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Photochemical reactions of digermanyl-substituted naphthalenes: The germyl migration to the aromatic ring

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Abstract

Photochemical reactions of digermanyl-substituted naphthalenes have been investigated by chemical studies using trapping agents, laser flash photolysis, and ab initio MO calculations. Irradiation of 1-(pentamethyldigermanyl)naphthalene (**1**) afforded mainly an isomer, 1-(dimethylgermyl)-8-(trimethylgermyl)naphthalene (**4**), via photochemical formation of a pair of trimethylgermyl radical and 1-naphthyldimethylgermyl radical, and then recombination at the 8-position of the latter followed by an intramolecular 1,4-hydrogen shift. At the same time a small amount of 1-(trimethylgermyl)naphthalene (**5**) was formed through the dimethylgermylene extrusion from **1**. From photolysis of 2-(pentamethyldigermany)naphthalene a high molecular weight polymer was obtained. The excited states of digermanyl-substituted naphthalenes responsible for the photodecomposition are also discussed. © 1998 Elsevier Science S.A.

Keywords: Photolysis; Migration; Naphthylgermane; Laser photolysis; Germyl radical

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1. Introduction

Recently, much attention has been focused on the photochemistry of aryl-substituted dimetals of group-14 elements (E) from both mechanistic and synthetic viewpoints [1–28]. In the photolysis of these σ (E–E)-π conjugated systems, highly reactive group-14 element species such as $R_2E{=}CR_2$, $R_2E{=}ER_2$, R_3E, and R_2E: (R = alkyl, aryl, etc.) are formed via various modes of reactions, and lead to many novel group-14 element compounds. However, studies of photochemical reactions of arylated digermanes are very limited compared with those of the corresponding disilanes.

We have recently reported the results of a study on photochemical reactions of arylated digermanes by chemical reactions using trapping agents and nanosecond laser flash photolysis techniques [29–37]. Photolysis of the arylated digermanes results in germanium–germanium bond homolysis to give a pair of two germyl radicals, which abstract a hydrogen atom from hydrogen sources to give the corresponding hydromonogermanes, or couple to afford digermanes as main products. In sharp contrast to the case of the aryldisilanes, germyl migration products to aromatic rings (formal 1,3-germyl migration products) could not be detected up to this time. Photochemical reaction pathways of aryldigermanes may depend on the nature of the π system. Thus, we have examined photochemical reactions of digermanyl-substituted naphthalenes and found the photochemical migration of a germyl group to the aromatic ring of arylated digermanes. In this paper, we report on the photochemical behavior of (digermanyl)naphthalenes by chemical studies using trapping agents, laser flash photolysis, and ab initio MO calculations. The excited states of (digermanyl)naphthalenes responsible for the photoreactions are also discussed.

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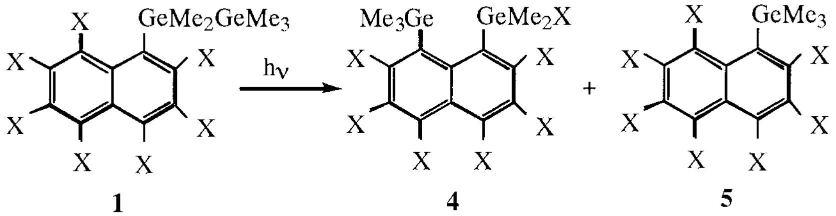
2. Results and discussion

2.1. Photolysis of 1-digermanyl-substituted naphthalenes

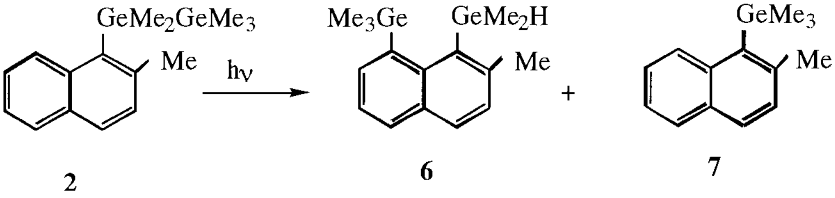
Each of cyclohexane solutions of 1-(pentamethyldigermanyl)naphthalene (**1**), 1-(pentamethyldigermanyl)-2-methylnaphthalene (**2**), and 1-(pentamethyldigermanyl)-8-methylnaphthalene (**3**) (ca. 0.1 M) in a quartz photolysis cell was degassed and then irradiated with a 110 W low pressure Hg arc lamp at room temperature under argon for 30 min. Photolysis of a cyclohexane solution of **1a** produced mainly an isomer, 1-(dimethylgermyl)-8-(trimethylgermyl)naphthalene (**4a**) (59%), along with 46% of recovered **1a** and of 1-(trimethylgermyl)naphthalene (**5a**) ($<1\%$) (Eq. (1)). Products **4a** and **5a** were isolated in pure state and their structures were confirmed by GC-mass, IR, and ^{1}H and ^{13}C NMR spectroscopic analysis. The IR, NMR, and GC-mass spectra of **5a** were identical with those of the authentic samples.



