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Photochemical reactions of germoxanes: generation of germyl and germoxy radicals

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Abstract

Photochemical reactions of phenyl-substituted digermoxanes, $(Ph_nMe_{3-n}Ge)_2O$ (n = 1–3), and a cyclic germoxane, $(Me_2GeO)_4$, have been investigated by chemical trapping and laser flash-photolysis. On irradiation, phenylated digermoxanes undergo homolysis of the germanium–oxygen bond to give germyl radicals and germoxy radicals. In the presence of nonhalogenated solvents, these germyl radicals and germoxy radicals couple to yield digermanes and digermyl peroxides, respectively. In polyhalomethanes (CCl_4, $CHCl_3$, and $BrCCl_3$), germyl radicals are converted to the corresponding halides by abstraction of a halogen atom. Germoxy radicals do not react with polyhalomethanes; they couple to produce digermyl peroxides which decompose to give either a pair of germoxy radicals or germyl radicals and germylperoxy radicals. Photolysis of a cyclic germoxane also results in cleavage of the germanium–oxygen bond.

Key words: Germanium; Digermoxane; Cyclic germoxane; Homolysis; Photochemistry

1. Introduction

Studies of polyorganogermoxanes are very limited compared with those on corresponding siloxanes [1]. Few studies of photochemical reactions of cyclic germoxanes directed towards the formation of germanium–oxygen double bonded species (germanones) resulting in ring contraction have been reported [2].

In this paper, we describe photochemical studies on phenylated digermoxanes and cyclic germoxanes. Laser flash photolysis of these compounds as well as trapping experiments show that irradiation of the digermoxanes breaks the germanium–oxygen bond, generating germyl and germoxy radicals.

2. Results and discussion

2.1. Photoreactions of phenylated digermoxanes and a cyclic germoxane

Aryl-substituted digermoxanes, $(Ph_nMe_{3-n}Ge)_2O$ (**1–3**, n = 1–3 respectively) and a cyclic germoxane, $(Me_2GeO)_4$ (**4**), (*ca.* 0.01–0.1 M) in cyclohexane were irradiated with a 110 W low pressure Hg arc lamp (λ = 254 nm) at room temperature under argon. Photolysis of **1–3** in cyclohexane gave high molecular weight products containing germanium atoms together with benzene. The polymers were shown to have wide molecular weight distributions by means of gel permeation chromatography (GPC). In each case, crude products contained a proportion of relatively high molecular weight materials: $\overline{M}w = 8.6 \times 10^3$ for **1**, 2.0×10^3 for **2**, and 1.2×10^3 for **3**. A typical elution profile from the GPC of **1** is shown in Fig. 1.

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The elemental compositions of the polymers obtained can be roughly determined from the ^{1}H NMR and IR spectra. The ratio phenyl group : methyl group on germanium atoms of polymers can be estimated by the integration of resonances, since the methyl group when attached to a germanium atom appears slightly upfield and resonates in different fields owing to the influence of germanium atoms. The ^{1}H spectra of polymers produced by photolysis of **1**–**3** showed several kinds of methyl groups attached to the germanium atom and the phenyl group : methyl group ratio decreased slightly as compared with the starting digermoxanes. IR spectroscopy showed that the spectra of polymers were similar to those of the digermoxanes, **1**–**3**, which were based on a germanium–oxygen bond framework. The UV spectra of polymers absorbed at slightly shorter wavelengths (λ_{max} = *ca.* 250 nm for **1**–**3**), but the end of these spectra extended even as far as 400 nm.

