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Preliminary communication

Photochemistry of aryl-substituted trigermanes

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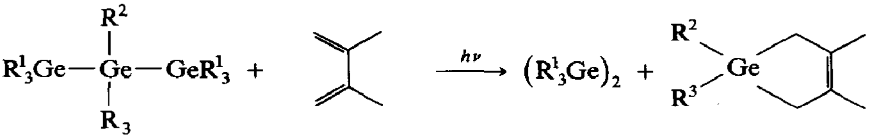
Abstract

The photolysis of phenyl-substituted trigermanes affords digermanes and germylenes. Trapping experiments, matrix isolation, and laser-photolysis studies indicate that the photoreaction of these compounds involves both the extrusion of germylenes and the formation of germyl radicals. The mechanism by which the germylenes are generated is discussed.

The photochemistry of organopolysilanes having a σ(Si–Si)/π(C–C) conjugated system has been the subject of considerable interest in synthetic chemistry. However, photochemical studies on the germanium analogue are scarce [1]. We describe herein the first photoreaction of the aryl-substituted trigermanes; $(PhMe_2Ge)_2GeMe_2$ (**1**) [2], $(Me_3Ge)_2GePhMe$ (**2**) [3], and $(Me_3Ge)_2GePh_2$ (**3**) [3].

Irradiation of the trigermanes **1**–**3** in cyclohexane with a 110-W low-pressure Hg arc lamp at room temperature under an argon atmosphere gave the digermanes: $(PhMe_2Ge)_2$ (33%) for **1**, and $(Me_3Ge)_2$ (25% and 40%) for **2** and **3**. In order to detect possible reaction intermediates, cyclohexane solutions of **1**–**3** and a large excess of 2,3-dimethylbutadiene were similarly irradiated. Digermanes and germacyclopentenes (18-33%) were obtained as the main products. 3-Butenylgermyl derivatives were also detected as minor products (< 5%). Formation of germacyclopentenes suggests the intermediacy of germylenes [4].



In the presence of carbon tetrachloride, photolysis of **1**–**3** in cyclohexane afforded chlorogermanes, chlorodigermanes, and dichlorogermanes, such as for example, $PhMe_2GeCl$, $PhMe_2GeGeMe_2Cl$, and $PhMeGeCl_2$, respectively, together with hexachloroethane. The formation of chlorogermane and chlorodigermane seems to indicate the intermediacy of the germyl and digermyl radicals produced by germanium–germanium bond cleavage of **1**–**3**. This may be further substantiated by

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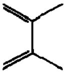
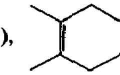
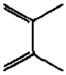
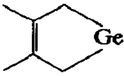
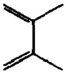
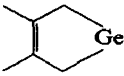
Table 1

The results of photochemical reactions of 1–3

Trigermane	Trapping agent	Main products (yield (%))
$(PhMe_2Ge)_2GeMe_2$ (1)	none	$(PhMe_2Ge)_2$ (33)
		$(PhMe_2Ge)_2$ (36),  GeMe$_2$ (18)
	CCl_4	$(PhMe_2Ge)_2$ (10), $PhMe_2GeCl$ (81), $PhMe_2GeMe_2GeCl$ (52)
$(Me_3Ge)_2GePhMe$ (2)	none	$(Me_3Ge)_2$ (25)
		$(Me_3Ge)_2$ (39),  GePhMe (32)
	CCl_4	$(Me_3Ge)_2$ (9), Me_3GeCl [a], $Me_3GePhMeGeCl$ (29)
$(Me_3Ge)_2GePh_2$ (3)	none	$(Me_3Ge)_2$ (40)
		$(Me_3Ge)_2$ (46),  GePh$_2$ (22)
	CCl_4	$(Me_3Ge)_2$ (17), Me_3GeCl [a], Me_3GePh_2GeCl (14)

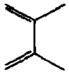
[a] The yield of Me_3GeCl could not be determined. The retention time of Me_3GeCl on GLC partially overlapped with that of CCl_4.

the presence of 3-butenylgermyl derivatives in the photo-products detected by means of GC-MS. The formation of dichlorogermane can be rationalized as evidence for interconversion of germylenes. The results of the photochemical reactions of 1–3 are summarized in Table 1.

