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Photochemistry of aryl-substituted trigermanes. Generation and mechanism of formation of germynes

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Abstract

Photochemical reactions of aryl-substituted trigermanes have studied by trapping experiments, matrix isolation, and laser flash-photolysis techniques. Photolysis of the phenylated trigermanes involved both the simple extrusion of germynes and the formation of germynyl radicals and digermynyl radicals. The photochemically generated germynes react with 2,3-dimethylbutadiene or CCl_4 to give germacyclopentenes or trichloromethylchlorogermanes, respectively. The germynyl radicals and digermynyl radicals abstract chlorine atoms from CCl_4 to produce chlorogermanes and chlorodigermanes. Two well-separated transient absorption bands (320–330 and 420–450 nm) obtained by laser flash-photolysis of the trigermanes in cyclohexane at 293 K were found to be due to phenylated digermynyl radicals and germynes, respectively. The rates of the reactions of phenylated digermynyl radicals and germynes with some substrates have been examined. In 3-methylpentane, glass germynes show an absorption band at 420–462 nm. The mechanism is discussed.

Introduction

The photochemistry of organopolysilanes having a $\sigma(\text{Si}-\text{Si})-\pi(\text{C}-\text{C})$ conjugated system has been the subject of considerable attention because of unexpected reactivity and interest of resulting products [1–3]. However, there have been few reports on photochemical studies of the germanium analogues. Masamune et al [4] and Ando et al [5] have studied photolysis of cyclic aryl-substituted trigermanes, in which generation of germynes is characterized. The generation of germynes produced by photolysis of another type of cyclic trigermanes [6] and dodecamethylcyclohexagermanes [7,8] has been also reported. Photolysis of polygermylmercury has been studied by Mazerolles et al [9] and Satgé et al [10].

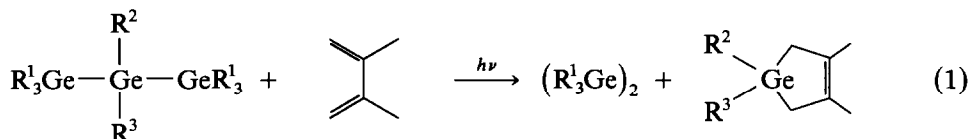
We previously reported that phenylated digermanes cause germanium–germanium bond homolysis which leads to the formation of germynyl radicals and germynes

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[11], and in a preliminary report we have described the photolysis of phenyl-substituted trigermanes [12]. In continuation of this study, we describe herein the first photoreaction of three phenyl-substituted trigermanes: $(\text{PhMe}_2\text{Ge})_2\text{GeMe}_2$ (**1**), $(\text{Me}_3\text{Ge})_2\text{GePhMe}$ (**2**), and $(\text{Me}_3\text{Ge})_2\text{GePh}_2$ (**3**). Laser flash-photolysis, matrix isolation techniques, and trapping experiments of the phenylated trigermanes involved both the simple extrusion of germynes and the formation of germyl radicals and digermyl radicals.

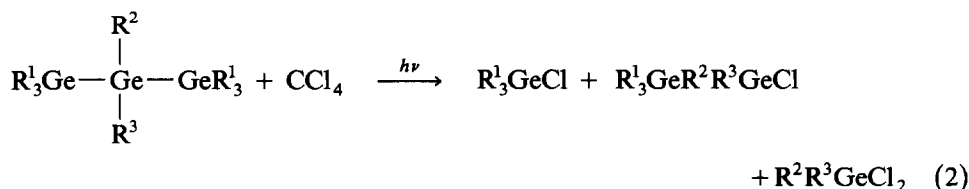
Results and discussion

Photoreactions of phenyl-substituted trigermanes. Irradiation of the phenylated trigermanes, $(\text{PhMe}_2\text{Ge})_2\text{GeMe}_2$ (**1**), $(\text{Me}_3\text{Ge})_2\text{GePhMe}$ (**2**), and $(\text{Me}_3\text{Ge})_2\text{GePh}_2$ (**3**), in cyclohexane with a 110-W low-pressure Hg arc-lamp at room temperature for 1 h gave the digermanes: $(\text{PhMe}_2\text{Ge})_2$ (33%) for **1**, and $(\text{Me}_3\text{Ge})_2$ (in 25% and 40%) yields for **2** and **3**, together with high-boiling unidentified products containing germanium. Cyclohexane solutions of **1–3** and a large excess of 2,3-dimethylbutadiene, a germylene trapping agent, were similarly irradiated to give digermanes and expected products, germacyclopentenes (in 18–33% yield), as main products. 3-Butenylgermyl derivatives were also detected as minor products by GC-MS. Formation of germacyclopentenes suggests the intermediacy of germynes [13].



