Intramolecular Reaction of Silene. Evidences for the Isomerization of Silaacrylate to Alkoxyketene

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Received February 17, 1987

Photolysis and thermolysis of ethyl pentamethyldisilanyldiazoacetate yield a conjugated silene, silaacrylate 8, followed by migration of the ethoxy group to give (ethoxydimethylsilyl)(trimethylsilyl)ketene 7. The reactions in the presence of alcohols and carbonyl compounds yield the products most simply attributed to the trapping of the silaacrylate along with the ketene. The silaacrylate was isolated in an argon matrix at 10 K. Photochemical conversion of the silaacrylate to the ketene also was studied.

Introduction

In recent years, interest in the chemistry of α-silylcarbenes has increased remarkably since they are potential precursors of silenes.[1] Previously, we have reported that the photolysis of ethyl (trimethylsilyl)diazoacetate produces a silene by intramolecular methyl migration in the formed carbomethoxy(trimethylsilyl)carbene.[2] Gas-phase generation of the carbene, followed by treatment with alcohol, however, gave product 3, which is not a simple alcohol addition product to the silene. The immediate precursor to 3 was (dimethylalkoxysilyl)ketene 2 (Scheme I).[3] Despite the amount of work in this area, a major question still remains as to the source of 2. One can anticipate that the trimethylsilyl group in carbene 5 should have a considerably higher migratory tendency than the methyl group because the carbene may have a conformation (6) due to σ–π conjugation between the Si–Si σ-bond and vacant carbon p orbital (Chart I).[4] We report here details of our studies of the isomerization of the ester-substituted silene (trimethylsilyl)dimethylsilaacrylate[5] to the ketene 2.

Scheme I

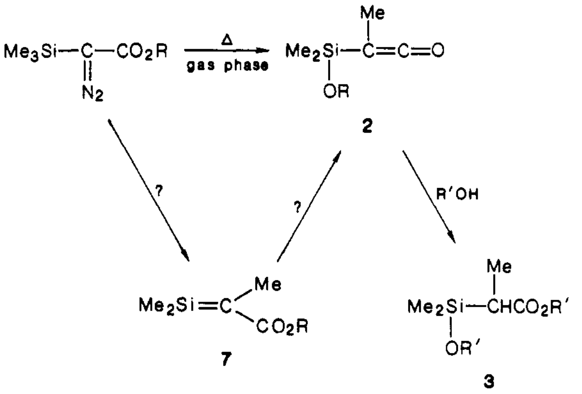
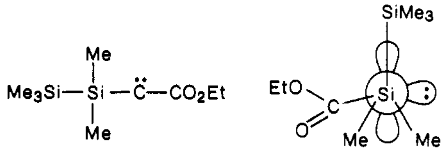


Chart I



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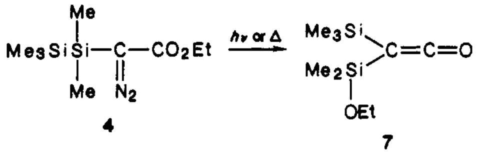
Results and Discussion

Thermolysis and Photolysis of Ethyl Pentamethyldisilanyldiazoacetate (4). When disilanyldiazoacetate 4 was pyrolyzed in vacuo by passing it through a Pyrex tube held at 360 °C, (ethoxydimethylsilyl)(trimethylsilyl)ketene (7) was isolated as a mobile oil in 94% yield (eq 1). Similarly, thermolysis of 4 at 180 °C without solvent gave 7 quantitatively. The photochemical decomposition of 4 in tetrahydrofuran using a high-pressure mercury l amp gave ketene 7 in 99% yield. An important mechanistic possibility involves isomerization of the silene 8 (Scheme II) to ketene 7. Silenes are known to react efficiently with alcohols to give alkoxysilane derivatives. When 4 was irradiated in methanol, 9a was produced in 70% yield together with the (methoxysilyl)ketene 12a (23%) and a small amount of 7. The reaction is general as photolysis of 4 in ethanol gave a similar product, 9b in 94% yield, together with 5% of 7. Interesting results were obtained with *tert*-butyl alcohol. Photolysis of 4 in *tert*-butyl alcohol gve 7 (25%), (*tert*-butoxysilyl)ketene 12b (31%), 9b (8%), and 9c (32%). The relative difficulty in forming the addition product and concomitant increases of ketenes 7 and 12b may reflect an increased steric barrier to addition, leaving the way open for rearrangement reaction to dominate (Scheme II). Alkoxysilane is almost certainly formed by addition of alcohol to silaacrylate 8.



$$\mathrm{Me_3Si\overset{Me}{\underset{Me}{Si}}-\underset{\underset{N_2}{\|}}{C}-CO_2Et} \xrightarrow{h\nu\ \text{or}\ \Delta} \mathrm{\begin{matrix}Me_3Si\\ Me_2\underset{OEt}{Si}\end{matrix}\!\!>\!C=C=O} \qquad (1)$$

