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Photochemical reactions of aryl-substituted catenates of group 4B elements, $\text{PhMe}_2\text{E}-\text{E}'\text{Me}_3$ ($\text{E}, \text{E}' = \text{Si}$ and Ge). Formation of a radical pair *

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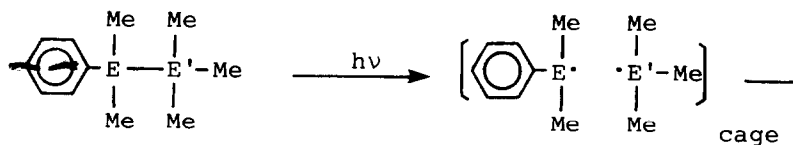
Abstract

Photochemical reactions of phenyl substituted catenates of group 4B elements, $\text{PhMe}_2\text{E}-\text{E}'\text{Me}_3$ ($\text{E}, \text{E}' = \text{Si}$ and Ge) have been investigated by chemical trapping experiments and laser flash-photolysis. On irradiation, the phenylated group 4B catenate undergoes $\text{E}-\text{E}'$ bond homolysis to give a pair of radicals ($\text{PhMe}_2\text{E}^\cdot$ and $\text{Me}_3\text{E}'^\cdot$). In CCl_4 , these radicals are converted to the corresponding chlorides by abstraction of a chlorine atom. In a nonhalogenated solvent, the radical pair couples at the ipso-position of the phenyl group of the pairing radical ($\text{PhMe}_2\text{E}^\cdot$) to yield the corresponding diradical. This undergoes either elimination of a divalent species ($\text{Me}_2\text{E}:$) with concomitant formation of trimethylphenyl group 4B element ($\text{PhMe}_3\text{E}'$) or intramolecular 1,2-group 4B element migration to yield group 4B metal-carbon double bonded species. The radical escapes from the solvent cage coupled to the metal atom of the radical to yield the dimetallic product. The reaction path observed is highly dependent on the nature of the group 4B element comprising the phenyl substituted catenate.

