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Photochemical reactions of 2-(pentamethyldisilanyl)furan and 2-(pentamethyldigermanyl)furan. Formation of a radical pair

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Abstract

Photochemical reactions of 2-(pentamethyldisilanyl)furan and 2-(pentamethyldigermanyl)furan have been investigated by chemical trapping experiments and laser flash-photolysis. On irradiation, the furylated catenates of Group 14 elements undergo silicon–silicon σ bond and germanium–germanium σ bond homolysis to give a pair of silyl radicals and germyl radicals, respectively. In CCl_4 , these radicals are converted to the corresponding chlorides by abstraction of a chlorine atom. In nonhalogenated solvents (cyclohexane and other hydrocarbons), the silyl radical pair undergoes a disproportionation to give as main products a monosilane and a silene. The trimethylgermyl radical mainly couples at the *ipso*-position of the furyl group of the pairing radical to yield the corresponding diradical. This diradical undergoes elimination of a divalent species, dimethylgermylene, with concomitant formation of 2-(trimethylgermyl)furan.

Key words: Photochemistry; Silanyl; Germanyl; Radical

1. Introduction

The photochemistry of aryl-substituted dimetals of Group 14 elements has attracted much attention as it is based on a $\sigma(\text{E}-\text{E})-\pi$ conjugated system ($\text{E} = \text{Si}$ and Ge). In the photolysis of aryl-substituted disilanes, highly reactive organosilicon species such as silicon–carbon double bonded species (silenes), silyl radicals, and divalent species (silylenes) are generated. The first studies on photolysis of methylpentaphenyldisilane reported the formation of the carbon–silicon double bonded species, 1,1-diphenylsilene, demonstrated by trapping experiments with alcohol [1]. Later, photochemical studies have shown that arylidisilanes undergo a formal 1,3-sigmatropic rearrangement of the silyl group to the aryl group to give unusual silicon–carbon double bonded species, as determined by trapping experiments [2]. At the same time, small amounts of products were found to be formed through the extru-

sion of silylenes on photolysis [2]. More recently, ESR studies have revealed the formation of the silyl radicals on photoinduced silicon–silicon σ bond homolysis of arylidisilanes, and a radical pair mechanism has been proposed to rationalize these photo-products [3]. Formation of silicon–oxygen double bonded species has been also reported by the photolysis of arylidisilanes in dimethylsulfoxide (DMSO) [4].

On the other hand, laser flash photolysis and trapping experiments on a series of aryl digermenes have shown that photolysis of these digermenes causes germanium–germanium σ bond homolysis to give the corresponding radical pair [5–7].

In this paper, we first describe the photochemical reactions of furylated catenates of Group 14 elements, as parts of photochemical studies of arylated Group 14 element catenates. Laser flash photolysis and trapping experiments on these compounds show that irradiation of the furylated Group 14 element catenates causes Group 14 element–Group 14 element σ bond homolysis to give rise to the corresponding radical pair. The difference in photochemical behaviour and mechanism

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between disilanylfuran and digermanylfuran is discussed.

2. Results and discussion

2.1. Photoreaction of disilanyl- and digermanyl-furans

Furylated Group 14 element catenates, 2-C₄H₃-OMe₂SiSiMe₃ (**1**) (*ca.* 0.03 M) and 2-C₄H₃OMe₂-GeGeMe₃ (**2**) (*ca.* 0.02–0.07 M) in cyclohexane or other hydrocarbon were irradiated with a 110 W low pressure Hg arc lamp (λ = 189 and 254 nm) at room temperature under argon. Photolysis of **1** in cyclohexane or pentadecane gave trimethylsilane (Me₃SiH, 22–38% and 14%, respectively) together with unidentified products of high molecular weight. Photolysis of **2** in cyclohexane afforded trimethylgermane (Me₃GeH, 3%), 2-(trimethylgermyl)furan (2-C₄H₃OMeGeMe₃, 20%), and hexamethyldigermoxane ((Me₃Ge)₂O, trace) to-

gether with unidentified products of high molecular weight. In tridecane, **2** was similarly irradiated to give Me₃GeH (5–13%) and 2-C₄H₃OMeGeMe₃ (9–11%). The photo-products generated with irradiation at 189 nm were almost the same as those at 254 nm. These results are summarized in Table 1.