(1)

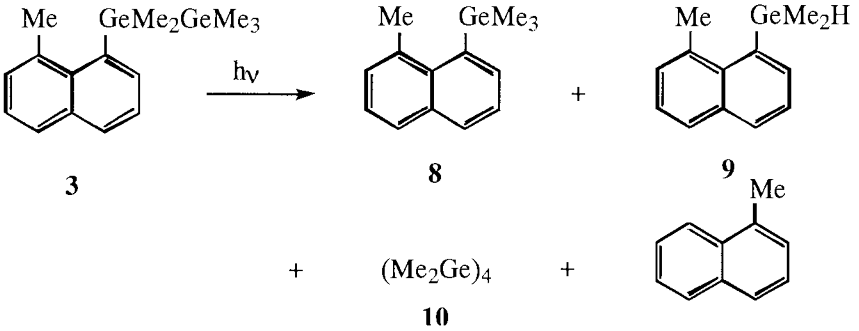
a: X=H; **b**: X=D

To get information on the origin of hydrogermane **4a**, photolysis of **1a** in deuteriocyclohexane (C_6D_{12}) were carried out under the same conditions. The ^{1}H NMR spectrum of **4a** thus obtained showed a septet resonance at δ 5.25 ppm due to a Ge–H proton. No deuterium is incorporated in the photoproducts. A similar irradiation of 1-(pentamethyldigermanyl)heptadeuterionaphthalene (**1b**) in cyclohexane gave 1-(dimethyldeuteriogermyl)-8-(trimethylgermyl)deuterio-naphthalene (**4b**), which showed no resonance due to a Ge–H proton by NMR. The mass spectrum of **4b** showed a parent ion (M^+) at m/z 355, indicating that **4b** contains a deuterium bonded to a germanium atom. These results indicate that the hydrogen on a germanium atom must come from the naphthyl ring, but not from the solvent used. Photolysis of **2**, in which the C_2 position is occupied by a methyl group, afforded an isomer, 1-(dimethylgermyl)-2-methyl-8-(trimethylgermyl)naphthalene (**6**) (33%), together with 1-(trimethylgermyl)-2-methylnaphthalene (**7**) (4%) in cyclohexane (Eq. (2)). The photoisomerization of **1** and **2** to **4** and **6**, respectively, clearly indicates that the trimethylgermyl group attached to the α-germanium at the C_1 position migrates to the C_8 position of the naphthyl ring. On the other hand, monogermanes **5** and **7** should be produced through the dimethylgermylene extrusion from **1** and **2**, respectively.



(2)

A similar photolysis of **3** in cyclohexane, in which the C_8 position of the naphthyl ring is occupied by a methyl group, yielded a variety of products; 1-(trimethylgermyl)-8-methylnaphthalene (**8**) (17%), 1-(dimethylgermyl)-8-methylnaphthalene (**9**) (1%), and octamethylcyclotetragermane (**10**) (1%), together with 1-methylnaphthalene ($<1\%$). Compound **10** may be formed via tetramerization of dimethylgermylene [37]. Expectedly, no migration products of the germyl group to C_8 position of the naphthyl ring were detected in the reaction mixture. A possible product formed migration of the germyl group to the C_2 position was not detected in the reaction mixture by means of GC-mass.



(3)

Formation of monogermanes, **5, 7, 8**, and cyclotetragermane **10** in the photolysate implies that dimethylgermylene is generated during the photolysis of **1–3**. However, the photolysis of **1a** in cyclohexane containing 10–20 fold excess of 2,3-dimethyl-1,3-butadiene as a germylene trap [38] afforded **4a** alone in 94% yield; no dimethylgermylene adduct was detected in the reaction mixture. The reason for no formation of germylene and remarkable increase of the yield of **4a** during photolysis of **1a** in the presence of 2,3-dimethyl-1,3-butadiene is described later. On the other hand, the formation of hydrogermane **9** on photolysis of **3** is indicative of an intermediacy of germyl radicals generated by homolysis of the germanium–germanium bond of 1-(digermanyl)naphthalenes. Since germyl radicals are well known to abstract a chlorine atom from polyhalomethanes effectively [39], the photolyses of **1–3** were carried out in cyclohexane containing a 5–10 fold excess of chloroform. A small amount of the corresponding chlorogermane, 1-(dimethylchlorogermyl)-8-methylnaphthalene (1%), was detected along with **10** (2%), pentamethylchlorodigermane (28%), and 1-methylnaphthalene ($<1\%$) during photolysis of **3**. No chlorogermanes, however, were formed in photolyses of **1a** and **2** in the presence of chloroform. Again, isomer **4a** (55%) and **6** (33%) were produced as major products in the reaction mixtures of **1** and **2**, respectively. A geminate pair of germyl radicals is expected to undergo a disproportionation to give the corresponding hydrogermanes and germenes. To prove the existence of the germene [40], the photolyses of **1–3** in cyclohexane containing a large excess (40- and 100-fold excess) of ethanol were examined. However, no ethanol addition products to the germenes were detected in the resulted photolysis mixture. The isomer **4a** (56%) and **6** (31%) were formed as the major products. In marked contrast to the photolysis of phenylated digermanes [31,32], the germenes are not involved as the reactive intermediates in the photolysis of the 1-naphthyl system.

The structure of **4a** was verified with GC-mass, IR, and ^{1}H and ^{13}C NMR spectroscopic methods. The positions of two germyl groups on the naphthyl ring in **4a** were carefully determined by ^{13}C NMR distortionless enhancement by polarization transfer (DEPT), ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and COLOC spectra, respectively.

2.2. Laser flash photolysis of 1-(digermanyl)naphthalene

To obtain more direct information on reactive intermediates in photochemical reactions of 1-(digermanyl)naphthalenes, measurements of nanosecond transient absorption spectra were performed on the degassed solutions containing **1a** at 293 K using both a XeCl laser and N_2 laser as excitatory light sources [41].