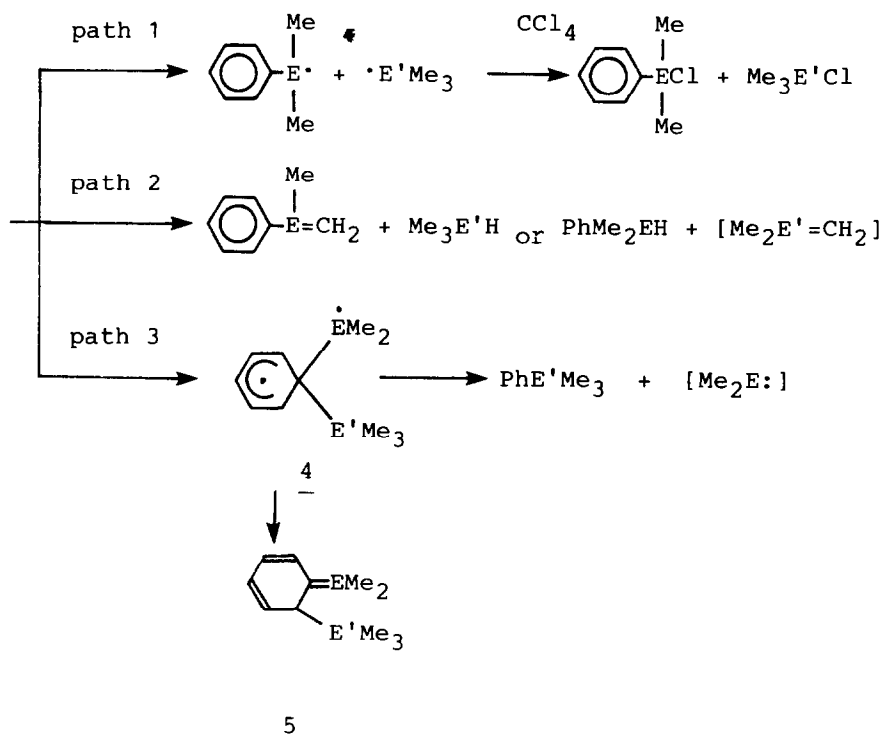
1. Introduction

Recently, much attention has been given to the photolysis of organosilanes based on a $\sigma(\text{Si}-\text{Si})-\pi$ conjugated system, especially the aryl-substituted disilanes [2–5]. In the photolysis of these disilanes, highly reactive organosilicon compounds such as silenes, silyl radicals, and silylenes are generated together with small amounts of stable monosilanes. Early studies on photolysis of methylpentaphenyldisilane reported production of a silene, namely 1,1-diphenylsilene (proved by trapping experiments with methanol) [2]. Later and more detailed photochemical studies have revealed that aryldisilanes undergo a formal 1,3-sigmatropic rearrangement of the silyl group to the aryl group to give another type of silicon-carbon double bonded

* Preliminary results of this study were reported in ref. 1



	E	E'
<u>1</u>	Si	Ge
<u>2</u>	Ge	Si
<u>3</u>	Ge	Ge



Scheme 1

species such as **5** ($\text{E} = \text{E}' = \text{Si}$ in Scheme 1). The structure of **5** has been determined by trapping experiments with various kinds of trapping agents [3]. At the same time, small amounts of products were found to be formed through the silylene extrusion reaction on photolysis [3]. More recently, esr studies show the generation of the silyl radicals on photo-induced homolysis of the corresponding aryldisilane. Furthermore, a radical pair mechanism has been proposed to rationalize these photoproducts [4].

To get more insight into the mechanism of the photolysis of arylsilylgermane, we have studied photolysis of various kinds of aryl-substituted dimetals of group 4B elements. Previously, we have reported on the photolysis of pentamethylphenyldigermene, in which the germyl radicals are generated on photo-induced homolysis of the Ge-Ge bond and constitute key intermediates of the photolysis [1]. In this paper, we describe the photolysis of the catenates, $\text{PhMe}_2\text{E}-\text{E}'\text{Me}_3$ ($\text{E}, \text{E}' = \text{Si}$ and Ge), 1-3, distinct from phenyldisilane ($\text{E} = \text{E}' = \text{Si}$). Laser flash-photolysis and trapping experiments on these compounds show that irradiation of the phenylated group 4B catenates causes E-E' bond homolysis to give rise to the corresponding radical pair.

Results and discussion

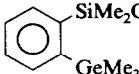

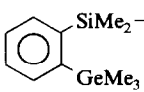
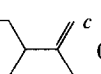

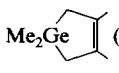
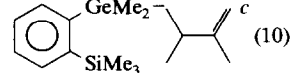

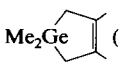
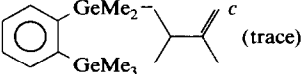
Photoreactions of the phenylated group 4B catenates, 1-3

Phenylated group 4B catenates, $\text{PhMe}_2\text{SiGeMe}_3$ (1), $\text{PhMe}_2\text{GeSiMe}_3$ (2), and $\text{PhMe}_2\text{GeGeMe}_3$ (3) in cyclohexane ($\sim 0.1 M$) were irradiated with a 110 W low pressure Hg arc lamp at room temperature under argon for 1-4 h. Photolysis of 1 in cyclohexane gave trimethylgermane (Me_3GeH , 35%), dimethylphenylsilane (PhMe_2SiH , 17%), hexamethyldigermene ($(\text{Me}_3\text{Ge})_2$, 9%), and tetramethyldiphenyldisiloxane ($(\text{PhMe}_2\text{Si})_2\text{O}$, 11%), respectively. Photolysis of 2 in cyclohexane afforded trimethylsilane (Me_3SiH , 4%) and trimethylphenylsilane (PhSiMe_3 , 24%), respectively. At the same time, trace amounts of dimethylphenylgermane (PhMe_2GeH), hexamethyldisilane ($(\text{Me}_3\text{Si})_2$), and tetramethyl-1,2-diphenyldigermene ($(\text{PhMe}_2\text{Ge})_2$) were detected by means of GC-MS. Photolysis of 3 in cyclohexane yielded a variety of products, monogermenes (Me_3GeH , 8%; PhMe_2GeH , 8%; PhMe_3Ge , 15%; $\text{Ph}_2\text{Me}_2\text{Ge}$, 8%) and digermenes ($(\text{Me}_3\text{Ge})_2$, 15%; $(\text{PhMe}_2\text{Ge})_2$, 1%), together with digermanoxane ($(\text{PhMe}_2\text{Ge})_2\text{O}$, 2%). Interestingly, a small amount of octamethyltrigermene ($(\text{Me}_3\text{Ge})_2\text{GeMe}_2$, 4%) was formed along with trace amounts of other possible trigermenes ($\text{PhMe}_2\text{GeGeMe}_2\text{GeMe}_3$ and $(\text{PhMe}_2\text{Ge})_2\text{GeMe}_2$) which were detected by means of GC-MS. These results are summarized in Table 1.