4 7

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(1) (a) Ando, W.; Sekiguchi, A.; Ogiwara, J.; Migita, T. *J. Chem. Soc., Chem. Commun.* **1975**, 145. (b) Kreeger, R. L.; Shechter, H. *Tetrahedron Lett.* **1975**, 2061. (c) Ando, W.; Sekiguchi, A.; Migita, T. *Chem. Lett.* **1976**, 779. (d) Chapman, O. L.; Chang, C.-C.; Jung, J.; Kilc, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844. (e) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 7846. (f) Ando, W.; Sekiguchi, A.; Rothschild, A. J.; Gallucci, R. R.; Jones, M., Jr.; Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6995. (g) Sekiguchi, A.; Ando, W. *Tetrahedron Lett.* **1979**, 4077. (h) Sekiguchi, A.; Ando, W. *J. Org. Chem.* **1980**, *45*, 5286. (i) Mal'tsev, A. K.; Korolev, V. A.; Khabashesku, V. N.; Nefedov, O. M. *Dokl. Akad. Nauk SSSR* **1980**, *251*, 1166. (j) Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584. (k) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1981**, *103*, 3579. (l) Ando, W.; Tanikawa, H.; Sekiguchi, A. *Tetrahedron Lett.* **1983**, *24*, 4245. (m) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1984**, *106*, 1486. (n) Sekiguchi, A.; Tanikawa, H.; Ando, W. *Organometallics* **1985**, *3*, 584.

(2) Ando, W.; Hagiwara, H.; Migita, T. *J. Am. Chem. Soc.* **1973**, *95*, 7518.

(3) (a) Ando, W.; Sekiguchi, A.; Migita, T.; Kammula, S.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3818. (b) Ando, W.; Sekiguchi, A.; Hagiwara, T. Migita, T.; Chowdhry, V.; Westheimer, F. H.; Kammula, S. L.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6393.

(4) (a) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. (b) Sekiguchi, A.; Ando, W. *Chem. Lett.* **1983**, 871.

(5) For the preliminary reports of the silylcarbene 5 see: (a) Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* **1981**, *103*, 5573. (b) Sekiguchi, A.; Ando, W.; Honda, K. *Tetrahedron Lett.* **1985**, *26*, 2337.

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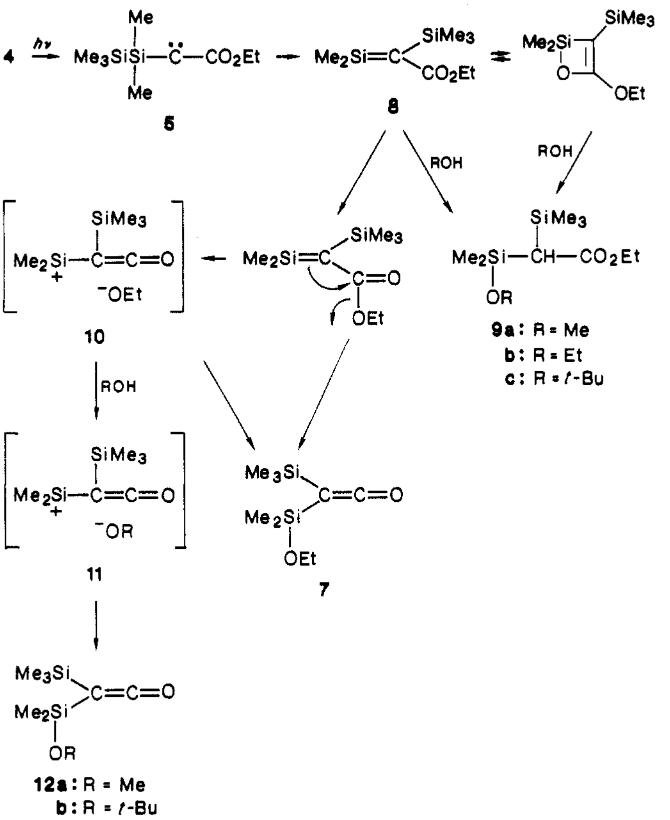
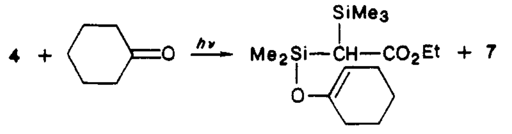
Scheme II



However, in our recent isolation of 1,2-oxasilacyclobutene from the photolysis of the silyl diazo ketone, a particularly attractive possibility is that **8** may be in equilibrium with isomeric 1,2-silaoxetene and the highly strained ring would probably react with the alcohol solvent.[1m]

Moreover, the ketene **7** is stable in alcohols at room temperature so the new ketene **12** should not be the product by the direct exchange of an ethoxy group on **7** for alkoxy solvents.[6] The reaction may involve the ion pair **10** and **11** on its way to the ketene **12**. The former can give the (ethoxysilyl)ketene **7**. At present, a reaction proceeding through a ion pair cannot be differentiated from the direct intramolecular alkoxy migration of the silene.

