1642 © 1992 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *65*, *1642—1647 (1992)* [Vol. 65, No. 6

Study of Photochemical Reactions of Decamethylcyclopentagermane

Kunio MOCHIDA* and Satoshi TOKURA
Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Tokyo 171

(Received January 21, 1992)

The photolysis of decamethylcyclopentagermane (**1**) in cyclohexane at room temperature proceeds readily along with the generation of dimethylgermylene to give octamethylcyclotetragermane. Photochemically generated dimethylgermylene reacts with 2,3-dimethylbuta-1,3-diene or carbon tetrachloride to give 1,1,3,4-tetramethyl-1-germa-3-cyclopentene or chlorodimethyl(trichloromethyl)germane, respectively. The transient absorption of **1** in cyclohexane at 490 nm, obtained by laser flash photolysis, is due to dimethylgermylene at 293 K. The reaction rates of dimethylgermylene with some trapping agents are examined. In 3-methylpentane, dimethylgermylene also shows an absorption band at 506 nm at 77 K. The photo-generated dimethylgermylene appears to be in the singlet ground state.

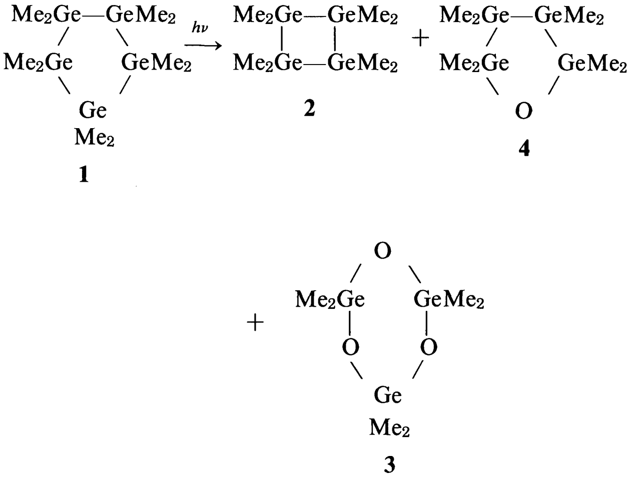
An investigation of the photochemical decomposition of polysilanes and polygermanes is of topical interest because of their importance as electric conduction, photoresists, and new materials.[1,2] However, studies of polygermanes are greatly limited, compared with those of polysilanes.[3-8] We previously reported the photoreactions of dodecamethylcyclohexagermane as part of an investigation of polygermanes.[8] In the photolysis of dodecamethylcyclohexagermane, the generation of dimethylgermylene was accompanied by the formation of decamethylcyclopentagermane.

The purpose of the studies described here was to clarify the photochemical behaviors of the cyclopentagermanes which were formed with a loss of dimethylgermylene by the photolysis of dodecamethylcyclohexagermane, and to compare those of the corresponding silicon compounds.

Results and Discussion

Photochemical Reactions of Decamethylcyclopentagermane. The irradiation of a cyclohexane solution of decamethylcyclopentagermane (**1**) with a 110-W low-pressure Hg arc lamp (254 nm, spiral type) at room temperature under argon gave several products. In addition to unidentified high-boiling products containing germanium, octamethylcyclotetragermane (**2**) and 1,3,5-trioxa-2,4,6-trigermacyclohexane (**3**) were obtained as the main products. 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 an accidental oxidation of the cyclotetragermane (**2**) by oxygen which could not be completely excluded during photolysis and/or a subsequent workup.

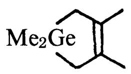
The photochemical degradation of **1** to **2** and the formation of **4**[9] strongly imply the generation of dimethylgermylene. To trap such a dimethylgermylene, a cyclohexane solution of containing ca. 20 molar amount of 2,3-dimethylbuta-1,3-diene[10] was similarly irradiated. The expected germylene trapping compound, 1,1,3,4-tetramethyl-1-germa-3-cyclopentene, was produced.