Along with hydrosilanes and hydrogermanes, formation of disilanes and digermenes on photolysis is indicative of the presence of an intermediate form of silyl and germyl radicals generated by homolysis of the E-E' bond of catenates 1-3. Since silyl and germyl radicals abstract a chlorine atom from CCl_4 effectively and rapidly [6], to trap these radical intermediates the photolyses of 1-3 were carried out in cyclohexane containing CCl_4 . As expected, the corresponding chlorosilanes and chlorogermenes were obtained in high yields, and neither di-silane and -germane nor hydro-silane and -germane were detected in the photolysate as shown in Table 1. In addition to dimerization, these radicals are expected to undergo a disproportionation to give hydro-silanes and -germanes, and silenes and germenenes, respectively. Silenes and germenenes are known to react quite efficiently with methanol to give corresponding methoxysilanes and methoxygermanes [7]. Hence, to confirm the presence of silenes and germenenes, the photolyses of 1-3 were examined in benzene containing a large excess of methanol (ca. 50 times excess). In the case of 1, methoxydimethylphenylsilane was obtained in fairly good yield, and is likely to arise from the polar addition of methanol to 1-methyl-1-phenylsilene formed from dimethylphenylsilyl radical via disproportionation (path 2 in Scheme 1). This

Table 1

Photoproducts and yields from the photolysis of the phenylated group 4B catenates 1–3 in cyclohexane

dimetal	trapping agent	photo-product (yield, %)
PhMe ₂ SiGeMe ₃ (1)	none	Me ₃ GeH (35), PhMe ₂ SiH (17), (Me ₃ Ge) ₂ (9), (PhMe ₂ Si) ₂ O (11)
	CCl ₄	Me ₃ GeCl (87), PhMe ₂ SiCl (98)
	MeOH ^a	Me ₃ GeH ^b , PhMe ₂ SiH (4), Ph ₂ SiMe ₂ (14) PhMe ₂ SiOMe (54),  (3)
		Me ₃ GeH (59), PhMe ₂ SiH (7), (PhMe ₂ Si) ₂ O (13),  (7),  (6)
	PhMe ₂ GeSiMe ₃ (2)	none
	CCl ₄	Me ₃ SiH (4), PhMe ₂ GeH (trace), PhSiMe ₃ (24), (Me ₃ Si) ₂ (trace), (PhMe ₂ Ge) ₂ (trace)
	MeOH ^a	Me ₃ SiCl (51), PhMe ₂ GeCl (41), PhSiMe ₃ (17), Me ₂ GeCl ₂ (trace) Me ₃ SiH ^b , PhMe ₂ GeH (trace), PhSiMe ₃ (37), (Me ₃ Si) ₂ (trace), (PhMe ₂ Ge) ₂ (trace)
		Me ₃ GeH (trace), PhMe ₂ GeH (trace), PhSiMe ₃ (23), (Me ₃ Si) ₂ (trace), (PhMe ₂ Ge) ₂ (trace),  (12),  (10)
	PhMe ₂ GeGeMe ₃ (3)	none
	CCl ₄	Me ₃ GeH (8), PhMe ₂ GeH (8), PhGeMe ₃ (15), Ph ₂ GeMe ₂ (8), (Me ₃ Ge) ₂ (15), (PhMe ₂ Ge) ₂ (1), (PhMe ₂ Ge) ₂ O (2), (Me ₃ Ge) ₂ GeMe ₂ (4), PhMe ₂ GeGeMe ₂ GeMe ₃ (trace), (PhMe ₂ Ge) ₂ GeMe ₂ (trace)
	MeOH ^a	Me ₃ GeCl (63), PhMe ₂ GeCl (43), PhGeMe ₃ (5), Me ₂ GeCl ₂ (trace) Me ₃ GeH ^b , PhMe ₂ GeH (6), PhGeMe ₃ (3), Ph ₂ GeMe ₂ (1), (Me ₃ Ge) ₂ (6), (PhMe ₂ Ge) ₂ (1), (PhMe ₂ Ge) ₂ O (10), (Me ₃ Ge) ₂ GeMe ₂ (1), PhMe ₂ GeMe ₂ GeGeMe ₃ (trace), (PhMe ₂ Ge) ₂ GeMe ₂ (trace)
		Me ₂ GeH (16), PhMe ₂ GeH (2), PhGeMe ₃ (3), (Me ₃ Ge) ₂ (1), (PhMe ₂ Ge) ₂ (6), (PhMe ₂ Ge) ₂ O (7),  (3),  (trace)