Similar irradiation of 2,2,4,4,6,6,8,8-octamethyl-1,3,5,7-tetraoxa-2,4,6,8-tetragermacyclooctane (**4**) in cyclohexane with a 110 W low pressure Hg arc lamp gave 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane (14%) and unidentified polymers of high molecular weight. At the same time, a trace amount of 2,2,4,4,6,6,8,8,10,10-decamethyl-1,3,4,7,9-pentaoxa-2,4,6,8,10-pentagermacyclodecane was also detected by means of gas chromatography–mass spectroscopy (GC–MS). Cyclic germoxanes are known to undergo ring contraction with extrusion of germanium–oxygen double bonded species (germanones) and ring expansion included germanones [2]. These photochemical results are summarized in Table 1.

TABLE 1. Photoproducts and yields from the photolysis of the germoxanes, **1**–**4** in cyclohexane [a]. The products were detected by GC–MS

Germoxane	Trapping agent	Photo-products (yield %)
(PhMe$_2$Ge)$_2$O **1**	none	high mw ($\overline{M}w$ = 8.62×10^3, $\overline{M}n$ = 8.57×10^3, $\overline{M}w/\overline{M}n$ = 1.01) (*ca.* 10)
	CCl$_4$	PhMe$_2$GeCl (168), (CCl$_3$)$_2$ (56), CHCl$_3$ ^{b}
	CHCl$_3$	PhMe$_2$GeCl (140), (CHCl$_2$)$_2$ (39), CH$_2$Cl$_2$ ^{b}
	BrCCl$_3$	PhMe$_2$GeCl (trace) PhMe$_2$GeBr (168), (CCl$_3$)$_2$ (157), CHCl$_3$ ^{b}
(Ph$_2$MeGe)$_2$O **2**	none	high mw ($\overline{M}w$ = 1.98×10^3, $\overline{M}n$ = 1.69×10^3, $\overline{M}w/\overline{M}n$ = 1.17) (10)
	CCl$_4$	Ph$_2$MeGeCl (200), (CCl$_3$)$_2$ (trace), CHCl$_3$ ^{b}
	CHCl$_3$	Ph$_2$MeGeCl (104), (CHCl$_2$)$_2$ (34), CH$_2$Cl$_2$ ^{b}
	BrCCl$_3$	Ph$_2$MeGeCl (trace) Ph$_2$MeGeBr (155), (CCl$_3$)$_2$ (128), CHCl$_3$ ^{b}
(Ph$_3$Ge)$_2$O **3**	none	high mw ($\overline{M}w$ = 1.19×10^3, $\overline{M}n$ = 1.01×10^3, $\overline{M}w/\overline{M}n$ = 1.18) (5)
	CCl$_4$	Ph$_3$GeCl (185), (CCl$_3$)$_2$ (25), CHCl$_3$ ^{b}
	CHCl$_3$	Ph$_3$GeCl (180), (CHCl$_2$)$_2$ (47), CH$_2$Cl$_2$ ^{b}
	BrCCl$_3$	Ph$_3$GeCl (trace) Ph$_3$GeBr (85), (CCl$_3$)$_2$ (77), CHCl$_3$ ^{b}
(Me$_2$GeO)$_4$ **4**	none	(Me$_2$GeO)$_3$ (14) (Me$_2$GeO)$_5$ ^{c}
	CCl$_4$	(Me$_2$GeO)$_3$ (23) Me$_2$GeCl$_2$ (43) (Me$_2$GeCl)$_2$O (150) (CCl$_3$)$_2$ (trace), CHCl$_3$ ^{b}
	CHCl$_3$	(Me$_2$GeO)$_3$ (6) Me$_2$GeCl$_2$ (41) (Me$_2$GeCl)$_2$O (172) (CHCl$_2$)$_2$ (118)

[a] Irradiation of 0.01–0.1 M cyclohexane solution with 110 W low pressure Hg arc lamp at room temperature for 3–10 h. The yields of conversion are *ca.* 40–50% for **1**–**4**. [b] Yields cannot be estimated due to the overlapping of the GLC peak of the product with that of the solvent and trapping agents employed.