The time dependence of absorbance of the transient absorption $A(t)$ was measured with cyclohexane solutions of **1a** (ca. 0.2 M). The $A(t)$ curves were measured in the wavelength region of 350–600 nm, where the time resolution of the apparatus was about 10 ns.

By using the $A(t)$ curves observed at various wavelengths, the time-resolved absorption spectra of **1a** were obtained at 240 ns and 20 μs after laser excitation as shown in Fig. 1. Two separated transient absorptions both at ca. 400 and 440 nm for **1a** were observed at 240 ns after photoexcitation. As shown in Fig. 1, both transients at 400 and 440 nm decayed, and a new transient peak at 460 nm appeared at 20 μs. The signals show a rapid rise and subsequent decay. The transient peak at 440 nm is reasonably assigned to that due to dimethylgermylene from comparison of the

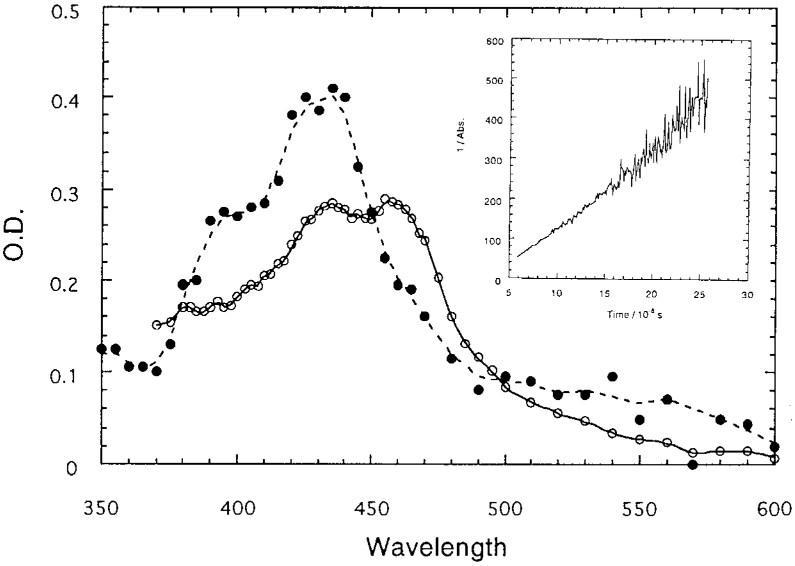


Fig. 1. Transient absorption spectra at 240 ns and 20 μs after photoexcitation of **1**.

spectral characteristics with those previously reported [39]. Analysis of the transient absorption due to dimethylgermylene revealed approximately second-order decay kinetics ($k/\varepsilon = 2.5 \times 10^7$, k is the second-order rate constant and ε is the molar extinction coefficient), suggesting the formation of digermene. The consistency of decay kinetics of the dimethylgermylene measured in this study with the life time of fluorescence for **1a** estimated from that of naphthalene derivatives [42] suggests that dimethylgermylene is generated through the singlet excited state of **1a**. The assignment of the transient peak at ca. 400 nm is tentatively ascribed to the corresponding digermene by comparing their spectral shapes and positions with those previously reported [37].

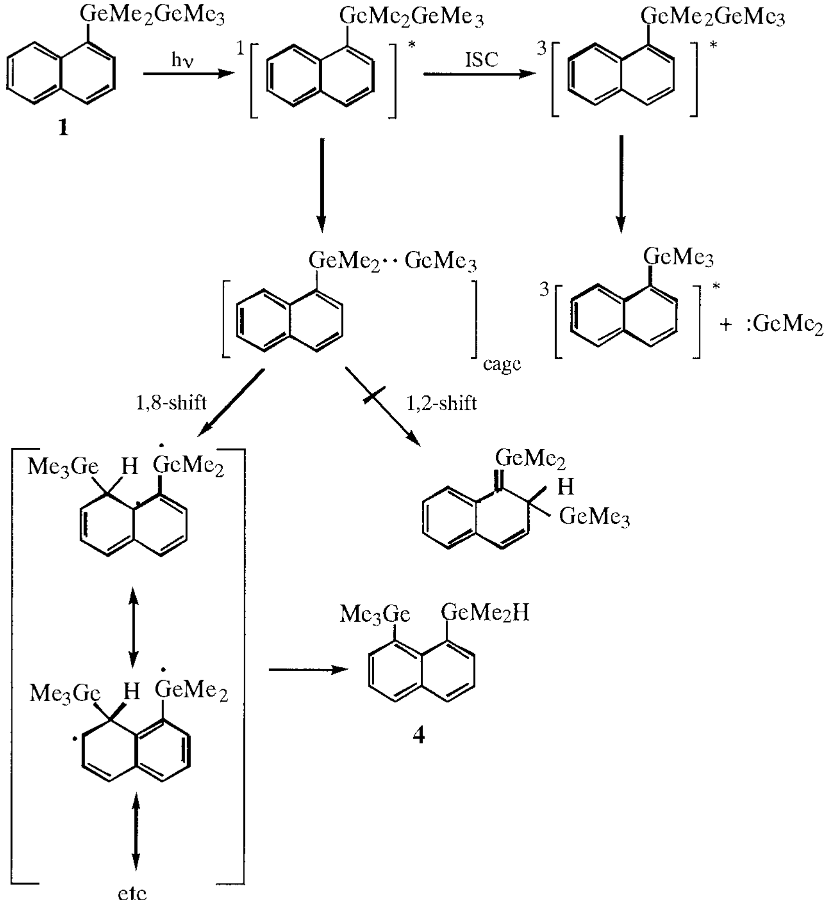
On the other hand, the transient peak at 460 nm is assigned to that of $T_n \leftarrow T_1$ of **1a**, by the following reasons: (1) The $T_n \leftarrow T_1$ transition in naphthalene has been reported to be 430 nm [40]. (2) The absorption peak at 460 nm did not appear at 10 ns after photoexcitation, but appeared at 10 μs.

