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Reactivity, absorption and emission of dimethylgermylene photo-generated from dodecamethylcyclohexagermane *

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Abstract

The UV photolysis of dodecamethylcyclohexagermane (**1**) in cyclohexane at room temperature proceeds readily with loss of dimethylgermylene species to give two of the lower homologs, decamethylcyclopentagermane (**2**) and octamethylcyclotetragermane (**3**). The photochemically generated dimethylgermylene species reacts with 2,3-dimethylbuta-1,3-diene or CCl_4 to give 1,1,3,4-tetramethyl-1-germacyclopent-3-ene or trichloromethyldimethylchlorogermane, respectively. The transient absorption of **1** in cyclohexane at 450 nm obtained by laser flash-photolysis is due to dimethylgermylene. The reaction rates of dimethylgermylene with some substances are examined. In 3-methylpentane glass dimethylgermylene shows an absorption band at 430 nm and a fluorescence peak at 650 nm. The photo-generated germylene appears to be the singlet ground state.

Introduction

The photolysis of organopolysilane compounds containing a silicon-silicon σ bond constitutes a very active research area [1]. One of the reactive intermediates observed in such photolysis contains divalent silicon species, silylenes. The photolysis of dodecamethylcyclohexasilane was first reported by Ishikawa and Kumada [2]. The generation of dimethylsilylene was accompanied by the formation of two homologs, namely decamethylcyclopentasilane and octamethylcyclotetrasilane. West and co-workers were the first to record the UV-visible spectrum of dimethylsilylene (λ_{max} 450 nm) generated from dodecamethylcyclohexasilane at 77 K [3]. The laser flash-photolysis technique was also applied by Nazaran et al. [4] and by Gasper et al. [5]. They studied the kinetics of the reactions of dimethylsilylene with various trapping agents. Recently, Sizuka et al. have presented the transient absorption (λ_{max} 470 nm) and its reaction kinetics [6]. Emission properties of dimethylsilylene

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* Dedicated to Professor H. Sakurai on the occasion of his 60th birthday.

were also described [3,6]. Levin et al. have reported on complexation of dimethylsilylene from dodecamethylcyclohexasilane with compounds containing a lone pair of electrons and its reaction kinetics [7].

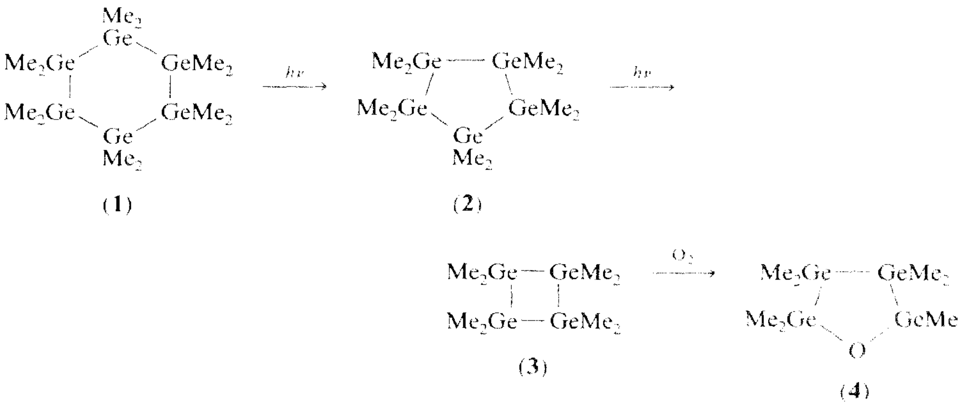
However, there have been few reports on photochemical studies on a germanium analogue, dodecamethylcyclohexagermane, prepared first by Nefedov et al. [8]. Carberry et al. have investigated photochemical reactions of dodecamethylcyclohexagermane, in which generation of dimethylgermylene is accompanied by the formation of the lower homolog, decamethylcyclopentagermane [9]. As far as we know, no photochemical studies on dodecamethylcyclohexagermane have been reported since Cohen's work. However, a few spectroscopic data on simple organogermylenes generated from different precursors have appeared [10–18].

