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Matrix Isolation of Silenes and Their Ultraviolet Absorptions

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Various silenes were isolated in 3-methylpentane matrix at 77 K by photolysis of the corresponding silyl diazo compounds and their ultraviolet spectra were measured.

Much interest has been expressed in multiply-bonded silicon compounds. Silenes and disilenes have been isolated as stable solids at room temperature or in the matrix at low temperature.[1)] Although there are many reports concerning silenes, very little is known about their ultraviolet spectra. 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),[2)] (2) silaaromatics like silabenzene (212, 272, 320 nm)[3)] and silatoluene (307, 314, 322 nm),[4)] (3) highly substituted silenes: $(Me_3Si)_2Si=C(OSiMe_3)R$ (ca. 340 nm) where R=CMe_3, CEt_3, and 1-adamantyl.[5,6)] We wish to report here various UV absorptions of silenes generated from photolysis of silyl diazo compounds. The matrix isolation technique was used for the measurement of UV spectra.

A dilute solution ($\approx 10^{-3}$ to $\approx 10^{-4}$ M) of pentamethyldisilanyldiazomethane ($Me_3SiSiMe_2CHN_2$) 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 of 265 nm appeared and grew on irradiation time (Fig. 1). The same absorption band was observed in 3-MP containing t-BuOH at 77 K and immediately disappeared on annealing the matrix with concurrent formation of the trapping product of the silene 2.[7)] Based on these results and our previous reports of silylcarbene chemistry,[8)] it is reasonable to assume that the absorption band at 265 nm is assigned to π-π^* of the silene 2. Similarly, various UV absorptions of silenes were measured by photolysis of the corresponding silyl diazo compounds. The results are summarized in Table 1.[9)]

The UV absorptions of tri or tetra substituted silenes are relatively shifted to the longer wavelength compared to the parent silene ($H_2Si=CH_2$, 258 nm), but shorter than the highly substituted silenes (Brook's silenes, ca. 340 nm). The introduction of trimethylsilyl group on carbon also results in slight red shifts. It is worthy to note that considerable bathochromic shifts of conjugated silenes such as 5, 6, and 7 have been observed.

Table 1. UV Absorptions of various silenes in 3-MP at 77 K

Silene	λmax/nm	Precursor
$Me_2Si=CHMe$ 1	255	Me_3SiCHN_2 a)
$Me_2Si=CHSiMe_3$ 2	265	$Me_3SiSiMe_2CHN_2$ a)
$Me_2Si=C(Me)SiMe_3$ 3	274	$(Me_3Si)_2CN_2$ a)
$Me_2Si=C(SiMe_3)_2$ 4	278	$Me_3SiSiMe_2C(N_2)SiMe_3$ a)
$Me_2Si=C(Ph)CO_2Me$ 5	280	$PhMe_2SiC(N_2)CO_2Me$ b)
$Me_2Si=C(SiMe_3)COAd$ c) 6	284	$Me_3SiSiMe_2C(N_2)COAd$ b)
$Me_2Si=C(SiMe_3)CO_2Et$ 7	293	$Me_3SiSiMe_2C(N_2)CO_2Et$ b)

a) Irradiated with $\lambda > 300$ nm.
b) Irradiated with $\lambda > 360$ nm.
c) Ad = 1-Adamantyl group.

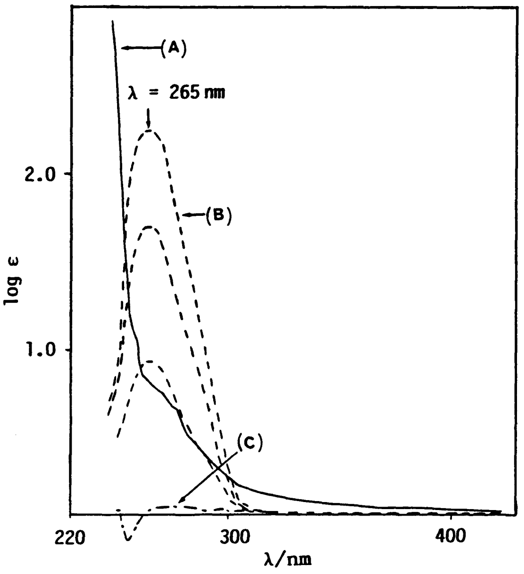

Fig. 1.
(———) $Me_3SiSiMe_2CHN_2$ prior to photolysis (A), (– – – –) After photolysis [40 s, 80 s, 120 s, 77 K, starting material subtracted (B)], (—·—·—) After annealing and recooling to 77 K, starting material subtracted (C).

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7) Alkoxysilane, $Me_2Si(O\text{-}t\text{-}Bu)CH_2SiMe_3$, was formed as a product.
8) A. Sekiguchi, H. Tanikawa, and W. Ando, Organometallics, 3, 584 (1985), and references cited therein.
9) Extinction coefficients cannot be given for methodological reasons. However, the absorption bands in Table 1 would be π-π^* transitions because the reactions were carried out with low concentration ($\approx 10^{-3}$ to $\approx 10^{-4}$ M).

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