

Preliminary communication

Kinetic spectroscopy of diphenylgermylene Ph_2Ge following laser flash photolysis of bis(trimethylsilyl)diphenylgermane $(\text{Me}_3\text{Si})_2\text{GePh}_2$ *

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Abstract

A transient, λ_{max} 445 nm, was observed in the 266 nm laser flash photolysis of cyclohexane solutions of $(\text{Me}_3\text{Si})_2\text{GePh}_2$, and rate constants were recorded for its disappearance in the presence of various trapping agents. The reactivity profile is in accord with the identification of the carrier as diphenylgermylene Ph_2Ge , that dimerizes to tetraphenyldigermene $\text{Ph}_2\text{Ge}=\text{GePh}_2$, λ_{max} 320 nm.

Given the rich harvest of synthetic and mechanistic chemistry that has resulted from the study of divalent carbon and silicon compounds [1*][†], carbenes and silylenes, an interest in compounds of divalent germanium, germylenes, is understandable [2*]. Surprises are to be expected. An example was the unanticipated stereospecific 1,4 addition of dimethylgermylene Me_2Ge : to 2,4-hexadienes [3] that undergo stepwise nonstereospecific addition by dimethylsilylene [4].

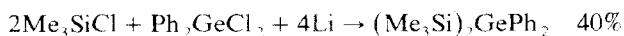
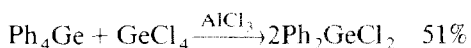
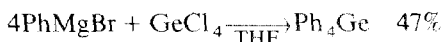
Photochemical generation of germylenes has been reported previously [5–9] and electronic absorption spectra of several matrix isolated germylenes have been published [7,9]. Here we report the first kinetic studies of germylene reactions in solution.

* This report is dedicated to Professor Colin Eaborn, whose lasting achievement it is to have greatly enhanced the understanding of organosilicon chemistry while the field has been rapidly growing under his influence.

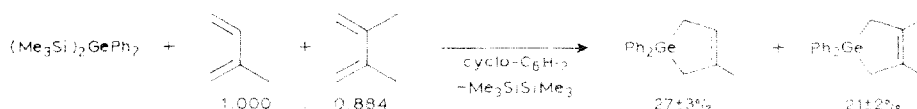
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[†] Reference numbers with asterisks indicate notes in the list of references.

For use as a precursor to diphenylgermylene bis(trimethylsilyl)diphenylgermane was synthesized by the following reaction sequence, and the product was fully characterized by NMR and mass spectroscopy.



Solutions of $(\text{Me}_3\text{Si})_2\text{GePh}_2$ in cyclohexane ($\lambda_{\text{max}} 238 \text{ nm}$, $\epsilon = 22\,100$) readily undergo photolysis to diphenylgermylene and hexamethyldisilane when irradiated by an array of low pressure mercury lamps through quartz vessels (60% conversion in 3 h) and reasonable yields of germylene adducts are obtained [10*]:



Since there are no reports of the photoinduced rearrangements of arylpolygermanes that are common features of arylpolysilane chemistry [5], we were encouraged to study the laser flash photolysis of bis(trimethylsilyl)diphenylgermane using techniques developed for the photolysis of silylene precursors [11,12].

The ca. 10 ns flashes from a Nd-YAG laser are frequency quadrupled to 266 nm pulses, ca. 18 mJ, that are used to photolyze 10^{-3} M solutions of $(\text{Me}_3\text{Si})_2\text{GePh}_2$ in cyclohexane ($A = 1.4$ at $\lambda 266 \text{ nm}$) producing reactive intermediates. These are detected by absorption of light from a continuous xenon source with wavelengths selected by monochromators before and after the sample. The change in the probe light intensity is monitored by a photomultiplier, the output of which is fed to a computer-controlled transient digitizer. The kinetic traces from at least 8 measurements are averaged. With this apparatus, a transient absorption spectrum at a particular time after excitation is constructed from the kinetic traces at many wavelengths. The spectrum obtained from photolysis of the title compound in a non-degassed solution at 295 K is shown in Fig. 1. The absorption maximum at 445 nm is shifted 21 nm to the blue from that reported in matrix isolation experiments at 77 K by Ando [9]. This shift between the low temperature glass and the room temperature solution spectra is of similar magnitude to that observed for transients identified as silylenes [12].

When the transient is generated in the presence of excess trapping agents, first-order decays are observed. The pseudo-first-order rate constants are obtained from the slopes of the linear plots of log absorbance versus time. The slopes of the linear plots of the pseudo-first-order rate constants versus substrate concentrations yield the second-order rate constants. Table 1 lists these second-order rate constants for reaction of the 445 nm transient with a range of substrates, all except dimethyldisulfide previously employed in kinetic experiments on the photolysis of silylene precursors [12]. Also included for comparison are data on the photolysis of 2,2-diphenylhexamethyltrisilane, a precursor of diphenylsilylene, believed to be the carrier of the transient absorption with $\lambda_{\text{max}} 460 \text{ nm}$ observed under identical photolysis conditions as used for the germylene precursor.

