl ring. The fact that no adducts arising from the reaction with the silenes **2b** and **12b** in the photolysis of **1** and **9** in the presence of methanol are produced may be ascribed to the formation of the adducts resulting in a loss of the aromatic sextet of the phenyl ring. Consequently, methanol adds to **2a** and **12a** to give thermodynamically more stable products.

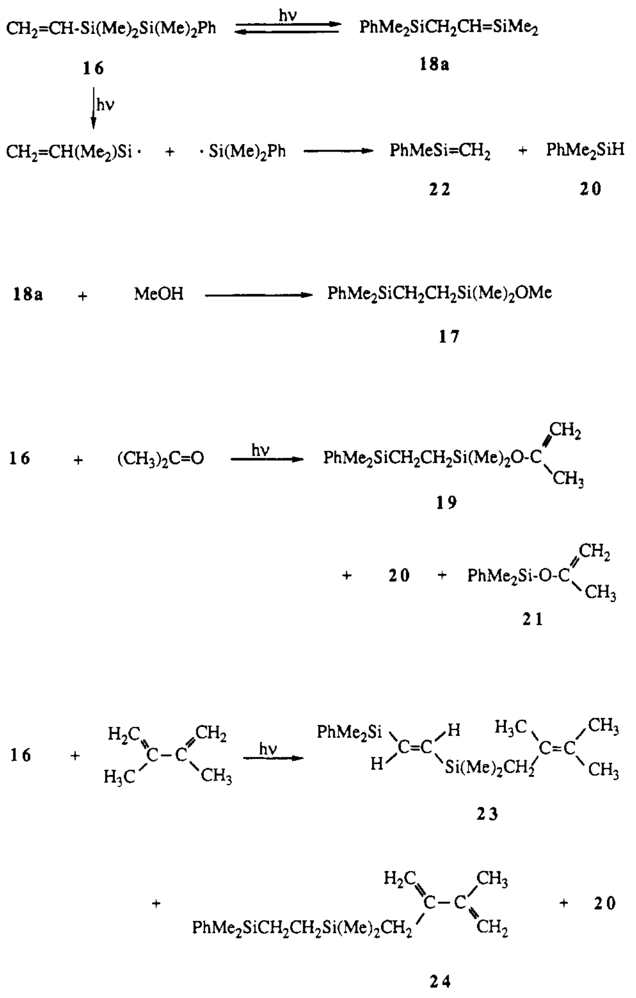
Next, we investigated the photolysis of 1,1,2,2-tetramethylphenylvinyldisilane (**16**). As reported previously,[3] the photolysis of **16** in the presence of methanol gives 1-(methoxydimethylsilyl)-2-(dimethylphenylsilyl)ethane (**17**) formed from the reaction of the silene (**18a**) arising from a 1,3-silyl to the vinyl moiety with methanol in 82% yield as the sole product. Similar photolysis of **16** in the presence of acetone as a trapping agent gave 1-[(isopropenyloxy)dimethylsilyl]-2-(dimethylphenylsilyl)ethane (**19**), which was produced by the ene reaction of **18a** with acetone in 66% yield. In this photolysis, dimethylphenylsilane (**20**) and (isopropenyloxy)dimethylphenylsilane (**21**) were also produced in 5 and 7% yields, respectively. However, neither the product derived from [2 + 2] cycloaddition of **18a** with acetone nor the product formed from the reaction of the silene (**18b**) arising from a 1,3-dimethylvinylsilyl shift to the benzene ring with acetone was detected in the reaction mixture by either spectrometric analysis or GLC analysis (Scheme IV). Compound **20** is probably formed by homolytic scission of a silicon–silicon bond of the photoexcited **16**, followed by redistribution of the resulting silyl radicals, while compound **21** is probably produced by the ene reaction of silene **22** formed from the redistribution of the silyl radicals with acetone.

Irradiation of **16** in the presence of 2,3-dimethylbutadiene, however, gave two products, 1-[dimethyl(2,3-dimethyl-2-butenyl)silyl]-2-(dimethylphenylsilyl)ethene (**23**) and 1-[dimethyl(3-methyl-2-methylene-3-butenyl)silyl]-2-(dimethylphenylsilyl)ethane (**24**) in 20 and 42% yields, in addition to 4% of the product **20**. The formation of products **23** and **24** can be best understood in terms of the ene reaction of silene **18a** with the trapping agent. Compound **24** is probably formed by an ene reaction of silene **18a** similar to that of **2a** with 2,3-dimethylbutadiene, in which a hydrogen shift from the methyl group of the butadiene to the silene carbon takes place. In contrast to **24**, compound **23** is probably produced by another type of the ene reaction involving a hydrogen shift from the methylene group of the silene **18a** to a terminal sp^2 carbon of the butadiene, analogous to the formation of **6**.

