

The First Matrix-Isolation and Electronic Structure of Vinyl-Substituted Silylenes¹

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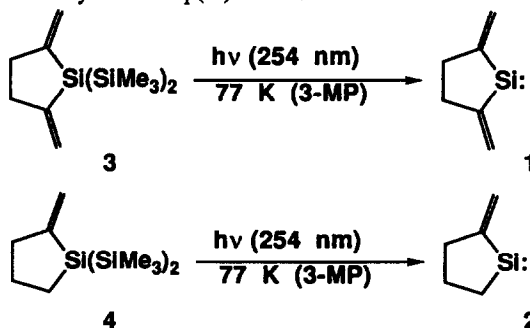
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Abstract: The first vinylsilylenes were isolated from photolysis of the corresponding trisilanes in 3-MP and 2-MeTHF matrices at 77 K. Contrary to the theoretical predictions, vinyl substitution caused a significant red shift of the $n(\text{Si})$ - $3p(\text{Si})$ transition of dimethylsilylene.

Much attention has been currently focused on the electronic structure of silylenes. Drahnak, Michl, and West have first reported that dimethylsilylene produced by the irradiation of dodecamethylcyclohexasilane shows a characteristic absorption maximum at ca. 450 nm in an argon matrix at 10 K or in a 3-methylpentane (3-MP) matrix at 77 K.^{2a} Recent extensive spectroscopic studies of dimethylsilylene by using matrix isolation,^{2,3} laser flash photolysis,⁴ and theoretical calculations^{5,6} have confirmed that the 450 nm absorption is ascribed to the $n(\text{Si})$ - $3p(\text{Si})$ transition of the singlet ground state. The absorption maximum shifted to 350 nm in a 2-methyltetrahydrofuran (2-MeTHF) matrix, being indicative of the formation of a silylene-ether complex.⁷ Remarkable substituent effects on the $n(\text{Si})$ - $3p(\text{Si})$ band maxima have been discussed on the basis of the limited experimental⁸ and theoretical results.⁵

We wish herein to report the first isolation of vinyl-substituted silylenes, **1** and **2**, in 3-MP and 2-MeTHF matrices at 77 K. The $n(\text{Si})$ - $3p(\text{Si})$ absorption maxima for the vinylsilylenes shifted to significantly longer wavelength than that for dimethylsilylene. The origin of the red shift is discussed in terms of the substantial conjugation between the vacant vinyl π^* and $3p(\text{Si})$ orbitals.



A purple color was induced by irradiation of a cyclic trisilane **3**⁹ in a 3-MP matrix at 77 K with a 125-W low pressure Hg arc lamp. The absorption spectrum showed a broad band at 505 nm and a relatively intense band at 290 nm (Figure 1a and Table 1). Upon annealing of the matrix, the two bands disappeared simultaneously. The purple species is assigned as the corresponding cyclic divinylsilylene **1** on the basis of the following experimental observation: (i) Similar photolysis of **3** in a 3-MP/2-MeTHF (95:5) matrix at 77 K

Table 1. Theoretical and Experimental Transition Energies of Vinylsilylenes **1** and **2**, and Dimethylsilylene

Silylene ^a	Transition Energies/eV		Assignment
	Obsd ^b	Calcd ^c	
1	2.46 (1.0)	2.459 (3x10 ⁻⁴)	n(Si) → 3p(Si)
	4.28 (7.4)	3.935 (0.132)	π → 3p(Si)
2	2.61	2.44 (4x10 ⁻⁴)	n(Si) → 3p(Si)
	---	4.23 (0.0665)	π → 3p(Si)
Me ₂ Si:	2.75 ^d	2.23 (5x10 ⁻⁵)	n(Si) → 3p(Si)

- a. Geometry optimized with the 3-21G basis set was used for the CNDO/S calculations.
 b. Relative absorption coefficients are shown in parentheses.
 c. Oscillator strengths are shown in parentheses.
 d. Ref 2.