Silenes are known to react efficiently with ketones to give alkenes. Yet photolysis of **4** in the presence of cyclohexanone led to silyl enol ether (30%) and the ketene **7** (53%). Similar results were obtained with benzophenone to yield vinylsilane **14** in 36% yield together with **7** (53%).



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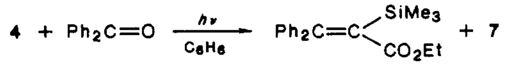

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These results suggest that both products, **13** and **14**, arise from the reaction of silaacrylate **8** with a carbonyl compound. Silyl enol ether **13** is probably formed by simultaneous hydrogen migration in the zwitterion (Scheme III).

Scheme III

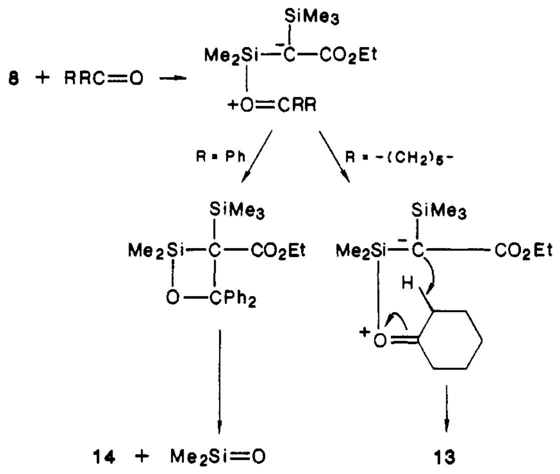

Table I. Stretching Vibration of Ester Carbonyl

compd	ν(CO), cm^{-1}
$Me_2C{=}C(Me)CO_2Et$	1715
$Me_2Si{=}C(SiMe_3)CO_2Et$ (**8**)	1670
$Me_2S^+{-}^-CHCO_2Et$	1600

The silene is known to produce the Diels-Alder adduct with 2,3-dimethylbutadiene, but silaacrylate was isolated; probably the silene has a ionic component, and the migration of alkoxy group can occur efficiently.

It is now clear that the formation of the silylketene **7** on thermolysis and photolysis of disilanyldiazoacetate does involve the isomerization of silaacrylate **8**. The formation of the ketene **7** is preferred in the absence of silene trapping reagents.

Matrix Isolation of 8 and Its Photochemical Rearrangement. A dilute mixture of **4** and argon, matrix isolated and cooled at 10 K, was irradiated with the filtered light of greater than 360 nm. To obtain the infrared spectrum, the mixture was deposited on a CsI window cooled at 10 K and irradiated with a high pressure mercury lamp. Analysis of the resulting spectrum and comparison with authentic samples of starting diazoacetate and the ketene **7** revealed that additional new bands were present. The additional bands at 1670 (s), 1242 (m), 1218 (s), 1138 (m), 1060 (m), 860 (m), 802 (m), and 762 (w) cm^{-1} are attributed to the silaacrylate **8**, which is slowly changed to the ketene **7** by the brief short wavelength ($\lambda > 240$ nm) irradiation (Figure 1C). No definitive assignment of these bands is possible, but the notable band at 1670 cm^{-1} is due to the stretching vibration of the ester carbonyl of **8**. The frequency of the ester band is approximately at the midpoint between that of ethyl 2,3-dimethylcrotonate[8] and dimethysulfonium (ethoxycarbonyl)methylide[9] (Table I). The lowered frequency of the ester carbonyl is attributed to weakened π-overlap in the silaacrylate **8** or to polarization of the Si=C double bond and delocalization of some of the negative charge onto oxygen. At present, we cannot assign the stretching vibration of a silicon–carbon double bond in the spectrum of the mixture of **7** and **8**. It is worth noting that the simultaneous generation of **7** via **8** was observed at even 10 K. A part of the hot silaacrylate can rearrange to the ketene **7** at 10 K, and such a process is calculated to be an extremely exothermic reaction (69 kcal/mol above singlet carbene).[10]

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[6] The ketene **7** reacted with refluxing methanol to give **12a** and the methoxysilane $MeOSi(Me_2)CH(SiMe_3)CO_2Me$. Similarly, the reaction of **7** with refluxing ethanol produced **9b**. See the Experimental Section.

[7] For general reviews of unsaturated organosilicon compounds see: (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[8] Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; Wiley: New York, London, 1977; p 344.

[9] Payne, G. B. *J. Org. Chem.* **1967**, *32*, 3351.