In the ^{1}H NMR spectrum of **23**, two vinylic protons show a singlet, and therefore we could not confirm the geometry from its ^{1}H NMR spectrum. However, since compounds **6** and **13**, which were produced from a similar reaction, could be identified to have trans geometry from their coupling constants, compound **23** seems to have trans geometry.

In conclusion, the photolysis of **1** and **9** produces two isomers of the silene arising from a 1,3-trimethylsilyl shift to the vinyl group and to the phenyl ring. The distribution of the products formed from two different silenes highly depends on the trapping agent used and also on substituents on the silicon atom at the C_2 position in the cyclohexadienyl ring of the silenes arising from a 1,3-silyl shift

Scheme IV



to the phenyl ring. In the photolysis of **16**, the products formed from the reaction of the silene produced from a 1,3-silyl shift to the vinyl moiety are obtained, in addition to the products derived from homolytic scission of a silicon–silicon bond of **16**. The fact that the photolysis of **1** in the presence of 2,3-dimethylbutadiene gives two products derived from both silenes in good yields strongly suggests the existence of equilibrium between the starting compound and the silenes formed.

Experimental Section

General Procedures. All photolyses were carried out under an atmosphere of purified argon. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. ^1H and ^{13}C NMR spectra were determined on a JEOL Model JNM-FX-90A spectrometer and a JEOL Model JNM-EX-270 spectrometer, using deuteriochloroform as a solvent. All photolyses were carried out by using a low-pressure mercury lamp (254 nm) at room temperature, and the yields of the products were calculated on the basis of the starting compounds photolyzed.

Materials. 1,2,2,2-Tetramethyl- and 1,1,2,2-tetramethylphenylvinyldisilane were synthesized by the method reported in the literature.[3] Tetrahydrofuran (THF) and hexane were dried over lithium aluminum hydride and distilled before use. Chloroform was dried over phosphorus pentachloride and distilled before use.

Preparation of 2-Ethyl-1,2,2-trimethyldiphenyldisilane. A (methyldiphenylsilyl)lithium solution prepared from 101.6 g (0.44 mol) of chloromethyldiphenylsilane and 10.1 g (1.4 mol) of lithium in 300 mL of THF was added to 51.9 g (0.42 mol) of chloroethyldimethylsilane in 100 mL of THF. The reaction mixture was stirred for 2 h at room temperature and hydrolyzed with water. The organic layer was separated from aqueous layer, and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined, washed with water, and then dried over anhydrous magnesium sulfate. The solvents were evaporated, and the residue was distilled under reduced pressure to give 56.0 g (58% yield) of 2-ethyl-1,2,2-trimethyldiphenylsilane: bp 105–110 °C (1 mmHg); MS *m/e* 284 (M^+); IR 1427, 1245, 1106, 958 cm^{-1}; ^1H NMR δ 0.15 (s, 6 H, Me_2Si), 0.64 (s, 3 H, MeSi), 0.68 (q, 2 H, C–CH_2Si, J = 7.9 Hz), 0.92 (t, 3 H, CH_3–CSi, J = 7.9 Hz), 7.34–7.53 (m, 10 H, phenyl ring protons); ^{13}C NMR δ –4.42 (MeSi), –4.02 (Me_2Si), 6.99 (CH_2Si), 7.89 (CH_3CSi), 127.82, 128.66, 134.83, 137.63 (phenyl ring carbons). Anal. Calcd for $C_{17}H_{24}Si_2$: C, 71.76; H, 8.50. Found: C, 71.65; H, 8.45.

Preparation of 1-Chloro-2-ethyl-1,2,2-trimethylphenyldisilane. Into a 200-mL three-necked flask fitted with a stirrer, gas inlet tube, and reflex condenser was placed a mixture of 49.4 g (0.17 mol) of 2-ethyl-1,2,2-trimethyldiphenyldisilane and 0.5 g (3.74 mmol) of anhydrous aluminum chloride in 120 mL of chloroform. Into the stirred mixture was passed gradually dry hydrogen chloride gas at room temperature. The reaction was monitored by GLC, and 10 mL of dry acetone was added to the mixture when the starting compound was consumed. After evaporation of the solvent, the residue was distilled under reduced pressure to give 34.1 g (81% yield) of 1-chloro-2-ethyl-1,2,2-trimethylphenyldisilane: bp 62–63 °C (2 mmHg); MS *m/e* 242 (M^+); IR 1428, 1248, 1107, 1007, 840 cm^{-1}; ^1H NMR δ 0.16 (s, 6 H, Me_2Si), 0.73 (q, 2 H, C–CH_2Si, J = 7.6 Hz), 0.74 (s, 3 H, MeSi), 0.96 (t, 3 H, CH_3–CSi, J = 7.6 Hz), 7.39–7.59 (m, 5 H, phenyl ring protons); ^{13}C NMR δ –4.99 (Me_2Si), 1.19 (MeSi), 6.11 (CH_2Si), 7.78 (CH_3–C), 128.09, 129.74, 133.26, 136.68 (phenyl ring carbons). Anal. Calcd for $C_{11}H_{10}ClSi_2$: C, 54.39; H, 7.88. Found: C, 54.21; H, 7.88.

