Photochemical Reactions of Aryl-Substituted Digermanes through a Pair of Organogermyl Radicals[1)]

Kunio Mochida,* Masanobu Wakasa, Yoshio Sakaguchi,† and Hisaharu Hayashi*,†
Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Tokyo 171
†The Institute of Physical and Chemical Research, Wako, Saitama 351-01

(Received January 11, 1991)

The photochemical reactions of aryl-substituted digermanes were investigated by trapping experiments and a laser flash photolysis technique. The photolysis of phenylated digermanes resulted in germanium–germanium bond homolysis to give a pair of two germyl radicals. The germyl radicals abstracted a chlorine atom from carbon tetrachloride to give chlorogermanes. The pair of germyl radicals also underwent ipso-substitution, which was a precursor of the germylenes. The mechanism for the photochemistry of phenylated digermanes is discussed.

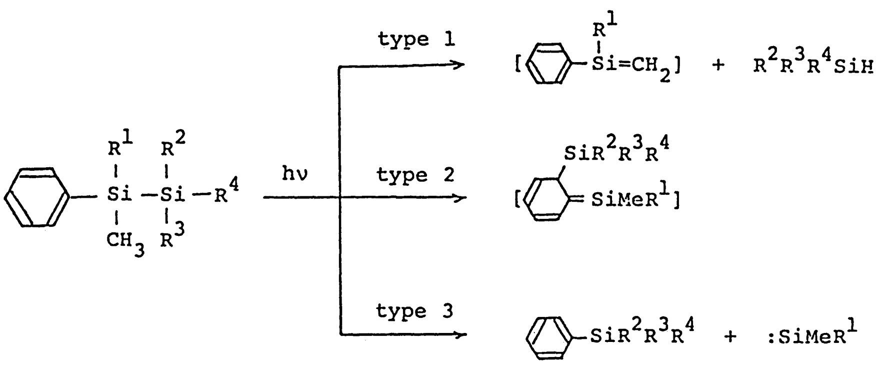
The photochemistry of organopolysilanes having a σ(Si–Si)-π(C=C) conjugated system has been the subject of considerable attention because of their unexpected reactivities as well as in the resulting products.[2—4)]

The photolysis of an aryldisilane was first reported by Boudjouk, Roberts, Golino, and Sommer[5)] for pentaphenylmethyldisilane. The generation of a silicon–carbon double-bonded species is the characteristic feature of the reaction (type 1 in Scheme 1). Later, Ishikawa, Fuchigami, Sugaya, and Kumada[6)] have reported on another type of reaction in which a rather unusual silicon–carbon double-bonded species is postulated as a key intermediate (type 2). The generation of a silylene has also been noted (type 3). Recently, Sakurai, Nakadaira, Kira, Sugiyama, Yoshida, and Takiguchi have presented a free radical mechanism for the photolysis of aryldisilanes. Okinoshima and Weber[8)] have also reported the formation of silicon–oxygen double-bonded species by the photolysis of aryldisilanes in dimethyl sulfoxide (DMSO).

However, there has been few papers on photochemical studies of the germanium analogues.[9)] We previously reported on the photolysis of phenylpentamethyldigermane, in which the generation of a pair of germyl radicals was indicated.[10)] In this paper, we described the photoreactions of phenylated digermanes studied via trapping experiments and a laser flash photolysis technique.

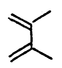
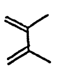
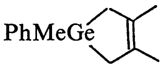
Results and Discussion

Photoreaction of the Phenylated Digermanes. Four kinds of phenyl-substituted digermanes, $(Ph_nMe_{3-n}Ge)_2$ (**1**—**3**, n=1—3, respectively) and $Me_3GeGePh_3$ (**4**), in cyclohexane or in tetrahydrofuran (THF) were investigated with a 110-W low-pressure Hg arc lamp at room temperature under an argon atmosphere for 1—2 h. The photolysis of **1** and **2** in cyclohexane gave $PhMe_2GeH$ (11%), Ph_2GeMe_2 (17%), and $(Me_2Ge)_4$ (4%) for **1**, and Ph_2MeGeH (20%) and Ph_3GeMe (17%) for **2**, as main products. The photolysis of **4** in cyclohexane mainly afforded Me_3GeH (15%), Ph_3GeH (32%), and $PhGeMe_3$ (19%). High-boiling unidentified products containing germanium were also formed in the photoreactions of **1**, **2**, and **4**. The formation of octamethylcyclotetragermane $(Me_2Ge)_4$ for **1** strongly suggests the intermediacy of a dimethylgermylene.[11)] In order to detect possible reaction intermediates, cyclohexane solutions of **1**, **2**, and **4** containing a large excess of 2,3-dimethylbutadiene, a germylene trapping agent,[12)] were similarly irradiated for 1—2 h. Monogermanes ($PhMe_2GeH$ and Ph_2GeMe_2) and $(Me_2Ge)_4$ were produced for **1**, regardless of the presence of 2,3-dimethylbutadiene. No 1,1-dimethylgermacyclopent-3-ene was formed. The rate of cycloaddition of 1,1,2,2-tetramethyldigermene (Me_2Ge=$GeMe_2$) formed by a



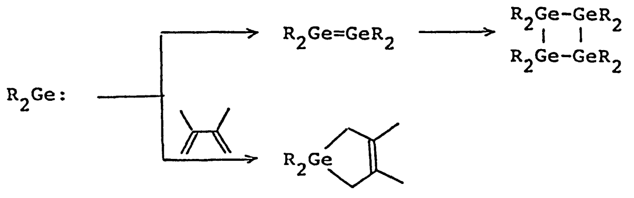
Scheme 1.