In the presence of carbon tetrachloride, the photolysis of **1** in cyclohexane afforded dimethyldichlorogermane in 21% yield. The formation of dimethyldichlorogermane may be a result of the thermal decomposition of chlorodimethyl(trichloromethyl)germane produced by the insertion of dimethylgermylene into the C–Cl bond of carbon tetrachloride,[11] or chlorine abstraction from carbon tetrachloride by dimethylgermylene, as is shown in the case of silicon.[12] Interestingly, 1,4-dichlorooctamethyltetragermane was also detected in 35% yield. The formation of the dichloride indicates that the germanium–germanium bond of **2** should be cleaved to produce the 1,4-tetragermanediyl biradical, which immediately abstracts chlorine atoms from carbon tetrachloride.[13]

The photolysis of **1** in cyclohexane containing ethanol did not produce any ethoxygermanes (which might be formed by the insertion of germylenes into the O–H bond of ethanol), but produced cyclotetragermane **2** under these conditions. This result is in sharply contrast to that of the silylenes. It is well known that silylenes react with alcohol to give alkoxysilanes effectively.[13]

Table 1. Photoreactions of Decamethylcyclopentagermane at 293 K

Run no.	Time h	Substrate	Products (Yield/%) $(Me_2Ge)_4$,	$(Me_2Ge)_4O$,	$(Me_2GeO)_3$,	Others	Conversion %
1	7	None	9	22	15		52
2	12	None	5	20	31		77
3	2.3	CCl_4	0	29		Me_2GeCl_2(21) $Cl(Me_2Ge)_4Cl$(35)	93
4	3	1,3-Diene	8	12		 (Trace)	91
5	2	EtOH	6	15			87

These photochemical results regarding **1** are summarized in Table 1.

In order to obtain more information concerning 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. Nanosecond transient absorption spectra measurements were performed on degassed solutions containing **1** at 293 K using the fourth-harmonic pulse of a Nd : YAG laser as the exciting light source (λ=266 nm).

The time dependence of the absorbance of the transient absorption (A(t)) was measured with cyclohexane solutions containing **1**. The A(t) curves were measured over the 300—700 nm wavelength region. The time resolution of the apparatus was about 10 ns. Transient absorption spectra with a peak at 490 nm were obtained (Fig. 1). As shown in Fig. 1, a transient peak at 490 nm disappeared, resulting in the build-up of a transient peak around 370 nm. An isosbestic point was observed around 400 nm. It is, therefore, clear that the 370 nm transient is not due to the primary photo-product of **1**. The transient at 490 nm may be ascribed to dimethylgermylene from a comparison of the spectral characteristics with those of reported for dimethylgermylene.3—7,11)

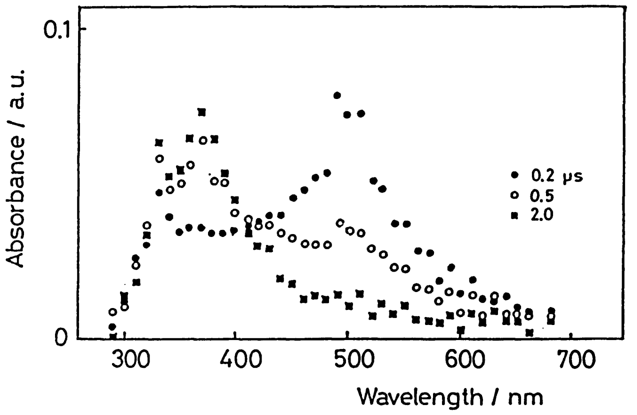


Fig. 1. Transient absorption spectra after photoexcitation of the cyclopentagermane at 293 K. ●; 200 ns, ○; 0.5 μs, ■; 2.0 μs.