Preparation of 2-Ethyl-1,2,2-trimethylphenylvinyldisilane (9). Into a 200-mL flask fitted with a stirrer, dropping funnel, and reflux condenser was placed 18.9 g (78 mmol) of 1-chloro-2-ethyl-1,2,2-trimethylphenyldisilane in 40 mL of THF. To this was added 80 mL (110 mmol) of a vinylmagnesium bromide–THF solution at room temperature. The mixture was heated to reflux for 8 h and hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic layer and extracts were combined, washed with water, and then dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was distilled under reduced pressure to give 14.6 g (81% yield) of **9**: bp 56–60 °C (2 mmHg); MS *m/e* 234 (M^+); IR 1425, 1402, 1237, 1102, 1002, 944 cm^{-1}; ^1H NMR δ 0.13 (s, 6 H, Me_2Si), 0.47 (s, 3 H, MeSi), 0.66 (q, 2 H, C–CH_2Si, J = 7.9 Hz), 0.97 (t, 3 H, CH_3–CSi, J = 7.9 Hz), 5.79 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{gem} = 3.6 Hz), 6.12 (dd, 1 H, vinylic proton, J_{cis} = 14.5 Hz, J_{gem} = 3.6 Hz), 6.42 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{cis} = 14.5 Hz), 7.36–7.54 (m, 5 H, phenyl ring protons); ^{13}C NMR δ –5.62 (MeSi), –4.33 (Me_2Si), 6.85 (C–CH_2Si), 7.98 (CH_3–CSi), 127.80, 128.50, 134.30, 137.70 (phenyl ring carbons), 132.69, 136.82 (vinylic carbons). Anal. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46. Found: C, 66.45; H, 9.37.

Photolysis of 1 in the Presence of Acetone. Into a 70-mL reaction vessel fitted with a low-pressure mercury lamp bearing a Vycor filter was placed a mixture of 0.8667 g (3.94 mmol) of **1**, 2.2250 g (38.4 mmol) of acetone, and 0.2315 g (1.48 mmol) of undecane as an internal standard in 60 mL of hexane. The mixture was irradiated at room temperature for 3.5 h with a slow stream of argon bubbling through the mixture. The reaction mixture was analyzed by GLC as being **4** (60% yield), **5** (5% yield), and the starting compound **1** (13%). The products **4** and **5** were isolated by preparative GLC. For **4**: MS *m/e* 278 (M^+); IR 1638, 1428, 1372, 1276, 1050 cm^{-1}; ^1H NMR δ 0.00 (s, 9 H, Me_3Si), 0.48 (s, 3 H, MeSi), 0.56–0.60 (m, 4 H, CH_2CH_2) 1.80 (br s, 3 H, Me), 4.04 (br s, 2 H, $H_2C{=}C$), 7.36–7.65 (m, 5 H, phenyl ring protons); ^{13}C NMR δ –3.9 (Me_3Si), –2.3 (MeSi), 7.7 (CH_2CH_2), 22.7 (CH_3), 91.6 ($CH_2{=}C$), 127.8, 129.6, 133.7, 136.8 (phenyl ring carbons), 155.9 (–O—C=CH_2). Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.52; H, 9.40. For **5**: IR 1370, 1243, 1114, 1014, 838 cm^{-1}; ^1H NMR δ 0.36 (s, 9 H, Me_3Si), 0.46 (s, 3 H, MeSi), 1.20 (d, 3 H, Me_aCH–O, J = 5.9 Hz), 1.22 (d, 3 H, Me_bCH–O, J = 5.9 Hz), 4.13 (sep, 1 H, HC–O, J = 5.9 Hz), 5.82 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{gem} = 4.0 Hz), 6.12 (dd, 1 H, vinylic proton, J_{cis} = 14.9 Hz, J_{gem} = 4.0 Hz), 6.32 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{cis} = 14.9 Hz), 7.29–7.68 (m, 4 H, phenyl ring protons); ^{13}C NMR δ -1.40 (MeSi), 1.58 (Me$_3$Si), 25.61 (Me$_2$CH-O), 65.98 (HC-O), 127.44, 128.27, 133.96, 135.27, 142.87, 146.81 (phenyl ring carbons), 135.00, 138.54 (vinylic carbons). High-resolution mass spectrum calcd for $C_{15}H_{26}Si_2O$: 278.1522. Found: 278.1505.