^a Irradiation of 0.1 M benzene solution containing large excess of methanol (ca 50 times excess).^b Yields cannot be estimated due to the overlapping of the GLC peak of the product with that of the solvent employed.^c The structure is assigned on the basis of its MS spectroscopic properties and by analogy with photolysis of phenyldisilane under similar conditions [33].

accords with the fact that the photolysis of **1** in the presence of methanol- d_1 (MeOD) under similar conditions gave monodeuterated methoxydimethylphenylsilane, $(\text{MeO})(\text{CH}_3)(\text{CH}_2\text{D})\text{PhSi}$ (M^+ : m/z 167; $M^+ - 15$: m/z 151 and 152). However, no methoxygermane was detected in the photolysate. In addition to the methoxysilane, appreciable amounts of dimethyldiphenylsilane was produced. Since the photolysis of **1** in cyclohexane-methanol did not yield dimethyldiphenylsilane at all, one of the phenyl groups of the silane should come from the benzene employed as a solvent. On the other hand, on the photolysis of **1**, a small amount of dimethylphenylsilane was formed also from the silyl radical possibly via disproportionation or hydrogen abstraction from the solvent, and interestingly, the photolysis in the presence of methanol- d_1 gave nondeuterated silane in ca 5:1 ratio. The mechanism of formation of monodeuterated silane is not clear yet. In contrast, on the photolysis of **2** and **3**, the methoxysilane and methoxygermane were not detected in the photolysate even by means of GC-MS, and photoproducts obtained under these conditions are found to be very similar to those from irradiation in cyclohexane as shown in Table 1.

On the other hand, the presence of PhSiMe_3 and PhGeMe_3 in the photolysate implies that dimethylgermylene should be generated on the photolysis of **2** and **3** under a variety of irradiation conditions. This is supported by the following trapping experiments. In cyclohexane containing a large excess of 2,3-dimethylbutadiene as a germylene trap, the photolysis of **2** and **3** gave 1,1-dimethyl-1-germacyclopent-3-ene (12 and 3% for **2** and **3**, respectively) together with PhSiMe_3 and PhGeMe_3 , respectively. However, on the photolysis of **1** in the presence of a large excess of the diene as a silylene trap, no 1,1-dimethyl-1-silacyclopent-3-ene was detected in the photolysate even by means of GC-MS. This is consistent with the fact that PhGeMe_3 is not formed on photolysis. In addition to the germacyclopentene, a 3-butenylsilyl derivative was detected in the photolysate. This seems to be formed by addition of the corresponding silyl radical to the diene.

