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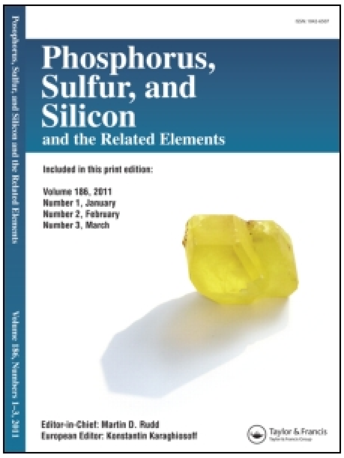

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Laser Flash Photolysis of Phenyl- Substituted Cyclic Oligogermanes

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Photochemical reactions of phenyl-substituted cyclic oligogermanes, $(Ph_2Ge)_n$ (n=4–6), were investigated by laser flash photolysis and chemical trapping experiments.

Keywords: phenyl-substituted cyclic oligogermanes; laser flash photolysis; chemical trapping experiments

INTRODUCTION

The chemistry of oligo- and polygermanes has been a subject of interest in recent years because of their unique physical, chemical, and optical properties arising from electronic delocalization in the Ge-Ge σ framework.[1-6] In continuation of our photochemical studies of cyclic oligogermanes,[7-9] we give herein the first data of photochemical studies of phenyl-substituted cyclic oligogermanes, $(Ph_2Ge)_n$ (n=4-6), by laser flash photolysis and chemical trapping experiments.

RESULTS

Laser flash photolysis (λ=266 nm, pulse width=5 ns, power=10 mJ/pulse) [10] of cyclohexane solutions of $(Ph_2Ge)_n$ (**1**: n=4, **2**: n=5) (ca. 0.001 M) at 293 K gave transient peaks at 340, 450, and 630 nm, as shown in Figures 1 and 2. The observed transient peaks for **1** and **2** appeared very rapidly within the duration of the laser pulse, suggesting that the photolysis originates from the excited singlet state of **1** and **2**. The transient peaks at 450 nm for **1** and **2** are relatively stable, since little change in absorbance was observed within the observable time limit of the laser pulse. The time dependence of absorbance A(t) for **1** is included in Figure 1. The peaks at 450 nm may be assigned to those of tetraphenyldigermene, $Ph_2Ge{=}GePh_2$, from comparison of their spectral characteristics with those of similar digermenes reported.[7-9] On the other hand, the transient peaks at 630 nm for **1** and **2** appeared rapidly just after laser pulsing and decayed with first-order kinetics ($k=1.0 \times 10^6$ s^{-1} for **1** and $k=1.4 \times 10^6$ s^{-1} for **2**). The transient peaks at 630 nm in cyclohexane in the presence of large excess amounts of 2,3-dimethyl-1,3-butadiene, a germylene trapping agent,[11] decayed with pseudo-first order kinetics. The transient peaks at 630 nm were also quenched rapidly with oxygen and carbon tetrachloride. Therefore, the transient peaks at 630 nm may be assigned to those of diphenylgermylene, Ph_2Ge: by taking into consideration the data of these trapping experiments and those previously reported for similar germylenes.[6,12] The value of λ_{max}

(630 nm) for Ph$_2$Ge: observed in this study was relatively red-shifted.[6,12]