afforded two bands at 290 nm and 505 nm; upon annealing of the matrix for several seconds, the two bands disappeared and a new band emerged at 390 nm (Figure 1c). The 390 nm band was also observed when **3** was irradiated in a pure 2-MeTHF matrix (Figure 1b), being assignable to the complex of **1** with 2-MeTHF. (ii) Upon irradiation of **3** in the presence of excess t-butyl alcohol in a 3-MP matrix at 77 K followed by warming to melt, the purple color of **1** was produced and then disappeared. After the procedure was repeated several times, GC-MS analysis of the mixture revealed the formation of a t-butyl alcohol adduct of **1** (**5**). (iii) Irradiation of a mixture of **3** and t-butyl alcohol in hexane at ambient temperature afforded **5** as a sole volatile product in the isolated yield of 51 %.¹⁰

Similar irradiation of **4**⁹ gave **2**, whose absorption maximum appeared at 475 nm in 3-MP and shifted to 345 nm in 2-MeTHF at 77 K. It is stressed that the successful observation of the vinylsilylenes would be an issue of the proper design of the cyclic substituents; photolysis of 2,2-divinylhexamethyltrisilane failed to give the corresponding divinylsilylene.

The transition energies for **1**, **2**, and dimethylsilylene calculated by using the CNDO/S theory¹¹ are shown in Table 1 together with the experimental values. A fairly good agreement was observed between the calculated and theoretical values, suggesting that a weak band at the longest wave-length is assigned to the n(Si)-3p(Si) transition. The calculation allows also to assign the relatively intense band at 290 nm for **1** to the π-3p(Si) transition.

The experimental n(Si)-3p(Si) bands for **1** and **2** red-shifted significantly relative to that for dimethylsilylene, in disagreement with a recent prediction on the basis of *ab initio* MO theory by Apeloig and Karni,⁵ they have predicted that a vinyl group serves as a π donor substituent on silylene to cause a substantial blue shift in the n(Si)-3p(Si) transition. Although the *ab initio* MO theory also predicted a red shift in the n(Si)-3p(Si) transition of silylenes when the apex angle increased, the apex angles for **1** and **2** were estimated by the *ab initio* MO calculations¹² to be even smaller than the angle for dimethylsilylene. The origin of the red shift in the n(Si)-3p(Si) transition would be ascribed to the lowering of the 3p(Si) orbital level caused by the vinyl substitution on the silylene. The relatively high-lying 3p(Si) orbital can be lowered by the more important interaction with the antibonding π* orbital than the interaction with the bonding π orbital of the vinyl groups. More elaborated theoretical calculations are indispensable to elucidate the electronic effects of π substituents on the silylene.