In the course of a study on the photochemical reactions of organopolygermane compounds [19–21] we have investigated the absorption and emission properties of germylenes formed from dodecamethylcyclohexagermane. This paper reports on the transient absorption and reaction kinetics of dimethylgermylene obtained by laser flash-photolysis at 266 nm and 293 K, and also on the absorption and emission properties of dimethylgermylene produced by photolysis at 254 nm (steady-state irradiation) in 3-methylpentane at 77 K.

Results and discussion

Photochemical reactions of dodecamethylcyclohexagermane at 293 K

Irradiation of cyclohexane solutions of dodecamethylcyclohexagermane (**1**) with a 110-W low-pressure Hg arc lamp (254 nm, spiral type) at room temperature under argon gave several products. These products included two of the lower permethylated cyclopolygermanes, namely decamethylcyclopentagermane (**2**), octamethylcyclotetragermane (**3**), and unidentified high-boiling products containing germanium. Sometimes an unexpected compound, 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetragermacyclopentane (**4**) was formed.



The formation of compound **4** may be ascribed to accidental oxidation of the cyclopentagermane (**3**) by oxygen which could not be excluded completely during photolysis and/or the subsequent work-up.

Prolonged irradiation of cyclohexane solutions containing **1** led to an increased yield of the cyclotetragermane (**3**). The photochemical degradation of **1** to **2** to **3** is

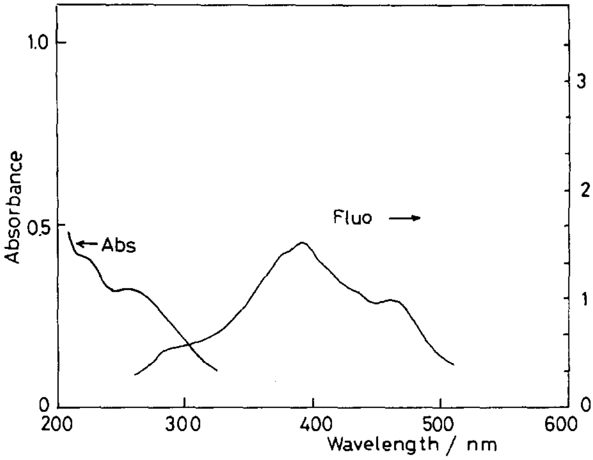


Fig. 1. Absorption and emission spectra of dodecamethylcyclohexagermane in cyclohexane at 293 K.

pictured as involving loss of the dimethylgermylene intermediate. The present photolysis of **1** is very useful in photo-generation of dimethylgermylene.

In order to obtain more information on photochemical degradation of **1**, use was made of reactive intermediates-trapping techniques. A cyclohexane solution of **1** containing ca 20 molar equivalents of 2,3-dimethylbuta-1,3-diene was similarly irradiated to produce the usual product of germylene trapping, 1,1,3,4-tetramethyl-1-germacyclopent-3-ene in 12% yield, based on the amount of **1** consumed. The conversion yields of **1** decreased with increasing concentration of the butadiene. This is in contrast to reported thermal reactions of dimethylgermylene; it may suggest that the lowest excited singlet state of **1** (S_1) is quenched by the 2,3-dimethylbuta-1,3-diene prior to the formation of dimethylgermylene from S_1 of **1**.

To clarify the effect of conversion yield of **1** upon the concentration of diene, studies of the fluorescence spectrum of **1** were made. The absorption and fluorescence spectra of **1** are shown in Fig. 1. The fluorescence spectrum of **1** excited at 250 nm has a maximum at 293 nm. Upon addition of 2,3-dimethylbuta-1,3-diene, the fluorescence intensity of **1** decreases with increasing concentration of the diene. The relative fluorescence quantum yields (ϕ_0/ϕ_q) of S_1 of **1** against the concentrations of the diene are shown in Fig. 2, where ϕ_0 and ϕ_q denote the fluoroscence quantum yields of S_1 emissions of **1** in the absence of the diene and in the presence of the diene, respectively. The value of the slope is taken to be 6.67 (M^{-1}). An analysis using the relationship estimated by Fig. 2 has revealed that about 60% of the lowest excited singlet state of **1** is quenched by the 2,3-dimethylbuta-1,3-diene (concentration ca 290 mM) before the formation of dimethylgermylene.