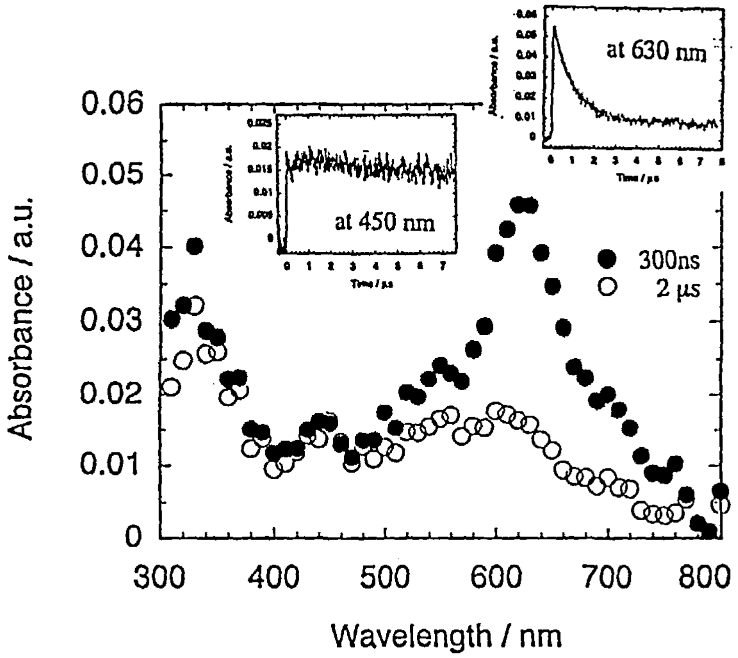


FIGURE 1 Transient absorption spectra after photoexcitation of **1**. Insert: absorption-time profiles.

This may be due to a conformational change in the C-Ge-C bond angle between the ground state and the lowest excited singlet state of **1** and **2**. Similar results have been reported for octaisopropylcyclotetragermane, (i-Pr$_2$Ge)$_4$.[9] The transient peaks at 340 nm are assigned to germyl radicals from comparison of their spectral data with those of similar germyl radicals.[12] The rate constants of the transient peaks at 340, 450, and 630 nm for **1** are summarized in Table 1.

TABLE 1 Rate constants for disappearance of the transients in the photolysis of $(Ph_2Ge)_4$ 1

Transient peak/nm	Rate constant ($M^{-1}s^{-1}$)		
	O_2	CCl_4	2,3-dimethyl-1,3-butadiene
340	6.8×10^9	2.6×10^8	3.7×10^8
450	1.4×10^9	2.5×10^7	–
630	7.3×10^9	2.5×10^8	8.5×10^8

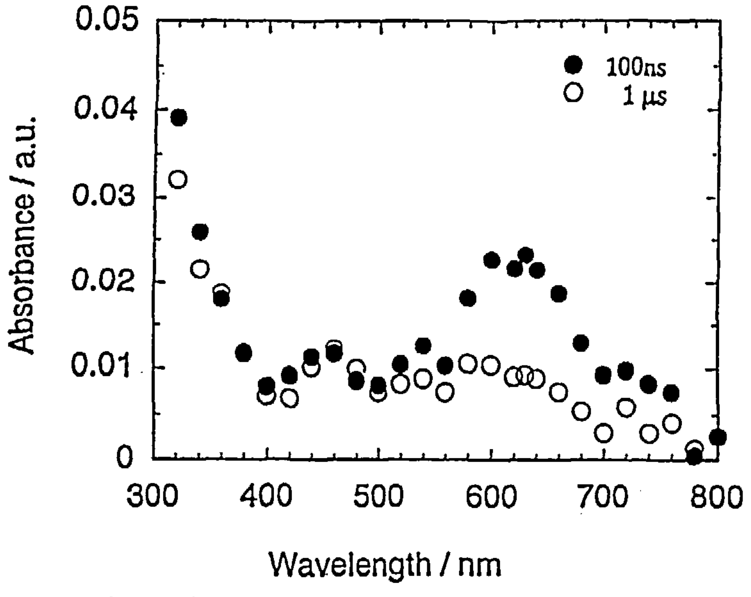


FIGURE 2 Transient absorption spectra after photoexcitation of 2.

Laser flash photolysis of $(Ph_2Ge)_6$ (3) in cyclohexane gave a transient peak at 350 nm together with weak transient peaks at 390 and 450 nm, as shown in Figure 3. The transient peaks at 390 and 450 nm were too weak to allow the decay constant to be estimated. The time dependence of absorbance A(t) for the transient peaks at 350 and 450 nm is included in Figure 3. The observed transient peaks at 350, 390, and 450 nm may be assigned to those of germyl radicals,[12] $Ph_2Ge{=}GePh_2$, [7-9] and

Ph_2Ge:, [6,12] respectively, from comparison of their spectral characteristics with those of similar species.