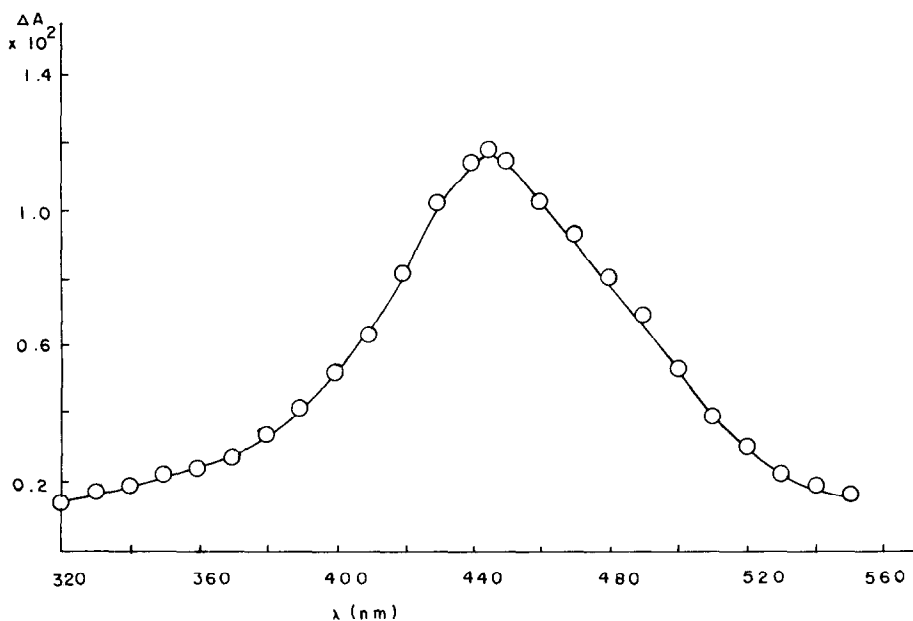


Fig. 1. Transient absorption spectrum recorded 400 ns after photolysis of a 1×10^{-3} M solution of $(\text{Me}_3\text{Si})_2\text{GePh}_2$ in undegassed cyclohexane with 266 nm pulses containing 18 mJ (average of 8 measurements).

Table 1

Laser flash photolysis at 266 nm of precursors to Ph_2Ge : and Ph_2Si : in cyclohexane solution

Precursor	$(\text{Me}_3\text{Si})_2\text{GePh}_2$	$(\text{Me}_3\text{Si})_2\text{SiPh}_2$
Concentration	1×10^{-3} M	3×10^{-4} M
Postulated transient	Ph_2Ge :	Ph_2Si :
λ_{max} , transient	445 nm	460 nm
$\tau_{1/2}$ self-reaction	270 μs	370 μs
k_2 ($M^{-1} \text{s}^{-1}$) (concentration of trapping agent, M)		
O_2	$1.02 \pm 0.08 \times 10^8$ (10^{-3})	$1.16 \pm 0.12 \times 10^8$ (10^{-3})
EtMe_2SiH	$1.01 \pm 0.03 \times 10^4$ (0.38–2.25)	$1.54 \pm 0.07 \times 10^3$ (1.50–3.75)
MeOH	no reaction (0.05–0.25)	$3.95 \pm 0.10 \times 10^7$ (0.01–0.06)
$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CH}_2$	$2.75 \pm 0.12 \times 10^4$ (0.037–0.187)	$8.26 \pm 0.34 \times 10^4$ (0.037–0.187)
$\text{CH}_2=\overset{\uparrow}{\text{C}}\text{C}(\text{CH}_3)=\text{CH}_2$	$5.07 \pm 0.22 \times 10^4$ (0.024–0.08)	–
$(\text{CH}_3)_2\text{CHCH}_2\text{Br}$	$6.36 \pm 0.21 \times 10^5$ (0.05–0.40)	–
MeSSMe	$5 \pm 3 \times 10^6$ (5×10^{-3})	–

