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Decompositions of Polysilylated Diazomethanes. Silene Formations by Selective Silyl Migration

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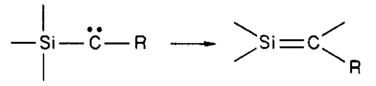
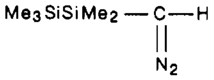
Photolyses and pyrolyses of (pentamethyldisilanyl)diazomethane (1), (pentamethyldisilanyl)(trimethylsilyl)diazomethane (2), and (tris(trimethylsilyl)silyl)(trimethylsilyl)diazomethane (3) resulted in the formation of the corresponding π-bonded silenes by the exclusive migration of a trimethylsilyl group to a carbene center. The silenes were efficiently trapped by alcohols and carbonyls. The ultraviolet absorptions of the silenes have also been measured.

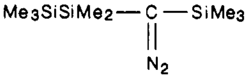
Introduction

Research on sp^2-hybridized silenes is of current interest, and the chemistry achieved has been summarized in many reports.[1] Although there are many methods to generate silenes, one typical approach to silenes is the intramolecular reactions of α-silylcarbenes (eq 1).[2] In a previous paper, we reported that the migrating ability of the groups on silicon atom to a carbene center was not influenced on the nature of substituents but was dependent on the statistical factor.[3] Since the Si–Si bond has shown σ-electron-donating properties[4] and the bond is relatively weaker than Si–C bonds,[5] silylcarbenes having an Si–Si bond are expected to undergo selective migration of a trimethylsilyl group to a carbene center, giving silenes. We report here such silyl migrations in the photoinduced and thermal decompositions of polysilylated diazomethanes 1, 2, and 3.[6]

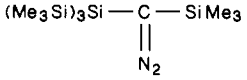

(1)


$\mathrm{Me_3SiSiMe_2{-}C(=N_2){-}H}$

1


$\mathrm{Me_3SiSiMe_2{-}C(=N_2){-}SiMe_3}$

2


$\mathrm{(Me_3Si)_3Si{-}C(=N_2){-}SiMe_3}$

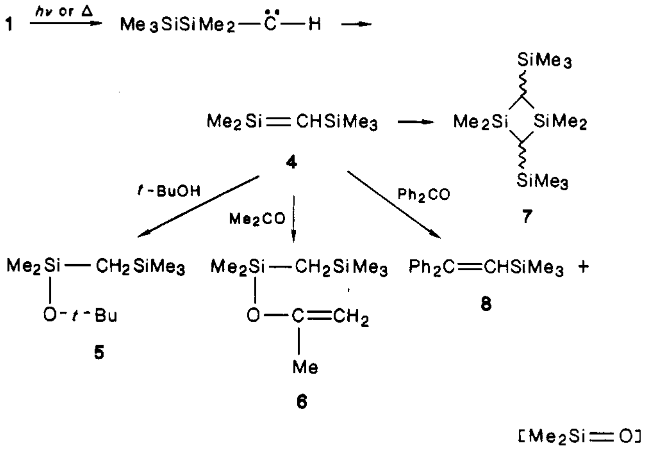
3

Results and Discussion

Photochemical and Thermal Decompositions of Polysilylated Diazomethanes 1, 2, and 3. Photolysis of (pentamethyldisilanyl)diazomethane (1) in *tert*-butyl alcohol with a high-pressure mercury lamp ($\lambda > 300$ nm) gave *tert*-butoxysilane 5 which arose from the trapping of silene 4 in 41% yield. Similarly, photolysis in the presence of acetone gave a silyl enol ether 6 in 28% yield (Scheme I).