In order to obtain more information on the reaction intermediates and primary photochemical processes, matrix isolation at 77 K and laser-photolysis at 293 K were also carried out. UV irradiation (low pressure Hg arc lamp for 30 min) of 1–3 (10^{-4} M) in rigid 3-methylpentane (3-MP) at 77 K produced yellow glasses with broad absorption bands at 422 nm for 1, 456 nm for 2, and 462 nm for 3. These bands disappeared upon warming-up. In a glass doped with 2,3-dimethylbutadiene,

Table 2

Rate constants for disappearance of the transients produced by photolysis of 1–3 in cyclohexane

Trigermane	λ_{max}/nm	k/ϵ [a]	Rate constant (M^{-1} s^{-1})		
				Et_3SiH	CCl_4
1	320	7.0×10^6	no	no	3.2×10^8
	420	2.5×10^7	2.4×10^7	4.2×10^6	quenched
2	320	5.5×10^5	no	no	1.3×10^8
	440	2.2×10^7	2.2×10^6	4.1×10^6	6.5×10^7
3	330	4.3×10^5	no	no	7.2×10^8
	450	3.0×10^6	7.2×10^5	6.6×10^5	1.5×10^8

[a] k is the rate constant of second-order decay and ϵ is the corresponding molar extinction coefficient.

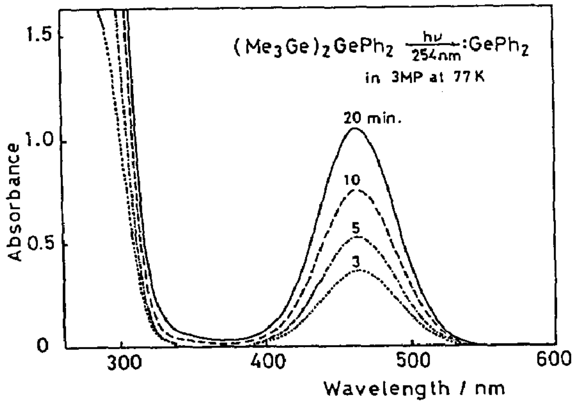


Fig. 1. Spectral change in absorption of $(Me_3Ge)_2GePh_2$ (**3**) during irradiation in 3-methylpentane glass at 77 K.

heating yielded the expected trapping products, germacyclopentenes. The yellow species with λ_{max} at 422, 456, and 462 nm, obtained in this study can be assigned to the corresponding germylenes on the basis of trapping experiments and from a comparison of the spectral characteristics with those of the germylenes previously reported [5–7]. The absorption spectrum of Ph_2Ge: generated from **3** is shown in Fig. 1.

Laser-photolysis (λ 266 nm, pulse width 5 ns, power 10 mJ per pulse) of **1–3** (10^{-3} *M*) gave two well-separated transient absorption bands as shown in Fig. 2. The transient at longer wavelength can be assigned to the absorption of a germylene by comparing its spectral and chemical properties with those previously reported [5,8,9]. The transients arising from **1–3** in cyclohexane decayed under second-order kinetics, suggesting the formation of digermenes [1,8]. This is substantiated further by quenching experiments with a germylene trapping agent, 2,3-dimethylbutadiene. The transients from **1–3** in cyclohexane in the presence of large excesses of the diene decayed under first-order kinetics. These transients were quenched with

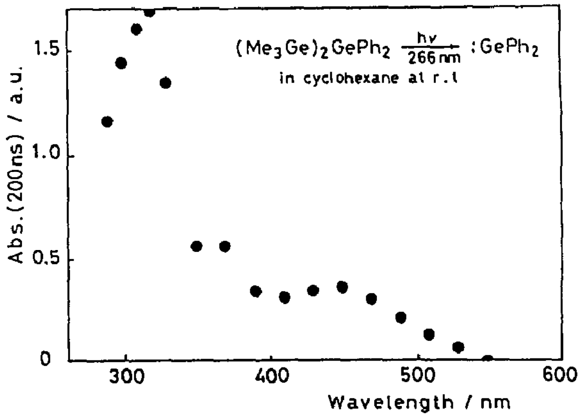
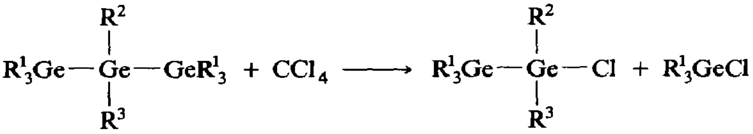


Fig. 2. Transient absorption spectrum at 200 ns after photoexcitation of $(Me_3Ge)_2GePh_2$ (**3**) in degassed cyclohexane solution at 293 K.