Photolysis of cyclohexane solutions of **1–3** containing carbon tetrachloride afforded chlorogermanes, chlorodigermanes, and dichlorogermanes, PhMe_2GeCl , $\text{PhMe}_2\text{GeMe}_2\text{GeCl}$, and PhMeGeCl_2 , respectively, together with hexachloroethane for **2**. The formation of chlorogermanes and chlorodigermanes indicates the intermediacy of the germyl radical and digermyl radical produced by germanium-germanium bond homolysis of phenylated trigermanes.

The formation of dichlorogermane can be rationalized as evidence for the conversion of germynes [14,15]. Thus, germynes insert into the C–Cl bond of









CCl_4 to give trichloromethylchlorogermane. This chlorogermane is thermally unstable to decompose dichlorogermane and dichlorocarbene.

Photolysis of **1–3** in cyclohexane containing ethanol gave a trace amount of ethoxymonogermanes. Thus, the ethoxymonogermanes are probably formed by alcoholysis of phenylated trigermanes **1–3** or unstable germanium-carbon double bonded species, germenes. Germenes are produced by disproportionation of germyl radicals and digermyl radicals generated from **1–3**. However, the mechanism of formation of ethoxygermanes is unclear at this moment. The results of photochemical reactions of **1–3** in cyclohexane are summarized in Table 1.

Table 1

The results of photochemical reactions of the trigermanes 1–3

Trigermane	Substrate	Main products (yield (%))
(PhMe ₂ Ge) ₂ GeMe ₂ (1)	none	(PhMe ₂ Ge) ₂ (33)
		(PhMe ₂ Ge) ₂ (36), Me ₂ Ge  (18)
(Me ₃ Ge) ₂ GePhMe (2)	CCl ₄	(PhMe ₂ Ge) ₂ (10), PhMe ₂ GeCl (81) PhMe ₂ GeMe ₂ GeCl (52), Me ₂ GeCl ₂ ^a
	EtOH	(PhMe ₂ Ge) ₂ (37), PhMe ₂ GeOEt (6)
	none	(Me ₃ Ge) ₂ (25)
(Me ₃ Ge) ₂ GePh ₂ (3)		(Me ₃ Ge) ₂ (39), PhGe  (32)
	CCl ₄	(Me ₃ Ge) ₂ (9), Me ₃ GePhMeGeCl (29), Me ₃ GeCl ^a , PhMeGeCl ₂ (7)
	EtOH	(Me ₃ Ge) ₂ (40), Me ₃ GeOEt (trace)
(Me ₃ Ge) ₂ GePh ₂ (3)	none	(Me ₃ Ge) ₂ (40)
		(Me ₃ Ge) ₂ (46), Ph ₂ Ge  (22)
	CCl ₄	(Me ₃ Ge) ₂ (17), Me ₃ GePh ₂ GeCl (14) Me ₃ GeCl ^a , Ph ₂ GeCl ₂ (10)
	EtOH	(Me ₃ Ge) ₂ (36), Me ₃ GeOEt (trace)

^a The yield of Me₃GeCl could not be determined. The retention time of Me₃GeCl of GLC partially overlapped with that of CCl₄ and cyclohexane.

In order to obtain more information on the reaction intermediates and primary photochemical processes, laser flash-photolysis at 293 K and matrix isolation studies of phenylated trigermanes 1–3 were also carried out.

Matrix isolation studies of the trigermanes at 77 K. The matrix isolation technique has been widely used in the observation of reactive species [16]. Irradiation of phenylated trigermanes 1–3 in rigid 3-methylpentane (3-MP) with a 110-W low-pressure Hg arc-lamp at 77 K produced yellow glasses with broad bands at 422 nm for 1, 456 nm for 2, and 462 nm for 3. These UV spectra from 1–3 are shown in Fig. 1. These bands disappear when the matrix melts. 3-MP matrix containing 1–3 and 2,3-dimethylbutadiene were similarly irradiated to produce yellow glasses. When this matrix was warmed to melt, the color of the matrix disappeared. As a result, germacyclopentenes were detected by means of GC-MS. The yellow species with λ_{\max} at 422, 456, and 462 nm, obtained in this study can be assigned to the germylenes on the basis of trapping experiments and from a comparison of the spectral characteristics with those of the germylenes previously reported [7,15,17]. UV data for the germylenes observed are listed in Table 2. As shown in Table 2, increasing replacement of methyl by phenyl in germylenes results in the red shift. The first transition in the UV-visible spectra of germylenes is due to an $n(\text{Ge}) \rightarrow 4p(\text{Ge})$ excitation. This absorption is shifted to longer wavelength by interaction of $4p(\text{Ge})$ with π^* orbital (benzene) or to longer wavelength by bulky substituents on the phenyl group.