Furthermore, the value of the slope obtained in Fig. 2 corresponds to $k_q\tau_s$, where k_q is the quenching rate constant and τ_s is the life time of the lowest excited singlet state. Assuming that k_q is almost equal to the diffusion controlled constant of cyclohexane ($k_{diff} = 6.9 \times 10^9\ M^{-1}\ s^{-1}$), the life time of the lowest excited singlet state of **1** (τ_s) is roughly estimated to be 1 ns.

In the presence of carbon tetrachloride, photolysis of **1** in cyclohexane afforded dimethyldichlorogermane in 41% yield. The formation of dimethyldichlorogermane may be a result of thermal decomposition of trichloromethyldimethylchlorogermane

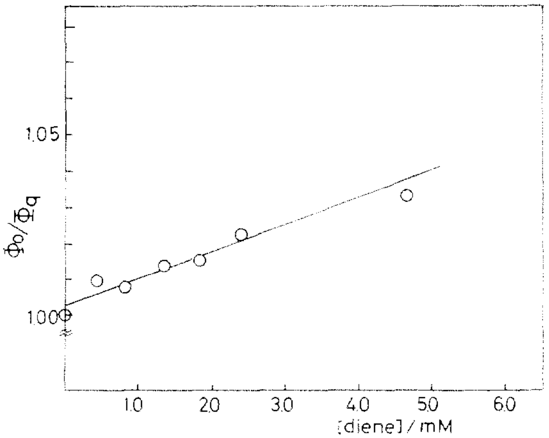


Fig. 2. Stern–Volmer plots for the quenching of the fluorescence of the cyclohexagermane with 2,3-dimethylbuta-1,3-diene at 293 K.

produced by insertion of dimethylgermylene into the C–Cl bond of carbon tetrachloride [14,23] or chlorine abstraction from carbon tetrachloride by dimethylgermylene as shown in the silicon cases [24]. No reaction of dimethylgermylene with methanol proceeded under these reaction conditions. This result contrasts sharply with that of silylenes [19,20]: it is well known that silylenes react effectively with methanol to give methoxysilanes.

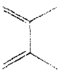
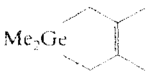
The photochemical results of **1** are summarized in Table 1. In order to obtain more information on the reactive intermediates and primary photochemical processes, laser flash-photolysis at 293 K and matrix isolation at 77 K of **1** were also carried out.

Transient absorption spectra of dimethylgermylene obtained by laser flash-photolysis

The UV absorption spectrum of a cyclohexane solution of the cyclohexagermane **1** is shown in Fig. 1. Nanosecond transient absorption spectra measurements were

Table 1

Photoreactions of dodecamethylcyclohexagermane at 293 K

Run No.	Time (min)	Substrate	Products (yield (%))			Recovery (%)
			$(Me_2Ge)_5$	$(Me_2Ge)_4$ or $(Me_2Ge)_4O$	other	
1	30	none	45	8		46
	60		54	26		20
	90		41	48		11
	120		47	45		9
2	30		18	0	 12	80
3	30	CCl_4	45	0	Me_2GeCl_2 41	47
4	30	MeOH	20	0		76

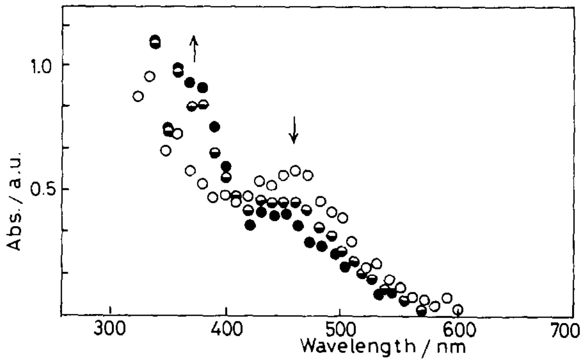


Fig. 3. Transient absorption spectra after photoexcitation of the cyclohexagermane at 293 K. ○ 200 ns; ◒ 1 μs; ● 2 μs.

performed on the degassed solutions containing **1** at 293 K using the fourth harmonic pulse on a Nd : YAG laser as the exciting light source ($\lambda = 266$ nm) [25].