2.3. Photolysis of 2-digermanyl-substituted naphthalene

In marked contrast to 1-(digermanyl)naphthalenes, photolysis of 2-(pentamethyldigermanyl)naphthalene (**11**) in cyclohexane gave high molecular weight polymer (Mw = 3.7×10^4). The molecular weight of the polymer is relative to polystyrene standards by means of gel permeation chromatography. The NMR spectrum of the polymers obtained roughly shows several kinds of methyl groups attached to the germanium atom and the naphthyl group. The photolysis of **11** gave polymeric products even in the presence of a trapping agent such as isobutene, ethanol, or 2-propanol. Ishikawa and co-workers have reported that photolysis of 2-(pentamethyldisilanyl)naphthalene in the presence of isobutene produces 2-isobutyldimethylsilyl-3-trimethylsilylnaphthalene, but in the absence of isobutene affords polymeric substances [20].

2.4. Mechanism for photoreactions of 1-digermanylnaphthalenes

Recently, Ishikawa and co-workers have reinvestigated the photolysis of 1-(pentamethyldisilanyl)naphthalene and related compounds and found the preferred migration of terminal trimethylsilyl group to the C_8 position of the



Scheme 1.

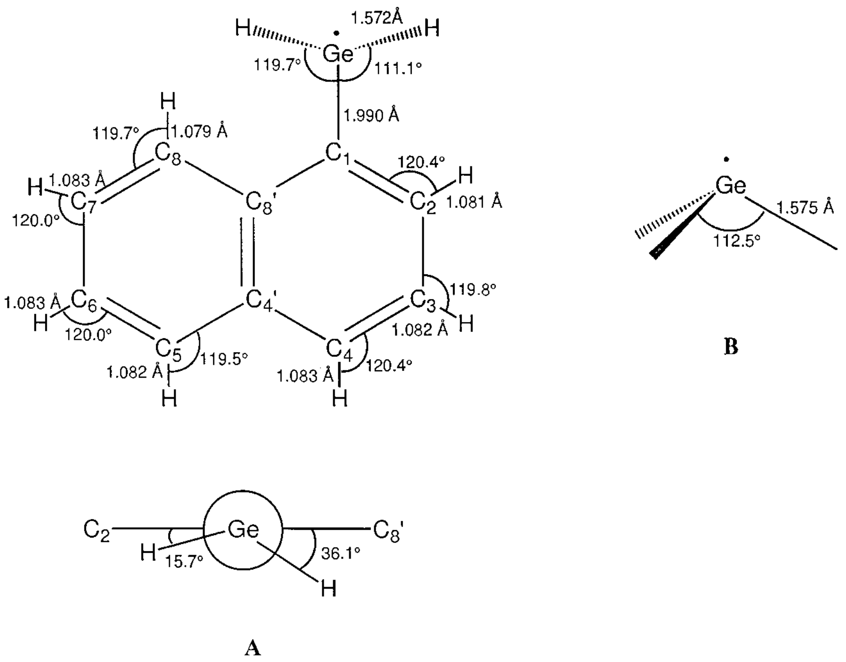
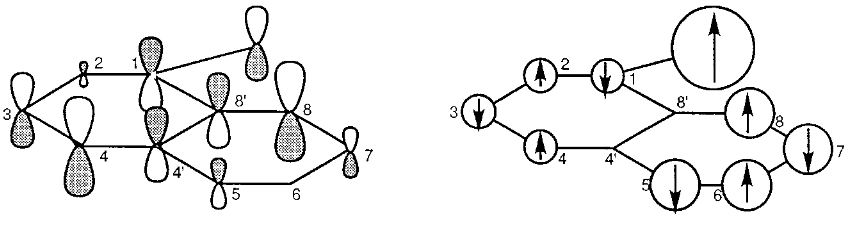


Fig. 2. Optimized structure at the UHF/LANL1MB level for naphthylgermyl radical (**A**). The geometry was optimized under the constraint of the planar naphthyl ring having a fixed C–C bond distance of 1.40 Å and a C–C–C bond angle of 120°.

naphthyl ring [21]. The major parts of the results of the photochemical studies of 1-digermanylnaphthalenes and related compounds are good in accord with the mechanism proposed by Isikawa et al. As shown in Scheme 1, during the photolysis of 1-pentamethyldigermanylnaphthalene (**1**), the homolytic scission of a germanium–germanium bond of the photoexcited molecule would take place to give a pair of trimethylgermyl and naphthyldimethylgermyl radicals, which recombine at the C_8 position of the latter in the solvent cage followed by a 1,4-hydrogen shift to give **4**. It is interesting to note that during photolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene, the formation of **5** was suppressed with increasing yield of **4**. Since the diene is well-known triplet quencher, the results suggest that the germylene extrusion occurs from the triplet excited state, while the homolytic Ge–Ge bond scission from the singlet excited state. However, there is possibility of the formation of other products except for germylene from the triplet excited state of **1**.