Interestingly, on the photolysis of **1**, and especially of **2**, small amounts of *o*-(trimethylgermyl)(2,3-dimethyl-3-butenyl)dimethylsilylbenzene and *o*-(trimethylsilyl)(2,3-dimethyl-3-butenyl)dimethylgermylbenzene respectively, were detected and their structures are deduced from their mass spectroscopic behaviour. On photolysis of aryldisilane, a similar type of product has been reported to arise from the reaction of a silicon-carbon double bonded species **5** ($\text{E} = \text{E}' = \text{Si}$) with the diene [3]. Formation of silicon and germanium-carbon double bonded intermediates **5** ($\text{E} = \text{Si}$, $\text{E}' = \text{Ge}$, and $\text{E} = \text{Ge}$, $\text{E}' = \text{Si}$) is reasonably inferred by analogy with the photolysis of aryldisilane. In the case of the photolysis of **3**, only a trace of the corresponding *o*-(trimethylgermyl)(2,3-dimethyl-3-butenyl)dimethylgermylbenzene was detected by GC-MS.

On photolysis of the digermene **3**, traces of trigermenes were detected in the photolysate and are accounted for by insertion of dimethylgermylene into the digermene produced by dimerization of appropriate germyl radicals. This is substantiated by the photolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorbornadiene, an efficient germylene precursor, in the presence of hexamethyldigermene. This produced octamethyltrigermene in 7% yield as expected [1,8]. This is in contrast to the behavior of a silylene which only undergoes insertion into an activated silicon-silicon bond, such as that of a 1,2-disilacyclobutene [9]. A trace of dimethyldiphenylgermane (Ph_2GeMe_2) probably originated from 1,2-di-

phenyltetramethyldigermene ($(\text{PhMe}_2\text{Ge})_2$) by way of photo-elimination of dimethylgermylene.

The origin of the oxygen atom involved in the siloxane and the germanoxane is not certain at this stage. In spite of efforts to minimize moisture and air, siloxane and the germanoxane were still obtained in appreciable amounts.

Laser flash-photolysis of the phenylated group 4B catenates

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 as an excitatory light source.

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 observed at various wavelengths, the time-resolved absorption spectra of 1–3 were obtained 200 ns after laser excitation, and are shown in Fig. 1. A transient absorption band is observed at 320 nm for 1, and two well-separated transient peaks are located at 320 and 430 nm for 2 and 3. The transient peak at 320 nm for 1–3 is assigned to that due to the phenyl-substituted group 4B element-centred radical, $\text{PhMe}_2\text{E}^\cdot$ ($\text{E} = \text{Si}, \text{Ge}$), from comparison of spectral characteristics with those previously reported [10,11]. Analysis of the transient absorption due to $\text{PhMe}_2\text{E}^\cdot$ revealed approximately second-order decay kinetics, suggesting the formation of group 4B dimetals. The experimentally determined decay constants of the transient at 320 nm in the presence of trapping agents and scavengers are summarized in Table 2. The transient absorption band at 320 nm arising from the photolysis of 1–3 decayed according to pseudo first-order kinetics under these conditions. The transient absorption was quenched effectively on addition of CCl_4 , an effective silyl and germly radical scavenger. The quenching rate constants observed agree nicely with the values reported for the silyl and germly radicals [10,11]. Similarly, oxygen and 2,3-dimethylbutadiene quenched the transient peak at 320 nm as shown.

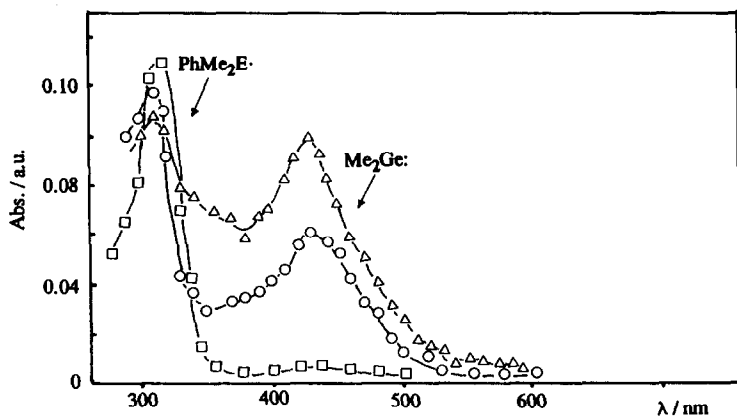


Fig. 1. Transient absorption spectra at 200 ns after photoexcitation of $\text{PhMe}_2\text{SiGeMe}_3$ (1) $-\square-\square-$, $\text{PhMe}_2\text{GeSiMe}_3$ (2) $-\triangle-\triangle-$, and $\text{PhMe}_2\text{GeGeMe}_3$ (3) $-\circ-\circ-$ in degassed cyclohexane solution.