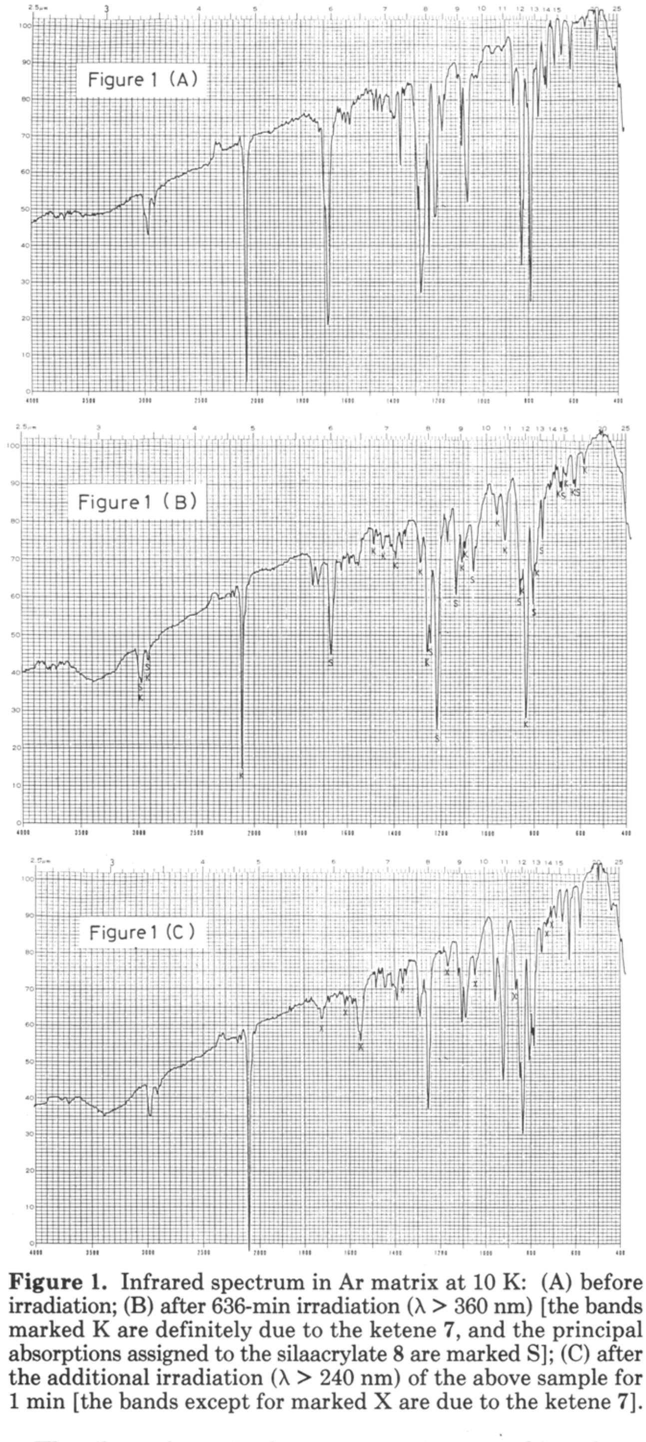


Figure 1. Infrared spectrum in Ar matrix at 10 K: (A) before irradiation; (B) after 636-min irradiation ($\lambda > 360$ nm) [the bands marked K are definitely due to the ketene **7**, and the principal absorptions assigned to the silaacrylate **8** are marked S]; (C) after the additional irradiation ($\lambda > 240$ nm) of the above sample for 1 min [the bands except for marked X are due to the ketene **7**].

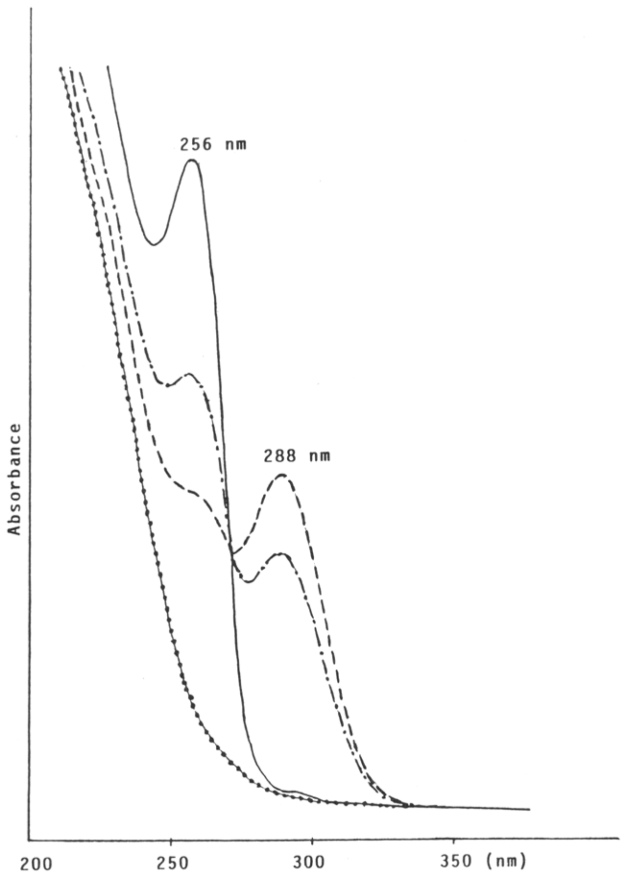
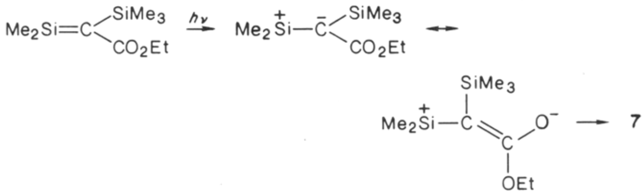


Figure 2. UV spectrum in Ar matrix at 10 K: before irradiation (—); after 25-min irradiation ($\lambda > 360$ nm) (-·-); after 70-min irradiation ($\lambda > 360$ nm) (---); after additional irradiation ($\lambda > 240$ nm) of the above sample for 1 min (···).