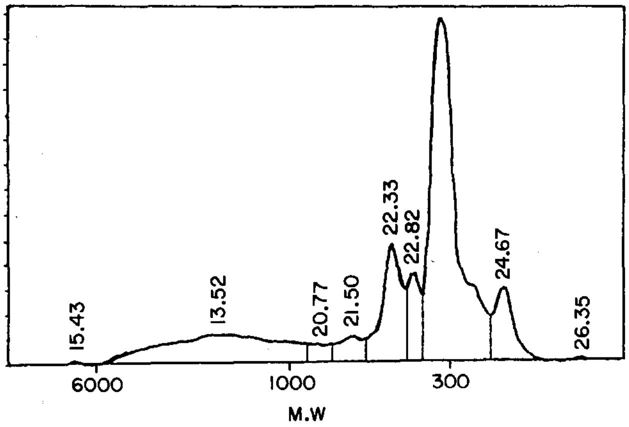

Fig. 1. Elution profile from permeation chromatography of polymers from (PhMe$_2$Ge)$_2$O (**1**). Molecular weights are relative to polystyrene standards.

To obtain possible reactive intermediates in photochemical reactions of digermoxanes, similar photolyses of **1**–**4** were carried out in cyclohexane containing polyhalomethanes (CCl$_4$, CHCl$_3$, and BrCCl$_3$). Germyl radicals effectively and rapidly abstract a chlorine (or bromine) atom from polyhalomethanes to give the corresponding halogermanes [3]. By photolysis of **1**–**3** with polyhalomethanes the corresponding halogermanes were obtained in unexpected high yields as shown in Table 1. As shown in Table 1, photolysis of **1** with CCl$_4$ and CHCl$_3$ gave phenyldimethylchlorogermane in 168% and 140% yields, respectively. With BrCCl$_3$, digermoxane **1** afforded phenyldimethylbromogermane

(168%). A trace amount of phenyldimethylchlorogermane was also detected by means of GC–MS. Cyclohexane solutions of phenylated digermoxanes, **2** and **3**, containing polyhalomethanes were similarly irradiated to afford the corresponding chlorogermanes (or bromogermanes) in all cases in high yields shown in Table 1. Photolysis of a cyclic germoxane **4** with CCl_4 gave tetramethyldichlorodigermoxane (150%), dimethyldichlorogermane (43%), 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane (23%), and other compounds. With $CHCl_3$, germoxane **4** showed similar results.

It is interesting to note that two molar amounts of halogermanes are obtained by photolysis of one molar amount of digermoxanes in the reaction of phenylated digermoxanes, **1–3**, with polyhalomethanes. Thus, two molar amounts of germyl radicals are generated by photolysis of one molar amount of digermoxanes.

Unfortunately, we only detected a small fraction of the theoretical amount of oxygen generated in the reactions of photochemical reactions of digermoxanes.

2.2. *Laser flash-photolysis of phenlyated germoxanes*

Nanosecond transient absorption spectra measurements were performed on the degassed solutions containing **1–3** at 293 K using the fourth harmonic pulse of a Nd:YAG laser ($\lambda = 266$ nm, power 10 mJ/pulse) as an exciting light source [4].

The time dependence of absorbance 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 wavelength region of 300–700 nm. Time resolution of the apparatus was about 10 ns.

Using the A_t curves at various wavelengths, the time-resolved absorption spectra of **1–3** were obtained at 200 ns after laser excitation and are shown in Fig. 2. A transient absorption around 360 nm for **1**, and two separated absorptions both at *ca.* 320–330 nm and 360 nm for **2** and **3** were observed. The signals show a rapid rise and subsequent decay. Careful examination of the transient peak of **1** shows it to have two components (λ_{max} *ca.* 320 and 360 nm). The transient peak at *ca.* 320 nm arising from **1** cannot be observed, apparently because of its molar coefficient being much smaller than that of the other transient peak at $\lambda_{max} =$ 360 nm.