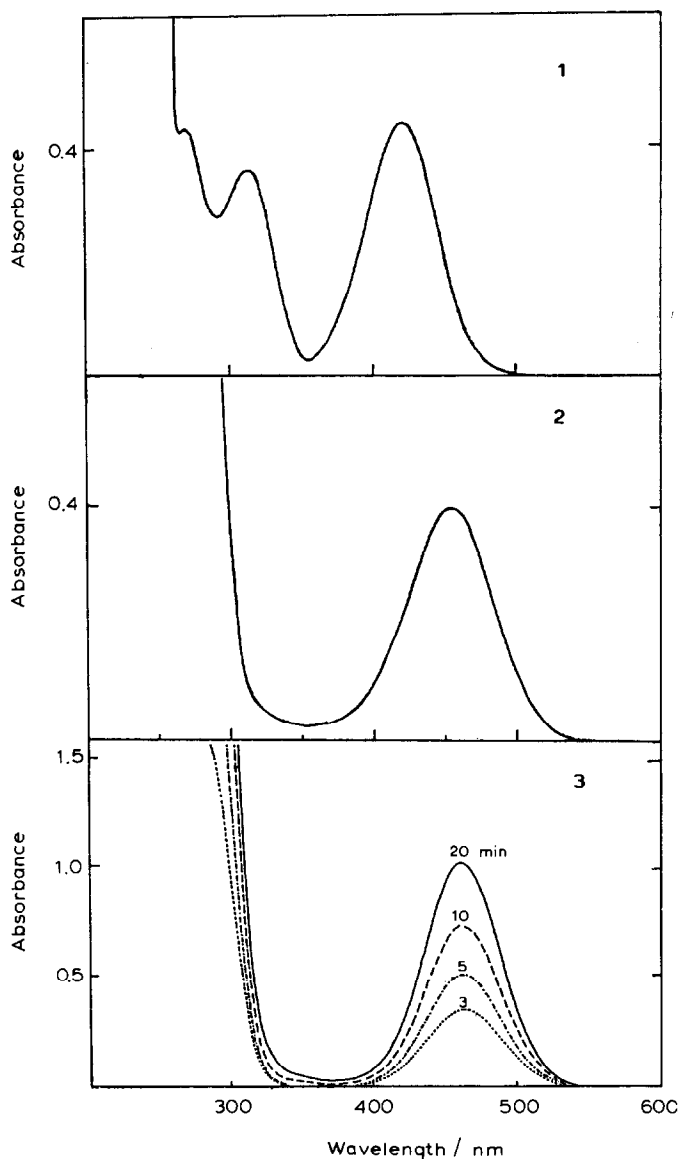


Fig. 1. UV spectra of the germylenes generated from $(\text{PhMe}_2\text{Ge})_2\text{GeMe}_2$ (1), $(\text{Me}_3\text{Ge})_2\text{GePhMe}$ (2), and $(\text{Me}_3\text{Ge})_2\text{GePh}_2$ (3) in 3-MP at 77 K.

Table 2

UV data for germylenes in 3-MP at 77 K

Germylene	λ_{max}	Reference
Me_2Ge :	422	this work
	420, 430	7, 15, 17
PhMeGe :	456	this work
Ph_2Ge :	462	this work
	466	17

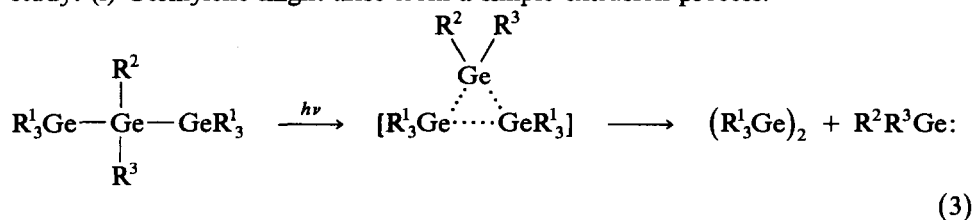
Laser flash-photolysis of the trigermanes at 293 K. Nanosecond transient absorption spectra measurements were performed on the degassed solutions containing 1–3 at 293 K by use of the fourth harmonic pulse of a Nd:YAG laser as the exciting light source [18].