The time dependence of absorbance of the transient absorption $A(t)$ was measured with cyclohexane solution containing **1**. The $A(t)$ curves were measured in the wavelength region of 300–700 nm. The time resolution of the apparatus was about 10 ns. The transient absorption spectra with a peak at 450 nm were obtained as shown in Fig. 3 [26]. As shown there, a transient peak at 450 nm disappeared, resulting in the build-up of a transient peak around 370 nm. An isosbestic point was observed at 400 nm. It is therefore clear that the 370 nm transient is not due to the primary photo-product of **1**. The transient peak at 450 nm may be ascribed to dimethylgermylene from a comparison of spectral characteristics with those reported for the dimethylgermylene (λ_{max} 420–450 nm) [14,19–21]. The transient peak at 450 nm of dimethylgermylene decayed under second-order kinetics ($k/\epsilon = 2.7 \times 10^7$ at 450 nm). Here k is the rate constant for the second-order decay and ϵ is the molar extinction coefficient. This is substantiated further by quenching experiments with germylene trapping agents. The transient arising from **1** in cyclohexane in the presence of a large excess of 2,3-dimethylbuta-1,3-dient and CCl_4 decayed with pseudo first-order kinetics. Rate constants for disappearance of the transient at 450 nm obtained from these quenching experiments (diene and CCl_4) were 2.2×10^7 M^{-1} s^{-1} and 4.9×10^8 M^{-1} s^{-1}, respectively. The present result for butadiene is well consistent with that of dimethylgermylene generated from photolysis of 1,3-diphenylhexamethyltrigermane reported previously [20]. The transient absorption peak at 450 nm was rapidly quenched by oxygen. The rate constants obtained in this study are listed in Table 2.

The transient absorption at 370 nm resulted from disappearance of that at 450 nm. The former may be ascribed to tetramethyldigermene, $Me_2Ge{=}GeMe_2$.

$$\underset{\lambda_{max}\ 450\ \mathrm{nm}}{2\ Me_2Ge:} \longrightarrow \underset{\lambda_{max}\ 370\ \mathrm{nm}}{Me_2Ge{=}GeMe_2}$$

Such dimerization of germylenes to digermenes was observed with UV [11] and IR [18]. The transient absorption at 370 nm decayed under second-order kinetics ($k/\epsilon = 3.9 \times 10^6$), suggesting the formation of cyclotetragermane. Rate constants

Table 2

Rate constants for disappearance of the transients produced by photolysis of the dodecamethylcyclohexagermane in cyclohexane at 293 K

Transient absorption λ_{max} (nm)	k/ϵ [a]	Rate constant (M^{-1} s^{-1})		
		O_2	CCl_4	
450	2.7×10^7	9.7×10^8	4.9×10^8	2.2×10^7
370	3.9×10^6	2.8×10^8	$< 10^7$	[b]

[a] k is the rate constant of second-order decay and ϵ is the corresponding molar extinction coefficient.
[b] Rate constant is too weak to be determined.

for disappearance of the transient at 370 nm are also summarized in Table 2. To the best of our knowledge, these are the first kinetics data for digermenes.

UV absorption spectra of dimethylgermylene obtained by matrix isolation studies at 77 K

The matrix isolation technique has been widely used in the observation of reactive species. Irradiation of **1** in rigid 3-methylpentane (3-MP) at 77 K with a 500-W xenon lamp or a 110-W low-pressure Hg arc lamp produced yellow glass with a broad band at 430 nm as shown in Fig. 4. The absorption peak at 430 nm is blue-shifted compared with the peak at 450 nm observed in the transient absorption at 293 K. After 30 min irradiation, the absorption maximum at 430 nm was distinctly visible and disappeared immediately on melting the matrix. The yellow species with the λ_{max} at 430 nm can be assigned to the dimethylgermylene from

