

MATRIX ISOLATION OF SILAACRYLATE AND ITS PHOTOCHEMICAL REACTION

Akira Sekiguchi and Wataru Ando\*

Department of Chemistry, The University of Tsukuba,  
Niihari-gun, Ibaraki 305, Japan

Koichi Honda

National Chemical Laboratory for Industry,  
Yatabe, Ibaraki 305, Japan

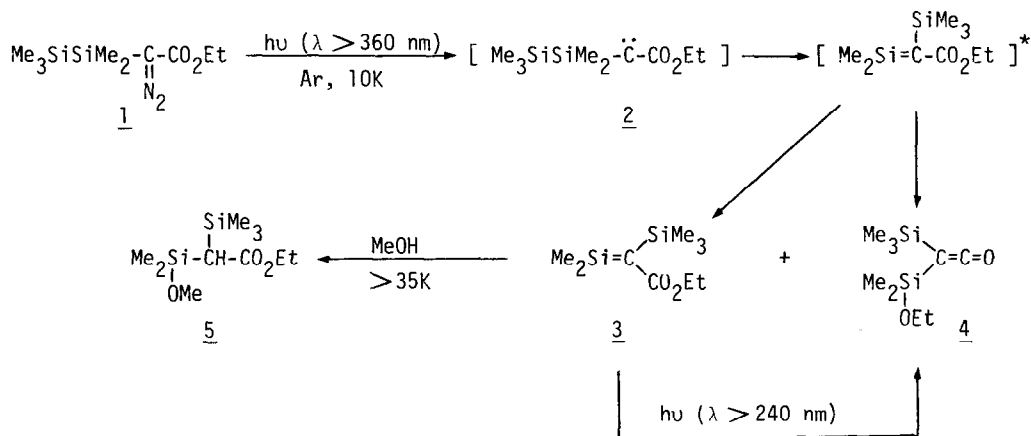
Summary:  $\pi$ -Bonded silaacrylate was isolated in argon matrix at 10K by the photolysis ( $\lambda > 360$  nm) of ethyl pentamethyldisilanyldiazoacetate. The silaacrylate immediately changed to (ethoxydimethylsilyl)(trimethylsilyl)-ketene at 10K by the brief irradiation with the light of shorter wavelength ( $\lambda > 240$  nm).

Studies on unsaturated organosilicon compounds have grown dramatically, and sterically stabilized silenes<sup>1</sup> and disilenes<sup>2</sup> were isolated by several groups. In contrast to the well documented photochemical reactions of alkenes, those of unsaturated organosilicon compounds are quite rare. To our knowledge, photochemical conversion of silenes to methylsilylenes,<sup>3</sup> valence isomerization of silabenzene to dewarsilabenzene,<sup>4</sup> and E/Z isomerization of disilenes<sup>5</sup> are only known examples. We wish to present here the first matrix isolation of silene with a functional group (silaacrylate)<sup>6</sup> and its entirely new type photochemical reaction.

A dilute mixture of ethyl pentamethyldisilanyldiazoacetate 1 and argon (1 : 500 to 1 : 1000), matrix isolated and cooled to 10K, was irradiated with the filtered light of greater than 360 nm.<sup>7</sup> The IR bands of 1 gradually disappeared and the irradiation for 636 min. resulted in the complete decomposition of the starting material. Analysis of the resulting spectrum revealed the formation of (ethoxydimethylsilyl)(trimethylsilyl)ketene 4 by comparison with the spectrum of matrix isolated authentic sample.<sup>8</sup> The additional bands at 1670 (s), 1242 (m), 1218 (s), 1138 (m), 1060 (m), 860 (m),

802 (m), and  $762\text{ cm}^{-1}$  (w) are attributed to the  $\pi$ -bonded silaacrylate 3 derived from 1,2-shift of trimethylsilyl group in carbene 2 (Scheme 1). However, no definitive assignment of these bands are possible at present time except for the notable band at  $1670\text{ cm}^{-1}$  due to the stretching vibration of ester carbonyl. The frequency of ester band is approximately at the midpoint between ethyl 2,3-dimethylcrotonate ( $1715\text{ cm}^{-1}$ ),<sup>9</sup> and dimethylsulfonium ethoxycarbonylmethylide ( $1603\text{ cm}^{-1}$ ).<sup>10</sup> The lower frequency shift of the ester carbonyl is consistent with the weakened  $\pi$ -overlap in 3. Unfortunately, it is not possible to assign the stretching vibration of a silicon-carbon double bond in the spectrum. It is worthy of note that the simultaneous generation of 4 with 3 at even 10K was observed. It is likely that a part of hot silene rearranges to the ketene 4.<sup>11</sup>

Scheme 1.



The silaacrylate 3 isolated in argon matrix was stable at least at ca. 35K. Evidence for the chemical identity of 3 is proved by the reaction with methanol. Silyldiazoacetate 1 was irradiated ( $\lambda > 360\text{ nm}$ ) at 10K in argon matrix containing methanol (730 : 30). The IR 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 isolated in a trap cooled by liquid nitrogen. GC-Mass revealed the presence of the ketene 4 and methoxysilane 5 as major products.<sup>12</sup> These results clearly show that the predominant species generated

by the photolysis of 1 are  $\pi$ -bonded silaacrylate 3 and the ketene 4 (ca. 1 : 3).

A major point of interest is the photochemical conversion of 3 to the ketene 4. The silaacrylate 3 immediately changed to 4 at 10K in argon matrix by the brief irradiation with the light of shorter wavelength ( $\lambda > 240$  nm). In this transformation, the disappearance of the infrared bands of 3 is concurrent with growth of the bands of 4.