The time dependence on time of the transient absorption $A(t)$ was measured with each of the cyclohexane solutions containing 1–3. The $A(t)$ curves were measured in the region 300–700 nm. Appreciable signals were two well-separated transient absorption bands at 320–330 and 420–450 nm. The rise time was about 10 ns, which was the time resolution of the instrument used. The $A(t)$ curves observed for 1–3 are shown in Fig. 2. The transient at longer wavelength (420–450 nm) can be assigned to the absorption of a germylene by comparing its spectral and chemical properties with those previously reported [12,15,19]. The transients arising from 1–3 in cyclohexane decayed under second-order kinetics, suggesting the formation of digermenes. This is substantiated by quenching experiments with a germylene trapping agent. The transient from 1–3 in cyclohexane in the presence of a large excess of 2,3-dimethylbutadiene, triethylsilane and carbon tetrachloride decayed under pseudo first-order kinetics. Rate constants for the disappearance of the transients at longer wavelength obtained in this study were consistent with those previously reported. The transient, however, was not quenched with ethanol and this is consistent with its chemical properties.

On the other hand, the transient at shorter wavelength (320–330 nm) can be assigned to the absorption of the phenyl-substituted digermyl radicals by comparing its spectral and chemical properties with those generated by photolysis of the hydrodigermanes. For example, laser flash-photolysis of 1,1-diphenyl,2,2,2-trimethyldigermene ($\text{Me}_3\text{GePh}_2\text{GeH}$) gave a transient signal at 320 nm. The transients arising from 1–3 in cyclohexane decayed under second-order kinetics, suggesting the dimerization of germyl radicals. Another transient absorption of alkyl-substituted germyl radicals generated by germanium–germanium bond homolysis is found below 300 nm [20]. The transient absorption at 320 nm was assigned to the digermene by Gaspar et al. [19]. Recently, the transient absorption band of digermene was found to be above 370 nm [21,22*].

The observed decay constants of the transients obtained in this study are listed in Table 3.

Mechanism of germylene formation. Various trapping experiments, matrix isolation, and laser flash-photolysis studies showed the photoreaction of phenylated trigermanes 1–3 to give germylenes, germyl radicals, and digermyl radicals. Germylene can be formed by two processes as deduced from the results obtained in this study: (i) Germylene might arise from a simple extrusion process.



In this process no germyl and digermyl radical formation can be expected.

* A reference number with an asterisk indicates a note in the list of references.