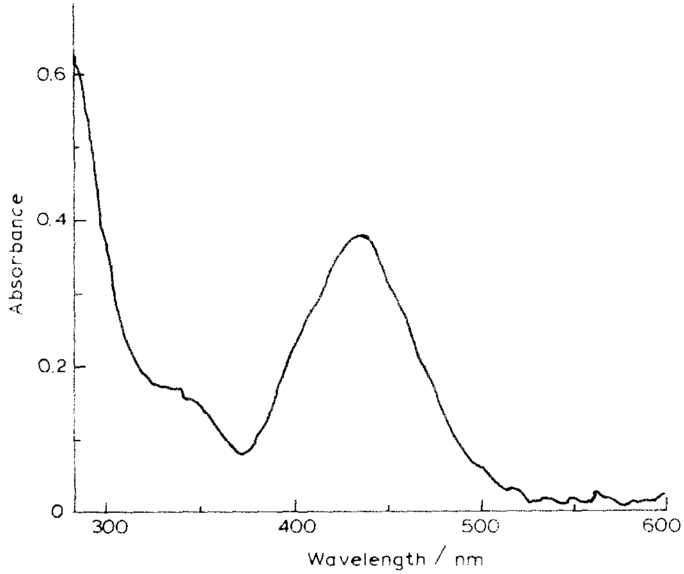


Fig. 4. UV absorption of cyclohexagermane in 3-methylpentane glass at 77 K.

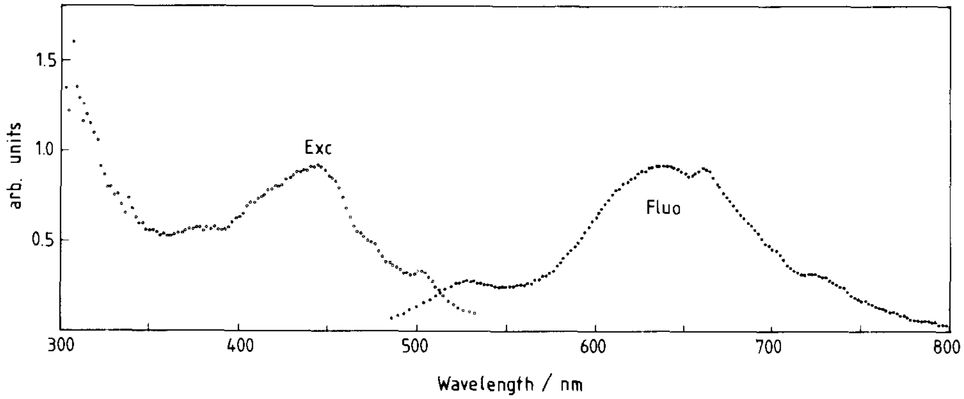


Fig. 5. Emission (Fluo) and excitation (Exc) spectra of dimethylgermylene in 3-MP glass at 77 K.

comparison of spectral characteristics with those of the dimethylgermylene reported previously (λ_{max} 420, 430 nm) [10,11,14].

Emission properties of dimethylgermylene in 3-MP glass at 77 K

In the photolysis of 3-MP glass containing **1** at 77 K by irradiation of a 500-W xenon lamp, the emission spectrum of dimethylgermylene was first observed. Figure 5 shows the excitation and emission spectra of dimethylgermylene. The absorption band at 430 nm may be due to the $S_1 \leftarrow S_0$ transition in dimethylgermylene, where S_0 is the singlet ground state. The emission of dimethylgermylene with a peak at 650 nm is observed in 3-MP glass at 77 K. The excitation spectrum monitored at 650 nm coincides with the absorption spectrum of dimethylgermylene. A good mirror-image relationship exists in the absorption and emission spectra of dimethylgermylene with a stokes shift of 7870 cm^{-1}. It may be justified to conclude that the emission of dimethylgermylene at 650 nm corresponds to the $S_1 \rightarrow S_0$ radiative transition. The 0–0 transition energy in dimethylgermylene is estimated to be 55.3 kcal mol^{-1} from the position of absorption (430 nm, 66.6 kcal mol^{-1}) and emission peaks (650 nm, 44.0 kcal mol^{-1}). Barthelat et al. have reported that the excited S_1 and T_0 states of dimethylgermylene are theoretically predicted to lie 50.9 and 13.7 kcal mol^{-1} above the S_0 ground state, respectively, where T_0 is the triplet ground state [27]. The experimental value of 55.3 kcal mol^{-1} of dimethylgermylene is virtually the same as the theoretical value for 0–0 S_1–S_0 transition energy. A relatively large Stokes shift of 7870 cm^{-1} for dimethylgermylene may be attributed to a conformational change in the C–Ge–C bond angle of dimethylgermylene between the lowest excited singlet state S_1 (122.0°) and the ground state (S_0) (97.8°) [27].