The transient peak at 490 nm of dimethylgermylene decayed under second-order kinetics($k/\varepsilon=3{,}5\mathrm{X}10^7$ at 490 nm) as is shown in Fig. 2. Here, k, is the rate constant for second-order decay, and ε is the molar extinction coefficient. The peak at 490 nm is further substantiated by quenching experiments with germylene trapping agents. The pseudo first-order rate constants (k_{obsd}) for decay depended linearly on the concentrations of such trapping agents as 2,3-dimethylbuta-1,3-diene and CCl_4. As a typical example, a plot of k_{obsd} vs. [diene] is shown in Fig. 3. The rate constants for the disapperance of the transient at 490 nm was obtained for these quenching experiments (diene and CCl_4) were

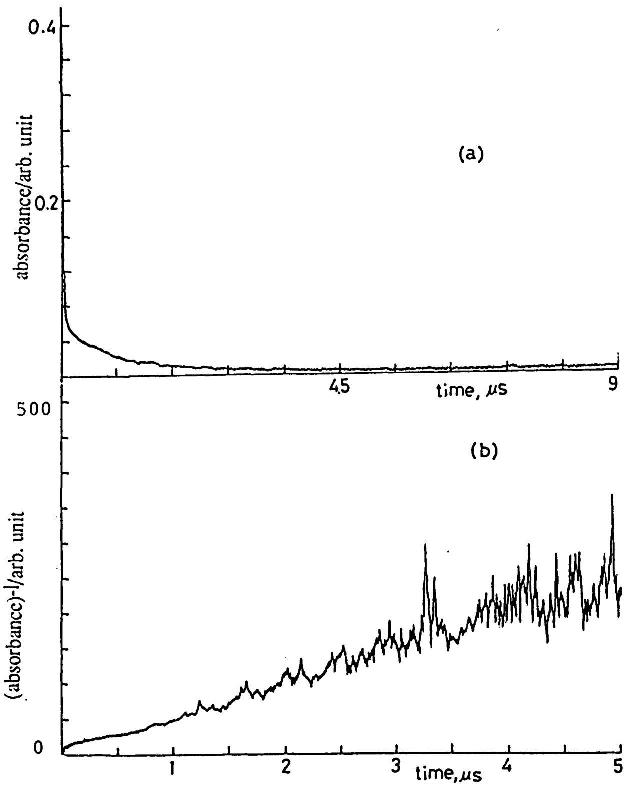


Fig. 2. Representative data displays from laser flash photolysis-kinetic spectroscopy experiments; (a) absorbance at 490 nm as a function of time (A(t)) upon irradiation of $(Me_2Ge)_5$ (**1**) (1.78 mM) in degassed cyclohexane solution, (b) 1/A(t) of **1**.

Table 2. Rate Constats for the Disappearance of the Transient Produced by the Photolysis of the Decamethylcyclopentagermane and 1,3-Diphenylhexamethyltrigermane in Cyclohexane at 293 K

Transient absorption λ_{max}	k/ε	Rate constant ($M^{-1}s^{-1}$)			Reference
		O_2	CCl_4	1,3-Diene	
490	1.5×10^{6} a)	1.6×10^{9}	7.3×10^{8}	1.5×10^{9}	This work
420	2.5×10^{7} a)		Quenched	2.4×10^{7}	(6)
370	4.8×10^{6} a)	1.8×10^{8}	1.4×10^{7}	2.6×10^{8}	This work

a) 2nd order decay.

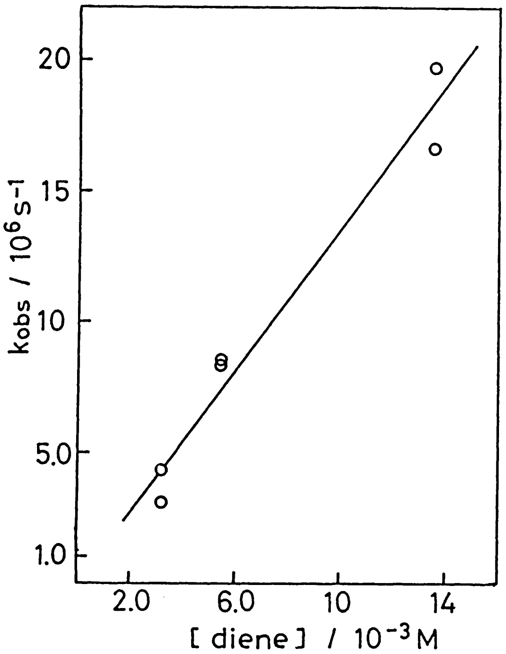


Fig. 3. Plot of the psuedo first-order rate constant for the decay of dimethylgermylene in cyclohexane against the diene concentration.