Table 1. The Results of Photochemical Reactions of the Phenylated Digermanes, **1**, **2**, and **4**

Digermane	Substrate	Main products (yield/%)
$(PhMe_2Ge)_2$	None	$PhMe_2GeH$ (11), Ph_2GeMe_2 (17), $(Me_2Ge)_4$ (4)
1	CCl_4	$PhMe_2GeCl$ (94)
		$PhMe_2GeH$ (21), Ph_2GeMe_2 (5), $(Me_2Ge)_4$ (4)
$(Ph_2MeGe)_2$	None	Ph_2MeGeH (20), Ph_3GeMe (15)
2	CCl_4	$Ph_2MeGeCl$ (95)
		 (1)
$Me_3GeGePh_3$	None	Me_3GeH (12), Ph_3GeH (32), $PhGeMe_3$ (19)
4	CCl_4	Me_3GeCl,[a) Ph_3GeCl[a)

a) The yield of products could not be determined by GLC.

dimethylgermylene may be much faster than that of the dimethylgermylene with 2,3-diemthylbutadiene under these reaction conditions. On the other hand, 1-methyl-1-phenylgermacyclopent-3-ene (1%) was formed together with mongermanes (Ph_2MeGeH and Ph_3GeMe) in the photolysis of **2** and 2,3-dimethylbutadiene. 3-Butenylgermyl derivatives were also detected by means of CC-MS in the photolysis of **1** and **2**.



No 1,1-diphenylgermacyclopent-3-ene and octaphenylcyclotetragermane $(Ph_2Ge)_4$ derived from diphenylgermylene were formed in the photolysis of **4**.

In the presence of carbon tetrachloride, the photolysis of **1**, **2**, and **4** in cyclohexane afforded chlorogermanes quantatively, together with hexachloroethane. The formation of chlorogermanes seems to indicate the intermediacy of the germyl radicals produced by germanium-germanium bond homolysis of the phenylated digermanes. The germyl radicals are known to abstract a chlorine atom from carbon tetrachloride to give the corresponding chlorogermanes and a trichloromethyl radical:[13)

$$R_3Ge\cdot + CCl_4 \longrightarrow R_3GeCl + \cdot CCl_3.$$

The germyl radicals add to 2,3-dimethylbutadiene to produce 3-butenylgermyl derivatives.

Hydrogermanes were formed in the absence of trapping agents. Germyl radicals do not abstract a hydrogen atom from solvents, such as THF or cyclohexane. This was confirmed by the fact that THF-d_8 or cyclohexane-d_{12} solutions containing **1** upon being irradiated gave no $PhMe_2GeD$ but $PhMe_2GeH$. It is unlikely that they can abstract a hydrogen atom from precursor C–H bonds, which are even stronger. Another route to the formation of hydrogermanes may be via a disproportionation of germyl radicals.[14) Germenes are also expected to form by the disproportionation of germyl radicals. The germenes are known to react with methanol to give methoxygermanes.[15) No methoxygermanes were formed in the photolysis of cyclohexane solutions of phenylated digermanes, **1**, **2**, **4** with methanol. At present, the formation processes of hydrogermanes are unclear.

The photolysis of **3** did not proceed since **3** was very difficult to dissolve in cyclohexane or in THF. The results of photochemical reactions of **1**, **2**, and **4** in cyclohexane are summarized in Table 1. Similar results regarding the photochemical reactions of **1**, **2**, and **4** in THF were obtained.

In order to obtain more information concerning the reaction intermediates and primary photochemical processes, laser flash photolysis at 293 K studies of phenylated **1**—**3** were also carried out.

Laser Flash photolysis Studies. Nanosecond transient absorption spectra measurements were performed on degassed solutions containing **1**—**3** at 293 K using the fourth-harmonic pulse of a Nd:YAG laser as the exciting light source.[16)

The time dependence of the transient absorbance, $A(t)$, was measured using each of the THF solutions containing **1**—**3**. The $A(t)$ curves were measured in the wavelength region 300—700 nm. Appreciable signals of two well-separated transient bands were obtained, as shown in Fig. 1. The signals show a fast rise and a following slow decay. The rise time was about 10 ns, the time resolution of the present apparatus. As a typical example, the $A(t)$ curve and the $\log A(t)$ curve observed with **2** at 320 nm for kinetic studies are shown in Fig. 2. Such a curve can be computer analyzed regarding composition of two components through the decay of pseudo first-order kinetics. The $A(t)$ curve