Table 2

Rate constants for disappearance at the shorter wavelength in photolysis of 1–3 in cyclohexane (ca $10^{-3} M$) at 293 K

Dimetal	λ_{\max} (nm)	k/ϵ^a	rate constant ($M^{-1}\cdot s^{-1}$)		
			CCl_4	O_2	diene
PhMe ₂ SiGeMe ₃ (1)	320	2.0×10^6	1.6×10^8	6.2×10^9	3.8×10^7
PhMe ₂ GeSiMe ₃ (2)	320	8.2×10^7	9.0×10^7	1.0×10^9	2.0×10^7
PhMe ₂ GeGeMe ₃ (3)	320	7.0×10^7	7.0×10^7	6.8×10^9	2.3×10^7

^a k is the second order rate constant and ϵ is the molecular extinction coefficient.

On the other hand, the transient peak at 430 nm arising from the photolysis of 2 and 3 can reasonably be assigned to that of a germylene by comparing its spectral and chemical properties with those reported previously [12,13]. These transients arising from the photolysis of 2 and 3 in cyclohexane decayed with second-order kinetics. This is substantiated further by quenching experiments with a germylene trap, such as 2,3-dimethylbutadiene, which gives the corresponding germacyclopentene as mentioned above. In cyclohexane containing a large excess of the diene, the transient absorption arising on the photolysis of 2 and 3 decayed with pseudo first-order kinetics, and the results are summarized in Table 3. Similarly, oxygen very rapidly quenched the transient peak at 430 nm as shown in Table 3. These transients were not quenched by ethanol, and this is in accord with the chemical properties of germylene observed.

Mechanism of photolysis of phenylated group 4B catenates

The results obtained from the analysis of photo-products and the laser flash-photolysis of 1–3 are best rationalized on the basis of a pair of group 4B element-centered radicals being generated from photo-induced homolysis of an E–E' bond as described in Scheme 1. A similar mechanism has been proposed for the photolysis of the silicon analogue, arylidisilane [4].

Table 3

Rate constants for disappearance at the longer wavelength in photolysis of 1–3 in cyclohexane (ca $10^{-3} M$) at 293 K

dimetal	λ_{\max} (nm)	k/ϵ^a	rate constant ($M^{-1}\cdot s^{-1}$)		
			O_2	diene	EtOH
PhMe ₂ SiGeMe ₃ (1)	–				
PhMe ₂ GeSiMe ₃ (2)	430	1.0×10^7	2.1×10^9	4.1×10^7	^b
PhMe ₂ GeGeMe ₃ (3)	430	3.2×10^7	1.7×10^9	2.1×10^7	^b

^a k is the second order rate constant and ϵ is the molecular extinction coefficient. ^b Not quenched.