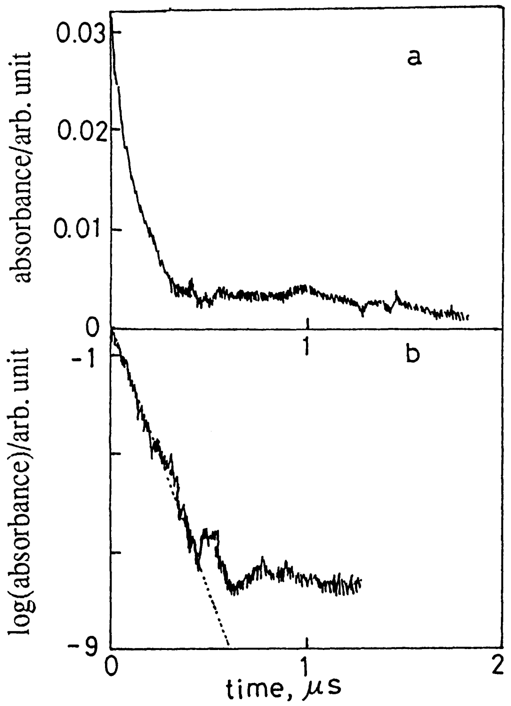


Fig. 4. Representative data displays from laser flash photolysis-kinetic spectroscopy experiments; (a) absorbance at 490 nm as a function of time upon the irradiation of $(Me_2Ge)_5$ (**1**) (1.78 mM) in a degassed cyclohexane solution containing butadiene (5.60 mM), (b) log absorbance at 490 nm as a function of time upon the irradiation of **1** containing butadiene.

1.5×10^{9} $M^{-1}s^{-1}$ and 7.3×10^{8} $M^{-1}s^{-1}$, respectively. The experimentally determined decay constants of **1** are summarized in Table 2, together with those of 1,3-diphenylhexamethyltrigermane.6) The transient at 490 nm from **1** slowly reacts with trapping agents, compared with that of the reported trigermane. The difference in the kinetic results may be explained by the interaction of Me_2Ge; with a π-system. Thus the Me_2Ge: generated from 1,3-diphenylhexamethyltrigermane interacts with the π-system of arylated germanium compound precursors, resulting in a decrease of their reactivities toward trapping agents, compared with the free dimethylgermylene obtained from **1**.14,15) The reactions of the dimethylsilyene with the trapping agents used in this study have been reported to be several orders of magnitude faster in the case of dimethylgermylene.16,17) Representative data displays from laser flash photolysis-kinetic spectroscopy experiments are shown in Figs. 4 and 5. The error limits of the rate constants in this study were about 10—20% due to the small molar coefficient of dimethylgermylene.

Transient absorption at 370 nm resulted from the disappearance of that at 490 nm. The former species may be ascribed to tetramethyldigermene, $Me_2Ge=GeMe_2$. Such dimerization of germylenes to digermenes was observed by both UV18) and IR.9) As is shown in Fig. 6, transient absorption at 370 nm decayed under second-order kinetics ($k/\varepsilon=4.8\times10^{6}$ at 370 nm), suggesting the formation of cyclotetragermane. The digermene are known to react very easily with such trapping agents as oxygen, CCl_4 and olefins.19) The rate constants for the disappearance of the transient at 370 nm with such trapping agents are also summarized in Table 2. As shown in Table 2, reactions of $Me_2Ge=GeMe_2$ with oxygen, CCl_4, and 1,3-diene are relatively slower than