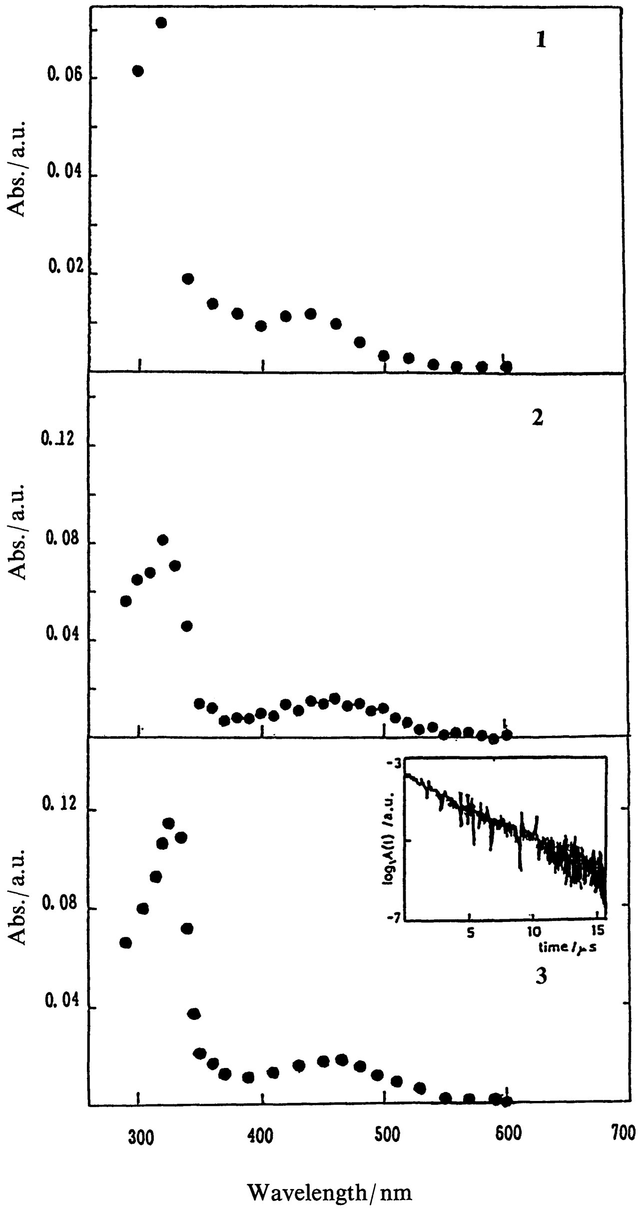


Fig. 1. Transient absorption spectra at 50 ns after photoexcitation of $(Ph_nMe_{3-n}Ge)_2$, **1**—**3** (n=1—3) (10^{-3} M) in degassed THF solutions. Insert (3): a first-order plot for decay of the absorption at 320 nm.

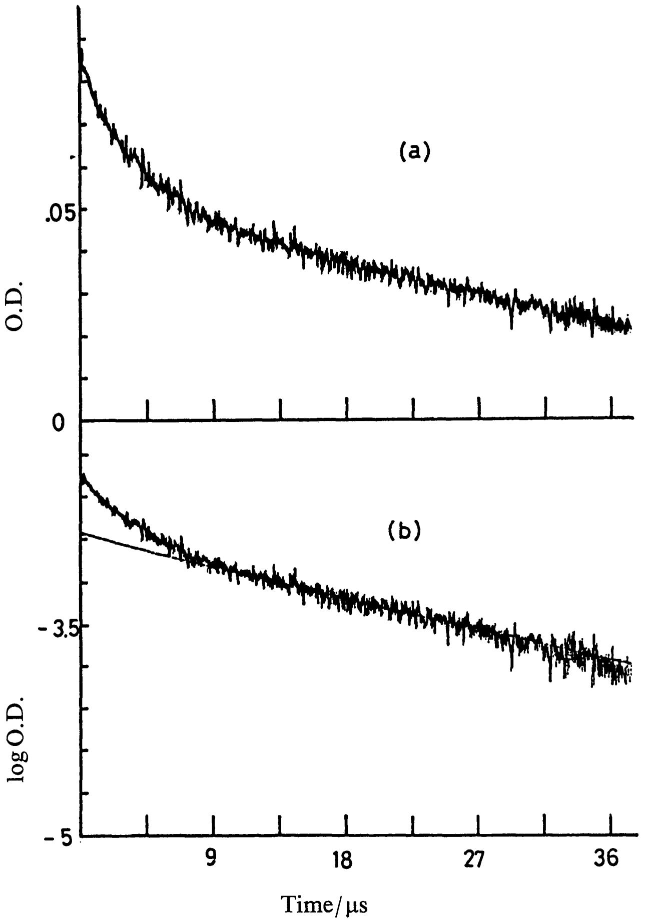


Fig. 2. Representative data displays from laser flash photolysis kinetic spectroscopy experiments: (a) absorbance at 320 nm as a function of time upon irradiation of $(Ph_2MeGe)_2$ (**2**) (2.6 mM) in degassed THF solution, (b) log absorbance at 320 nm as a function of time upon irradiation of **2** (the slope of linear plot is first-order rate constant).