Scheme IV



The silaacrylate **8** in the argon matrix was stable at least at ca. 35 K. Chemical evidence for **8** is provided by the reaction with methanol. Disilanyldiazoacetate **4** containing methanol was irradiated at 20 K in the argon matrix with the wavelength greater than 360 nm. The infrared spectrum of the irradiated mixture was completely identical with that obtained in the absence of methanol except for the bands of methanol. The matrix was warmed slowly to room temperature, and the volatile products were collected. GC–mass spectrometry revealed the presence of the ketene **7**, **12a**, and methoxysilane **9a** as major products.

Of interest is the photochemical conversion of the silaacrylate **8** to the ketene **7**.[11] The silaacrylate **8** immediately changed to **7** at 10 K in the argon matrix by brief irradiation with a low-pressure mercury lamp ($\lambda > 240$ nm). In this transformation, the disappearance of the infrared bands of **8** is concurrent with the growth of bands of the ketene **7**. To obtain the ultraviolet spectrum of **8**, the argon-diluted **4** was deposited on a sapphire window cooled at 10 K. Irradiation ($\lambda > 360$ nm) results in the disappearance of the UV absorption of **4** (256 nm) with concurrent formation of a new band with a maximum at 288 nm (Figure 2). Although some UV spectra of silenes are precedented, the absorption band of **8** is relatively shifted to a longer wavelength compared to those of the simple silenes such as $H_2Si{=}CH_2$ (258 nm)[12] and $Me_2Si{=}CHSiMe_3$ (265 nm)[13] but to a shorter wavelength compared

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[10] (a) Gordon, M. S. *Chem. Phys. Lett.* **1978**, *54*, 9. (b) Goddard, J. D.; Yoshioka, Y.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 7644. (c) Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884.

[11] Some photochemical reactions of silenes and disilenes are precedented. (a) Reisenauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 854. (b) Maier, G.; Mihm, G.; Reisenauer, H. P.; Littmann, D.; *Chem. Ber.* **1984**, *117*, 2369. (c) Maier, G.; Mihm, G.; Baumgärtner, R. O. W.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2337. (d) Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821. (e) Murakami, S.; Collins, S.; Masamune, S. *Tetrahedron Lett.* **1984**, *25*, 2131. (f) Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. K. *J. Am. Chem. Soc.* **1985**, *107*, 4338.

[12] Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 597.

to those of the highly substituted silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (ca. 340 nm) where R = CMe_3, CEt_3, and adamantyl.[14] Disappearance of the 288 nm band by the additional brief irradiation at 240 nm supports the conversion of **8** to the ketene **7**.[15] Excitation of this band results in the polarization of Si=C double bond, and the bond cleavage of C–OEt followed by migration led to the formation of the ketene **7** (Scheme IV).

The ultraviolet absorption attributed to **8** is also observable at 293 nm in isopentane/methylcylohexane (3:1) and the 3-methylpentane matrix at 77 K.[16] Yet the band did not appear in the EPA (5:5:2) matrix at 77 K, suggesting that the silaacrylate **8** reacts with alcohols at 77 K. Indeed, photolysis of **4** in the methanol/tetrahydro-2-methylfuran matrix at 77 K gave methoxysilane **9a** (83%) along with **7** (11%) and **12a** (4%).

In conclusion, we regard the migration of the alkoxy group in the ester-substituted silene is much more efficient in aprotic solvent and is accelerated by the excitation of the Si=C double bond.

Experimental Section

The NMR and IR spectra were recorded on Varian EM 360A and Hitachi 260-50 spectrometers. Mass and UV spectra were obtained on a Hitachi RMU-6M mass spectrometer and a Shimazu UV-365 spectrometer. Gas chromatographic analyses were done by a Hitachi gas chromatograph with a 4 mm × 1.5 m glass column of 10% SF-96 on Celite 545. Preparative gas chromatographic separations were carried out on an Ohkura gas chromatograph with a 8 mm × 1 m glass column of 10% SF-96 on Celite 545.

Preparation of Ethyl Pentamethyldisilanyldiazoacetate (4). The diazoacetate **4** was prepared by a modification of the method of Schöllkopf.[17] The mixture of bis(pentamethyldisilanyl)thiane (50 g, 0.17 mol), diethyl mercuribis(diazoacetate) (70 g, 0.16 mol), and benzene (250 ML) was heated at 80 °C with stirring for 12 days. The precipitated mercury(II) sulfide was filtered off. The filtrate was concentrated, and the residue was distilled to give yellow oil **4**: bp 61–62 °C (1 mmHg); yield 30 g (38%); NMR (CCl_4, δ) 0.12 (s, 9 H, $SiMe_3$), 0.25 (s, 6 H, $SiMe_2$), 1.27 (t, 3 H, $OCCH_3$), 4.17 (q, 2 H, OCH_2); IR (NaCl) 2100 ($C{=}N_2$), 1690 cm^{-1} (C=O); mass spectrum, *m/e* 244 (M^+); UV (hexane) λ_{max} 261 (ϵ 7900), 382 nm (138).