Flash vacuum pyrolysis of 1 at 450 °C produced 1,3-disilacyclobutane 7 in 47% yield (a mixture of cis and trans isomers; ratio 41:59), apparently formed by the head-to-tail dimerization of the silene 4. The silene was further intercepted by *tert*-butyl alcohol and carbonyl compounds. When 1 was pyrolyzed with *tert*-butyl alcohol at 450 °C in a stream of nitrogen, *tert*-butoxysilane 5 was obtained in 53% yield. Co-pyrolysis of 1 with acetone gave the silyl enol ether 6 in 54% yield and with benzophenone led to the formation of vinylsilane 8 in 58% yield via the Wittig-type reaction of the silene 4 with the ketone (Scheme

Scheme I



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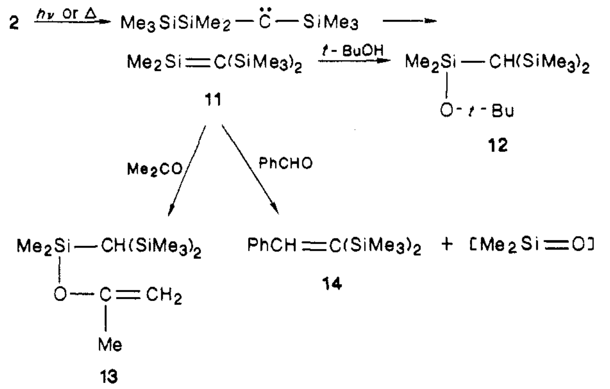
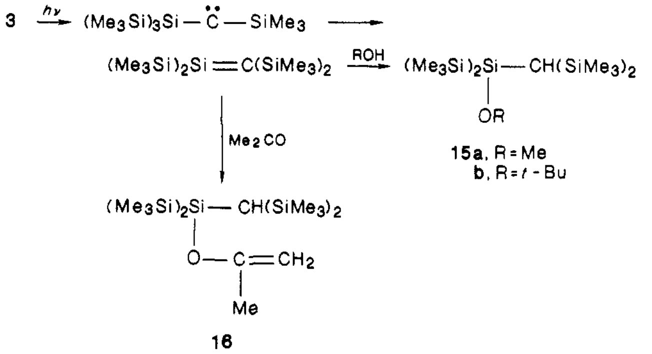
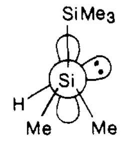
Scheme II



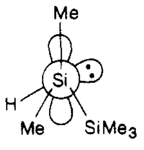
Scheme III



I). It is interesting to note that the exclusive migration of a trimethylsilyl group to a carbene center was observed in both thermal and photochemical decompositions of **1**. No detectable amount of methyl migration product was observed. This probably is due to the difference of the conformation of the pentamethyldisilanylcarbene. Since the Si–Si σ-bond can interact with vacant p orbitals via σ–π conjugation, the conformation **9** will be more favorable than **10**.



9



10

Similar selective migration of a trimethylsilyl group to a carbene center was observed in the reactions of (pentamethyldisilanyl)(trimethylsilyl)diazomethane (**2**). When **2** was pyrolyzed with *tert*-butyl alcohol at 450 °C under flowing nitrogen, *tert*-butoxysilane **12** arising from the silene **11** was obtained in 59% yield as sole product.[7] Silyl enol ether **13** and vinylsilane **14** were formed in 52% and 48% yields, respectively, when **2** was pyrolyzed with acetone or benzaldehyde. Photolysis of **2** in *tert*-butyl alcohol and acetone also led to the same products, **12** and **13**, in 58% and 29% yields, respectively. No methyl migration product could be found in the photo and thermal decompositions of **2** (Scheme II).

Photolysis of (tris(trimethylsilyl)silyl)(trimethylsilyl)diazomethane (**3**) in alcohols also cleanly produced the corresponding alkoxysilanes **15a** and **15b** in 50% and 60% yields, respectively. Silyl enol ether **16** was also obtained by the photolysis of **3** in acetone in 38% yield. Again, a methyl migration product was not found (Scheme III).

