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Matrix Isolation and Ultraviolet Spectra of Germylenes

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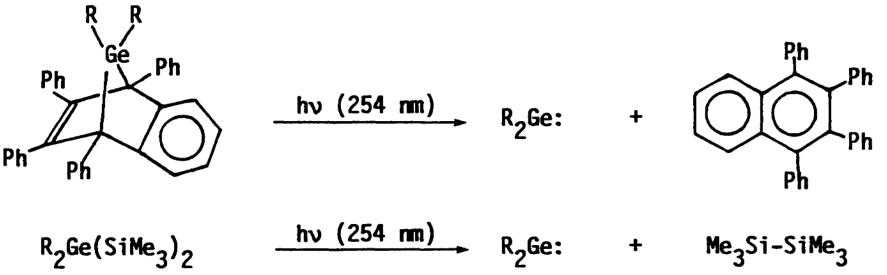
Some organogermylenes were isolated in a hydrocarbon matrix at low temperature by the photolysis of 7-germanorbornadienes or bis(trimethylsilyl)germanes. The germylenes show electronic absorption bands at 420-560 nm.

The matrix isolation technique has been widely used in the observation of reactive species such as silylenes or unsaturated silicon compounds.1) Although organogermylenes have been postulated as reactive intermediates,2) only dimethylgermylene has been observed at low temperature in a hydrocarbon matrix.3) There is no systematic study on the spectroscopic properties of germylenes. In this communication we report the matrix isolation and electronic absorptions of various organogermylenes in 3-methylpentane (3-MP) at 77 K.

Germylenes were generated by the photolysis of 7-germanorbornadienes2) or bis(trimethylsilyl)germanes.4) We found that 7-germanorbornadienes were effective photochemical precursors of germylenes.5)



Irradiation of cyclohaxane solution of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorbornadiene 1 (0.3 mmol) and 2,3-dimethyl-1,3-butadiene 2 (3.0 mmol) with a low pressure mercury lamp produced 1,1,3,4-tetramethyl-1-germacyclopent-3-ene 3 in 90% yield together with 1,2,3,4-tetraphenylnaphthalene. The formation of 3 can be rationalized by the reaction of dimethylgermylene with 2. When 3-MP solution of 1 ($\approx 10^{-4}$ M) was cooled to 77 K, and irradiated with a low pressure mercury lamp, the matrix turned to intense yellow and a broad electronic absorption band with a maximum of 420 nm was observed (Fig. 1). This band immediately disappeared on melting the matrix. Since it is precedent that dimethylgermylene is a yellow species with λmax 430 nm in 3-MP,3) the yellow species from 1 may be ascribed to dimethygermylene. Convincing evidence for identification of the yellow species as dimethylgermylene is provided by the results of a chemical trapping experiment. About 1 mg of 1 and 0.5 ml of 2 were dissolved in 3.5 ml of 3-MP, cooled to 77 K, and the resulting matrix was irradiated with 254 nm, producing pale yellow color of dimethylgermylene. When matrix was warmed to melt, the color disappeared. 3 was detected by GC-MS. Ultraviolet absorptions of germylenes obtained by the photolysis of 7-germanorbornadienes or bis(trimethysilyl)germanes at 77 K in 3-MP glasses are listed in Table 1.

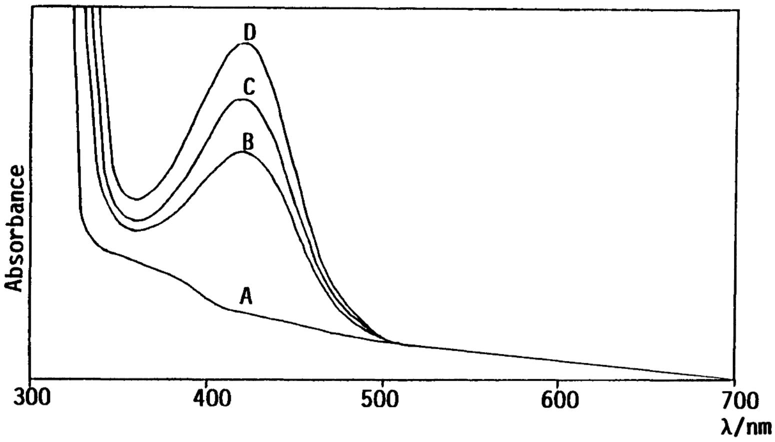


Fig. 1. UV spectra of dimethylgermylene in 3-MP at 77 K.
A: UV spectrum of 1 before irradiation.
B: 5 min irradiation.
C: 15 min irradiation.
D: 30 min irradiation.

Table 1. Electronic absorptions of germylenes in 3-MP at 77 K

Germylenes	λmax/nm	(color of the matrix)	Precursors
Mes_2Ge:	550	(purple)	$Mes_2Ge(SiMe_3)_2$
$Mes(^tBu)Ge$:	508	(red)	$Mes(^tBu)Ge(SiMe_3)_2$
Ph_2Ge:	466	(yellow-orange)	$Ph_2Ge(SiMe_3)_2$
Ph_2Ge:	466	(yellow-orange)	7-germanorbornadiene,R=Ph
Et_2Ge:	440	(yellow)	7-germanorbornadiene,R=Et
Me_2Ge:	420	(yellow)	7-germanorbornadiene,R=Me

The introduction of aryl group on germanium resulted in the dramatical red shift compared to the alkylgermylenes. This is probably due to the stabilization of the excited state.

When the matrix contaning dimesitylgermylene was annealed, the yellow species (λmax 406 nm at 77 K) due to tetramesityldigermene was observed.[4] This absorption band is identical with that obtained from the photolysis of hexamesitylcyclotrigermane giving tetramesityldigermene.

References
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2) M. Schriewer and W. P. Neumann, J. Am. Chem. Soc., 105, 897 (1983).
3) H. Sakurai, K. Sakamoto, and M. Kira, Chem. Lett., 1984, 1379.
4) S. Collins, S. Murakami, J. T. Snow, and S. Masamune, Tetrahedron Lett., 26, 1281 (1985).
5) D. Griller et al. reported that 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene 4 decomposed by the photolysis in isopentane glass at 77 K (Organometallics, 3, 1123 (1984)), but in our experiment 4 was photochemically stable in 3-MP at 77 K.

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