The transient peaks at shorter wavelength ($\lambda_{max} =$ *ca.* 320–330 nm for **1–3**) are reasonably assigned to those of the phenyl-substituted germyl radicals, $Ph_nMe_{3-n}Ge\cdot$ ($n = 1$–3), for the reasons listed. (1) The spectral shapes and peak positions of **1–3**, respectively, agree well with those of the germyl radicals generated by abstraction of hydrogen of the phenylated hydrogermanes ($Ph_nMe_{3-n}GeH$) with *t*-butoxy radicals and other precursors [5,6]. The transient peaks of $Ph_nMe_{3-n}Ge\cdot$ have been reported to be at 315 nm for $n = 1$, 330 nm for $n = 2$, and 330 nm and 332 nm for $n = 3$. (2) The transients from **1–3** in cyclohexane decayed with second-order kinetics ($k/\varepsilon = 7.3$–9.1×10^5; k is the rate constant of second-order decay, ε is the molar extinction coefficient), suggesting dimerization of germyl radicals to give digermanes. The values observed in this study agree with those previously reported within experimental error [5,6]. The decay constants of these transients determined experimentally, are summarized in Table 2. The assignment of the shorter wavelength transient is further substantiated by quenching experiments with carbon tetrachloride, oxygen, and dimethyl-1,3-butadiene. Addition of carbon tetrachloride, an effective radical scavenger [3], quenched the transient absorption as shown in Table 2. The quenching rate constants observed agreed with the values reported for the germyl radicals.

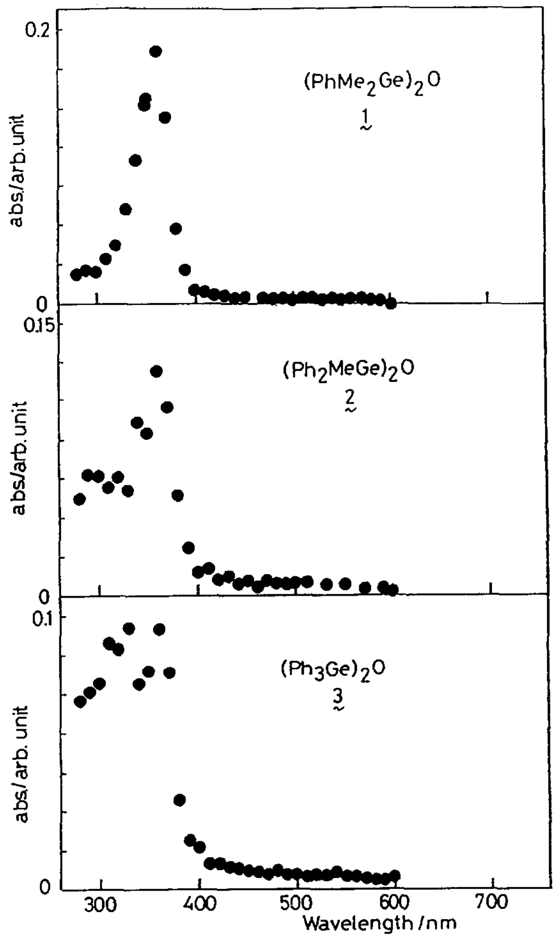

Fig. 2. Transient absorption at 200 ns after photoexcitation of $(Ph_nMe_{3-n}Ge)_2O$ (**1–3**, $n = 1-3$, respectively) in the degassed cyclohexane solution at 293 K.

$$Ph_nMe_{3-n}Ge\cdot + CCl_4 \rightarrow Ph_nMe_{3-n}GeCl + \cdot CCl_3$$

TABLE 2. Rate constants for disappearance in the photolysis of **1–4** in cyclohexane (*ca.* 0.1 M) at 293 K