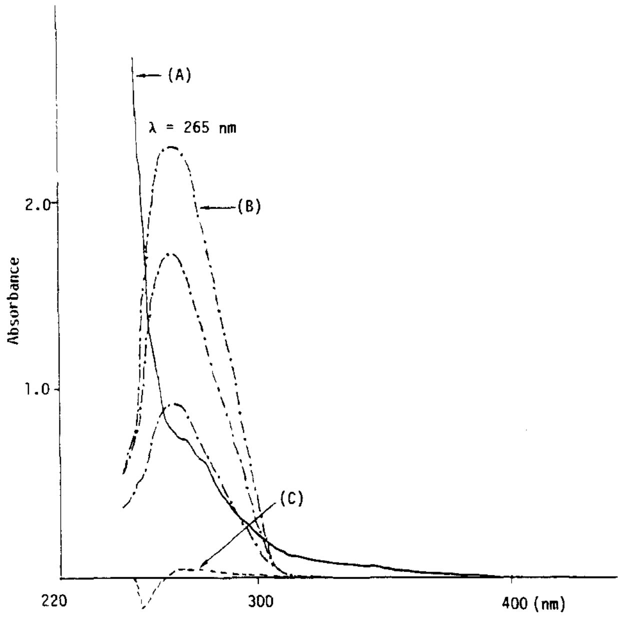
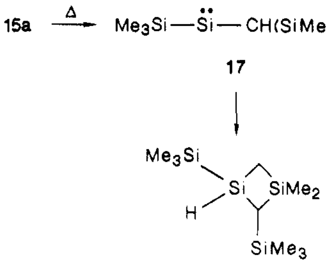


Figure 1. UV spectrum in 3-MP at 77 K: (A) prior to photolysis of **1** (—); (B) after photolysis with λ > 300 nm (40 s, 80 s, 120 s, 77 K, starting material subtracted) (-·-); (C) after annealing and recooling to 77 K, starting material subtracted (---).

Scheme IV



The alkoxysilane **15** was not stable under the pyrolytic conditions and underwent α-elimination to give silylene **17** and methoxytrimethylsilane. Thus, when a benzene solution of **15a** was pyrolyzed at 450 °C under flowing nitrogen, 1,3-disilacyclobutane **18** and methoxytrimethylsilane were obtained as volatile products in 57% and 79% yields, respectively. The disilacyclobutane **18** is apparently formed by intramolecular insertion of silylene **17** into γ-C–H bonds on the methyl groups on silicon (Scheme IV).

Ultraviolet Spectra of Silenes. The matrix-isolation technique has been used widely for the observation of the reactive species.[8] Although there are many reports concerning silenes, very little is known about their ultraviolet spectra.[1] The UV absorptions of silenes reported so far are (1) simple silenes such as $H_2Si{=}CH_2$ (258 nm), $D_2Si{=}CH_2$ (259 nm), and $Cl_2Si{=}CH_2$ (246 nm),[9] (2) conjugated silene like silaacrylate $Me_2Si{=}C(SiMe_3)CO_2Et$ (288 nm),[10] (3) silaaromatics like silabenzene (212, 272, 320 nm)[11] and silatoluene (307, 314, 322 nm),[12] and highly

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(6) For the preliminary reports of polysilylated carbenes see: (a) Sekiguchi, A.; Ando, W. *Chem. Lett.* **1983**, 871. (b) Sekiguchi, A.; Ando, W. *Tetrahedron Lett.* **1983**, *24*, 2791. (c) Sekiguchi, A.; Ando, W. *Chem. Lett.* **1985**, 2025.

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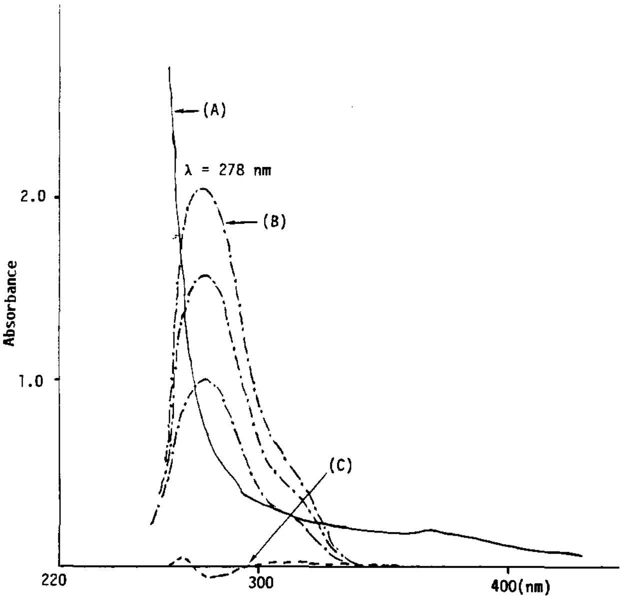

Figure 2. UV spectrum in 3-MP at 77 K: (A) prior to photolysis of **2** (—); (B) after photolysis with λ > 300 nm (80 s, 140 s, 220 s, 77 K, starting material subtracted) (-·-); (C) after annealing and recooling to 77 K, starting material subtracted (---).