and the $\log A(t)$ curve of the short-lived component, excluding those of the longer-lived one, is shown in Fig. 3. Thus, a careful examination of the transient peak at shorter wavelengths shows that it comprises two components (half lifetimes, $t_{1/2}$<5 μs and $t_{1/2}$>20 μs, respectively, for **1** and **2** in THF and hydrocarbon media). On the other hand, the transient peak at shorter wave-

Table 2. Rate Constants for Disappearance of the Shorter-Lived Transients at Shorter Wavelength in the Photolysis of **1**—**3** in THF (10^{-3} M) at 293 K

Digermane	λ_{max}/nm	Rate constant/ $M^{-1} s^{-1}$			
		None[a)]	CCl_4	O_2	2,3-Dimethylbutadiene
$(PhMe_2Ge)_2$ **1**	315	4.3×10^5	2.2×10^8	5.3×10^9	b)
$(Ph_2MeGe)_2$ **2**	325	3.2×10^5	4.7×10^8	4.0×10^9	b)
$(Ph_3Ge)_2$ **3**	330	1.9×10^5	5.8×10^8	3.8×10^9	b)

a) s^{-1}. b) The transient decays too fast to be observed.

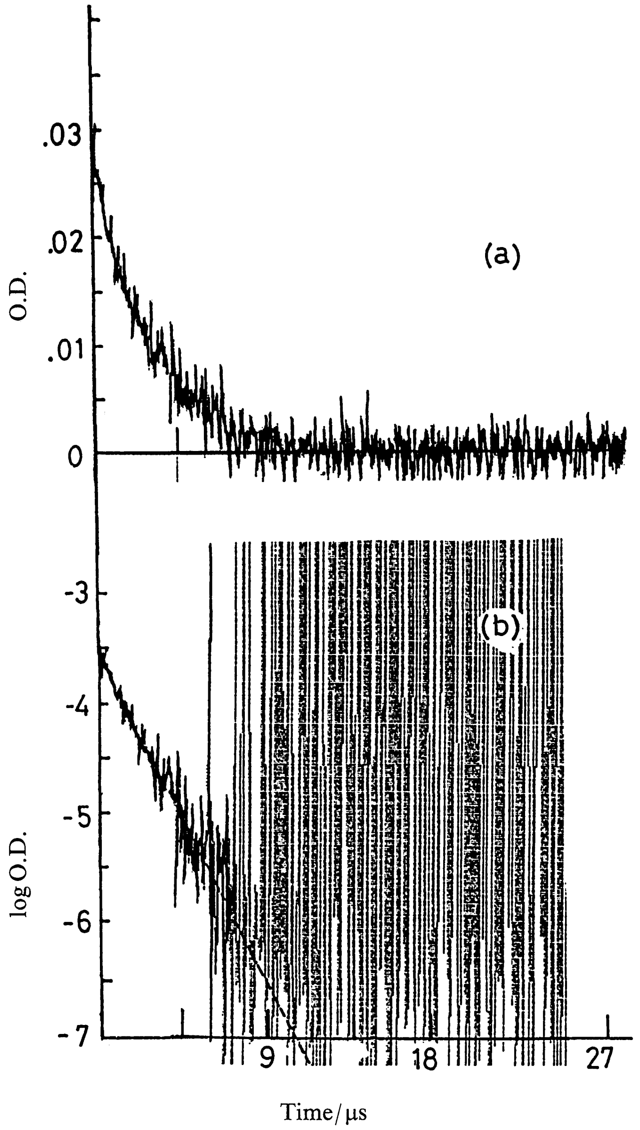


Fig. 3. Representative data displays from laser flash photolysis kinetic spectroscopy experiments: (a) absorbance of short-lived component at 320 nm as a function of time upon irradiation of $(Ph_2MeGe)_2$ (**2**) (2.6 mM) in degassed THF solution, (b) log absorbance of short-lived component at 320 nm as a function of time upon irradiation of **2** (the slope of linear plot is first-order rate constant).