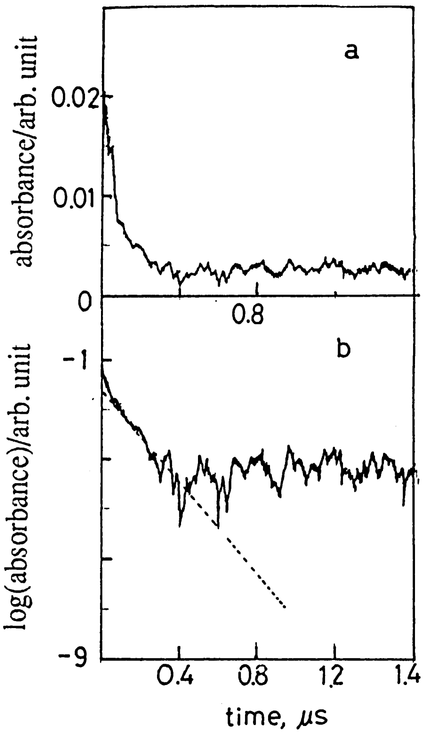


Fig. 5. Representative data displays from laser flash photolysis-kinetic spectroscopy experiments: (a) absorbance at 490 nm as a function of time upon the irradiation of $(Me_2Ge)_5$ (**1**) (1.78 mM) in a degassed cyclohexane solution containing CCl_4(2.28 mM), (b) log absorbance at 490 nm as a function of time upon irradiation of **1** containing CCl_4.

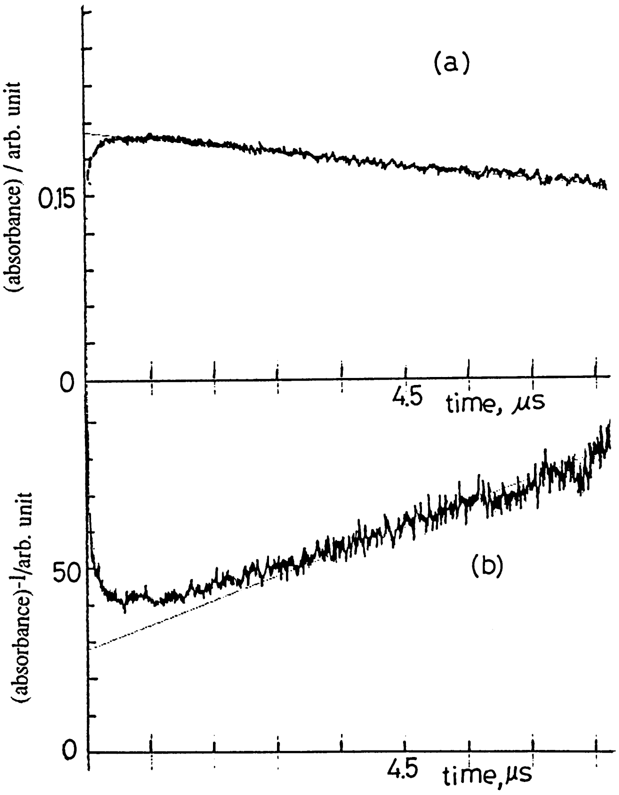


Fig. 6. Representative data displays from laser flash pbotolysis-kinetic spectroscopy experiments: (a) absorbance at 370 nm as a function of time (A(t)) upon the irradiation of **1** in a degassed cyclohexane solution, (b) I/A(t) of **1**.

those in the case of the dimethylgermylene. Digermenes are a limiting form of 1,2-digermanediyl biradicals. In general, 1,2-digermanediyl biradicals react slowly with CCl_4, olefins, as well as some substrates, compared with cases involving germylene.[8,18]