Whereas rather unusual migration of the terminal germyl group of **1** to C_8 position may be explained in line with the orbital interaction method developed by Ishikawa et al., the radical recombination mechanism may also be compatible with the results. The latter possibility was proved by ab initio MO UHF calculations of 1-naphthylgermyl radical (**A**) using the LANL1MB basis set. The geometry was optimized under the constraint of the planar naphthyl ring having a fixed C–C bond distance of 1.40 Å and a C–C–C bond angle of 120°. As shown in Fig. 2, at the optimized structure, the sp^3-like singly occupied atomic orbital on germanium overlaps well with the naphthyl pπ orbital. The SOMO and spin density distribution of **A** are shown schematically in Fig. 3. Whereas the largest spin density of **A** was observed at the germanium atom as expectedly, the second largest spin density was found at the C_5 (-0.555) and C_8 $(+0.562)$ positions. Recombination of the radical pair would occur favorably at a position having large spin density such at the C_8 position.



SOMO **Spin Density**

Fig. 3. Schematic representation of SOMO and spin density distribution for 1-naphthylgermyl radical calculated at the UHF/LANL1MB level.

3. Experimental details

^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 MHz, Varian 400 MHz, Hitachi H-90 MHz, and JNM-MY60 60 MHz NMR spectrometers. 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-8A and Okura Model 802 instruments with 1 m 20% SE30 and 1 m Apiezon L columns. Liquid chromatography was performed with a JAI LC-908 with AJ 1H and 2H columns.

3.1. Materials

Chloroform, ethanol, 2-propanol, isobutene, 2,3-dimethyl-1,3-butadiene, 1-methylnaphthalene, and 1-boromonaphthalene were commercially obtained. Octamethylcyclotetragermane [43] and pentamethylchlorodigermane [44] were prepared as described in the literature. Cyclohexane and deuteriocyclohexane as solvents were dried over sodium wire and purified under argon.

*3.2. Preparation of 1-(pentamethyldigermanyl)naphthalene (**1a**)*

A solution of 1-naphthylmagnesium bromide prepared from 3.0 g (0.12 mol) of magnesium and 27 g (0.13 mol) of 1-bromonaphthalene in a mixed solvent (THF–ether–benzene, 13:25:38 ml) was added to 20 g (0.078 mol) of pentamethylchlorodigermane in 50 ml of THF at room temperature. The mixture was then refluxed for 3 h and then hydrolyzed with dilute hydrochloric acid. After work-up in the usual manner, fractional distillation gave 20.5 g (76%) of **1a**: bp 109–110°C/1 mmHg; ^{1}H NMR (δ in CDCl$_3$) 0.50 (s, 9H), 0.92 (s, 6H), 7.3–8.1 (m, 7H); IR (neat, cm^{-1}) 3072, 2970, 2903, 1504, 1232, 825, 790, 731, 594, 561; UV (cyclohexane) λ_{max}/nm (ϵ) 226 (5.44×10^4), 285 (9.91×10^3); mass spectrum m/z 348. Anal. Calcd. for $C_{15}H_{22}Ge_2$: C, 51.84; H, 6.38%. Found: C, 51.93; H, 6.24%.

*3.3. Preparation of 1-(pentamethyldigermanyl)perdeuterionaphthalene (**1b**)*

A solution of 1-(perdeuterionaphthyl)magnesium bromide prepared from 0.9 g (0.037 mol) of magnesium and 3.3 g (0.015 mol) of 1-bromo(perdeuterionaphthalene) in a mixed solvent (THF–ether–benzene) was added to 3.1 g (0.012 mol) of pentamethylchlorodigermane in 10 ml of THF. The mixture was refluxed for 3 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was washed and dried over anhydrous magnesium sulfate. After work-up in the usual manner, fractional distillation gave 3.4 g (80%) of **1b**: bp 123 °C/2 mm Hg. ^{1}H NMR (δ in CDCl$_3$) 0.37 (s, 9H), 0.70 (s, 6H); IR(neat, cm^{-1}) 2969, 2905, 2272, 1439, 1410, 1233, 825, 733, 629, 594, 572, 561; UV (cyclohexane) λ_{max}/nm (ϵ) 226 (4.91×10^4), 284 (1.78×10^3); mass spectrum m/z 355. Anal. Calcd. for $C_{15}H_{15}D_7Ge_2$: C, 51.84; H + D, 6.38%. Found: C, 51.21; H + D, 6.16%.

*3.4. Preparation of 1-(pentamethyldigermanyl)-2-methylnaphthalene (**2**)*

A solution of 2-methyl-1-naphthylmagnesium bromide prepared from 6.1 g (0.25 mol) of magnesium and 4.4 g (0.02 mol) of 1-bromonaphthalene in a mixed solvent (THF–ether–benzene) was added to 4.0 g (0.016 mol) of pentamethylchlorodigermane in 25 ml of THF at room temperature. The mixture was then refluxed for 3 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was washed and dried over anhydrous magnesium sulfate. After work-up in the usual manner, fractional distillation gave 0.8 g (14%) of **2**: bp 120–122°C/2 mm Hg; ^{1}H NMR (δ in CDCl$_3$) 0.40 (s, 9H), 0.89 (s, 6H), 2.70 (s, 3H), 7.1–8.1 (m, 6H); IR (neat, cm^{-1}) 2967, 1506, 1420, 1232, 828, 792, 775, 738, 590; UV (cyclohexane) λ_{max}/nm (ϵ) 231 (5.01×10^4), 290 (7.379×10^3); mass spectrum m/z 362. Anal. Calcd. for $C_{15}H_{24}Ge_2$: C, 53.15; H, 6.69%. Found: C, 53.12; H, 6.45%.