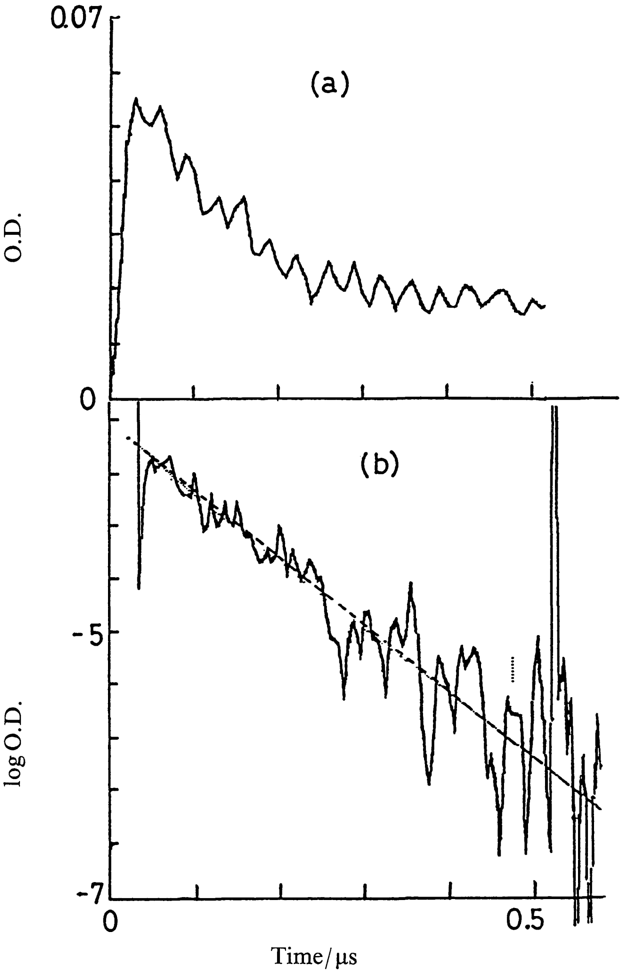


Fig. 4. Representative data displays from laser flash photolysis-kinetic spectroscopy experiments: (a) absorbance of short-lived component at 320 nm as a function of time upon irradiation of $(PhMe_2Ge)_2$ (**1**) (2.6 mM) in degassed THF solution containing CCl_4 (10 mM), (b) log absorbance of short-lived component at 320 nm as a function of time upon irradiation of **1** containing CCl_4.

lengths arising from **3** has only the short-lived component. This component has been reasonably assigned to that of the phenyl-substituted germyl radicals, $Ph_nMe_{3-n}Ge\cdot$ (n=1—3), from a comparison of the spectral characteristics with those reported for germyl radicals.[17] The experimentally determined decay constants of these transient species are summarized in Table 2. The transient arising from **1**—**3** decayed under pseudo first-order kinetics and are dependent on the concentrations of the employed phenylated digermanes. Such kinetics can be explained by the addition of the generated germyl radical to the aromatic ring on a germanium atom. This is very different from the situation reported regarding the addition of germyl radicals to aromatic compounds in solutions.[18] The assignment of a shorter-lived transient has been further substantiated by quenching experiments with carbon tetrachloride, oxygen, and 2,3-dimethylbutadiene. The addition of carbon tetrachloride, an effective germyl radical scavenger, quenched the transient absorption (Table 2). The quenching-rate constants observed nicely agree with the values reported for germyl radicals.[17] Similarly, oxygen quenched the shorter-lived transient very quickly (Table 2). Representative data displays from laser flash photolysis-kinetic spectroscopy experiments are shown in Fig. 4.

What is the latter carrier of the longer-lived transient at shorter wavelengths? The concentration of this species appeared to be correlated with that of the shorter-lived species assigned to the germyl radicals as well as that of the longer-wavelength transient arising from the germylene described below. Furthermore, the change in the intensity of the transient was examined in isooctane as well as in more viscous solvents, such as dodecane. Figure 5 shows the intensity of the longer-lived transient in isooctane tends to increase in dodecane. This implies that this transient species may be a product of a radical which had escaped from the cage. Accordingly, the longer-lived species may be tentatively assigned to a coupling product of the germyl radicals at the ipso-position, as described in Scheme 2. The possibility of germenes and digermenes, suggested as another species, is excluded the UV data of germenes and digermenes are below 300 nm[19] and above 370 nm[20] respectively.

The experimentally determined decay constants of longer-lived transients are summarized in Table 3.

On the other hand, the transient at the longer wavelength (Fig. 1) could be assigned to that of a germylene by comparing its chemical and spectral properties with those reported.[21–23] These transients arising from **2** and **3** in THF decayed with first-order kinetics. However, the transient arising from **1** in THF is too weak to observe its decay constant. This kinetic behavior implies that the germylene reacts with THF in a similar as do the silylenes.[24] In contrast, in inert solvents, such as isooctane, the transient due to the germylene decayed with second-order kinetics, suggesting the formation of digermenes. This was further substantiated by quenching experiments with a germylene trapping agent, 2,3-dimethylbutadiene, which gives the corresponding germacyclopentenes. The transient from **2** and **3** in THF in the presence of large excess amounts of the diene decayed with pseudo first-order kinetics; the obtained rate constants are summarized in Table 4. The fact that these transients were not quenched by ethanol is in accord with the observed chemical property.