Photolysis of 1 in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.5005 g (2.28 mmol) of 1, 0.5241 g (6.39 mmol) of 2,3-dimethylbutadiene, and 0.0480 g (0.261 mmol) of tridecane in 60 mL of hexane was photolyzed for 7 h at room temperature. The mixture was analyzed as being **6** (9% yield), **7** (31% yield), and **8** (28% yield), in addition to the starting compound 1 (11%). Pure **6**–**8** were isolated by preparative GLC. For **6**: MS *m/e* 302 (M$^+$); IR 1425, 1248, 1167, 1108, 861 cm^{-1}; ^{1}H NMR δ 0.06 (s, 9 H, Me$_3$Si), 0.33 (s, 3 H, MeSi), 1.53 (br s, 3 H, CH$_3$), 1.60 (br s, 3 H, CH$_3$), 1.64 (br s, 3 H, CH$_3$), 1.83 (br s, 2 H, CH$_2$), 6.65 (d, 1 H, H$_a$C=C, *J* = 22.4 Hz), 6.75 (d, 1 H, H$_b$C=C, *J* = 22.4 Hz), 7.32–7.51 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -4.54 (MeSi), -1.69 (Me$_3$Si), 20.42 (CH$_2$), 21.15 (CH$_3$), 21.08 (CH, 23.58 (CH$_3$), 121.67 (C(Me)=CMe$_2$), 124.12 (C(Me$_2$)=CMe), 127.64, 128.88, 134.14, 138.22 (phenyl ring carbons), 147.31 (C$_a$(Si)=C), 153.42 (C$_b$(Si)=C). Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.45; H, 9.99. Found: C, 71.45; H, 9.89. For **7**: MS *m/e* 302 (M$^+$); IR 1590, 1427, 1248, 1133, 1113, 1053 cm^{-1}; ^{1}H NMR δ -0.05 (s, 9 H, Me$_3$Si), 0.24 (s, 3 H, MeSi), 0.37–0.63 (m, 4 H, CH$_2$CH$_2$), 1.87 (s, 3 H, CH$_3$), 2.02 (s, 2 H, H$_2$C), 4.90–4.96 (m, 4 H, H$_2$C$_a$= and H$_2$C$_b$=), 7.23–7.47 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -5.5 (MeSi), -2.2 (Me$_3$Si), 6.3 (CH$_2$), 8.9 (CH$_2$), 21.1 (CH$_2$), 21.3 (CH$_3$), 110.9 (CH$_2$=C), 113.6 (CH$_2$=C), 127.6, 128.8, 134.0, 138.0 (phenyl ring carbons), 143.6 (C=CH$_2$), 145.2 (C=CH$_2$). Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.45; H, 9.99. Found: C, 71.41; H, 9.79. For **8** (diastereomeric mixture): MS *m/e* 302 (M$^+$); IR 1590, 1427, 1248, 1111 cm^{-1}; ^{1}H NMR δ 0.34 (s, 9 H, Me$_3$Si), 0.46 and 0.48 (s, 3 H, MeSi), 0.93–1.11 (m, 5 H, CH$_2$ and CH$_3$), 1.64 (s, 3 H, CH$_3$), 2.16–2.49 (m, 1 H, HC), 4.59–4.64 (m, 2 H, H$_2$C=C), 5.68 and 5.70 (dd, 1 H, vinylic proton, J_{trans} = 19 Hz, J_{gem} = 5 Hz), 6.04 and 6.06 (dd, 1 H, vinylic proton, J_{cis} = 15 Hz, J_{gem} = 5 Hz), 6.45 and 6.48 (dd, 1 H, vinylic proton, J_{trans} = 19 Hz, J_{cis} = 15 Hz), 7.25–7.70 (m, 4 H, phenyl ring protons); ^{13}C NMR δ -1.6 and -1.1 (MeSi), 2.2 (Me$_3$Si), 18.8 and 18.9 (CH$_3$), 22.7 (CH$_2$), 22.9 (CH$_3$), 37.4 (CH), 108.4 and 108.5 (CH$_2$=C), 127.5, 127.7, 132.9, 135.5, 136.2, 143.7, 143.8, 144.6 (phenyl ring carbons), 139.4 and 139.6 (C=CH$_2$), 152.2 and 152.3 (C=CH$_2$). Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.45; H, 9.99. Found: C, 71.41; H, 10.00.

