Transient and Matrix Ultraviolet Absorption Spectra of Dimethylgermylene (Dimethylgermanediyl)

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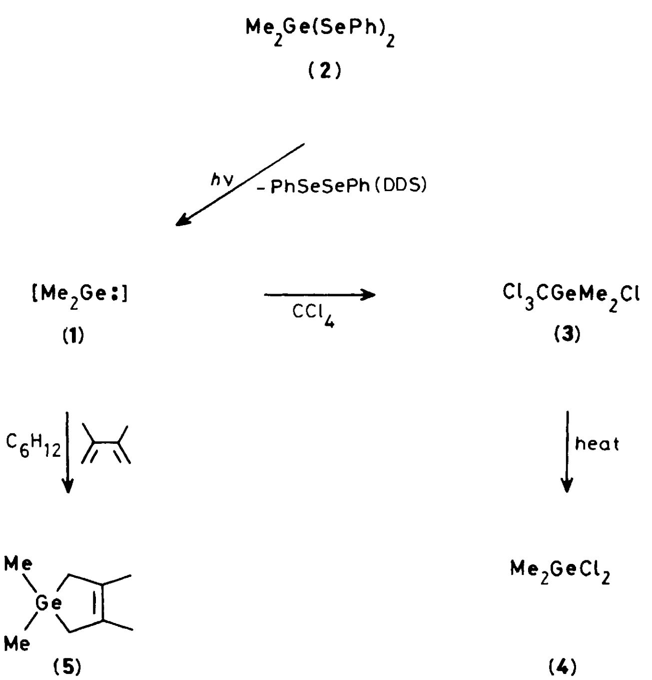
Dimethylgermylene (**1**), generated from a new precursor dimethylbis(phenylseleno)germane (**2**), has been observed as a transient species by time-resolved laser flash photolysis at room temperature.

Following the rapid progress in the area of silylene chemistry during the last decade,[1] much attention has recently been paid to its heavier analogue germylene.[2] We now report the first observation of the transient u.v. absorption of the simplest diorganogermylene, dimethylgermylene (**1**), generated by irradiation of dimethylbis(phenylseleno)germane (**2**) with an excimer laser at 308 nm; its assignment has been fully supported by matrix isolation and e.s.r. spectroscopic studies.

The precursor (**2**) was chosen because chemical bonds involving selenium are generally light-sensitive and readily undergo homolytic cleavage:[3] it was therefore expected that simultaneous homolytic cleavage of the two Ge–Se bonds



Scheme 1

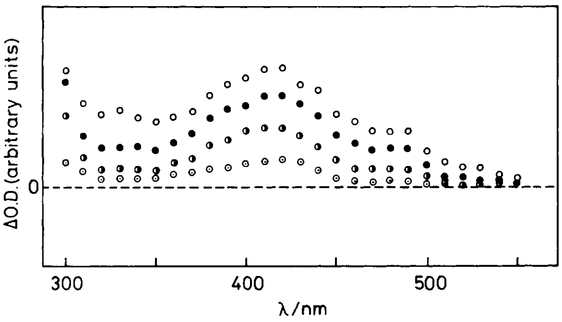


Figure 1. Time-resolved absorption spectra of dimethylgermylene (**1**) (420 nm) generated from dimethylbis(phenylseleno)germane (**2**) in cyclohexane by irradiation with XeCl excimer laser at 308 nm and room temperature; measured (top to bottom) 0.4, 6.6, 23.6, and 106 μs after excitation,.

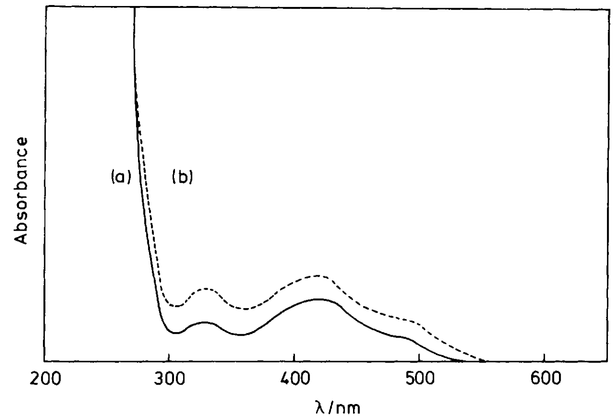


Figure 2. Absorption spectra of dimethylgermylene (**1**) (420 nm) generated from dimethylbis(phenylseleno)germane (**2**) by irradiation with a low-pressure Hg lamp (253.7 nm): (a) rigid matrix solution in 3-methylpentane at 77 K; (b) argon matrix at 21 K. The baseline was corrected by subtracting the end absorption due to residual precursor (**2**) ($\lambda_{max.}$ < 300 nm).