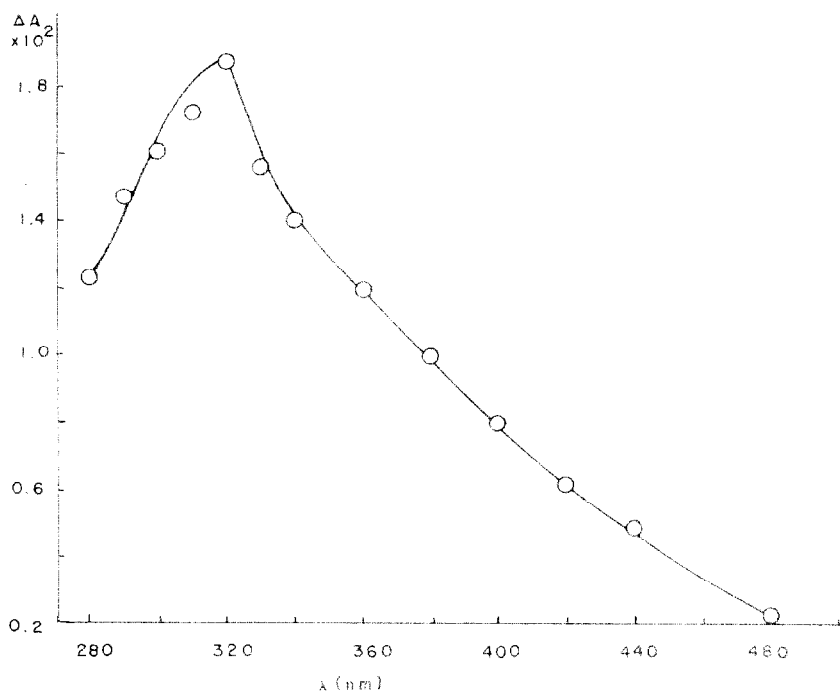
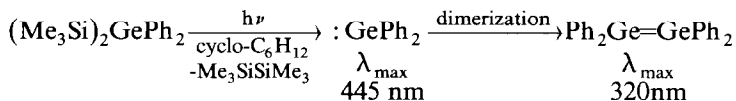


Fig. 2. Transient absorption spectrum recorded 800 μs after the flash using a degassed sample. Other conditions as in Fig. 1.

The reactivity profile is clearly consistent with the identification of the 445 nm transient from $(\text{Me}_3\text{Si})_2\text{GePh}_2$ as diphenylgermylene. Germylenes are known to react rapidly with oxygen forming germoxanes via germanone intermediates [13]. While insertion into Si-H bonds by germylenes is not common, several examples have been reported, the first in a recoil experiment [14]. The slow reaction with methanol contrasts markedly with the behavior of silylenes, and could have been anticipated from Masamune's report that germylenes undergo dimerization in the presence of methanol [18]. Germylenes are well known to react with 1,3-dienes forming 1-germacyclopent-3-enes in high yield [15,16]. Insertion of germylenes into carbon-halogen bonds is also widely precedented [2], and germylenes have been shown to insert quantitatively into disulfide linkages [17].

Further evidence consistent with an identification of the 445 nm transient as diphenylgermylene is its second-order decay in the absence of added trapping agents. As the 445 nm transient decays, with an initial "half-life" of 270 μs , a second transient with an absorption maximum at 320 nm grows, reaching a maximum at ca. 700 μs after the laser flash. The second transient subsequently decays in a second-order process with an initial half-life of 630 μs . Figure 2 shows a transient absorption spectrum recorded 800 μs after the laser flash, when the 445 nm transient has nearly disappeared, and the 320 nm transient is at nearly its maximum concentration. The 320 nm transient, in contrast with the 445 nm transient, reacts, albeit rather sluggishly, with methanol ($k_2 = 7.14 \pm 0.22 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$). The 320 nm transient is clearly formed by dimerization of the 445 nm

transient. The shift in absorption maximum is exactly that reported for dimesitylgermylene upon dimerization to the digermene [9]. Thus it seems very likely that the 320 nm transient is tetraphenyldigermene, formed by dimerization of diphenylgermylene. Masamune has reported absorption of tetrakis(2,6-diethylphenyl)digermene at 263 and 412 nm [18].



While the identification of the 445 nm transient from photolysis of $(\text{Me}_3\text{Si})_2\text{GePh}_2$ as diphenylgermylene is tentative, a few comments are in order concerning the rate constants reported in Table 1. For comparison, the table also includes rate constants for the 460 nm transient formed by photolysis of the diphenylsilylene precursor $(\text{Me}_2\text{Si})_2\text{SiPh}_2$ under nearly identical conditions. The only qualitative difference between the reactivity of the two transients is toward methanol, and this is in accord with differences observed between germylenes and silylenes in steady-state irradiations [1*,18]. The quantitative differences are a greater reactivity of the transient believed to be diphenylgermylene toward Si-H bonds by ca. 6/1 and a lower reactivity, ca. 1/3, toward 2,3-dimethylbutadiene. Thus this first opportunity to compare the reactivity of analogous germylenes and silylenes has indicated that the germylene is more reactive in an Si-H "insertion", but less reactive in addition to a π -system. It would be premature to offer detailed explanations for these observations, but they do suggest that much is to be learned from kinetic studies of germylenes as well as silylenes.

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References

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