Photolysis of 9 in the Presence of Methanol. A mixture of 0.7045 g (3.01 mmol) of **9**, 1.3057 g (40.8 mmol) of methanol, and 0.0976 g (0.530 mmol) of tridecane as an internal standard in 60 mL of hexane was photolyzed for 2.2 h. The resulting mixture was analyzed by GLC as being 2-(ethyldimethylsilyl)-1-(methoxymethylphenylsilyl)ethane (94% yield), in addition to 30% of the starting compound **9**. The product was isolated by preparative GLC: MS *m/e* 266 (M$^+$); IR 1428, 1252, 1090, 1052, 789 cm^{-1}; ^{1}H NMR δ -0.06 (s, 6 H, Me$_2$Si), 0.37 (s, 3 H, MeSi), 0.48 (q, 2 H, C-CH$_2$-Si, *J* = 7.9 Hz), 0.72 (t, 2 H, CH$_2$, *J* = 3.6 Hz), 0.78 (t, 2 H, CH$_2$, *J* = 3.6 Hz), 0.90 (t, 3 H, CH$_3$-CSi, *J* = 7.9 Hz), 3.50 (s, 3 H, Me-O), 7.38–7.58 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -5.00 (MeSi), -4.47 (Me$_2$Si), 5.88 (CH$_2$), 6.31 (C-CH$_2$Si), 6.67 (CH$_2$), 7.35 (CH$_3$-CSi), 50.86 (Me-O), 127.84, 129.56, 133.76, 136.68 (phenyl ring carbons). Anal. Calcd for $C_{14}H_{26}OSi_2$: C, 63.09; H, 9.83. Found: C, 63.03; H, 9.98.

Photolysis of 9 in the Presence of Acetone. A solution of 0.7307 g (3.12 mmol) of **9**, 1.3868 g (23.9 mmol) of acetone, and 0.1080 g (0.587 mmol) of tridecane as an internal standard in 60 mL of hexane was photolyzed for 2 h. The mixture was analyzed by GLC as being **10** (67% yield) and **11** (5% yield), in addition to 26% of the starting compound **9**. Compounds **10** and **11** were isolated by preparative GLC. For **10**: MS *m/e* 263 (M$^+$ - 29); IR 1428, 1372, 1277, 1134, 1049, 785 cm^{-1}; ^{1}H NMR δ -0.06 (s, 6 H, Me$_2$Si), 0.45 (s, 3 H, MeSi), 0.46 (q, 2 H, C—CH$_2$Si, *J* = 7.9 Hz), 0.78 (t, 2 H, CH$_2$, *J* = 3.6 Hz), 0.83 (t, 2 H, CH$_2$, *J* = 3.6 Hz), 0.89 (t, 3 H, CH$_3$-CSi, *J* = 7.9 Hz), 1.77 (s, 3 H, Me—CO), 4.00 (s, 1 H, H$_a$C(H$_b$)=CO), 4.02 (s, 1 H, H$_b$C(H$_a$)=CO), 7.33–7.60 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -4.47 (Me$_2$Si), -3.95 (MeSi), 5.77 (CH$_2$), 6.29 (CH$_2$), 7.32 (CH$_2$—C), 7.55 (CH$_3$—C), 22.73 (CH$_3$), 91.61 (CH$_2$=CO), 127.78, 129.61, 133.66, 136.77 (phenyl ring carbons), 155.90 (C(O)=CH$_2$). Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.64. Found: C, 65.68; H, 9.52. For **11**: IR 1390, 1243, 1114, 1009, 814 cm^{-1}; ^{1}H NMR δ 0.33 (s, 6 H, Me$_2$Si), 0.45 (s, 3 H, MeSi), 0.86–0.93 (m, 5 H, EtSi), 1.19 (d, 3 H, Me, *J* = 5.9 Hz), 1.21 (d, 3 H, Me, *J* = 5.9 Hz), 4.12 (sept, 1 H, CH-O, *J* = 5.9 Hz), 5.82 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{gem} = 4.0 Hz), 6.11 (dd, 1 H, vinylic proton, J_{cis} = 14.8 Hz, J_{gem} = 4.0 Hz), 6.31 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{cis} = 14.8 Hz), 7.26–7.65 (m, 4 H, phenyl ring protons); ^{13}C NMR δ -1.40 (MeSi), -0.88 (Me$_2$Si), 7.64 (C—CH$_2$Si), 8.65 (CH$_3$—CSi), 25.57 ((CH$_3$)$_2$CO), 65.9 (C—O), 127.39, 128.18, 135.29, 138.56, 143.07, 145.86 (phenyl ring carbons), 135.36 (C=CHSi), 139.75 (CH(Si)=C). High-resolution mass spectrum calcd for $C_{16}H_{28}OSi_2$: 292.1679. Found: 292.1755.