Photoreaction Mechanism of Phenylated Digermanes. The results of photochemical reactions and laser flash photolysis studies of **1**—**4** are best rationalized as a pair of germyl radicals according to the path described in Scheme 2. The photolysis of aryldigermanes cleaves the germanium-germanium bond to give a pair of germyl radicals. The generated germyl radicals readily abstract a chlorine atom from carbon

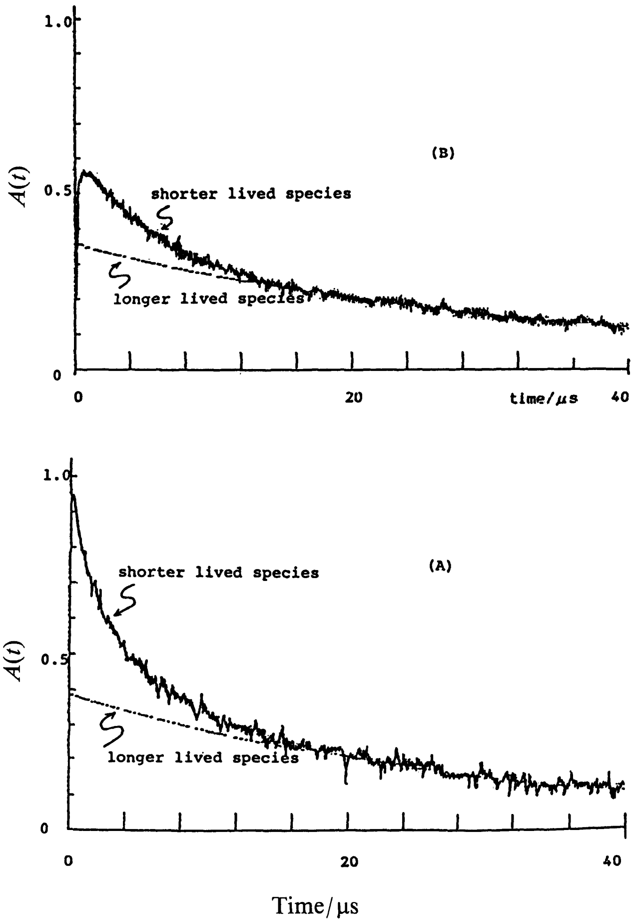


Fig. 5. Plots of the absorbance at 320 nm against t observed with the isooctane (A) and dodecane (B) of **1**.

Table 3. Rate Constants for Disappearance of the Longer-Lived Transients at Shorter Wavelength in the Photolysis of **1**—**3** in THF (10^{-3} M) at 293 K

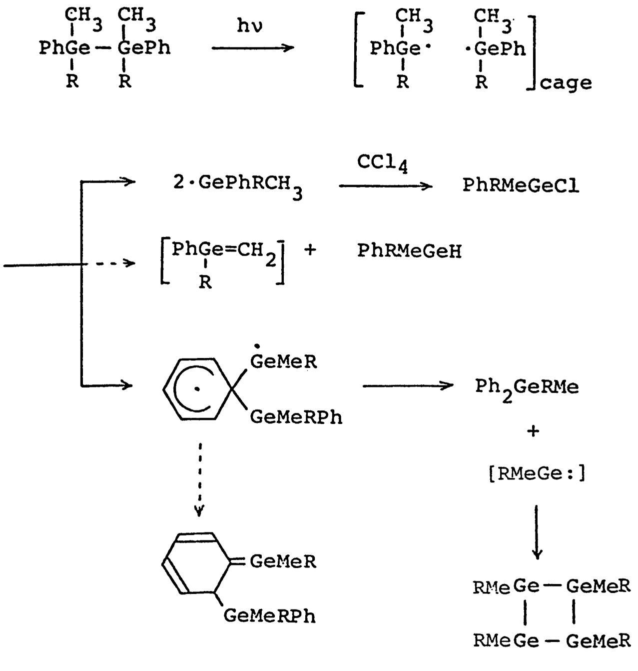
Digermane	Rate constant/$M^{-1}\,s^{-1}$		
	CCl_4	O_2	2,3-Dimethylbutadiene
$(PhMe_2Ge)_2$ **1**	a)	5.8×10^8	a)
$(Ph_2MeGe)_2$ **2**	3.8×10^7	2.1×10^8	8.5×10^4
$(Ph_3Ge)_2$ **3**	a)	a)	1.5×10^5

a) The transient decays too fast to be observed.

Table 4. Rate Constants for Disappearance of the Transient at Longer Wavelength in the Photolysis of **1**—**3** in THF (10^{-3} M) at 293 K

Digermane	λ_{max}/nm	Rate constant/$M^{-1}\,s^{-1}$			
		None[a)]	2,3-Dimethylbutadiene	O_2	EtOH
$(PhMe_2Ge)_2$ **1**	440	b)	b)	b)	c)
$(Ph_2MeGe)_2$ **2**	450	1.1×10^5	4.5×10^6	2.3×10^8	c)
$(Ph_3Ge)_2$ **3**	470	2.0×10^5	1.0×10^6	1.8×10^8	c)

a) s^{-1}. b) The absorption of **1** is too weak to determine rate constants. c) Not quenched.



Scheme 2.

tetrachloride to give the corresponding chlorogermanes and trichloromethyl radical. The formation mechanism of hydrogermanes are unclear.