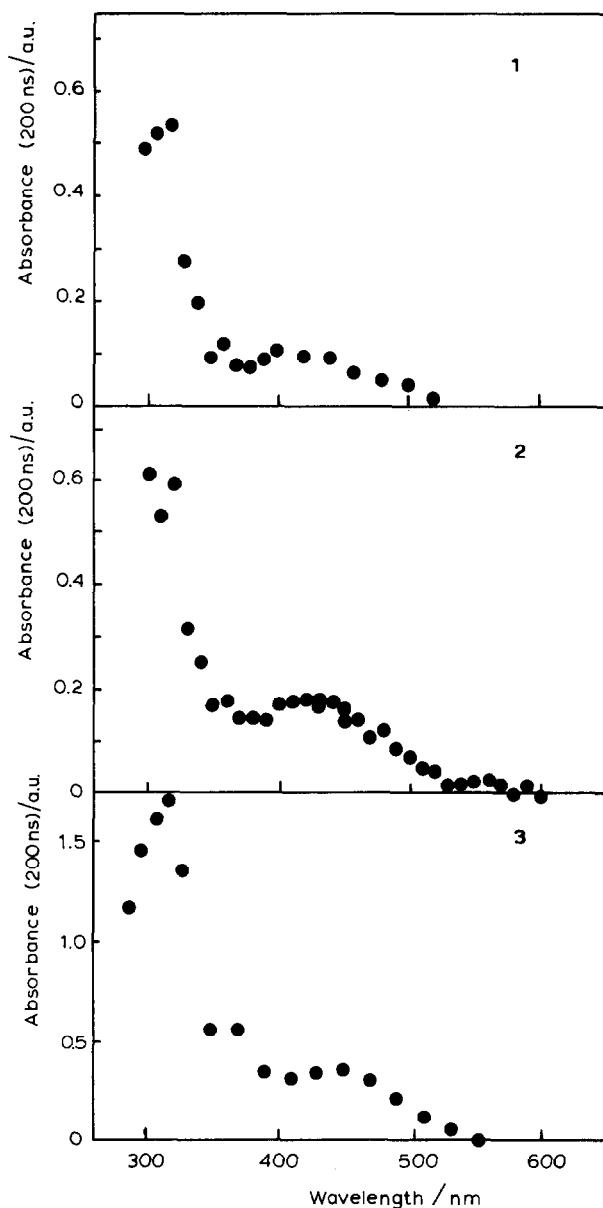


Fig. 2. Transient absorption spectra at 200 ns after photoexcitation of $(\text{PhMe}_2\text{Ge})_2\text{GeMe}_2$ (1), $(\text{Me}_3\text{Ge})_2\text{GePhMe}$ (2), and $(\text{Me}_3\text{Ge})_2\text{GePh}_2$ (3) in degassed cyclohexane solutions at 293 K.

(ii), Germylene might be produced by the photodecomposition of the digermyl radical generated from the homolysis of the germanium–germanium bond in 1–3.

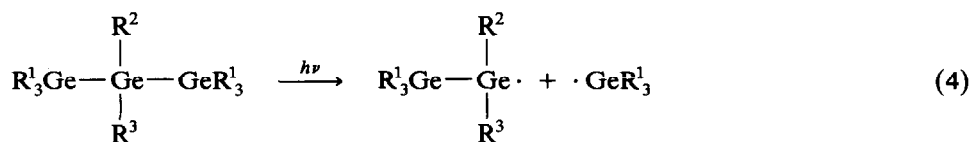

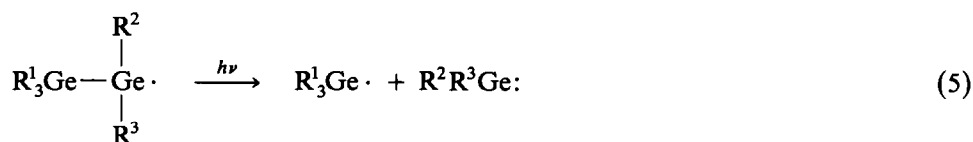


Table 3

Rate constants for the disappearance of the transients produced by photolysis of the trigermans 1–3 in cyclohexane at 293 K

Trigermans	λ_{\max}	k/ϵ^a	Rate constant ($M^{-1} s^{-1}$)			
				Et ₃ SiH	CCl ₄	EtOH
(PhMe ₂ Ge) ₂ GeMe ₂	320	7.0×10^6	no	no	3.2×10^8	no
(1)	420	2.5×10^7	2.4×10^7	4.2×10^6	quenched	no
(Me ₃ Ge) ₂ GePhMe	320	5.5×10^5	no	no	1.3×10^8	no
(2)	440	2.2×10^7	2.2×10^6	4.1×10^6	6.5×10^7	no
(Me ₃ Ge) ₂ GePh ₂	330	4.3×10^5	no	no	7.2×10^8	no
(3)	450	3.0×10^6	7.2×10^5	6.6×10^5	1.5×10^8	no

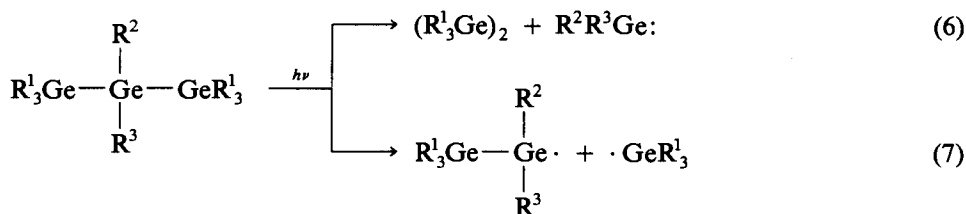
^a k is the rate constant of second-order decay and ϵ is the the corresponding molar extinction coefficient.