At first, photolysis of phenylated group 4B catenates 1–3 causes E–E' bond cleavage to yield a pair of group 4B element-centred radicals ($\text{PhMe}_2\text{E}'$ and $\text{Me}_3\text{E}'$). In CCl_4 the two group 4B element-centred radicals generated were able effectively to abstract a chlorine atom to give the corresponding group 4B element chlorides (path 1). Considering the formation of chlorides in high yields as shown in Table 1, a group 4B element-centred radical pair appears to be a key intermediate in these photoreactions. However, together with the corresponding chlorides, there were obtained small but noticeable amounts of a trimethylphenyl group 4B element compound ($\text{PhMe}_3\text{E}'$), such as trimethylphenylsilane and trimethylphenylgermane accompanied by a trace of dichlorogermane, except in the photolysis of 1. This may be rationalized on the basis of the nature of the intervening radical pair. In general, the silyl radical abstracts a chlorine atom and adds to an aromatic ring much more rapidly than the corresponding germyl radical. This is substantiated by the results given in Table 2. In the presence of CCl_4 , the pseudo first-order quenching rate constants of the phenylated silyl radical are larger than those of the corresponding germyl radical. The quenching rate constants show that the silyl radical should be trapped by CCl_4 more readily than the germyl radical. In the photolysis of 1, the pairing phenyl silyl radical may be trapped by CCl_4 quite rapidly and efficiently. So the life time of the radical pair may not be long enough for the trimethylgermyl radical to add to the aromatic ring of the pairing silyl radical. This may also be partly because the germyl radical is reluctant to add to the aromatic ring of the silyl radical. These lead to the formation of only the corresponding chlorides as shown in Table 1. In the case of 2, a part of the trimethylsilyl radical may add successfully to the phenyl group of the pairing germyl radical in competition with chlorine abstraction, and the diradical 4 ($\text{E} = \text{Ge}$, $\text{E}' = \text{Si}$) thus formed evolves dimethylgermylene to give trimethylphenylsilane. In the case of 3, since the germyl radical is not trapped by CCl_4 as rapidly as the corresponding silyl radical, the germyl radical pair thus formed survives long enough to couple at the *ipso*-position of the phenyl of the pairing germyl radical to give a diradical 4 ($\text{E} = \text{E}' = \text{Ge}$). This gives rise to evolution of germylene to yield trimethylphenylgermane.

On the other hand, group 4B element-centred radicals may undergo disproportionation to give group 4B element–carbon double bonded species and group 4B element hydrides (path 2). However the results in Table 1 show that this route is conceivably unfavorable except in the case of the dimethylphenylsilyl radical. This is in contrast to the carbon radical. Since the trimethylgermyl radical is not able to add to the phenyl group of the pairing silyl radical as efficiently as the silyl radical, in a nonhalogenated solvent the lifetime of a radical pair composed of dimethylphenylsilyl and trimethylgermyl radicals is probably long enough for escape from the solvent cage. Disproportionation of the free dimethylphenylsilyl radical thus formed gives the corresponding hydrosilane and silene which is trapped by methanol to give methoxydimethylphenylsilane. On the other hand, in the case of 2, trimethylsilyl radical generated adds preferentially to the benzene ring of the pairing dimethylphenylgermyl radical to give the corresponding cyclohexenyl radical 4 ($\text{E} = \text{Ge}$, $\text{E}' = \text{Si}$) which yields trimethylphenylsilane and dimethylgermylene.

The group 4B element-centred radical pair couples at the *ipso*-position to give a group 4B element-substituted cyclohexadienyl radical 4 [14]. Diradical 4 undergoes further intramolecular 1,2-migration of the group 4B atom to produce a group 4B element–carbon double bonded intermediate 5. At the same time, 4 evolves a group

4B divalent species as shown in Scheme 1. The competition between these two processes depends upon the nature of the central atom of the radical species involved, and possibly also upon the nature of the medium employed.

Experimental

^1H NMR spectra were recorded on a JEOL GX270 using tetramethylsilane as the internal standard. GC-MS spectra were obtained with a JEOL JMS-DX 303 mass spectrometer, and only major mass peaks are shown. Infrared spectra were recorded on a Shimadzu FT IR 4200 spectrometer. UV and UV-Vis spectra were recorded on a JASCO Ubest 50 spectrometer. Gas chromatography was performed on a Shimadzu GC-6A and 8A with 2 m 20% SE30 and 1 m 30% Apiezon L columns.