The germyl radicals couple at the ipso-position to give germyl-substituted cyclohexadienyl type radicals. The germyl-substituted cyclohexadienyl type radicals undergo further elimination to produce a gemylene and arylgermanes. The photo-generated germylene dimerize to give digermenes or react with 2,3-dimethylbutadiene to give germacyclopentenes. The arylgermanes produced by elimination processes are Ph_2GeMe_2 for **1**, Ph_3GeMe for **2**, and $PhGeMe_3$ for **4**. In contrast to the case of the aryldisilane, we have no concrete evidence for the presence of formal 1,3-germyl migration products in the photolysis of **1**, **2**, and **4**. This difference in the photochemical behavior between an arydigermane and an aryldisilane may be accounted for in terms of the following reasons. The bond dissociation energy of a germanium-carbon bond (318 kJ mol^{-1}) is less than that of a silicon-carbon bond (343 kJ mol^{-1}), and π-bonding of carbon must be formed more effectively with a silicon atom than with a germanium atom.[18]

In addition, organogermylene is more thermodynamically stable than is silylene. All of those factors favor the formation of germylene and germylene elimination products from the coupling products of germyl radicals at the ipso-position over the formation of germyl migration products.

The formation of germylenes and arylgermanes cannot necessarily be explained by a 1,2-phenyl shift of the phenylated digermanes, since the transient signal of the germylenes was observed with that of the germyl radicals immediately after photoexcitation of the phenylated digermanes. Taking the results of the trapping experiments with carbon tetrachloride, the 1,2-phenyl shift proceeds as a minor path.

Experimental

^1H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as an internal standard. GC-MS spectra were obtained with a JEOL JMX-DX 303 mass spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed on a Shimadzu GC-6A and 8A with 2 m 20% SE30 and 1 m 10% SE columns.

Materials. 2,3-Dimethylbutadiene, CCl_4, and ethanol were commercially available. $PhMe_2GeGeMe_2Ph$, bp 170—174 °C/4 mmHg (1 mmHg=133,322 Pa),[25] $Ph_2MeGeGeMePh_2$, mp 132—133 °C,[25] $Ph_3GeGePh_3$, mp 335—340 °C,[25] $Me_3GeGePh_3$, mp 108—109 °C,[26] $PhMe_2GeH$, bp 65—66 °C/20 mmHg,[27] Me_3GeH, bp 26 °C,[28] Ph_2MeGeH, bp 105—106 °C/6 mmHg,[29] Ph_3GeH, mp 39.5 °C,[30] Me_3GeCl, bp 98 °C,[28] $PhMe_2GeCl$, bp 90 °C/10 mmHg,[31] $Ph_2MeGeCl$, bp 140 °C/14 mmHg,[32] Ph_3GeCl, mp 145 °C,[33] Ph_2GeMe_2, bp 145 °C/14 mmHg,[34] Ph_3GeMe, mp 71 °C,[35] $PhGeMe_3$, bp 80 °C/20 mmHg,[36] 1-methyl-1-phenylgermacyclopent-3-ene,[37] and $(Me_2Ge)_4$[11] were prepared as described in the cited references.

Solvents. Cyclohexane, isooctane, dodecane, and THF were distilled from sodium-benzophenone under an argon atmosphere.

Photochemical Reactions of the Phenylated Digermanes. The digermanes (ca. 200 mg) were dissolved in dry cyclohexane (6 cm^3) in a quartz tube. The tube was degassed in a vacuum and charged with argon. The sample was irradiated with a 110-W low-pressure Hg arc lamp at room temperature for 2 h. After irradiation, the photoproducts were verified by comparing the retention times on GLC and GC-MS with those of authentic samples.

Photochemical Reactions of the Phenylated Digermanes with Various Trapping Agents. As a representative example, photolysis of a cyclohexane solution containing 1,1-diphenyltetramethyldigermane with CCl_4 is described. Compound **1** (200 mg, 0.56 mmol) and CCl_4 (0.45 g, 30 mmol) were dissolved in dry cyclohexane (6 m^3) in a quartz tube. The sample tube was degassed in a vacuum and charged with argon. The sample was irradiated at room temperature for 20 min. After irradiation, the photoproducts were verified by comparing the retention time on GLC and GC-MS with those of authentic samples.

Time-Resolved Optical Absorption. Samples in quartz cells with an optical length of 5 mm were degassed by four freeze-pump-thaw cycles. The concentrations of the phenylated digermanes were ca. 10^{-3} M (1 M=1 mol dm^{-3}). Laser flash photolysis experiments were performed at room temperature (293 K) by using the fourth-harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser as the exciting light source. The laser pulse was about 5 ns. Details concerning the laser flash photolysis apparatus have been published elsewhere.[16] 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 an NEC PC 8801 microcomputer.

The authors thank Professor Yasuhiro Nakadaira of The University of Electro-Communications for valuable discussion. This research was supported in part by a Grant-in-Aid for Scientifc Research Nos. 0649518 and 63790213 from the Ministry of Education, Science and Culture. One of the authors (M. Wakasa) thanks the Japan Chemical Society for Promotion of Science for the Fellowship for Japan Junior Scientists.

References

1) Preliminary results of the study were reported in: K. Mochida, M. Wakasa, Y. Nakadaira, Y. Sakaguchi, and H. Hayashi, *Organometallics,* **7**, 1869 (1988).