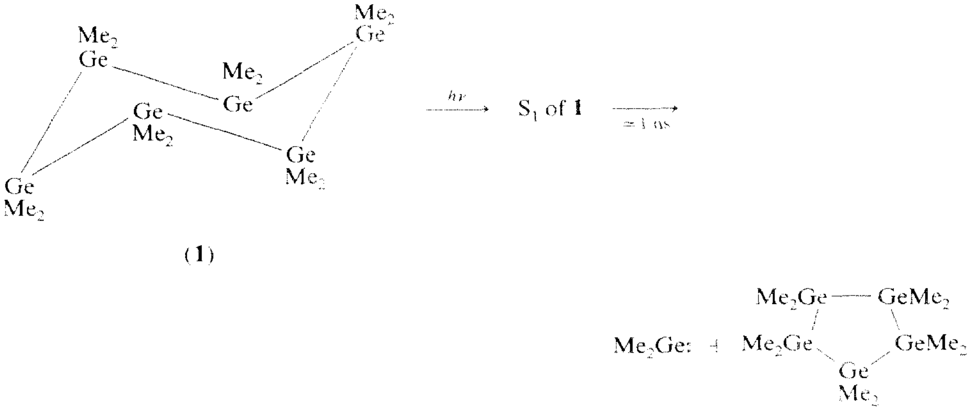
The life time of emission of dimethylgermylene was observed to be 1–2 ns in 3-MP glass at 77 K for the first time.

ESR studies of dimethylgermylene in cyclohexane at 77 K and 10 K

In order to clarify the electric state of dimethylgermylene from **1**, ESR measurements were carried out at 77 K and 10 K. No triplet ESR signal was obtained for dimethylgermylene in rigid cyclohexane at 77 K and 10 K. Thus, the photo-generated germylene should be the singlet ground state. This result is consistent with that of the calculation by Barthelat et al. [27]: the germylene of singlet state is more stable than the triplet one. The ESR spectra ($g = 2.014$, $\Delta H_{1/2} \approx 5$ mT) due to some organogermyl radicals were observed with moderate intensities in the photolysis of **1**.

Photodecomposition mechanism of dodecamethylcyclohexagermane

The photochemical decomposition of **1** proceeds from S_1 of **1**, resulting in the formation of dimethylgermylene and cyclopentagermane (**2**). Assuming spin conservation within the life time of the emission of **1** (ca. 1 ns), dimethylgermylene is expected to be in the singlet state. In fact, no ESR signals due to the triplet state of dimethylgermylene were observed.



(**1**)

(**2**)

The formation of cyclopentagermane (**2**) from **1** may be explained by the simple extrusion of dimethylgermylene, or by bigermyl radicals generated by germanium–germanium bond homolysis. However, we have no data to elucidate the formation of **2**.

Conclusion

The photolysis of dodecamethylcyclohexagermane involves ring contraction of their skeletal germanium–germanium chain with loss of divalent germanium species, dimethylgermylene. The photo-generated dimethylgermylene is thought to be produced through the singlet state of the cyclohexagermane and is the singlet ground state.

Experimental section

^{1}H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as the internal standard. GC-MS spectra were obtained with a JEOL JMX-DX 303 mass spectrometer. Gas chromatography was performed on a Shimazu GC-6A and 8-A with 1-m 10% SE30 columns.