*3.5. Preparation of 1-(pentamethyldigermanyl)-8-methylnaphthalene (**3**)*

A solution of 8-methyl-1-naphthylmagensium bromide prepared from 0.51 g (0.021 mol) of magnesium and 3.9 g (0.017 mol) of 8-methyl-1-bromonaphthalene in a mixed solvent (THF–ether–benzene, 12:18:29 ml) was added to 5.1 g (0.02 mol) of pentamethylchlorodigermane in 25 ml of THF. The mixture was refluxed for 1 week and then hydrolyzed with dilute hydrochloric acid. The organic layer was washed and dried over anhydrous magnesium sulfate. After work-up in the usual manner, fractional distillation gave 1.4 g (23%) of **3**: bp 121–123°C/1 mm Hg. ^{1}H NMR

(δ in $CDCl_3$) 0.37 (s, 9H), 0.75 (s, 6H), 2.90 (s, 3H), 7.1–7.9 (m, 6H); UV (cyclohexane) λ_{max}/nm (ϵ) 233 (5.61×10^4), 293 (1.28×10^4); mass spectrum m/z 362. Anal. Calcd. for $C_{16}H_{24}Ge_2$: C, 53.15; H, 6.69%. Found: C, 53.86; H, 6.59%.

*3.6. Preparation of 2-(pentamethyldigermanyl)naphthalene (**11**)*

A solution of 2-naphthylmagensium bromide prepared from 1.0 g (0.041 mol) of magnesium and 8.5 g (0.041 mol) of 2-bromonaphthalene in a mixed solvent (THF–ether–benzene, 24:36:58 ml) was added to 5.2 g (0.02 mol) of pentamethylchlorodigermane in 10 ml of THF at room temperature. The mixture was then refluxed for 3 h. The mixture was hydrolyzed with dilute hydrochloric acid. After work-up in the usual manner, fractional distillation gave 5.3 g (76%) of **11**: bp 118–120°C/2 mm Hg. ^{1}H NMR (δ in $CDCl_3$) 0.43 (s, 9H), 0.70 (s, 6H), 7.2–8.2 (m, 6H); IR (neat, cm^{-1}) 3072, 2970, 2901, 2359, 1498, 1238, 815, 791, 739, 594, 559; UV (cyclohexane) λ_{max}/nm (ϵ) 229 (7.49×10^4), 291 (4.16×10^3); mass spectrum m/z 348. Anal. Calcd. for $C_{15}H_{22}Ge_2$: C, 51.84 ; H, 6.38%. Found: C, 51.95; H, 6.29%.

*3.7. Preparation of 1-(trimethylgermyl)naphthalene (**5a**)*

This compound was prepared in 60% yield, according to the method for 1-(pentamethyldigermanyl)naphthalene. **5a**: bp 80–82°C/1 mm Hg; ^{1}H NMR (δ in $CDCl_3$) 0.4 (s, 9H), 7.5–8.5 (m, 7H); mass spectrum m/z 246.

*3.8. Photolysis of 1-(pentamethyldigermanyl)naphthalene (**1a**)*

A mixture of 12 mg (0.33 mol) and *n*-eicosane as an internal standard in 2 ml of cyclohexane was placed in a quartz photolysis cell. The cell was degassed in a vacuum and replaced with argon. The sample was irradiated with a 110 W low-pressure Hg arc lamp at room temperature for 30 min. After irradiation, the photoproducts were identified by IR, GC-mass, and NMR spectra. Quantitative analysis of the product by GC shows the formation of 1-(dimethylgermyl)-8-(trimethylgermyl)naphthalene (**4a**) (59%), 1-(trimethylgermyl)naphthalene (**5a**) (< 1%), and unreacted **1a** (46%) were formed. Isomer **4a** was isolated by preparative GC. ^{1}H NMR (δ in $CDCl_3$) 0.394 (d, 6H, $J = 3.1$ Hz), 0.562 (s, 9H), 5.25 (sept., 1H, $J = 3.1$ Hz), 7.38 (dd, 1H, $J = 8.3$, 7.1 Hz), 7.40 (dd, 1H, $J = 8.3$, 6.8 Hz), 7.66 (d, 1H, $J = 6.8$ Hz), 7.75 (d, 1H, $J = 8.3$ Hz), 7.77 (d, 1H, $J = 7.1$ Hz), 7.78 (d, 1H, $J = 8.3$ Hz); ^{13}C NMR (δ in $CDCl_3$)-1.7, 3.6, 124.2, 124.3, 130.2, 130.6, 133.8, 134.3, 135.9, 140.8, 140.9, 142.6; IR (neat, cm^{-1}) 3050, 2975, 2907, 2104, 1489, 1414, 1305, 1237, 831, 816, 777, 700, 692, 599, 582, 569; mass spectrum M^+ m/z 348.

*3.9. Photolysis of **1a***

*3.9.1. Photolysis of **1a** in the presence of ethanol*

A mixture of 16 mg (0.045 mmol) of **1a** and *n*-eicosane in 20 ml of cyclohexane containing 11 mg (0.24 mmol) of ethanol was irradiated for 4 h. The compounds **4a** (56%) and **5a** (< 1%) were formed with recovery of **1a** (55%).