UV Absorption Spectra of Dimethylgermylene Obtained by Matrix Isolation Studies at 77 K. The matrix isolation technique has been widely used for observing reactive species. The 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 reddish-orange glass with a broad band at 506 nm (Fig. 7). The absorption peak at 506 nm is red-shifted, compared with the peak at 490 nm observed in the transient absorption at 293 K. After 20 min of irradiation, the absorption maximum at 509 nm was distinctly visible, but immediately disappeared upon melting the matrix. A reddish-orange species with a λ_{max} at 509 nm can be assigned to dimethylgermylene from a comparison of the spectral characterisitics with those of dimethylgermylene, previously reported for 77 K.[6,18,20] The value of λ_{max} (506 nm) for dimethylgermylene observed in this study was relatively red-shifted. This may be due to a conformational change in the C–Ge–C bond angle between the ground and lowest excited singlet states of the photo-generated dimethylgermylene from **1** at 77 K.

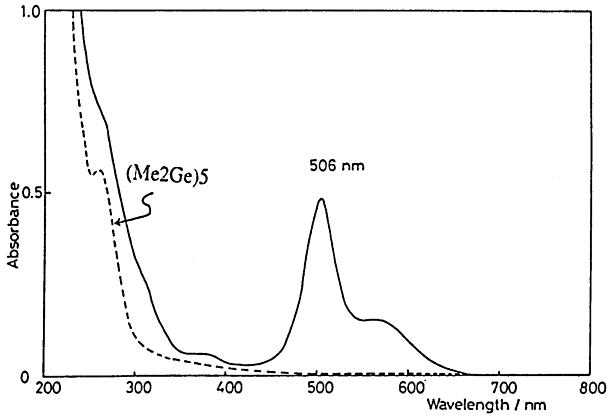
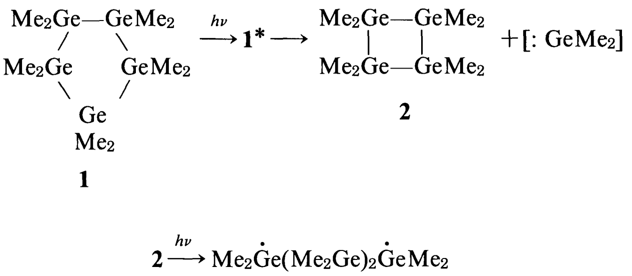


Fig. 7. UV absorption of the cyclopentagermane in 3-methylpentane glass at 77 K.

ESR Studies of Dimethylgermylene in Cyclohexane at 77 K. ESR measurements were carried out at 77 K in order to clarify the electric state of dimethylgermylene photochemically generated from **1**. No triplet ESR signal was obtained for dimethylgermylene in either methyltetrahydrofuran or benzene at 77 K. Thus, the photo-generated dimethylgermylene is in the singlet ground state. The ESR spectra (g=2.014, $\Delta H_{1/2}$=ca. 5

mT) due to some organogermyl radicals[21] were observed with moderate intensities during the photolysis of **1**.

Photodecomposition Mechanism of Decamethylcyclopentagermane. The photochemical degradation of decamethylcyclopentagermane may be rationalized on the basis of Scheme 1 which is similar to that proposed regarding the photolysis of permethylated cyclic polysilanes.[22] Thus, the photochemical degradation of the cyclopentagermane (**1**) may proceed along with the generation of dimethylgermylene to give octamethylcyclotetragermane (**2**) from the lowest excited singlet state. The reactions of dimethylgermylene with some substrates are orders of magnitude of the diffusion-controlled rate. Upon on prolonged irradiation of **2**, a homolytic scission of the germanium-germanium bond of **2** occurs to give the 1,4-tetragermanediyl biradical.



Scheme 1.

Experimental

^{1}H NMR spectra were recorded on a JEOL GX 270 using tetrmethylsilane as the internal standard. GC-MS spectra were obtained with a JEOL JMX-DX 303 mass spectrometer. Gas chromatography was performed an a Shimadzu GC-6A, and 8A with 1 m SE30 Columns.