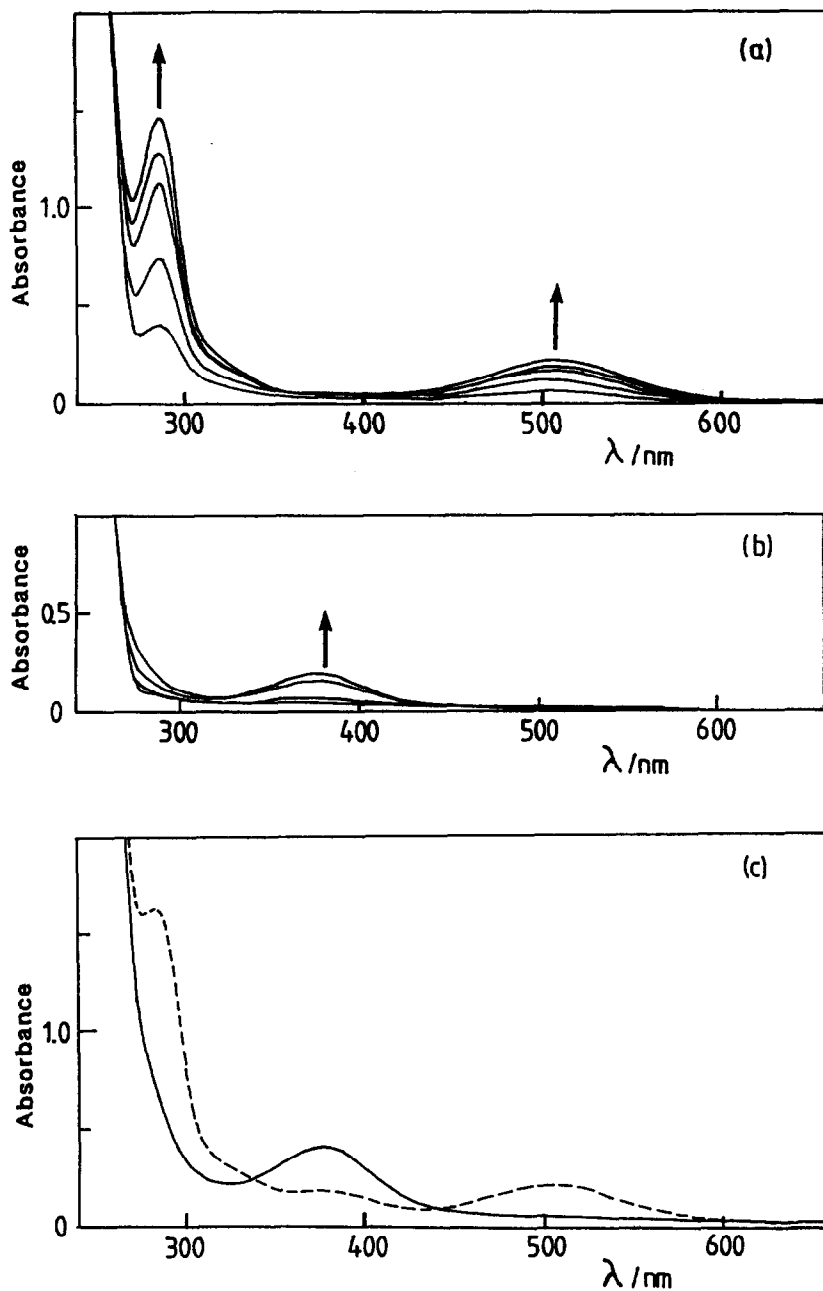


Figure 1. UV spectra obtained in photolysis of **3** at 77 K: (a) In 3-MP, at 80, 160, 220, 280, and 400 s, respectively, after irradiation, (b) in 2-MeTHF at 0, 60, 180, and 210 s, respectively, after irradiation, and (c) in 95:5 3-MP/2-MeTHF, (----) after 10 min irradiation and (—) after annealing of the matrix for several seconds.

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9. Compounds **3** and **4** were prepared in 63 and 44% yields, respectively, by the reaction of the corresponding dilithium reagents with 2,2-dichlorohexamethyltrisilane in ether. **3**: bp 105 °C/10 mmHg; white crystals; mp 63 °C; ¹H NMR (CDCl₃) δ 0.13 (s, 18H), 2.36 (s, 4H), 5.19 (d, J = 2.7 Hz, 2H), 5.71 (d, J = 2.7 Hz, 2H); ¹³C NMR (CDCl₃) δ -1.3, 40.7, 121.0, 153.9; ²⁹Si NMR (CDCl₃) δ -52.2, -15.5; MS m/z (relative intensity) 254 (M⁺, 13), 239 (44), 73 (100); UV (hexane) λ_{max}/nm (ε) 249 (4230); HRMS m/z 254.1346 (calcd for C₁₂H₂₆Si₃ m/z 254.1344). **4**: bp 115 °C/15 mmHg; ¹H NMR (CDCl₃) δ 0.11 (s, 18H), 0.95 (t, J = 7.0 Hz, 2H), 1.68 (t of t, J = 6.7 and 7.0 Hz, 2H), 2.21 (t of t, J = 6.7 and 2.0 Hz, 2H), 5.17 (q, J = 2.0 Hz, 1H), 5.70 (q, J = 2.0 Hz, 1H), ¹³C NMR (CDCl₃) δ -1.0, 9.5, 28.1, 41.2, 120.1, 153.9; ²⁹Si NMR (CDCl₃) δ -44.2, -15.9; MS m/z (relative intensity) 242 (M⁺, 23), 227 (16), 141 (62), 73 (100); HRMS m/z 242.1341 (calcd for C₁₁H₂₆Si₃ m/z 242.1342).
10. The products which were expected to be derived from photochemical 1,3-migration of a trimethylsilyl group in **3** were not found in the reaction mixture, whereas the 1,3-silyl migration occurred efficiently in the photoreaction of a closely related vinyldisilane, 2,5-dimethylene-1-methyl-1-trimethylsilyl-1-silacyclopentane, as reported in the following paper: Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986-3987.
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12. The geometry was fully optimized with the 3-21G basis set by using the GAMESS program¹³ at the Computer Center of Tohoku University. The calculated apex angles for **1**, **2**, and dimethylsilylene were 87.4, 88.1, and 97.7°, respectively.
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