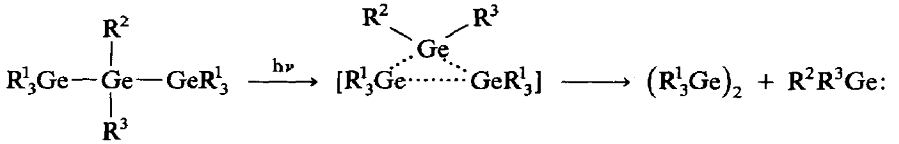
carbon tetrachloride [5]. However, the transient was not quenched with ethanol [8] and this is consistent with its chemical properties. On the other hand, the transient at shorter wavelength can be assigned to the absorption of the phenyl-substituted digermyl radical produced by germanium–germanium bond cleavage of **1–3**. The assignment of the transient at shorter wavelength is further substantiated by quenching experiment with carbon tetrachloride. Addition of carbon tetrachloride, an effective germyl radical scavenger [10,11], quenched the transient absorption. The transient absorption of alkyl-substituted germyl radicals is below 300 nm [12].



$$R^1_3Ge-\underset{R^3}{\overset{R^2}{Ge}}-GeR^1_3 + CCl_4 \longrightarrow R^1_3Ge-\underset{R^3}{\overset{R^2}{Ge}}-Cl + R^1_3GeCl$$

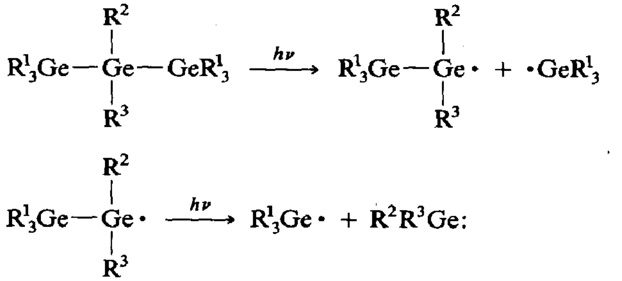
The experimentally determined decay constants of these transient species are summarized in Table 2.

Formation of germylene can be accounted by two mechanisms from the results described above. First, germylene might be formed by a simple extrusion process.



$$R^1_3Ge-\underset{R^3}{\overset{R^2}{Ge}}-GeR^1_3 \xrightarrow{h\nu} [R^1_3Ge\cdots\overset{R^2\ \ R^3}{Ge}\cdots GeR^1_3] \longrightarrow (R^1_3Ge)_2 + R^2R^3Ge:$$

Second, germylene might be produced by photodecomposition of digermyl radical generated from germanium–germanium bond cleavage of **1–3**.



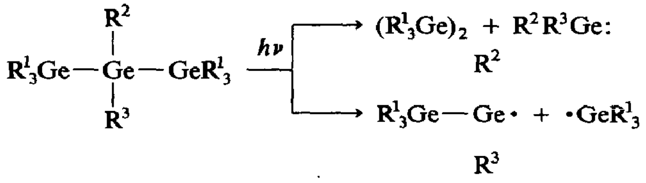
$$R^1_3Ge-\underset{R^3}{\overset{R^2}{Ge}}-GeR^1_3 \xrightarrow{h\nu} R^1_3Ge-\underset{R^3}{\overset{R^2}{Ge}}\cdot + \cdot GeR^1_3$$

$$R^1_3Ge-\underset{R^3}{\overset{R^2}{Ge}}\cdot \xrightarrow{h\nu} R^1_3Ge\cdot + R^2R^3Ge:$$

To elucidate the mechanism of germylene formation, we carried out the photodecomposition of a digermyl radical by both isolation matrix and laser-photolysis techniques. The phenyltetramethyldigermyl radical was photochemically generated from its parent digermane (phenyltetramethyldigermane) in 3-MP at 77 K. However, there was no signal of a germylene by succesive irradiation of the phenyltetramethyldigermyl radical. In a 3-MP glass doped with carbon tetrachloride, heating yielded the expected trapping product, phenyltetramethylchlorodigermane [13].

The laser-photolysis of **1–3** was carried out by two-step excitation. The 308 nm laser-photolysis of the transient at shorter wavelength with a decay time of 1 μs produced by the 266 nm laser-photolysis of **1–3** in cyclohexane was performed. However, there was no change in intensity of either transient because the digermyl radical was at shorter wavelength and the germylene at longer wavelength [13]. Thus, germylenes are not produced via digermyl radicals but may be photo-extruded from the trigermane itself.

Consequently, the photolysis of phenyl-substituted trigermanes involves both the simple extrusion of germylenes and the formation of germyl and digermyl radicals as shown in Scheme 1.



Scheme 1

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