Materials. 2,3-Dimethyl-1,3-butadiene, CCl_4, and ethanol were commercially available. $(Me_2Ge)_5$,[23] $(Me_2Ge)_4$,[20] $(Me_2Ge)_4O$,[20] Me_2GeCl_2,[24] 1,1,3,4-tetramethyl-1-germa-3-cyclopentene[25] and $(Me_2GeO)_3$[9] were prepared as described in the cited references.

Photochemical Reactions of Decamethylcyclopentagermane at 293 K. Cyclopentagermane (ca. 20 mg, 0.039 mmol) was dissolved in dry cyclohexane (6 cm^3) in a quartz tube. The tube was degassed in a vacuum and argon inserted. The sample was irradiated with a 110-W low-pressure Hg arc lamp (Sen Tokushu Kogen Co., Ltd.) at room temperature for 30 min. After irradiation, the photoproducts were identified by comparing the retention times on GLC and GC-MS with those of authentic samples. $(MeGe_2)_4$ (25%) and $(Me_2GeO)_3$ (31%) were formed.

Photochemical Reactions of Decamethylcyclopentagermane in the Presence of Trapping Agents. As a representative example, the photolysis of a cyclohexane solution of decamethylcyclopentagermane containing carbon tetrachloride is described. Cyclopentagermane (ca. 20 mg, 0.039 mmol) and CCl_4(0.26 g 1.71 nunol) was dissolved in dry cyclohexane (6 cm^3) in a quartz tube. The tube was degassed in a vacuum and argon inserted. Me_2GeCl_2 (21%) and $Cl(Me_2Ge)_4Cl$ (35%) were formed. The reaction products were separated by preparative GLC and the structures were assigned by comparing the NMR and GC data of similar reported compounds. $Cl(Me_2Ge)_4Cl$:MS (70 eV) *m/z* 447(5), 343(80), 323(5), 255(4), 221(75), 191(15), 161(6), 139(18), 119(100), 105(10), 89(35).

Time-Resolved Optical Absorption Samples contained in quartz cells with an optical length of 5 cm were degassed by four freeze-pump-thaw cycles. The concentrations of cyclopentagermane were ca. 10^{-3} M. Laser flash photolysis experiments were performed at room temperature by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-11 Nd:YAG laser exciting light source. The laser pulse width was about 5 ns. Details concerning the laser photolysis apparatus have been published elsewhere.[26] The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and recorded with an Iwatsu DM-901 digital memory (10 ns/point, 8 bit) controlled by an NEC PC 8801 microcomputer.

Matrix Isolation of the Cyclopentagermane at 77 K. Cyclopentagermane (ca. 0.1 mM) was dissolved in 3-MP and sealed in the vacuum of a quartz cell connected to a Pyrex tube. The cell was introduced into an Oxford cryostat. The sample was cooled to 77 K, and then 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.

ESR Measurement. ESR signals were recorded on a JEOL FE-2X ESR spectrometer at 77 K. The 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.

We thank Drs. Hisaharu Hayashi and Masanobu Wakasa of The Institute of Physical and Chemical Research for measuring laser flash photolysis. This research was partly supported by a Grant-in-Aid for Scientific Research No. 03215228 from the Ministry of Education, Science and Culture.

References

1) For examples: R. West, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, Frankfurt (1982), Vol. 2, Chap. 9.4; H. Sakurai Synthesis and Application of Organopolysilanes," CMC, Tokyo (1989); R. West, *J. Organomet. Chem.*, **300**, 327 (1986), and references cited therein; M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, **19**, 51 (1981), and references cited therein; H. Sakurai, *Yuki Gosei Kagaku Kyokaishi*, **47**, 1051 (1989), and references cited therein; R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

2) P. Trefonas and R. West, *J. Polym. Sci., Polmy. Chem. Ed.*, **23**, 2099 (1985); R. D. Miller and R. Sooriyakumaran *ibid.*, **25**, 111 (1987); J. C. Baumert, G. C. Bjorklund, D. H. Jundt, M. C. Jurich, H. Looser, R. D. Miller, J. Rabolt, R. Sooariyakumaran, J. D. Swalen, and R. J. Tweig, *Appl. Phys. Lett.*, **53**, 1147 (1988), G. Meyer and Wohrle, *Makromol. Chem.*, **175**, 714 (1974); H. Ban and A. Tanaka, *J. Appl. Polym. Sci.*, **37**, 1589 (1989).