Table I. UV Absorptions of Silenes in 3-MP at 77 K

silene	λ_{max}, nm	precursor
$Me_2Si{=}CHMe$	255	Me_3SiCHN_2
$Me_2Si{=}CHSiMe_3$ (4)	265	$Me_3SiSiMe_2CHN_2$ (1)
$Me_2Si{=}C(Me)SiMe_3$	274	$(Me_3Si)_2CN_2$
$Me_2Si{=}C(SiMe_3)_2$ (11)	278	$Me_3SiSiMe_2C(N_2)SiMe_3$ (2)

substituted silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (ca. 340 nm) where R = CMe_3, CEt_3, and 1-adamantyl.[13] Since the selective migration of a trimethylsilyl group to a carbene center has been found, we have taken ultraviolet spectra of the silene formed in the reactions of polysilylated diazomethanes. A dilute solution (~10^{-3} to ~10^{-4} M) of **1** in 3-methylpentane (3-MP) was placed in a quartz cell and cooled to 77 K. The resulting matrix was irradiated with the filtered light of greater than 300 nm. A band with a maximum at 265 nm appeared on irradiation time (Figure 1). The same absorption band was observed in 3-MP containing *tert*-butyl alcohol at 77 K and immediately disappeared on annealing the matrix with concurrent formation of the trapping product **5** of the silene **4**. It is quite reasonable to assume that the absorption band at 265 nm is assigned to the π–π^* transition of silene **4**. Similarly, silene **11** was also spectroscopically observable. Photolysis of **2** in 3-MP matrix at 77 K resulted in the formation of a band with a maximum at 278 nm (Figure 2). For comparison, UV spectra of silenes $Me_2Si{=}CHMe$[2e,f] and $Me_2Si{=}C(Me)SiMe_3$[21] were also measured by the photolyses of (trimethylsilyl)diazomethane and bis(trimethylsilyl)diazomethane in 3-MP at 77 K, respectively. The results are summarized in Table I.[14] The UV absorptions of tri- or tetrasubstituted silenes are shifted to longer wavelength compared to the parent silene ($H_2Si{=}CH_2$, 258 nm) but are at shorter wavelength than those of the highly substituted silenes (Brook's silenes, ca. 340 nm).[13] The introduction of a trimethylsilyl group on carbon also results in a slight bathchromic shift.

In summary, the effective migratory aptitude of a trimethylsilyl group to a carbene center was observed in the reactions of polysilylated diazomethanes. This may reflect a vertical charge stabilization by the donating effect of the Si–Si σ-electrons to the vacant p orbitals of the silylcarbenes.

Experimental Section

General Data. The NMR and IR spectra were recorded on Varian EM 360A and Hitachi 260-50 spectrometers. Mass spectra were obtained on a Hitachi RMU-6M mass spectrometer and JEOL JMS-D300 spectrometer. UV spectra were recorded on a Shimazu UV-365 spectrometer. Preparative gas chromatographic separations were carried out on an Ohkura gas chromatograph with 8 mm × 1 m, 8 mm × 1.5 m, and 8 mm × 2 m glass columns of 20% SF-96 on Celite 545.