Germoxane	λ_{max} (nm)	k/ϵ [a] (s^{-1} cm)	Rate constant (M^{-1} s^{-1})		
			O_2	CCl_4	Diene
$(PhMe_2Ge)_2O$	320	9.1×10^5 [b]	2.0×10^9	1.1×10^8	– [d]
1	360	6.5×10^5 [c]	2.3×10^9	not quenched	2.0×10^9
$(Ph_2MeGe)_2O$	320	8.2×10^5 [b]	1.2×10^9	2.0×10^8	– [d]
2	360	1.3×10^6 [c]	2.2×10^9	not quenched	1.4×10^9
$(Ph_3Ge)_2O$	330	7.5×10^5 [b]	1.1×10^9	1.2×10^9	– [d]
3	360	2.5×10^6 [c]	2.6×10^9	not quenched	2.0×10^9

[a] k is the rate constant of second-order kinetics and ε is the molar extinction coefficient. [b] At 330 nm. [c] At 370 nm. [d] The absorption is too weak to permit determination of rate constants.

Similarly, oxygen very rapidly quenched the transient peaks at the shorter wavelength as shown in Table 2. Laser flash photolysis of **1–3** in cyclohexane containing oxygen was also performed. Interestingly, the transients at shorter wavelength ($\lambda_{max} = ca.$ 320–330 nm), due to germyl radicals, disappeared, resulting in the build-up of the transient peaks at the longer wavelengths ($\lambda_{max} = ca.$ 360 nm). Thus, the species at shorter wavelengths react with oxygen to give the species at longer wavelengths.

However, the transient peaks at the longer wavelength in Fig. 2 may be assigned to germoxy radicals. This assignment of transients can be justified for the following reasons. (1) The spectral characteristics of **1–3** agree with those generated by laser flash photolysis of phenylated germyl-*t*-butylperoxide ($Ph_nMe_{3-n}GeOO^tBu$, $n = 1$–3). The formation of the germoxy radical by photolysis of germyl-*t*-butylperoxide has been reported [7]. The spectra of $PhMe_2GeO\cdot$, $Ph_2MeGeO\cdot$, and $Ph_3GeO\cdot$ have not been reported until now. However, the spectral shapes, peak positions, and large molar coefficients ε for **1–3** resemble those generated by photolysis of phenylated germyl-*t*-butylperoxide [8*]

$$Ph_nMe_{3-n}GeOO^tBu \xrightarrow{h\nu} Ph_nMe_{3-n}GeO\cdot + \cdot O^tBu$$

(2) The laser flash photolysis of **1–3** containing oxygen led to the disappearance of the transients at shorter wavelengths, resulting in the build-up of the transient peaks at the longer wavelengths.

$$\begin{array}{ccc} R_3Ge\cdot & \xrightarrow{h\nu,\, O_2} & R_3GeO\cdot \\ \lambda_{max} = 320\text{–}330 \text{ nm} & & \lambda_{max} = ca.\ 360 \text{ nm} \end{array}$$

These transient peaks arising from **1–3** in cyclohexane decayed with second-order kinetics, suggesting dimerization of germoxy radicals to give digermyl peroxides. The transients from **1–3** in cyclohexane in the presence of a large excess of 2,3-dimethyl-1,3-butadiene and oxygen decayed with pseudo first-order kinetics, and the rate constants obtained are also shown in Table 2. However, the transients at the longer wavelengths were not quenched with carbon tetrachloride under reaction conditions.

$$(Ph_nMe_{3-n}Ge)_2O \xrightarrow{h\nu} Ph_nMe_{3-n}Ge\cdot + \cdot OGePh_nMe_{3-n}$$

$$2Ph_nGe_{3-n}Ge\cdot \longrightarrow (Ph_nMe_{3-n}Ge)_2$$

$$2Ph_nMe_{3-n}GeO\cdot \longrightarrow (Ph_nMe_{3-n}GeO)_2$$

$n = 1$–3, **1–3**

Scheme 1.