Pyrolysis of 4 in the Gas Phase. Gas-phase pyrolysis was carried out by using a vacuum pyrolysis apparatus that consists of an injecting part, a Pyrex pyrolysis tube (1 cm × 37 cm), and a collector. The pyrolysis tube was heated at 360 °C by an electric oven. The sample of **4** (350 mg, 1.43 mmol) was introduced into the Pyrex tube through the septum under 1 mmHg. The pyrolysates were collected in a receiver cooled by liquid nitrogen. Separation of the reaction mixture by preparative GLC gave ketene **7** in 94% yield; NMR (CCl_4, δ) 0.22 (s, 9 H, $SiMe_3$), 0.26 (s, 6 H, $SiMe_2$), 1.17 (t, 3 H, $OCCH_3$), 3.68 (q, 2 H, OCH_2); IR (NaCl) 2080 (C=C=O), 1080 cm^{-1} (Si–O–C); mass spectrum, *m/e* 216 (M+); UV(hexane) λ_{max} 273 nm (ϵ 43). Anal. Calcd for $C_9H_{20}O_2Si_2$: C, 49.94; H, 9.31. Found: C, 49.64; H, 9.25.

Thermolysis of 4. **4** (263 mg, 1.08 mmol) was placed in a Pyrex tube and heated at 180 °C for 30 min under nitrogen. Separation of the reaction mixture by GLC gave **7** in 98% yield.

Photolysis of 4 in THF. A solution of **4** (217 mg, 0.889 mmol) and THF (4 g) was irradiated with a 400-W high-pressure mercury lamp for 2 h through a Pyrex tube. Separation of the reaction mixture by GLC gave **7** in 99% yield.

Photolysis of 4 in Methanol. A solution of **4** (282 mg, 1.21 mmol) and methanol (3.9 g) was irradiated with a high-pressure mercury lamp for 0.8 h. Separation of the reaction mixture by preparative GLC gave ketene **12a** (23%), methoxysilane **9a** (70%), and a small amount of **7**.

Compound **12a**: NMR (CCl_4, δ) 0.20 (s, 9 H, $SiMe_3$), 0.22 (s, 6 H, $SiMe_2$), 3.37 (s, 3 H, OMe); IR (NaCl) 2085 (C=C=O), 1090 cm^{-1} (Si–O–C); mass spectrum, *m/e* 202 (M^+). Anal. Calcd for $C_8H_{18}O_2Si_2$: C, 47.47; H, 8.96. Found: C, 47.27; H, 9.03.

Compound **9a**: NMR (CCl_4, δ) 0.09 (s, 9 H, $SiMe_3$), 0.13 (s, 3 H, SiMe), 0.17 (s, 3 H, SiMe), 1.21 (t, 3 H, $OCCH_3$), 1.67 (s, 1 H, SiCH), 3.38 (s, 3 H, OMe), 4.00 (q, 2 H, OCH_2); IR (NaCl) 1700 cm^{-1} (C=O); mass spectrum, *m/e* 233 ($M^+ - Me$). Anal. Calcd for $C_{10}H_{24}O_3Si_2$: C, 48.33; H, 9.73. Found: C, 48.36; H, 9.88.

Photolysis of 4 in Ethanol. A solution of **4** (202 mg, 0.82 mmol) and ethanol (3.4 g) was irradiated with a high-pressure mercury lamp for 1.5 h. Separation of the reaction mixture by preparative GLC gave **7** (5%) and ethoxysilane **9b** (94%).

Compound **9b**: NMR (CCl_4, δ) 0.11 (s, 9 H, $SiMe_3$), 0.15 (s, 3 H, SiMe), 0.18 (s, 3 H, SiMe), 1.13 (t, 3 H, $OCCH_3$), 1.20 (t, 3 H, $OCCH_3$), 1.66 (s, 1 H, SiCH), 3.66 (q, 2 H, OCH_2), 4.02 (q, 2 H, OCH_2); IR (NaCl) 1690 cm^{-1} (C=O); mass spectrum, *m/e* 247 ($M^+ - Me$). Anal. Calcd for $C_{11}H_{26}O_3Si_2$: C, 50.33; H, 9.98. Found: C, 50.23; H, 10.11.

Photolysis of 4 in *tert*-Butyl Alcohol. A solution of **4** (226 mg, 0.93 mmol), *tert*-butyl alcohol (3 g), and benzene (0.7 g) was irradiated with a high-pressure mercury lamp for 1 h. Separation of the reaction mixture by preparative GLC gave **7** (25%), (*tert*-butoxysilyl)ketene **12b** (31%), **9b** (8%), and *tert*-butoxysilane **9c** (32%).