2) R. West, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York (1982), Vol. 2, Chap. 9. 4.

3) M. Ishikawa, *Pure Appl. Chem.,* **50**, 11 (1978); M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.,* **19**, 51 (1981).

4) H. Sakurai, *J. Organomet. Chem.,* **200**, 261 (1980); H. Sakurai, Y. Nakadaira, and H. Tobita, *Kagaku no Ryoiki,* **33**, 879, 973 (1979).

5) P. Boudjouk, J. R. Roberts, C. M. Gollino, and L. H. Sommer, *J. Am. Chem. Soc.,* **94**, 7926 (1975).

6) M. Ishikawa T. Fuchigami, T. Sugaya, and M. Kumada, *J. Am. Chem. Soc.,* **97**, 5926 (1975).

7) H. Sakurai, Y. Nakadaira, M. Kira, K. Yoshida, H. Sugiyama, and T. Takiguchi, *J. Organomet. Chem.,* **184**, C36 (1980).

8) H. Okinoshima and W. Weber, *J. Organomet. Chem.,* **149**, 279 (1978).

9) M. Kira, K. Sakamoto, and H. Sakurai, *J. Am. Chem. Soc.,* **105**, 7469 (1983).

10) K. Mochida, H. Kikkawa, and Y. Nakadaira, *Chem. Lett.,* **1988**, 1089.

11) H. Sakurai, K. Sakamoto, and M. Kira, *Chem. Lett.,* **1984**, 1379.

12) M. Schriewer and W. P. Neumann, *J. Am. Chem. Soc.,* **105**, 897 (1983).

13) H. Sakurai, K. Mochida, A. Hosomi, and F. Mita, *J. Organomet. Chem.,* **38**, 275 (1972).

14) K. Mochida, I. Yoneda, and M. Wakasa, *J. Organomet. Chem.,* **339**, 53 (1990).

15) J. Barrau, J. Escudié, and J. Satgé, *Chem. Rev.,* **90**, 283 (1990).

16) For example: Y. Sakaguchi, H. Hayashi, and S. Nagakura, *J. Phys. Chem.,* **86**, 3177 (1982).

17) K. Mochida, M. Wakasa, Y. Sakaguchi, and H. Hayashi, *J. Am. Chem. Soc.,* **109**, 7942 (1987).

18) H. Sakurai, "Free Radicals," ed by J. K. Kochi, Wiley, New York (1973), Vol. II, Chap. 25.

19) K. Mochida, M. Wakasa, Y. Sakaguchi, and H. Hayashi, *Nippon Kagaku Kaishi,* **1987**, 1171.

20) W. Ando, H. Itoh, T. Tsumuraya, and H. Yoshida, *Organometallics,* **7**, 1880 (1988).

21) M. Wakasa, I. Yoneda, and K. Mochida, *J. Organomet. Chem.,* **366**, C1 (1989).

22) S. Tomoda, M. Shimoda, Y. Takeuchi, Y. Kaji, K. Obi, I. Tanaka, and K. Honda, *J. Chem. Soc., Chem. Commun.,* **1988**, 910.

23) S. Konieczzy, S. J. Jacobs, J. K. B. Wilking, and P. P. Gaspar, *J. Organomet. Chem.,* **341**, C17 (1988).

24) H. Vancik, G. Raabe, M. J. Michalczyk, R. West, and J. Michl, *J. Am. Chem. Soc.,* **107**, 4097 (1985); G. R. Gillette, G. H. Noren, and R. West, *Organometallics,* **6**, 2617 (1987).

25) H. Bauer and K. Burcshkies, *Chem. Ber.,* **1934**, 2617.

26) D. B. Chambers and F. Glockling, *J. Chem. Soc. A,* **1968**, 735.

27) R. H. Fish and H. G. Kuivila, *J. Org. Chem.,* **31**, 2445 (1966).

28) A. E. Finholt, *Nucl. Sci. Abstr.,* **6**, 617 (1957).

29) J. Satgé and P. Riviere, *Bull. Soc. Chim. Fr.,* **1966**, 1773.

30) O. H. Johnson and W. H. Nebergall, *J. Am. Chem. Soc.,* **71**, 1720 (1949).

31) J. Satgé, P. Riviere, and A. Boy, *Trans. R. Acad. Sci. Ser. C,* **278**, 1309 (1974).

32) M. Kumada, S. Sakamoto, and M. Ishikawa, *J. Organomet. Chem.,* **17**, 1309 (1974).

33) E. H. Brooks and F. Glockling, *J. Chem. Soc. A,* **1966**, 1241.

34) L. A. Leites, Y. P. Egorov, G. Y. Zueva, and V. A. Ponomarenko, *Izv. Akad. Nauk SSSR,* **1961**, 2132.

35) C. Eaborn, A. Leyshon, and K. C. Pande, *J. Chem. Soc.,* **1960**, 3423.

36) H. Bauer and K. Burschkies, *Chem. Ber.,* **1933**, 1156.

37) P. Riviere, J. Satgé, and D. Soula, *J. Organomet. Chem.,* **63**, 167 (1973).