Materials

2,3-Dimethylbutadiene, CCl_4 , MeOH, and EtOH were commercially obtained. $\text{PhMe}_2\text{GeGeMe}_3$ [15], $\text{PhMe}_3\text{GeSiMe}_3$ [16], $\text{PhMe}_2\text{SiGeMe}_3$ [16], Me_3GeH [17], PhMe_2GeH [18], PhGeMe_3 [19], Ph_2GeMe_2 [20], $(\text{Me}_3\text{Ge})_2$ [21], $(\text{PhMe}_2\text{Ge})_2$ [22], $(\text{PhMe}_2\text{Ge})_2\text{O}$ [1], $(\text{Me}_3\text{Ge})_2\text{GeMe}_2$ [22], $(\text{PhMe}_2\text{Ge})\text{GeMe}_2$ [23], Me_3GeCl [17], PhMe_2GeCl [24], Me_2GeCl_2 [17], 1,1-dimethyl-1-germacyclopent-3-ene [25], PhMe_2SiH [26], $(\text{PhMe}_2\text{Si})_2\text{O}$ [27], PhMe_2SiCl [27], Ph_2SiMe_2 [26], $\text{PhMe}_2\text{SiOMe}$ [28], Me_3SiH [29], PhSiMe_3 [30], $(\text{Me}_3\text{Si})_2$ [31], and Me_3SiCl [32] were prepared as described in the cited references.

Solvent

Cyclohexane was distilled from sodium/benzophenone under argon.

Identification of the photo-products

These compounds were separated by preparative GLC and their structures assigned by comparing the NMR and GC data of similar compounds previously reported [33]. *o*-(Trimethylsilyl)(2,3-dimethyl-3-butenyl)dimethylgermylbenzene: MS m/z (%): 336 (3, M^+ calculated based on ^{74}Ge), 321 (20), 263 (14), 253 (100), 237 (39), 187 (31), 119 (46), 105 (26), 73 (69). ^1H NMR (δ in CDCl_3): 0.35 (s, 9H, SiMe); 0.49 (s, 3H, GeMe); 0.50 (s, 3H, GeMe); 1.01 (d, $J = 7.0$ Hz, 3H, CHMe); 1.08 (dd, $J = 13.9, 8.1$ Hz, 1H, CH_2); 1.25 (dd, $J = 13.9, 6.6$ Hz, 1H, CH_2); 1.66 (br. s, 3H, =CMe); 2.37 (m, 1H, CHMe); 4.60 (s, 1H, = CH_2); 4.64 (s, 1H, = CH_2); 7.28–7.66 (m, 4H, ArH). *o*-(trimethylgermyl)(2,3-dimethyl-3-butenyl)dimethylsilylbenzene: MS m/z (%): 336 (20, M^+ calculated based on ^{74}Ge) 217 (53), 202 (15), 171 (21), 135 (100), 119 (100). ^1H NMR (δ in CDCl_3): 0.36 (s, 3H, SiMe); 0.39 (s, 3H, SiMe); 0.47 (s, 9H, GeMe); 0.88 (dd, $J = 13.5, 7.5$ Hz, 1H, CH_2); 1.00 (d, $J = 6.9$ Hz, 3H, CHMe); 1.03 (dd, $J = 13.5, 6.5$ Hz, CH_2); 1.65 (br. s, 3H, =CMe); 2.37 (m, 1H, CHMe); 4.60 (s, 1H, = CH_2); 4.67 (s, 1H, = CH_2); 7.30–7.63 (m, 4H, ArH). *o*-(Trimethylgermyl)(2,3-dimethyl-3-butenyl)dimethylgermylbenzene: MS m/z (%): 380 (3, M^+ calculated based on ^{74}Ge), 263 (12), 181 (100), 151 (6), 119 (27). Methoxydimethyl(2-trimethylgermylphenyl)silane: MS m/z (%): 286 (4, M^+ calculated based on ^{74}Ge), 151 (100), 119 (52), 89 (60), 74 (10), 59 (30). (2,3-Dimethyl-3-butenyl)dimethylphenylsilane: MS m/z (%): 218 (100, M^+), 203 (52), 137 (40), 135 (60), 127 (80), 75 (56).

Photochemical reactions of the phenyl-substituted group 4B catenates

The catenate compound (ca. 200 mg) was dissolved in dry cyclohexane (6 cm³) 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 1 h. After irradiation, the photo-products were identified by comparing the retention times on GLC and GC-MS with those of authentic samples.

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-dump-thaw cycles. The concentrations of the catenate compounds 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-1 Nd:YAG laser as an excitatory light source. The laser pulse was about 5 ns, and the details of the laser photolysis apparatus have been published elsewhere [34]. 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 a NEC PC 8801 microcomputer.

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