Preparation of (Trimethylsilyl)diazomethane and (Pentamethyldisilanyl)diazomethane (1). (Trimethylsilyl)diazomethane (Me_3SiCHN_2) was prepared by the method of Shioiri by using ((trimethylsilyl)methyl)magnesium chloride and diphenylphosphoryl azide, $(PhO)_2P(O)N_3$.[15] (Pentamethyldisilanyl)diazomethane (1) was also prepared by a similar manner. Thus, ((pentamethyldisilanyl)methyl)magnesium chloride was prepared by adding a solution of (chloromethyl)pentamethyldisilane (22.7 g, 0.126 mol) in ether (80 mL) to magnesium (3.68 g, 0.151 mol) with stirring under argon. To a solution of diphenylphosphoryl azide (31.1 g, 0.113 mol) in ether (100 mL) was added the Grignard reagent at ca. −20 °C. The mixture was stirred at 0 °C for 1 h and at room temperature overnight. The reaction mixture was poured into ice water and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and concentrated. The residual yellow oil was distilled to give **1** (10.8 g, 50%): bp 62–65 °C (22 mmHg) (yellow oil); NMR (CCl_4, δ) 0.12 (s, 9 H, $SiMe_3$), 0.18 (s, 6 H, $SiMe_2$), 2.53 (s, 1 H, $SiCHN_2$); IR (NaCl) 2050 cm^{-1} ($C{=}N_2$); MS, *m/e* 144 ($M^+ - N_2$).

Preparation of (Pentamethyldisilanyl)(trimethylsilyl)diazomethane (2), (Tris(trimethylsilyl)silyl)(trimethylsilyl)diazomethane (3), and Bis(trimethylsilyl)diazomethane. Lithio(trimethylsilyl)diazomethane [$LiC(N_2)SiMe_3$] was prepared by adding lithium diisopropylamide (LDA) (9.63 mmol) in ether (10 mL) to a solution of Me_3SiCHN_2 (1.69 g, 14.8 mmol) in ether (15 mL) at −40 °C under argon. To a solution of the $LiC(N_2)SiMe_3$ was added a solution of chloropentamethyldisilane (1.30 g, 7.78 mmol) in ether (10 mL) at −55 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. The reaction mixture was poured into ice water and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and concentrated. The residual yellow oil was distilled to give **2** (870 mg, 93%): bp 43–45 °C (0.4 mmHg) (yellow oil); NMR (CCl_4, δ) 0.05 (s, 9 H, $SiMe_3$), 0.09 (s, 9 H, $SiMe_3$), 0.12 (s, 6 H, $SiMe_2$); IR (NaCl) 2025 cm^{-1} ($C{=}N_2$); MS, *m/e* 216 ($M^+ - N_2$); high-resolution mass calcd for $C_9H_{24}N_2Si_3$ 244.1245, found 244.1244. In a similar manner, (tris(trimethylsilyl)silyl)(trimethylsilyl)diazomethane (**3**) was prepared in quantitative yield by the reaction of tris(trimethylsilyl)chlorosilane (2.19 g, 7.74 mmol) and $LiC(N_2)SiMe_3$ prepared from Me_3SiCHN_2 (1.09 g, 9.60 mmol) and LDA (9.60 mmol) in ether. After the workup, the mixture was chromatographed on a alumina column containing 10% water at 0 °C with hexane. Evaporation of the solvent afforded the yellow wax of **3**: NMR (CCl_4, δ) 0.17 (s, 9 H, $SiMe_3$), 0.22 (s, 27 H, $SiMe_3$); IR (NaCl) 2020 cm^{-1} ($C{=}N_2$); MS *m/e* 360 (M^+); high-resolution mass calcd for $C_{13}H_{36}N_2Si_5$ (360.1723, found 360.1716. Bis(trimethylsilyl)diazomethane was prepared by the reaction of lithio(trimethylsilyl)diazomethane with trimethylchlorosilane in ether.[16]

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(14) Extinction coefficients cannot be given for the methodological reasons. However, the absorption bands in Table I would be π–π^* transitions because the reactions were carried out with low concentrations (~10^{-3} to ~10^{-4} M).