Compound **12b**: NMR (CCl_4, δ) 0.21 (s, 9 H, $SiMe_3$), 0.28 (s, 6 H, $SiMe_2$), 1.27 (s, 9 H, *t*-Bu); IR (NaCl) 2080 (C=C=O), 1045 cm^{-1} (Si–O–C); mass spectrum, *m/e* 244 (M^+); high-resolution mass calcd for $C_{11}H_{24}O_2Si_2$ 244.1314, found 244.1299.

Compound **9c**: NMR (CCl_4, δ) 0.10 (s, 9 H, $SiMe_3$), 0.18 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe), 1.20 (t, 3 H, $OCCH_3$), 1.24 (s, 9 H, *t*-Bu), 1.62 (s, 1 H, SiCh), 3.97 (q, 2 H, OCH_2); IR (NaCl) 1695 cm^{-1} (C=O); mass spectrum, *m/e* 275 ($M^+ - Me$). Anal. Calcd for $C_{13}H_{30}O_3Si_2$: C, 53.74; H, 10.40. Found: C, 53.69; H, 10.57.

Photolysis of 4 in Cyclohexanone. A solution of **4** (199 mg, 0.817 mmol) and cyclohexanone (5.7 g, 58 mmol) was irradiated with a high-pressure mercury lamp for 2 h. Separation of the reaction mixture by preparative GLC gave silyl enol ether **13** (30%) and **7** (53%).

Compound **13**: NMR (CCl_4, δ) 0.10 (s, 9 H, $SiMe_3$), 0.23 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 1.21 (t, 3 H, $OCCH_3$), 1.76 (s, 1 H, SiCH), 1.38–2.22 (m, 8 H, aliphatic CH), 4.02 (q, 2 H, OCH_2), 4.78 (m, 1 H, C=CH); IR (NaCl) 1705 (C=O), 1670 cm^{-1} (C=C); mass spectrum, *m/e* 314 (M^+); high-resolution mass calcd for $C_{15}H_{30}O_3Si_2$ 314.1732, found 314.1736.

Photolysis of 4 in Presence of Benzophenone. A benzene solution of **4** (277 mg, 1.14 mmol) and benzophenone (1.93 g, 10.6 mmol) was irradiated with a high-pressure mercury lamp for 2.5 h. Separation of the reaction mixture by preparative GLC gave vinylsilane **14** (36%) and **7** (53%).

Compound **14**: NMR (CCl_4, δ) −0.08 (s, 9 H, $SiMe_3$), 0.94 (t, 3 H, $OCCH_3$), 3.86 (q, 2 H, OCH_2), 7.18 (br s, 5 H, ArH), 7.26 (br s, 5 H, ArH); IR (NaCl) 1710 (C=O), 1665 cm^{-1} (C=C); mass spectrum, *m/e* 324 (M^+), high-resolution mass calcd for $C_{20}H_{24}O_2Si$ 324.1544, found 324.1521.

Reaction of (Ethoxysilyl)ketene 7 with Alcohols. The ketene **7** was stable in methanol at room temperature, but on heating it gave **12a** and the methoxysilane $MeOSi(Me_2)CH(SiMe_3)CO_2Me$: NMR ($CCl_4$, δ) 0.11 (s, 9 H, $SiMe_3$), 0.14 (s, 3 H, SiMe), 0.18 (s, 3 H, SiMe), 1.70 (s, 1 H, SiCH), 3.41 (s, 3 H, OMe), 3.56 (s, 3 H, OMe); IR (NaCl) 1700 cm^{-1} (C=O), mass spectrum, *m/e* 234 (M^+, very weak), 219 ($M^+ - Me$); high-resolution mass calcd for $C_8H_{19}O_3Si_2$ ($M^+ - Me$) 219.0872, found 219.0842. Similarly, the ketene **4** reacted with refluxing ethanol to give ethoxysilane **9b**.

Photolysis of 4 in Ar Matrix at 10 K. Matrix isolation was conducted by using Air Products Inc. Displex refrigerator. Matrix-isolated samples (**4**:Ar = 1:500 ≈ 1:1000) were prepared by gas-phase deposition onto a CsI window cooled at 10 K. The resulting matrix was irradiated with an Ushio 500-W high-pressure

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(15) The ketene **7** has an absorption band at 273 nm (hexane) with a small extinction coefficient (ϵ 43).

(16) Extinction coefficient cannot be given for methological reasons. However, the absorption band at 293 nm would be $\pi-\pi^*$ transition of the silaacrylate **8** because the reaction was carried out with low concentration ($\sim 10^{-3}$ to $\sim 10^{-4}$ M).

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mercury lamp through a cutoff filter (λ > 360 nm). The reaction was followed by the infrared spectrum. The formation of the ketene 7 was confirmed by comparison of the infrared spectrum of matrix-isolated authentic sample. For the ultraviolet absorption, the argon-diluted sample was deposited on a sapphire window cooled at 10 K and irradiated with the wavelength greater than 360 nm. The ultraviolet spectrum was taken at periodic intervals.