The values of k/ε in Table 2 increase in the order: $Ph_3Ge\cdot < Ph_2MeGe\cdot < PhMe_2Ge\cdot$ for the phenylated germyl radicals, and $PhMe_2GeO\cdot < Ph_2MeGeO\cdot < Ph_3GeO\cdot$ for the phenylated germoxy radicals respectively. The decrease of k/ε values for $Ph_nMe_{3-n}Ge\cdot$ with increasing number of phenyl groups is explained by the steric hindrance of phenyl group. On the other hand, the increase of values of k/ε for $Ph_nMe_{3-n}GeO\cdot$ with increasing number of phenyl groups may be explained by the electronic effect of phenyl-substituted germyl groups on the oxygen atom.

2.3. *Photochemical mechanism of digermoxanes*

The results of photochemical reactions and laser flash photolysis studies of digermoxanes **1–4** are best rationalized by a homolytic scission of the germanium–oxygen bonds of the digermoxanes as described in Scheme 1.

At first, photolysis of digermoxanes causes germanium–oxygen bond cleavage to yield germyl and germoxy radicals. In nonhalogenated solvents, these germyl and germoxy radicals dimerize to yield digermanes and digermyl peroxides, respectively. In the presence of polyhalomethanes such as CCl_4, $CHCl_3$, and $BrCCl_3$, germyl radicals can abstract a halogen atom to give the corresponding halides. Germoxy radicals, which do not react with polyhalomethanes, couple to produce digermyl peroxides.

Considering the yields of germyl chlorides in the reactions of **1–3** with polyhalomethanes, germyl radicals, which abstract halogen atoms from polyhalomethanes, may be effectively formed by the photolysis of digermyl peroxides. In fact, chemical trapping experiments and laser flash photolysis studies of digermyl peroxides showed both cleavage of (1) germanium–oxygen bonds, and (2) oxygen–oxygen bonds shown in Scheme 2. Germyl peroxy radicals generated from germanium–oxygen bond homolysis decompose to yield germyl radicals and oxygen [8].

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

$$\mathrm{R_3GeOOGeR_3} \longrightarrow \mathrm{R_3Ge}\cdot + \cdot\mathrm{OOGeR_3} \qquad (1)$$

$$\mathrm{R_3GeOO}\cdot \longrightarrow \mathrm{R_3Ge}\cdot + \mathrm{O_2}$$

$$\mathrm{R_3GeOOGeR_3} \longrightarrow \mathrm{R_3GeO}\cdot + \cdot\mathrm{OGeR_3} \qquad (2)$$

Scheme 2.

Consequently, germyl radicals appear to be intermediates in these photochemical reactions.

The bathochromic shift of the observed germoxy radicals relative to that of the corresponding carbon analogue, such as *t*-butoxy radical ($\lambda_{max} = 320$ nm), may be explained by a contribution from the Ge=O resonance structure as follows:

$$\equiv \mathrm{Ge{-}O}\cdot \leftrightarrow \equiv\mathrm{G}\overset{\dot{-}}{\mathrm{e}}{=}\mathrm{O}^{+}$$

3. Experimental details

^{1}H NMR spectra were recorded on a JEOL GX270 using tetramethylsilane (TMS) as the internal standard. GC-MS spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded on a Shimadzu FT IR 4200 spectrometer. UV and UV-Vis spectra were recorded on a Shimadzu 2200 UV spectrometer. Gas chromatography was performed on Shimadzu GC-6A and 8A instruments with 1 m 20% SE30 and 1 m 20% Apiezon L columns. GPC was performed with a Shimadzu HLC-8020.