3) K. Mochida, M. Wakasa, Y. Nakadaira, Y. Sakaguchi, and H. Hayashi, *Organometallics*, **7**, 1869 (1988); K. Mochida, M. Wakasa, Y. Sakaguchi, and H. Hayashi, *Bull. Chem. Soc. Jpn.*, **64**, 1899 (1991).

4) K. Mochida, H. Kikkawa, and Y. Nakadaira, *Chem. Lett.*, **1988**, 1089; K. Mochida, H. Kikkawa, and Y. Nakadaira, *J, Organomet. Chem.*, **412**, 9 (1991).

5) K. Mochida, H. Chiba, and M. Okano, *Chem. Lett.*, **1991**, 109.

6) M. Wakasa, I. Yoneda, and K. Mochida, *J. Organomet. Chem.*, **366**, Cl (1989); K. Mochida, I. Yoneda, and M. Wakasa, *ibid.*, **399**, 53 (1990).

7) M. Okano and K. Mochida, *Chem. Lett.*, **1990**, 701.

8) K. Mochida, N. Kanno, R. Kato, M. Kotani, S. Yamauchi, M. Wakasa, and H. Hayashi, *J. Organomet. Chem.*, **415**, 191 (1991).

9) J, Barrau, D. L. Bean, K. M. Welsh, R. West, and J. Michl, *Organometallics*, **8**, 2606 (1989).

10) For example: M. Schriewer and W. P. Neumann, *J. Am. Chem. Soc.*, **105**, 897 (1983).

11) W. P. Neumann and M. Schriewer, *Tetrahedron Lett.*, **1980**, 3273; S. Tamoda, M. Shimoda, Y. Takeuchi, Y. Kaji, K. Obi, I. Tanaka, and K. Honda, *J. Chem. Soc., Chem. Commun.*, **1988**, 910.

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

13) For examples: P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, **1973**, 54.

14) K. Mochida, S. Tokura, and S. Murata, *J. Chem. Soc., Chem. Commun.*, **1992**, 250.

15) G. Levin, P. K. Das, C. Bilgrien, and C. Lee, *Organometallics*, **8**, 1206 (1989).

16) P. P. Gaspar, D. Holten, S Konieczny, and J. Y. Corey, *Acc. Chem. Res.*, **20**, 329 (1987).

17) H. Shizuka, H. Tanaka, K. Tonokura, K. Murata, H. Hiratsuka, J. Ohshita, and M. Ishikawa, *Chem. Phys. Lett.*, **143**, 225 (1988).

18) For example: J. Barrau, J. Escudie, and J. Satge, *Chem. Rev.*, **90**, 283 (1990).

19) W. Ando, T. Tsumuraya, and A. Sekiguchi, *Chem. Lett.*, **1987**, 317; W. Ando, H. Itho, T. Tsumuraya, and H. Yoshida, *Organometallics*, **7**, 1880 (1988).

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

21) H. Sakurai, K. Mochida, and M. Kira, *J. Am. Chem. Soc.*, **94**, 929 (1975); *idem, J. Organomet. Chem.*, **154**, 353 (1978).

22) M. Ishikawa and M. Kumada, *J. Chem. Soc., Chem. Commun.*, **1970**, 612; *idem, J. Organomet. Chem.*, **42**, 325 (1978).

23) E. Caberry, B. D. Domberk, and S. C. Cohen, *J. Organomet. Chem.*, **36**, 61 (1972).

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

25) P. Mazerolles and G. Manuel, *Bull. Chim. Fr.*, **1973**, 1.

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