Photolysis of 9 in the Presence of 2,3-Dimethylbutadiene. A mixture of 1.6607 g (7.10 mmol) of **9**, 1.3237 g (16.1 mmol) of 2,3-dimethylbutadiene, and 0.1176 g (0.640 mmol) of tridecane in 120 mL of hexane was photolyzed for 7 h. The mixture was analyzed by GLC as being **13** (5% yield), **14** (57% yield), and **15** (20% yield), in addition to 27% of the starting compound **9**. Compounds **13**–**15** were isolated by preparative GLC. For **13**: MS *m/e* 316 (M$^+$); IR 1420, 1243, 1167, 1108, 808 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6 H, Me$_2$Si), 0.33 (s, 3 H, MeSi), 0.53 (q, 2 H, C—CH$_2$Si, *J* = 7.9 Hz), 0.92 (t, 3 H, CH$_3$—CSi, *J* = 7.9 Hz), 1.48 (br s, 3 H, CH$_3$), 1.54 (br s, 3 H, CH$_3$), 1.60 (br s, 3 H, CH$_3$), 1.83 (br s, 2 H, CH$_2$), 6.65 (d, 1 H, H$_a$C(Si)=CH$_b$, *J* = 22.6 Hz), 6.75 (d, H$_b$C(Si)=C, *J* = 22.6 Hz), 7.31–7.53 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -4.49 (MeSi), -3.97 (Me$_2$Si), 6.99 (C—CH$_2$Si), 7.33 (CH$_3$—CSi), 20.40 (CH$_2$), 21.06 (CH$_3$), 21.13 (CH$_3$), 23.56 (CH$_3$), 123.90 (C(Me$_2$)—C), 127.80 (C=CMe$_2$), 127.62, 128.86, 134.12, 137.57 (phenyl ring carbons), 147.96 (C$_a$(Si)=C$_b$), 152.31 (C$_b$(Si)=C$_a$). High-resolution mass spectrum calcd for $C_{19}H_{32}Si_2$: 316.2043. Found: 316.2054. For **14**: MS *m/e* 316 (M$^+$); IR 1458, 1248, 1132, 1114, 1053, 1010, 879 cm^{-1}; ^{1}H NMR -0.09 (s, 6 H, Me$_2$Si), 0.23 (s, 3 H, MeSi), 0.41 (q, 2 H, C—CH$_2$Si, *J* = 7.9 Hz), 0.64–0.66 (m, 4 H, CH$_2$CH$_2$), 0.87 (t, 3 H, CH$_3$—CSi, *J* = 7.9 Hz), 1.89 (br s, 3 H, CH$_3$), 2.00 (br s, 2 H, CH$_2$), 4.71 (br s, 1 H, H$_a$C(H$_b$)=C), 4.90 (br s, 1 H, H$_b$C(H$_a$)C=C), 4.95 (br s, 2 H, H$_2$C=C), 7.32–7.49 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -5.55 (MeSi), -4.44 (Me$_2$Si), 6.18 (CH$_2$), 6.33 (CH$_2$), 6.88 (C—CH$_2$Si), 7.35 (CH$_3$—CSi), 21.06 (CH$_3$), 21.19 (CH$_2$), 110.94 (CH$_2$=C), 113.59 (CH$_2$=C), 127.60, 128.79, 133.96, 139.39 (phenyl ring carbons), 143.56 (C=CH$_2$), 145.10 (C=CH$_2$). Anal. Calcd for $C_{19}H_{32}Si_2$: C, 72.07; H, 10.19. Found: C, 72.01; H, 10.17. For **15**: MS *m/e* 316 (M$^+$); IR 1427, 1248, 1130, 1010, 788 cm^{-1}; ^{1}H NMR δ -0.09 (s, 3 H, MeSi), -0.08 (s, 3 H, MeSi), 0.25 (s, 3 H, MeSi), 0.39 (dd, 1 H, H$_a$C(H$_b$)Si, *J* = 15.0, 10.4 Hz), 0.44 (q, 2 H, C–CH$_2$Si, *J* = 7.9 Hz), 0.67 (dd, 1 H, H$_b$C(H$_a$)Si, *J* = 15.0, 3.8 Hz), 0.86 (t, 3 H, CH$_3$-CSi, *J* = 7.9 Hz), 1.12 (four d, 1 H, HC, *J* = 10.4, 10.2, 5.3, 3.8 Hz), 1.36 (br d, 1 H, H$_a$C(H$_b$), *J* = 16.8 Hz), 1.49 (br d, 1 H, H$_b$C(H$_a$), *J* = 16.8 Hz), 1.68 (br s, 3 H, CH$_3$), 1.72 (br s, 3 H, CH$_3$), 1.93 (br dd, 1 H, H$_c$C(H$_d$), *J* = 15.4, 10.2 Hz), 2.26 (br dd, 1 H, H$_d$C(H$_c$), *J* = 15.4, 5.3 Hz), 7.28–7.51 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -7.31 (MeSi), -3.12 (MeSi), -2.96 (MeSi), 7.37 (C—CH$_2$Si), 7.59 CH$_3$—CSi), 14.90 (CH$_2$), 16.55 (CH$_2$), 19.97 (CH), 21.33 (CH$_3$), 23.15 (CH$_3$), 40.24 (CH$_2$), 125.03 (C$_a$(Me)=C$_b$), 128.03 (C$_b$(Me)=C$_a$), 127.67, 128.88, 133.85, 138.76 (phenyl ring carbons). Anal. Calcd for $C_{19}H_{32}Si_2$: C, 72.07; H, 10.19. Found: C, 71.91; H, 10.13.