Materials. 2,3-Dimethylbuta-1,3-diene, CCl_4, and methanol were commercially available. $(Me_2Ge)_6$, m.p. 229 °C [9], $(Me_2Ge)_5$, m.p. 170–173 °C [9], $(Me_2Ge)_4$ [11],

$(Me_2Ge)_4O$ [11], Me_2GeCl_2, b.p. 123° C [28] and 1,1-dimethyl-1-germacyclopenta-3-ene [29] were prepared as described in the cited references.

Solvent. Cyclohexane was distilled from sodium/benzophenone under argon. 3-Methylpentane was dried over calcium chloride and distilled under argon.

Photochemical reactions of dodecamethylcyclohexagermane at 293 K

The cyclohexagermane (ca 52.6 mg, 0.085 mmol) was dissolved in dry cyclohexane (6 cm^3) in a quartz tube. The tube was degassed in vacuum and filled with argon. The sample was irradiated with a 110-W low-pressure Hg arc lamp (Sen Tokushu Kogan Co., Ltd.) at room temperature for 30 min. After irradiation, the photo-products were identified by comparing the retention times on GLC and GC-MS with those of authentic samples. Decamethylcyclopentagermane, $(Me_2Ge)_5$, and octamethyltetragermane, $(Me_2Ge)_4$, were formed in 45 and 8% yields, respectively.

Photochemical reactions of dodecamethylcyclohexagermane in the presence of trapping agents

As a representative example, photolysis of a cyclohexane solution of dodecamethylcyclohexane containing 2,3-dimethylbuta-1,3-diene is described. The cyclohexagermane (52.4 mg, 0.085 mmol) and 2,3-dimethylbuta-1,3-diene (140.8 mg, 1.71 mmol) were dissolved in dry cyclohexane (6 cm^3) in a quartz tube. The tube was degassed in vacuum and filled with argon. The sample was similarly irradiated and the photo-products were determined by GLC and GC-MS.

Time-resolved optical absorption

The samples contained in quartz cells with an optical length of 5 cm were degassed by four freeze–pump–thaw cycles. The concentration of the cyclohexagermane was ca 10^{-3} *M*. Laser flash-photolysis experiments were performed at room temperature using the fourth harmonic (266 nm) of a Quanta-Ray DCR-11 Nd : YAG laser as an exciting light source. The laser pulse width was about 5 ns. The details of the laser photolysis apparatus have been published elsewhere [15]. The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and stored in an Iwatsu DM-901 digital memory (10 ns/point, 8 bit) controlled by a NEC PC 8801 microcomputer.

Matrix isolation of the cyclohexagermane at 77 K

The cyclohexagermane (ca 0.1 m*M*) was dissolved in 3-MP and sealed in vacuum in a quartz cell connected to a Pyrex tube. The cell was introduced into an Oxford cryostat. The sample was cooled to 77 K and irradiated with a 500-W xenon lamp or 110-W low-pressure Hg arc lamp. The UV spectra were recorded on a JASCO Ubest 50 spectrometer.

Emission spectrum in 3-MP at 77 K

The sample preparation procedure was the same as in the matrix isolation measurement. The cell was introduced into a quartz dewar with liquid nitrogen. The cell was irradiated with a 500-W xenon lamp for photolysis of 3-MP glass containing **1**. The emission and excitation spectra were measured with a Hitachi MPF 2A fluorescence spectrometer. The life time of the emission was measured with a sampling type streak camera (Hamamatsu, OOS-01). Dye laser (Lambda Physik, FL3002) pumped by XeCL excimer laser (Lambda Physik, EMG 101 MSC) was used as the exciting light source, pulse duration of this laser, also measured with the streak camera, was 3 ns. Emission life time was computed by deconvolution using a microcomputer (Epson, PC-286VS).

ESR measurement

ESR signals were recorded on a JEOL FE-2X ESR spectrometer at 77 K and 10 K. Temperature was controlled with an Oxford CF 204 continuous flow cryostat. Samples were irradiated at 77 K with a 500-W high-pressure Hg arc lamp.

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