*3.9.2. Photolysis of **1a** in the presence of 2,3-dimethyl-1,3-butadiene*

A mixture of 16 mg (0.041 mmol) of **1a** and *n*-eicosane in 20 ml of cyclohexane containing 25 mg (0.3 mmol) of 2,3-dimethyl-1,3-butadiene was irradiated for 4 h. The compounds **4a** (70%) were formed with recovery of **1a** (26%).

*3.10. Photolysis of 1-(pentamethyldigermanyl)heptadeuterionaphthalene (**1b**)*

A cyclohexane solution (4 ml) of **1b** (10 mg, 0.028 mmol) was irradiated and analyzed by GC, GC-MASS, and NMR spectra. Isomer **4b** was isolated by preparative GC. ^{1}H NMR (δ in $CDCl_3$) 0.394 (s, 6H), 0.562 (s, 9H); ^{13}C NMR (δ in $CDCl_3$) -1.7, 3.6, 124.2, 124.3, 130.2, 130.6, 133.8, 134.3, 135.9, 140.8, 140.9, 142.6; IR (neat, cm^{-1}) 1237; MS M^+ m/z 355.

*3.11. Photolysis of 1-(pentamethyldigermanyl)-2-methylnaphthalene (**2**)*

A mixture of 10 mg (0.03 mmol) of **2** and *n*-eicosane in 20 ml of cyclohexane was irradiated for 1 h. Unreacted **2** (66%), 1-(dimethylgermyl)-8-(trimethylgermyl)-2-methylnaphthalene (**6**) (33%), and 1-(trimethylgermyl)-2-methylnaphthalene (**7**) (45%) were observed. Photoproducts **6** and **7** were separated by preparative GC and their structures were assigned by comparing the NMR and GC data of similar compounds. **6:** ^{1}H NMR (δ in CCl_4) 0.40 (d, 6H,

$J = 2.5$ Hz), 0.60 (s, 9H), 2.70 (s, 3H), 5.30 (sept., 1H, $J = 3.0$ Hz), 7.2–8.2 (m, 5H); mass spectrum, m/z 362, 345, 229, 213, 155, 141, 119, 104, 89. **7:** ^{1}H NMR (δ in CCl_4) 0.45 (s, 9H), 2.70 (s, 3H), 7.2–8.2 (m, 6H); mass spectrum m/z 260, 245, 213, 155, 141, 115, 87.

*3.12. Photolysis of **2** in the presence of 2,3-dimethyl-1,3-butadiene*

A cyclohexane solution of 12 mg (0.033 mmol) of **5** with 27 mg (0.32 mmol) of 2,3-dimethyl-1,3-butadiene was irradiated for 36 h. Unreacted **2** (50%) and **6** (81%) were detected by GC in the reaction mixture.

*3.13. Photolysis of 1-(pentamethyldigermanyl)-8-methylnaphthalene (**3**)*

A mixture of 12 mg (0.033 mmol) of **3** and *n*-eicosane in 20 ml of cyclohexane was irradiated for 2 h. 1-(Trimethylgermyl)-8-methylnaphthalene (**8**) (17%), 1-(dimethylgermyl)-8-methylnaphthalene (**9**) (1%), and octamethylcyclotetragermane (1%), and 1-methylnaphthalene (< 1%) were formed with recovery of **3** (40%). Photoproducts **8** and **9** were separated by preparative GC and assigned by comparing the NMR and GC data of similar compounds. **8:** ^{1}H NMR (δ in CCl_4) 0.40 (s, 9H), 2.90 (s, 3H), 7.2–8.2 (m, 6H); mass spectrum m/z 260, 245, 213, 153, 141, 115, 89. **9:** IR (neat, cm^{-1}) 2095; mass spectrum m/z 246, 231, 199, 173, 141, 127, 111, 99, 87, 77.

*3.14. Photolysis of **3** in the presence of chloroform*

Photolysis of **3** in 20 ml of cyclohexane containing 36 mg (0.3 mmol) of chloroform for 2 h gave **8** (2%), 1-(dimethylchlorogermyl)-8-methylnaphthalene (1%), pentamethylchlorodigermane (28%), and 1-methylnaphthalene (< 1%) with recovery of **3** (30%). Mass spectrum of 1-(dimethylchlorogermyl)-8-methylnaphthalene: m/z 280, 265, 229, 141, 115.

*3.15. Photolysis of 2-(pentamethyldigermanyl)naphthalene (**11**)*

A mixture of 15 mg (0.042 mmol) of **11** and *n*-eicosane as an internal standard in 20 ml of cyclohexane was obtained for 100 min. A high molecular weight polymer (Mw = 37000, $M_w/M_n = 2.5$, 25%) was obtained with unreacted starting **11** (70%).

3.16. Time-resolved optical absorption

The sample **1a** (1.9 mmol) in cyclohexane was placed in quartz cell with an optical length of 5 mm and was degassed by four freezed-pump-thaw cycles. Laser flash-photolysis experiments were performed at room temperature by use of XeCl laser as an excitatory light source. The laser pulse was about 10 ns, and the details of the laser photolysis apparatus have been published elsewhere [39].

3.17. MO calculation

MO calculations were carried out by the ab initio MO using the Gaussian 92 program. The LANL1MB basis set was employed for the calculations. The calculations were carried out by IBM/RS6000.

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References

[1] P. Boudjouk, J.R. Robert, C.M. Gollino, L.H. Sommer, J. Am. Chem. Soc. 94 (1972) 7926.
[2] M. Ishikawa, T. Fuchigami, T. Sugaya, M. Kumada, J. Am. Chem. Soc. 97 (1975) 5923.
[3] M. Ishikawa, M. Kuamda, Adv. Organomet. Chem. 19 (1981) 51.