Photolysis of 16 in the Presence of Acetone. A mixture of 0.8931 g (4.06 mmol) of **16**, 1.3110 g (22.6 mmol) of acetone, and 0.0817 g (0.528 mmol) of undecane as an internal standard in 60 mL of hexane was photolyzed for 4 h. The mixture was analyzed by GLC as being **19** (66% yield), **20** (5% yield), and **21** (7% yield), in addition to 2% of the starting compound **16**. Products **19**–**21**, were isolated by preparative GLC. For **19**: MS *m/e* 263 (M$^+$ - 15); IR 1427, 1406, 1371, 1278, 1250, 1047 cm^{-1}; ^{1}H NMR δ 0.19 (s, 6 H, Me$_2$Si), 0.28 (s, 6 H, Me$_2$Si), 0.60–0.71 (m, 4 H, CH$_2$CH$_2$), 1.77 (br s, 3 H, CH$_3$), 4.04 (br s, 2 H, CH$_2$=C), 7.31–7.58 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -3.6 (Me$_2$Si), -2.2 (Me$_2$Si), 7.0 (CH$_2$), 7.4 (CH$_2$), 22.7 (CH$_3$), 91.1 (CH$_2$=C), 127.7, 128.8, 133.6, 139.2 (phenyl ring carbons), 156.0 (C(O)=C). Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.56, H, 9.35. For **20**: All spectral data obtained from this compound were identical with those of the authentic sample prepared from lithium aluminum hydride reduction of chlorodimethylphenylsilane. For **21**: MS *m/e* 192 (M$^+$); IR 1489, 1427, 1276, 1120 cm^{-1}; ^{1}H NMR δ 0.51 (s, 6 H, Me$_2$Si), 1.78 (s, 3 H, CH$_3$), 4.01 (br s, 2 H, CH$_2$), 7.14–7.67 (m, 5 H, phenyl ring protons); ^{13}C NMR δ -1.2

(Me$_2$Si), 22.8 (CH$_3$), 91.8 (CH$_2$=C), 127.9, 129.7, 133.3, 137.7 (phenyl ring carbons), 155.8 (C=CH$_2$). Anal. Calcd for $C_{11}H_{16}OSi_2$: C, 68.69; H, 8.38. Found: C, 68.46; H, 8.35.