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Photolysis of 1 in *tert*-Butyl Alcohol and Acetone. A solution of 1 (85 mg, 0.49 mmol) and *tert*-butyl alcohol (1.5 mL) was irradiated with a high-pressure mercury lamp for 1.3 h. Separation of the reaction mixture by preparative GLC gave *tert*-butoxysilane 5 in 41% yield: NMR (CCl_4, δ) −0.25 (s, 2 H, $SiCH_2Si$), 0.00 (s, 9 H, $SiMe_3$), 0.10 (s, 6 H, $SiMe_2$), 1.23 (s, 9 H, *t*-Bu); IR (NaCl) 1050 cm^{-1} (Si–O–C); MS, *m/e* 203 (M^+ − Me). Anal. Calcd for $C_{10}H_{26}OSi_2$: C, 54.97; H, 11.99. Found: C, 55.10; H, 10.21.

Photolysis of 1 in acetone gave the silyl enol ether 6 in 28% yield: NMR (CCl_4, δ) −0.10 (s, 2 H, $SiCH_2Si$), 0.04 (s, 9 H, $SiMe_3$), 0.18 (s, 6 H, $SiMe_2$), 1.72 (s, 3 H, C=CMe), 3.92 (br s, 2 H, $C=CH_2$); IR (NaCl) 1630 (C=C) and 1050 cm^{-1} (Si–O–C); MS, *m/e* 187 (M^+ − Me). Anal. Calcd for $C_9H_{22}OSi_2$: C, 53.99; H, 10.95. Found: C, 53.08; H, 11.12.

Vacuum Pyrolysis of 1. The vacuum pyrolysis apparatus consisted of a Pyrex tube (1 × 37 cm) heated at 450 °C by an electric oven. The sample (93 mg, 0.54 mmol) was introduced through a septum by using a syringe at 10 mmHg. The products were collected in a trap cooled by liquid nitrogen. Separation of the reaction mixture by preparative GLC gave disilacyclobutane 7 (a mixture of trans and cis) in 53% yield: NMR (CCl_4, δ) −0.43 (s, Si_3CH), −0.40 (s, Si_3CH), −0.10 (s, $SiMe_3$), −0.09 (s, $SiMe_3$), 0.15 (s, $SiMe_2$), 0.20 (s, $SiMe_2$), 0.23 (s, $SiMe_2$); MS, *m/e* 288 (M^+). Anal. Calcd for $C_{12}H_{32}Si_4$: C, 49.91; H, 11.17. Found: C, 50.02; H, 11.44.

General Pyrolysis Procedures under Flowing Nitrogen. The pyrolysis apparatus consisted of a 28 cm × 1 cm Pyrex glass tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for syringe introduction of the sample and a nitrogen gas inlet. The pyrolysis tube was maintained at 450 °C, and the nitrogen flow was ca. 11 mL/min. The sample was introduced drop by drop by using a 1-mL syringe. The pyrolysates were trapped in a receiver cooled by liquid nitrogen.

Pyrolysis of 1 with *tert*-Butyl Alcohol, Acetone, and Benzophenone. Pyrolyses were carried out at 450 °C under flowing nitrogen. Pyrolysis of 1 (86 mg, 0.50 mmol) with *tert*-butyl alcohol (1.5 mL) produced the *tert*-butoxysilane 5 in 52% yield. Similarly, pyrolyses of 1 with acetone or benzophenone gave the silyl enol ether 6 (54%) and the vinylsilane 8 (58%),[17] respectively.

Pyrolysis of 2 with *tert*-Butyl Alcohol, Acetone, and Benzaldehyde. Pyrolyses were carried out at 450 °C under flowing nitrogen. Pyrolysis of 2 (86 mg, 0.35 mmol) with *tert*-butyl alcohol (1.5 mL) produced the *tert*-butoxysilane 12[7b] in 59% yield: NMR (CCl_4, δ) −0.80 (s, 1 H, Si_3CH), 0.07 (s, 18 H, $SiMe_3$), 0.16 (s, 6 H, $SiMe_2$), 1.22 (s, 9 H, *t*-Bu); IR (NaCl) 1040, and 1010 cm^{-1} (Si–O–C); MS, *m/e* 275 (M^+ − Me). Anal. Calcd for $C_{13}H_{34}OSi_3$: C, 53.71; H, 11.79. Found: C, 53.64; H, 12.01.