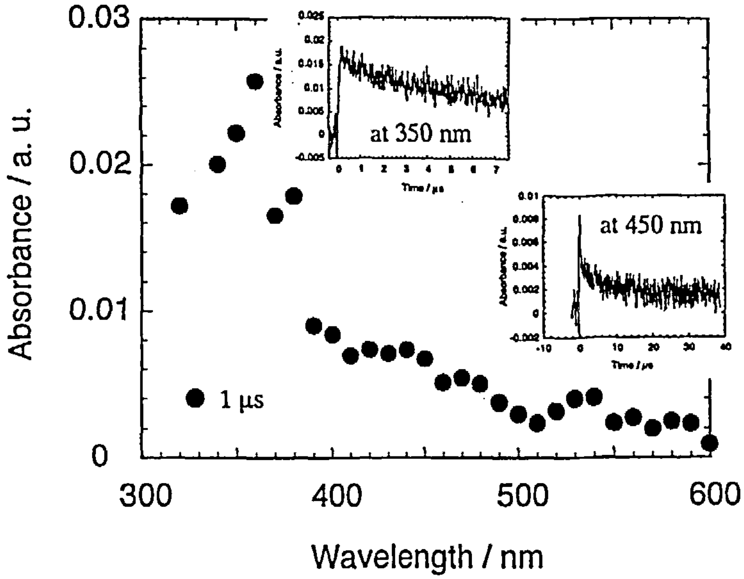
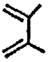
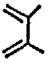
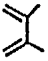


FIGURE 3 Transient absorption spectra after photoexcitation of **3**. Insert: absorption-time profiles.

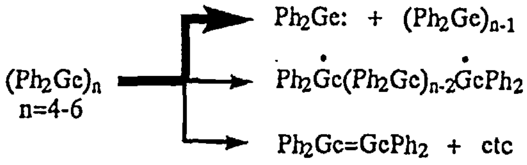
Along with laser flash photolysis of $(Ph_2Ge)_n$ (n=4-6), product studies were carried out by photolyzing **1**-**3** (0.04 M) in cyclohexanes with 110-W low-pressure Hg arc lamp at room temperature for 4 h under argon. Together with unidentified high molecular weight products (M_w=2000-5000) ring-contracted products and hydrogermanes were identified in the photolysate by means of GC-MS and NMR methods. The photolysis of **1**-**3** in cyclohexane containing carbon tetrachloride (CCl_4)[13] gave diphenyldichlorogermane (Ph_2GeCl_2) and hexachloroethane (Cl_6C_2) as the main products. As expected, photolysis of **1**-**3** in cyclohexane containing a large excess of 2,3-dimethyl-1,3-butadiene gave the corresponding germylene trapped product, 1,1-diphenyl-3,4-dimethyl-1-germacyclopent-3-ene. The results are summarized in Table 2.

TABLE 2 Photochemical reactions of cyclic oligogermanes

$(Ph_2Ge)_n$	Conditions	Reagent	Products (Yield/%)
$(Ph_2Ge)_4$ 1	<300 nm, 4 h	No	$H(Ph_2Ge)_3H$ (51), Ph_3GeH (7), Ph_2GeH_2 (trace), $PhGeH_3$ (trace)
		CCl_4	Ph_2GeCl_2 (82)
			 (82)
$(Ph_2Ge)_5$ 2	<300 nm, 4 h	No	$(Ph_2Ge)_4$ (88), Ph_3GeH (5), Ph_2GeH_2 (20), $PhGeH_3$ (trace)
		CCl_4	Ph_2GeCl_2 (98)
			 (98)
$(Ph_2Ge)_6$ 3	<300 nm, 4 h	No	$(Ph_2Ge)_5$ (66), Ph_3GeH (18), Ph_2GeH_2 (26), $PhGeH_3$ (trace)
		CCl_4	Ph_2GeCl_2 (59)
			 (59)

The above laser flash photolysis and chemical trapping studies are rationalized by Scheme 1. A similar mechanism has been proposed for the photolysis of $(i\text{-}Pr_2Ge)_4$.[9]

Scheme 1



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