To elucidate the mechanism of germylene formation, we carried out the photodecomposition of a digermyl radical by trapping experiments, matrix isolation, and laser flash-photolysis techniques.

Photolysis of cyclohexane solution of phenyltetramethyldigermene, PhMe₂GeMe₂GeH (4), containing CCl₄ with a 110-W low-pressure Hg arc-lamp at room temperature for 1 h quantitatively gave the corresponding chlorodigermene. This result suggests the quantitative formation of phenyltetramethyldigermyl radical. A cyclohexane solution of 4 and a large excess of 2,3-dimethylbutadiene was similarly irradiated but no germacyclopentene was detected. Irradiation of 4 in 3-MP with a 110-W low-pressure Hg arc-lamp at 77 K produced a pale yellow glass with a band at 320 nm. This band immediately disappeared when the matrix melted. A 3-MP solution of the digermene 4 and carbon tetrachloride was similarly irradiated at 77 K to produce a yellow glass. When the matrix was warmed to melt, the color of the matrix disappeared. Phenyltetramethylchlorodigermene (PhMe₂GeMe₂GeCl) was detected by GC-MS. The pale yellow species with λ_{\max} at 320 nm obtained from the digermene 4 was identified as the digermyl radical on the basis of trapping experiments. Successive irradiations of the absorption band due to the digermyl radical, failed to give a signal due to a germylene.

The laser flash-photolysis of 1–3 was carried out at 293 K by a two-step excitation. The 308 nm laser flash-photolysis of the transient at shorter wavelength (320–330 nm) with a decay time of 1 μ s produced by the 266 nm laser flash-photolysis of 1–3 in cyclohexane was performed. However, there was no change in the intensity of either transient. Thus, germynes are not produced via digermyl radicals but via photoexcited state of phenylated trigermene itself under these reaction conditions.



Scheme 1

Consequently, the photolysis of phenylated trigermanes involves both simple extrusion of germynes and the formation of germyle radicals and digermyle radicals resulting from germanium–germanium bond homolysis.

Experimental

^1H NMR spectra were recorded with a Varian FT 80A, with tetramethylsilane as an internal standard. GC-MS spectra were recorded with a JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded with a Hitachi 260-10 spectrometer. UV-visible spectra were recorded on a JASCO Ubest 50 spectrometer. Gas chromatography was performed with a Shimadzu GC-6A and 8A equipped with 2 m 20% SE30 and 3 m 30% Apiezon L columns, Liquid chromatography was performed with a JASCO TWINCLE in a Finepeak SIL C_{18} column.

Material. 2,3-Dimethylbutadiene, CCl_4 , methanol, and ethanol were commercial products $(\text{PhMe}_2\text{Ge})_2\text{GeMe}_2$, bp 145–150 °C/4 Torr [23], $(\text{Me}_3\text{Ge})_2\text{GePhMe}$, bp 90–95 °C/2 Torr [24], $(\text{Me}_3\text{Ge})_2\text{GePh}_2$, bp 150–154 °C/4 Torr [24], $(\text{Me}_3\text{Ge})_2$, bp 137 °C [25], $(\text{PhMe}_2\text{Ge})_2$, bp 170–174 °C/25 Torr [26], 1,1,3,4-tetramethyl-1-germacyclopent-3-ene [27], 1-phenyl-1,3,4-trimethyl-1-germacyclopent-3-ene [38], 1,1-diphenyl-3,4-dimethyl-1-germacyclopent-3-ene [27], Me_3GeCl , bp 98 °C [29], PhMe_2GeCl , bp 90 °C/10 Torr [23], $\text{PhMe}_2\text{GeMe}_2\text{GeCl}$, bp 51–54 °C/4 Torr [23], $\text{Me}_3\text{GePhMeGeCl}$, bp 48–55 °C/4 Torr [23], Me_3GeOEt , bp 100 °C [30], Me_2GeCl_2 , 122 °C [29], PhMeGeCl_2 , bp 60–75 °C/12 Torr [31], Ph_2GeCl_2 , bp. 223 °C/12 Torr [32], and Et_3SiH , bp 108 °C [33] were prepared as described in the cited references.