Pyrolysis of 2 (88 mg, 0.36 mmol) with acetone (1.5 mL) gave the silyl enol ether 13 in 52% yield: NMR (CCl_4, δ) −0.63 (s, 1 H, Si_3CH), −0.03 (s, 18 H, $SiMe_3$), 0.13 (s, 6 H, $SiMe_2$), 1.63 (s, 3 H, C=CMe), 3.77–3.92 (m, 2 H, $C=CH_2$); IR (NaCl) 1630 (C=C), 1040 and 1010 cm^{-1} (Si–O–C); MS, *m/e* 375 (M^+ − Me). Anal. Calcd for $C_{12}H_{30}OSi_3$: C, 52.48; H, 11.01. Found: C, 52.19; H, 11.16.

Pyrolysis of 2 (87 mg, 0.35 mmol) with benzaldehyde (1.5 mL) gave the vinylsilane 14 in 48% yield: NMR (CCl_4, δ) −0.07 (s, 9 H, $SiMe_3$), 0.19 (s, 9 H, $SiMe_3$), 7.27 (br s, 5 H, ArH), 7.83 (s, 1 H, C=CH); IR (NaCl) 1540 cm^{-1} (C=C); MS, *m/e* 248 (M^+). Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.40; H, 9.80.

Photolysis of 2 in *tert*-Butyl Alcohol and Acetone. A solution of 2 (86 mg, 0.35 mmol), *tert*-butyl alcohol (1.5 mL), and benzene (0.5 mL) was irradiated with a high-pressure mercury lamp for 2 h. *tert*-Butoxysilane 12 was obtained in 58% yield. Similarly, photolysis of 2 in acetone gave the silyl enol ether 13 in 29% yield.

Photolysis of 3 in Methanol, *tert*-Butyl Alcohol, and Acetone. A solution of 3 (89 mg, 0.25 mmol), *tert*-butyl alcohol (1.5 mL), and benzene (0.5 mL) was irradiated with a high-pressure mercury lamp for 1.4 h. Separation of the reaction mixture by preparative GLC gave the *tert*-butoxysilane **15b** in 60% yield: NMR (CCl_4, δ) −0.53 (s, 1 H, Si_3CH), 0.06 (s, 18 H, $SiMe_3$), 0.12 (s, 18 H, $SiMe_3$), 1.18 (s, 9 H, *t*-Bu); IR (KBr) 1030 and 1015 cm^{-1} (Si–O–C). Anal. Calcd for $C_{17}H_{46}OSi_5$: C, 50.17; H, 11.39. Found: C, 49.93; H, 11.57.

Photolysis of 3 (1671 mg, 4.59 mmol) in methanol for 4.3 h produced the methoxysilane **15a** in 50% yield: mp 140–142 °C; NMR (CCl_4, δ) −0.02 (s, 18 H, $SiMe_3$), 0.10 (s, 18 H, $SiMe_3$), 3.33 (s, 3 H, OMe), and the signal of the methine proton on carbon coincides with those of trimethylsilyl group; ^{13}C NMR ($CDCl_3$, δ) 0.94 (q, $SiMe_3$), 3.60 (q, $SiMe_3$), 6.25 (d, Si_3CH), 53.27 (q, OMe); IR (KBr) 1100 and 1010 cm^{-1} (Si–O–C); MS, *m/e* 349 (M^+ − Me). Anal. Calcd for $C_{14}H_{40}OSi_5$: C, 46.08; H, 11.04. Found: C, 46.02; H, 11.23.

Photolysis of 3 (89 mg, 0.25 mmol) in acetone gave the silyl enol ether 16 in 38% yield: NMR (CCl_4, δ) −0.02 (s, 18 H, $SiMe_3$), 0.07 (s, 18 H, $SiMe_3$), 0.19 (s, 1 H, Si_3CH), 1.58 (s, 3 H, C=CMe), 3.70 (br s, 1 H, C=CH), 3.85 (br s, 1 H, C=CH); IR (KBr) 1640 (C=C), 1030 cm^{-1} (Si–O–C); MS, *m/e* 375 (M^+ − Me). Anal. Calcd for $C_{16}H_{42}OSi_5$: C, 49.16; H, 10.83. Found: C, 49.03; H, 10.62.