Photolysis of 16 in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.9011 g (4.10 mmol) of **16**, 1.5650 g (19.1 mmol) of 2,3-dimethylbutadiene, and 0.0386 g (0.250 mmol) of undecane as an internal standard in 120 mL of hexane was photolyzed for 2 h. The mixture was analyzed by GLC as being **20** (4% yield), **23** (20% yield), and **24** (42% yield), in addition to 23% of the starting compound **16**. Products **20**, **23**, and **24** were isolated by preparative GLC. For **23**: MS *m/e* 302 (M$^+$); IR 1427, 1247, 1011, 833 cm^{-1}; ^{1}H NMR δ 0.07 (s, 6 H, Me$_2$Si), 0.33 (s, 6 H, Me$_2$Si), 1.57 (br s, 9 H, three CH$_3$), 1.90 (s, 2 H, CH$_2$), 6.69 (s, 2 H, HC(Si)=CH(Si)), 7.30–7.53 (m, 5 H, phenyl ring protons); ^{13}C NMR δ −2.7 (Me$_2$Si), −2.6 (Me$_2$Si), 20.4 (CH$_2$), 21.2 (CH$_3$), 24.5 (two CH$_3$), 121.0 (C_a=C_b), 127.8 (C_b=C_a), 127.7, 128.7, 133.9, 138.7 (phenyl ring carbons), 148.3 (C_aH=C_bH), 152.4 (C_bH=C_aH). Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.45; H, 9.99. Found: C, 71.16; H, 9.99. For **24**: MS *m/e* 302 (M$^+$); IR 1426, 1428, 1159, 1132 cm^{-1}; ^{1}H NMR δ −0.04 (s, 6 H, Me$_2$Si). 0.27 (s, 6 H, Me$_2$Si), 0.42–0.61 (m, 4 H, CH$_2$CH$_2$), 1.79 (s, 2 H, CH$_2$), 1.99 (s, 3 H, CH$_3$), 4.75 (br s, 1 H, HC=C), 4.95–5.03 (m, 3 H, H$_2$C=C and HC=C), 7.32–7.58 (m, 5 H, phenyl ring protons); ^{13}C NMR δ −3.6 (Me$_2$Si), −3.5 (Me$_2$Si), 7.6 (CH$_2$), 7.9 (CH$_2$), 21.0 (CH$_3$), 21.9 (CH$_2$), 110.2 (CH$_2$=C), 113.4 (CH$_2$=C), 127.7, 128.7, 132.9, 133.6 (phenyl ring carbons), 145.6 (two C=CH$_2$). Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.45; C, 9.99. Found: C, 71.37; H, 10.00.

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Oxidative-Addition Reactions of Alkyl Chlorides with Chlorobis(cyclooctene)rhodium(I) and the Bis(oxazolinyl)pyridine Ligand: Formation of Stable (Chloromethyl)rhodium(III) Complexes and Their Reactions

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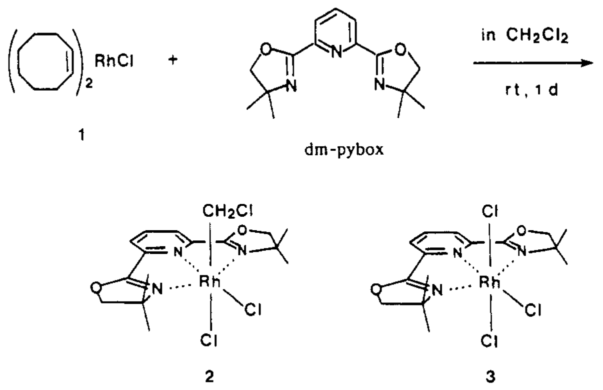
Dichloromethane and chloroform readily react with chlorobis(cyclooctene)rhodium(I) (1) and 2,6-bis(4,4-dimethyloxazolin-2-yl)pyridine, dm-pybox, at room temperature to give the stable (chloromethyl)rhodium(III) complex 2 and (dichloromethyl)rhodium(III) complex 4, respectively. Several organic halides also react with 1 to give the corresponding substituted alkylrhodium(III) complexes. Some reactions of the chloromethyl complexes were also demonstrated. Decomposition of 2 and 3 in methanol at 100–130 °C gave the methylrhodium(III) complex, in which the origin of the methyl group can be traced to be methanol.

We have prepared new terdentate nitrogen ligands, bis(oxazolinyl)pyridine (pybox), for asymmetric hydrosilylation of ketones with rhodium catalysts.[1] During the study of the pybox–rhodium complexes as catalysts, we have unexpectedly found an oxidative addition reaction of dichloromethane and chloroform to chlorobis(cyclooctene)rhodium(I) in the presence of the pybox, giving (chloromethyl)rhodium(III) complexes. Halomethyl transition-metal complexes have been well investigated from the aspect of the activation of halogenomethanes and the intermediates of catalytic systems.[2] We report here the formation and some reactions of the stable (chloromethyl)- and (dichloromethyl)rhodium(III) pybox complexes.

Scheme I



Results and Discussion

A mixture of chlorobis(cyclooctene)rhodium(I) (1)[3] and bis(4,4-dimethyloxazolin-2-yl)pyridine,[1b] dm-pybox, in

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