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

Preparation of phenyldimethylethoxygermane. Phenyldimethylethoxygermane was prepared from phenyldimethylchlorogermane (2.5 g, 10 mmol) and sodium ethoxide (1.4 g, 20 mmol) in ethanol (20 cm^3) at room temperature. The mixture was extracted with ether. Fractional distillation gave the ethoxygermane, bp 38–43 °C/4 Torr; ^1H NMR (δ , CDCl_3) 0.63 (s, 6H), 1.13 (t, J 7.0 Hz, 3H), 3.60 (q, J 7.0 Hz, 2H), 7.27–7.67 (m, 5H); n_D 1.5000; M^+ 226, 211, 181, 167, 151, 123, 103, 90, 79. Anal. Found: C, 53.70; H, 7.20. $\text{C}_{10}\text{H}_{16}\text{GeO}$ calcd. C, 53.42; H, 7.17%.

Preparation of phenyltetramethyldigermane and 1,1,1-trimethyl-2,2-diphenyldigermane. As a representative example, the preparation of phenyltetramethyldigermane is described. Reduction of phenyltetramethylchlorodigermane (1.0 g, 4 mmol) with lithium aluminum hydride (0.2 g, 5 mmol) in ether (20 cm^3) gave the crude digermane, bp 70–85 °C/22 Torr. Pure digermane was obtained by preparative GC (1 m 20% SE30). ^1H NMR (δ , CDCl_3) 0.30 (d, J 2 Hz, 6H), 0.50 (s, 6H),

3.67 (sept., J 2 Hz, 1H), 7.0–7.6 (m, 5H); n_D 1.5466; IR (cm^{-1} , neat) 2000 ($\nu_{\text{Ge-H}}$); M^+ 284, 265, 179, 165, 151, 119, 89. Anal. Found: C, 57.03; H, 8.86%. $\text{C}_{10}\text{H}_{18}\text{Ge}$ calcd. C, 56.97; H, 8.60%. Pure 1,1,1-trimethyl-2,2-diphenyldigermene was also obtained by preparative GC. ^1H NMR (δ , CDCl_3) 0.36 (s, 9H), 4.06 (s, 1H), 7.0–7.5 (m, 10H); n_D 1.5791; IR (cm^{-1} , neat) 2000 ($\nu_{\text{Ge-H}}$); M^+ 346, 331, 268, 243, 228, 181, 165, 151, 119, 87, 78. Anal. Found; C, 66.22; H, 7.52. $\text{C}_{15}\text{H}_{20}\text{Ge}$ calcd. C, 66.02; H, 7.39%.

Preparation of 1,1,1-trimethyl-2,2-diphenylchlorodigermene. A crude chlorodigermene was obtained by chlorodephenylation of 1,1,1-trimethyl-2,2,2-triphenyldigermene [34] with chlorine in carbon tetrachloride at room temperature; bp 65–87°C/3 Torr; NMR (δ , CDCl_3) 0.52 (s, 9H), 7.13–7.79 (m, 10H); n_D 1.5899; M^+ 380, 361, 341, 263, 243, 228, 203, 181, 149, 119, 109, 99, 89, 77, 63.

Photochemical reactions of phenylated trigermenes. The trigermene (ca. 200 mg) was dissolved in dry cyclohexane (6 cm^3) in a quartz tube. The tube was degassed in vacuum and charged with argon. The sample was irradiated with a 110-W low-pressure Hg arc-lamp (Sen Tokushu Kogen Co. Ltd.) at room temperature for 1 h. After irradiation, the photo-products were verified by comparing the retention times on GLC and GC-MS with those of authentic samples.

Time-resolved optical absorption. The samples contained in quartz cells with an optical length of 5 mm were degassed by four freeze–pump–thaw cycles. The concentrations of the trigermenes were ca. 10^{-3} M. Laser flash-photolysis experiments were performed at room temperature by use of the fourth harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser as the exciting light source. The duration of the laser pulse was about 5 ns. The details of the laser photolysis apparatus have appeared elsewhere [18]. The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and recorded by an Iwatsu DM-901 digital memory (10 ns/point, 8 bit) controlled by a NEDC PC 8801 microcomputer. Two-step excitation of the trigermenes was carried out with Nd:YAG and Xe-Cl lasers.

Matrix isolation of the phenylated trigermenes at 77 K. The trigermene (ca. 0.1 mM) was dissolved in 3-MP and sealed in vacuum in a quartz cell connected to a Pyrex tube as the upper part. The cell was introduced into an Oxford cryostat. The sample was cooled to 77 K and irradiated with a 110-W low-pressure Hg arc lamp. The UV spectra were recorded on a JASCO Ubest 50 spectrometer.

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