Pyrolysis of Methoxysilane 15a. A solution of methoxysilane **15a** (108 mg, 0.30 mmol) and benzene (1.5 Ml) was pyrolyzed at 450 °C under flowing nitrogen. Separation of the reaction mixture by preparative GLC gave methoxytrimethylsilane (79%) and disilacyclobutane 18 (57%). Compound **18**: NMR (CCl_4, δ) −0.33 (d, *J* = 7 Hz, 1 H, Si_3CH), −0.08 (s, 9 H, $SiMe_3$), 0.09 (s, 9 H, $SiMe_3$), 0.18 (s, 3 H, SiMe), 0.24 (s, 3 H, SiMe), 4.35 (q, *J* = 7 Hz, 1 H, SiH), the signals of the ring methylene protons are superimposed on those of two trimethylsilyl group, but the integration of the silyl region signals shows these should arise from 27 protons in total; ^{13}C NMR ($CDCl_3$, δ) −4.42 ($SiCH_2Si$), −1.93 ($SiMe_3$), 1.21 ($SiMe_3$), 1.76 (Si_3CH), 2.51 (SiMe), 4.57 (SiMe), $SiCH_2Si$ and Si_3CH carbons were easily differentiated for SiMe carbons by INEPT technique; IR (NaCl) 2070 cm^{-1} (SiH); MS, *m/e* 260 (M^+). Anal. Calcd for $C_{10}H_{28}Si_4$: C, 46.07; H, 10.82. Found: C, 46.05; H, 11.02.

Photolysis of Silyldiazomethanes 1 and 2, (Trimethylsilyl)diazomethane, and Bis(trimethylsilyl)diazomethane in 3-MP Matrix at 77 K. A mixture of 1 (ca. 0.1 mg) and 3-methylpentane (3-MP) (5 mL) was placed in a quartz UV cell and degassed for several times. The mixture was cooled to 77 K, and the resulting matrix was irradiated through a filter ($\lambda >$ 300 nm). The ultraviolet absorptions were taken at periodic intervals. An absorption band with a maximum at 265 nm appeared and grew on irradiation (Figure 1). The same absorption band was observed in 3-MP containing *tert*-butyl alcohol at 77 K and immediately disappeared on annealing the matrix. Gc-mass spectrometry revealed the formation of *tert*-butoxysilane 5. Similarly, silyldiazomethane 2, (trimethylsilyl)diazomethane, and bis(trimethylsilyl)diazomethane was irradiated in 3-MP at 77 K with $\lambda >$ 300 nm, giving absorption bands at 278, 255, and 274 nm, respectively, due to the corresponding silenes. These bands immediately disappeared on annealing the matrix.

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Registry No. 1, 87161-27-1; 2, 87161-28-2; 3, 86997-48-0; 4, 18143-89-0; 5, 87161-29-3; 6, 87161-30-6; *trans*-7, 82113-62-0; *cis*-7, 82113-61-9; 8, 51318-07-1; 9, 87161-33-9; 11, 62139-73-5; 12, 87161-31-7; 13, 80431-41-0; 14, 18415-23-1; **15a**, 86997-46-8; **15b**, 87161-32-8; 16, 87161-34-0; 18, 86997-49-1; $LiC(N_2)SiMe_3$, 84655-21-0; $(Me_3Si)_3SiCl$, 5565-32-2; $Me_2Si{=}CHMe$, 55395-25-0; Me_3SiCHN_2, 18107-18-1; $(Me_3Si)_2CN_2$, 30006-66-7; $Me_3SiSi(Me_2)CH_2Cl$, 5181-46-4; $(PhO)_2P(O)N_3$, 26386-88-9; $Me_3SiSiMe_2Cl$, 1560-28-7; Me_3SiCl, 75-77-4; *t*-BuOH, 75-65-0; Me_3SiOMe, 1825-61-2; 3-MP, 96-14-0; benzaldehyde, 100-52-7.

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[17] Gröbel, B. -T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.