Photolysis of 4 in Argon Matrix in the Presence of Methanol. The sample was deposited on a CsI window cooled at 20 K together with Ar and methanol (Ar:methanol = 730:30). The matrix was irradiated with λ > 360 nm. The infrared spectrum after the photolysis was completely identical with that obtained in the absence of methanol except for the bands of methanol. The matrix was warmed slowly to room temperature, and the volatile products were collected in a trap cooled by liquid nitrogen. Gc–MS revealed the presence of **12a** (8%), **7** (74%), and **9a** (18%).

Photolysis of 4 in Hydrocarbon Matrix at 77 K. A mixture of 4 (ca. 0.1 mg) and 3-methylpentane (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 (λ > 360 nm) through the windows of a quartz Dewar. The ultraviolet absorption was taken at periodic intervals. An absorption band with a maximum of 293 nm appeared and grew on irradiation time. The isopentane/methylcyclohexane (3:1) matrix containing 4 also resulted in the appearance of band with a maximum of 293 nm due to 8 at 77 K on irradiation (λ > 360 nm).

Photolysis of 4 in Methanol/2-Methyltetrahydrofuran Matrix at 77 K. A mixture of 4 (326 mg, 1.34 mmol), methanol (4 mL), and 2-methyltetrahydrofuran (4 mL) was cooled to 77 K. The resulting matrix was irradiated through a Pyrex tube with a high-pressure mercury lamp for 9 h. Separation of the reaction mixture by GLC gave **7** (11%), **12a** (4%), and methoxysilane **9c** (83%).

Acknowledgment. We are grateful to the Shinetsu Chemical Co. for partial support of this work. This research is supported by Grant-in Aid for Scientic Research (No. 61740280).

Registry No. 4, 79251-24-4; **7**, 79251-25-5; **8**, 79251-29-9; **9a**, 79251-30-2; **9b**, 79251-28-8; **9c**, 79251-32-4; **12a**, 79251-26-6; **12b**, 79257-68-4; **10**, 79251-31-3; **14**, 110046-19-0; MeOSi(Me)$_2$CH(SiMe$_3$)CO$_2$Me, 79251-27-7; bis(pentamethyldisilanyl)thiane, 110077-40-2; benzophenone, 119-61-9.

Synthesis, Reactivity, and Electrochemical Behavior of [η^5-(Alkoxysilyl)cyclopentadienyl]iron Dicarbonyl Complexes

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Received February 18, 1987

The binuclear iron complexes [(η^5-C$_5$H$_4$SiMe$_2$OEt)Fe(CO)$_2$]$_2$ (**1**) and [(η^5-C$_5$H$_4$(CH$_2$)$_3$Si(OMe)$_3$)Fe(CO)$_2$]$_2$ (**2**) have been prepared by thermal reaction between the cyclopentadienylalkoxysilane C$_5$H$_5$SiMe$_2$OEt or C$_5$H$_5$(CH$_2$)$_3$Si(OMe)$_3$ and Fe(CO)$_5$ in good yield. From these compounds new mononuclear iron complexes are formed. The oxidation of **1** and **2** with ferricinium hexafluorophosphate in the presence of PPh$_3$ gives the cationic complexes [(η^5-C$_5$H$_4$SiMe$_2$OEt)Fe(CO)$_2$PPh$_3$]PF$_6$ (**3**) and [(η^5-C$_5$H$_4$(CH$_2$)$_3$Si(OMe)$_3$)Fe(CO)$_2$PPh$_3$]PF$_6$ (**4**). The anions [(η^5-C$_5$H$_4$SiMe$_2$OEt)Fe(CO)$_2$]$^-$ (**5**) and [(η^5-C$_5$H$_4$(CH$_2$)$_3$Si(OMe)$_3$)Fe(CO)$_2$]$^-$ (**6**) were obtained by treatment of **1** and **2** with potassium benzophenone ketyl. The compounds are characterized by ^{1}H and ^{13}C NMR and IR spectroscopy. The electrochemistry of the dinuclear compounds **1** and **2** indicates that two-electron oxidation products are stable on the voltammetry time scale. However, the results show that the kinetic stability of the oxidation products is very dependent upon the donor properties of the solvent and the nature of the ring substituents.

Introduction

In the last years, there has been considerable interest focused on the multiple functionalization of the cyclopentadienyl ligand, which often results in considerable kinetic stabilization of its complexes with transition metals,[1,2] and, depending on the desired oxidation state, this may result in thermodynamic stabilization as well. It is known, from a redox viewpoint, that permethylation on the η^5-C$_5$H$_5$ ring leads to the stabilization of the higher oxidation states.[3-5] However, recently, it has been found that η^5-C$_5$Ph$_5$ ligand is capable of stabilizing lower oxidation states because of the electron-withdrawing ability of phenyl ring substituent.[6-9]

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