would give dimethylgermylene (**1**), with concomitant formation of the phenylseleno radical and/or diphenyl diselenide (DDS). A preliminary experiment was carried out in carbon tetrachloride. Thus a dilute (10^{-2} M) solution of (**2**) in CCl_4 was irradiated with a low-pressure mercury lamp (253.7 nm) under argon for 4 h at room temperature. Clean quantitative conversion into the insertion product (**3**), dichlorodimethylgermane (**4**), and DDS was demonstrated by ^1H and ^{13}C n.m.r. (Scheme 1). Upon heating at 80 °C for 3 h, the primary product (**3**) was converted quantitatively into (**4**). Since the formation of (**3**) has previously been recognized as evidence for the intervention of dimethylgermylene (**1**),[4] it was highly likely that (**1**) had been generated quantitatively under these conditions. Furthermore when a solution of (**2**) in cyclohexane was irradiated in the presence of a large excess of 2,3-dimethylbuta-1,3-diene under similar conditions, 3,4-dimethyl-1-germacyclopent-3-ene (**5**)[5] was obtained in 20% yield (of isolated material), strongly suggesting the intermediacy of dimethylgermylene (**1**)[5] (Scheme 1). Encouraged by these results, we turned our attention to direct observation of the elusive intermediate (**1**) by u.v. spectroscopy. Time-resolved laser flash photolysis was clearly the first choice of technique. A dilute solution (10^{-4} M; degassed under 10^{-6} Torr) of (**2**) in cyclohexane in a quartz cell (path-length 50 mm) was irradiated with a XeCl excimer laser at 308 nm. Transmitted light from a pulsed xenon lamp through the sample cell was monitored at right angles with respect to the excitation laser beam after a delay period indicated in the caption to Figure 1 (0.4—106 μs). The time-resolved u.v. absorption spectrum of the transient species formed from (**2**) (Figure 1) exhibited a weak band at 330 nm and a medium band at 420 nm, with shoulders around 380 and 490 nm. Since the precursor (**2**) showed no distinct absorption beyond 300 nm, these bands must be due to the photolysis product. The 330 nm band was readily assigned to DDS. The 490 nm band has been assigned previously to the phenylseleno radical generated from DDS.[6] In order to assign the remaining two bands (380 and 420 nm), we measured the u.v. absorption spectra of the photoproducts from (**2**) under long life conditions. A degassed solution of (**2**) (10^{-3} M) in 3-methylpentane (3-MP) in a quartz cell was introduced into an Oxford cryostat. The sample was cooled to 77 K and irradiated with a low-pressure Hg lamp. After 20 min irradiation, the system showed distinct absorption maxima at 330 and 420 nm, with shoulders around 380 and 490 nm. As shown in Figure 2(a), the spectral pattern closely resembled that observed in laser flash photolysis. To prove the formation of DDS and its secondary photolysis product(s), control experiments using DDS ($\lambda_{max.}$ 330 nm) were carried out under similar conditions (10^{-3} M; 3-MP glass matrix at 77 K). After irradiation at 253.7 nm for 20 min, the spectrum showed two new absorptions, at 380 and 490 nm. This strongly suggested that the remaining absorption at 420 nm was due to dimethylgermylene (**1**).

To eliminate the possibility that the absorption at 420 nm might arise from a dimeric form of (**1**) or from a germanium radical such as $Me_2\dot{G}eSePh$, two further experiments were performed. One involved argon matrix isolation at 21 K,[7]† where dimerization of (**1**) should be highly unlikely. Thus a carefully prepared argon matrix of the diselenogermane (**2**)

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† An Air Products 202 Displex cryogenic refrigeration system, equipped with standard instrumentation skirt, optical spectroscopy shroud (DMX-1A) with sapphire window, and an optical sample heating system, was employed.[7]

[(**2**): argon 1:3000 to 1:5000) was irradiated at 21 K with a low-pressure Hg lamp for 15 min. The u.v. spectrum, obtained by computer subtraction of the bands due to the precursor (**2**), showed two distinct bands at 330 and 420 nm in addition to shoulders near 380 and 490 nm [Figure 2(b)]. The spectral pattern is remarkably similar not only to that obtained by laser flash photolysis (Figure 1), but also to that of the glass-matrix experiment at 77 K [Figure 2(a)]. The other experiment, which eliminates the possibility of intervention of a germanium radical, was the e.s.r. spectroscopic comparison between the 3-MP matrix samples of (**2**) and DDS (irradiated at 253.7 nm at 77 K). The spectra consisted of complex, somewhat broadened multiplets, but were entirely coincident.[8] Two important conclusions can be drawn from the e.s.r. studies. First, irradiation of (**2**) (3-MP; 77 K) gives a radical(s) which exhibit(s) a spectral pattern identical with that derived from photodecomposition of DDS under similar conditions. It should be noted that the product(s) derived from photodecomposition of DDS are responsible for the absorption bands at 380 and 490 nm. Secondly, a germanium-centred radical is unlikely to be involved in the reaction system.

The foregoing experimental observations seem consistent only with the statement that the electronic absorption band of (**1**) occurs at 420 nm between room temperature and 21 K. This agrees with the results of Sakurai *et al.* (430 nm in 3-MP at 77 K)[2b] and with those obtained very recently by Ando *et al.* (420 nm in 3-MP at 77 K),[2c] although these workers employed different precursors.

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