To obtain the ultraviolet spectrum, the argon-diluted 1 was deposited on a sapphire window cooled to 10K.<sup>13</sup> Irradiation ( $\lambda > 360$  nm) results in the disappearance of the UV absorption of 1 (256 nm) with formation of a new band with a maximum at 288 nm assignable to  $\pi \rightarrow \pi^*$  of 3 since 4 has absorption at 273 nm with a small extinction coefficient ( $\epsilon$ ; 43). Disappearance of this band by additional brief irradiation with  $\lambda > 240$  nm indicates the conversion of 3 to 4 (Figure 1). The ultraviolet absorption attributed to 3 is also observable at 293 nm in isopentane/methylcyclohexane (3 : 1) matrix at 77K. However, the band does not appear in EPA (5 : 5 : 2) matrix at 77K. This indicates that the silaacrylate 3 reacts with alcohol at the temperature of 77K. Indeed, photolysis of 1 in methanol/tetrahydro-2-methylfuran matrix at 77K gave the methoxysilane 5 (83%) and the ketene 4 (11%) along with a small amount of (methoxydimethylsilyl)(trimethylsilyl)ketene (4%).<sup>8</sup>

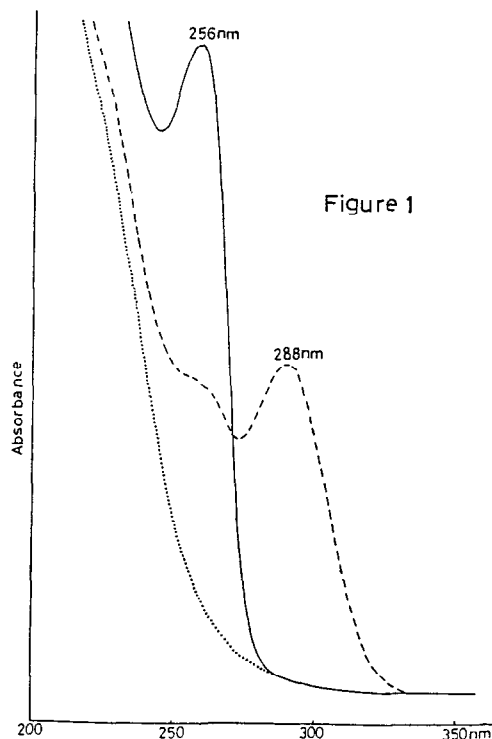


Figure 1.

UV spectrum of 1 matrix isolated in argon at 10K: before irradiation (—), after 70 min. irradiation ( $\lambda > 360$  nm) (-----), after additional irradiation ( $\lambda > 240$  nm) of the above sample for 1 min. (.....).

## References and Notes

1. (a) A. G. Brook, J. W. Harris, I. Lennon, and M. El Sheikh, *J. Am. Chem. Soc.*, 101, 83 (1979); (b) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, and R. K. Kallury, *Chem. Commun.*, 191 (1981); (c) A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, Y. C. Poon, Y. M. Chang, and W. Wong-Ng, *J. Am. Chem. Soc.*, 104, 5667 (1982); (d) N. Wiberg and G. Wagner, *Angew. Chem. Int. Ed. Engl.*, 22, 1005 (1983).
2. (a) R. West, *Science*, 225, 1109 (1984); (b) R. West, *Pure & Appl. Chem.* 56, 163 (1984), and references cited therein.
3. (a) H. P. Reisenauer, G. Mihm, and G. Maier, *Angew. Chem. Int. Ed. Engl.*, 21, 854 (1982); (b) G. Maier, G. Mihm, H. P. Reisenauer, and D. Littmann, *Chem. Ber.*, 117, 2369 (1984).
4. G. Maier, G. Mihm, R. O. W. Baumgärtner, and H. P. Reisenauer, *Chem. Ber.*, 117, 2337 (1984).
5. (a) M. J. Michalczyk, R. West, and J. Michl, *J. Am. Chem. Soc.*, 106, 821 (1984); (b) S. Murakami, S. Collins, and S. Masamune, *Tetrahedron Lett.*, 25, 2131 (1984).
6. Although the silene isolated by Brook has a functional group on the  $sp^2$ -hybridized carbon, it is quite different from ours.
7. Matrix-isolated samples were prepared by gas-phase deposition onto a CsI window cooled by an Air Products Inc., Displex refrigerator. Irradiations were performed with an Ushio 500W high pressure mercury lamp through a cutoff filter.
8. W. Ando, A. Sekiguchi, and T. Sato, *J. Am. Chem. Soc.*, 103, 5573 (1981).
9. D. Dolphin and A. Wick, "Tabulation of Infrared Spectral Data", p-344, John Wiley & Sons., Inc., New York, London (1977).
10. G. B. Payne, *J. Org. Chem.*, 32, 3351 (1967).
11. The rearrangement of silylcarbene to silene is extremely exothermic reaction because singlet silylmethylene is calculated to be 69 Kcal/mol above singlet silene (DZ + d CI). (a) M. S. Gordon, *Chem. Phys. Lett.*, 54, 9 (1978); (b) J. D. Goddard, Y. Yoshioka, and H. F. Schaefer III, *J. Am. Chem. Soc.*, 102, 7644 (1980); (c) H. J. Köhler and H. Lischka, *J. Am. Chem. Soc.*, 104, 5884 (1982).
12. Both compounds had identical retention times and mass spectra with those of authentic samples.
13. Ultraviolet spectrum of 1: UV  $\lambda_{\max}$  (hexane) 261 nm ( $\epsilon$ ;  $7.90 \times 10^3$ ), 382 nm ( $\epsilon$ ; 138).

(Received in Japan 29 January 1985)