[4] M. Ishikawa, Pure Appl. Chem. 50 (1978) 11.
[5] H. Sakurai, Y. Nakadaira, H. Tobita, Kagaku no Ryoiki, 33 (1979) 879, 973.
[6] H. Sakurai, Y. Nakadaira, M. Kira, H. Sugiyama, K. Yoshida, T. Takiguchi, J. Organomet. Chem. 184 (1980) C36.
[7] H. Sakurai, J. Organomet. Chem. 200 (1980) 261.
[8] R. West, in: G. Wilkinson, G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 2, Chap. 9.4, Pergamon, New York, 1980.
[9] H. Okinoshima, W. Weber, J. Organomet. Chem. 149 (1991) 297.
[10] H. Sakurai, Y. Kamiyama, Y. Nakadaira, J. Am. Chem. Soc. 98 (1976) 7424.
[11] M. Ishikawa, T. Fuchigami, M. Kumada, J. Organomet. Chem. 117 (1976) C58.
[12] M. Ishikawa, T. Fuchigami, M. Kumada, J. Organomet. Chem. 149 (1978) 37.
[13] P. Boudjouk, L.H. Sommer, J. Chem. Soc., Chem. Commun. (1973) 54.
[14] R.D. Bush, C.M. Gollino, C.M. Homer, L.H. Sommer, J. Organomet. Chem. 80 (1974) 37.
[15] R.L. Lambert, D. Seyferth, J. Am. Chem. Soc. 94 (1972) 9246.
[16] D. Seyferth, C.K. Hess, D.C. Annavelli, J. Organomet. Chem. 80 (1973) 37.
[17] D. Seyferth, D.P. Duncan, S.C. Vicks, J. Organomet. Chem. 125 (1977) C5.
[18] D. Seyferth, S.C. Vick, M.L. Shannon, T.F. Olin, D.P. Duncan, J. Organomet. Chem. 56 (1977) C7.
[19] M. Kira, H. Sakurai, H. Yoshida, J. Am. Chem. Soc. 107 (1985) 7767.
[20] M. Ishikawa, M. Oda, N. Miyoshi, L. Fabry, M. Kumada, T. Yamabe, K. Fukui, J. Am. Chem. Soc. 101 (1979) 4612.
[21] J. Ohsita, H. Ohsaki, M. Ishikawa, A. Tachibana, Y. Kurosaki, T. Yamabe, A. Minato, Organometallics 10 (1991) 880.
[22] H. Shizuka, H. Hiratsuka, Res. Chem. Intermed. 18 (1992) 131.
[23] J. Braddock-Wilking, M.Y. Chiang, P.P. Gaspar, Organometallics 12 (1993) 197.
[24] M. Kira, T. Miyazawa, H. Sugiyama, M. Yamaguchi, H. Sakurai, J. Am. Chem. Soc. 115 (1883) 3116.
[25] M. Ishikawa, M. Kikuchi, A. Kunai, T. Takeuchi, T. Tsukihara, M. Kido, Organometallics 12 (1993) 3474.
[26] W.J. Leigh, G.W. Sluggett, J. Am. Chem. Soc. 115 (1993) 7531.
[27] W.J. Leigh, G.W. Sluggett, Organometallics 13 (1994) 269.
[28] G.W. Sluggett, W.J. Leigh, Organometallics 13 (1994) 1005.
[29] K. Mochida, H. Kikkawa, Y. Nakadaira, Chem. Lett. (1988) 1089.
[30] K. Mochida, H. Kikkawa, Y. Nakadaira, J. Organomet. Chem. 412 (1991) 9.
[31] K. Mochida, M. Wakasa, Y. Nakadaira, Y. Sakaguchi, H. Hayashi, Organometallics 7 (1988) 1869.
[32] K. Mochida, M. Wakasa, Y. Sakaguchi, H. Hayashi, Bull. Chem. Soc. Jpn. 64 (1991) 1889.
[33] M. Wakasa, I. Yoneda, K. Mochida, J. Organomet. Chem. 366 (1989) C1.
[34] K. Mochida, I. Yoneda, M. Wakasa, J. Organomet. Chem. 399 (1990) 53.
[35] K. Mochida, H. Kikkawa, Y. Nakadaira, Bull. Chem. Soc. Jpn. 64 (1991) 2772.
[36] K. Mochida, K. Kimijima, M. Wakasa, H. Hayashi, J. Organomet. Chem. 465 (1994) 101.
[37] K. Mochida, N. Kanno, M. Wakasa, R. Kato, M. Kotani, H. Hayashi, J. Organomet. Chem. 415 (1991) 191.
[38] W.P. Neumann, M. Schriever, Tetrahedron Lett. (1980) 3273.
[39] H. Sakurai, K. Mochida, A. Hosomi, F. Mita, J. Organomet. Chem. 38 (1972) 275.
[40] J. Barrau, J. Escudie, J. Satge, Chem. Rev. 90 (1990) 283.
[41] Y. Sakaguchi, H. Hayashi, S. Nagakura, J. Phys. Chem. 86 (1982) 3177, For example.
[42] N.J. Turro, Molecular Photochemistry, W.A. Benjamin, New York, 1967, p. 75.
[43] K. Mochida, S. Tokura, Bull. Chem. Soc. Jpn. 65 (1992) 1642.
[44] K. Yamamoto, M. Kumada, J. Organomet. Chem. 35 (1972) 297.