3.1. Materials

CCl_4, $CHCl_3$, $BrCCl_3$, $(CCl_3)_2$, $(CHCl_2)_2$, $(CBrCl_2)_2$, 2,3-dimethyl-1,3-butadiene, bicyclohexyl, and cyclohexyl chloride were commercially obtained. $(Ph_3Ge)_2O$ [9], $(Me_2GeO)_3$ [10], $(Me_2GeO)_4$ [11], $PhMe_2GeCl$ [12], $Ph_2MeGeCl$ [13], Ph_3GeCl [14], $Ph_2MeGeBr$ [15], Ph_3GeBr [14], Me_2GeCl_2 [16], and $(ClMe_2Ge)_2$ [17] were prepared as described. Cyclohexane for use as solvent was dried over sodium wire and purified by distillation under argon.

3.2. Identification of the photo-products

Photo-products were separated by preparative GLC and their structures assigned by comparing the NMR and GC data of similar compounds previously reported. Crude 1,3-dichlorotetramethyldigermoxane was prepared by oxidation of 1,2-dichlorotetramethyldigermane with *m*-chloroperbenzoic acid, bp. 35°C/35 mmHg, MS *m/z* (%) 275 ($M^+ - Me$) (100), 255 (30), 245 (15), 225 (15), 195 (18), 176 (8), 158 (12), 138 (50), 108 (20), 88 (20), 73 (5). Crude phenyldimethylbromogermane was prepared by bromination of 1,1-diphenyl,2,2,2,2-tetramethyldigermane in carbon tetrachloride, bp. 90–95°C/10 mmHg, MS *m/z* 260 (15), 245 (100), 201 (10), 181 (20), 151 (20), 91 (15), 51 (15).

3.3. Preparation of diphenyltetramethyldigermoxane and tetraphenyldimethylgermoxane

Phenylated digermoxanes in this study were prepared by hydrolysis of the corresponding chlorides. $(PhMe_2Ge)_2O$: bp. 114°C/0.5 mmHg, NMR (δ in $CDCl_3$) 0.47 (s, 6H), 7.34–7.51 (m, 5H), n20 1.5462. Anal. Calcd. for $C_{16}H_{22}G_2O$: C, 51.17; H, 5.91. Found: C, 51.21; H, 6.02%. $(Ph_2MeGe)_2O$: bp. 125°C/0.6 mmHg, mp. 52–54°C, NMR (δ in $CDCl_3$) 0.52 (s, 3H), 7.10–7.29 (m, 10H). Anal. Calcd. for $C_{26}H_{26}Ge_2O$: C, 62.50; H, 5.26. Found: C, 62.48; H, 5.52%.

3.4. Photochemical reactions of phenylated digermoxanes, 1–3, and of a cyclic germoxane (4)

As a representative example, photolysis of diphenyltetramethyldigermoxane, $(PhMe_2Ge)_2O$, is described. The digermoxane (30 mg, 0.08 mmol) was dissolved in dry cyclohexane (4 ml) in a quartz tube. The tube was degassed in vacuum and replaced with argon. The sample was irradiated with a 110 W low-pressure Hg arc lamp (Sen Tokushu Kogen Co. Ltd.) at room temperature for 10 h. After irradiation, the photo-products were identified by comparing the retention times on GLC and GC–MS with those of authentic samples. UV spectra of phenylated digermoxanes, $(Ph_nMe_{3-n}Ge)_2O$ absorbed at 266 nm ($\varepsilon = 406$) for $n = 1$, 266 nm ($\varepsilon = 790$) for $n = 2$, and 266 nm ($\varepsilon = 1560$) for $n = 3$.

3.5. Time-resolved optical absorption

The sample was placed in a quartz cell with an optical length of 5 mm and was degassed by four freeze–pump–thaw cycles. The concentrations of digermoxanes were *ca.* 10^{-1} M. Laser flash photolysis experiments were performed at room temperature by the fourth harmonic ($\lambda = 266$ nm) of a Quanta-Ray DCR-1 Nd:YAG laser as an exciting light source. The laser pulse was about 5 ns, and the details of the laser photolysis apparatus have been published elsewhere [4]. The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and recorded by a NEC PC 8801 microcomputer.

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