To trap possible reactive intermediates, the photolyses of **1** and **2** were carried out in cyclohexane (or other hydrocarbon solvents) containing various trapping agents. Since silyl and germyl radicals abstract a chlorine atom from polyhalomethanes (CCl₄ or CHCl₃) effectively and rapidly [8], the photolyses of **1** and **2** were carried out in hydrocarbon solvents containing CCl₄ (or CHCl₃). The corresponding chlorosilanes and chlorogermanes were obtained as shown in Table 1. The chlorodigermene was also produced by photolysis of **2** in CCl₄ (or CHCl₃). However, furylated chlorosilanes were not detected. Addition reactions of fury-

TABLE 1. Photoproducts and yields from the photolysis of the furylated Group 14 catenates **1** and **2** in cyclohexane ^a

dimetal	trapping agent ^b	irradiation conditions	conv./%	photo-products (yield%) ^c
 1	none	189 nm, 2 min	58–85	Me ₃ SiH (22–38)
	none ^d	189 nm, 2 min	42	Me ₃ SiH (14)
	CCl ₄	189 nm, 2 min	41–44	Me ₃ SiH (2–17), Me ₃ SiCl (3)
	t-BuOH	189 nm, 2 min	54	Me ₃ SiH (19),  SiMe ₂ (O ^t Bu) (43)
	EtOH	189 nm, 2 min	53	Me ₃ SiH (23), (Me ₃ Si) ₂ O (5)
	Et ₃ SiH	189 nm, 2 min	56	 SiMe ₃ (5),  SiMe ₂ (OEt) (37)
 2	none	254 nm, 3–5 h	46	Me ₃ GeH (3–5),  GeMe ₃ (11–20)
	none ^e	189 nm, 10 min	72	Me ₃ GeH (13),  GeMe ₃ (9), (Me ₃ Ge) ₂ O (trace)
	CCl ₄ ^d	254 nm, 40 min	52	Me ₃ GeCl ^f , ClMe ₂ GeGeMe ₃ (17)
	CHCl ₃ ^e	254 nm, 60 min	61	Me ₃ GeCl (14), ClMe ₂ GeGeMe ₃ (10)
				 GeMe ₂ Cl (trace)
	t-BuOH	254 nm, 3 h	57	Me ₃ GeH (3),  GeMe ₃ (8)
		254 nm, 10 h	42	Me ₃ GeH (3–10),  GeMe ₃ (8–18)
		254 nm, 9 h	51	Me ₃ GeH (9),  GeMe ₃ (11)

^a Irradiation of cyclohexane solutions of **1** (*ca.* 0.03 M) and **2** (*ca.* 0.07 M) with low pressure Hg arc lamp (189 nm and 254 nm). ^b Molar ratio of furylated Group 14 catenates to trapping agents = 1:20. ^c The yield of photoproducts was based on **1** and **2** consumed. ^d In pentadecane. ^e In tridecane. ^f Yields cannot be estimated due to the overlapping of the GLC peak of the product with that of the solvent employed.

lated silyl radicals may be faster than the reactions whereby these silyl radicals abstract chlorine from polyhalomethanes. Hydrosilane was detected and no hydrogermane was formed on photolysis in CCl_4 . Silyl and germyl radicals are expected to undergo a disproportionation to give hydrosilanes and hydrogermanes, and silenes and germenes, respectively [9]. Silenes and germenes are known to react effectively with alcohols to give the corresponding alkoxysilanes and alkoxygermanes [10]. Hence, to confirm the presence of silenes and germenes, **1** and **2** were similarly irradiated in cyclohexane solution containing a large excess of ethanol or *t*-butanol.

In the case of **1**, ethoxy- and *t*-butoxysilanes were obtained in good yields, and are likely to arise from the polar addition of ethanol and *t*-butanol, respectively, to 2-(1-methylsilyl)furan formed from 2-furyldimethylsilyl radical and trimethylsilyl radical via disproportionation. This accords with the fact that the photolysis of **1** in the presence of ethanol- d_1 (EtOD) under similar conditions gave monodeuterated 2-(ethoxydimethylsilyl)furan, $2\text{-C}_4\text{H}_3\text{OSi}(\text{EtO})(\text{CH}_3)(\text{CH}_2\text{D})$. The low yield of trimethylhydrosilane may be due to its low volatility. Dimethylsilene (and 2-furyldimethylsilane) arising from 2-furyldimethylsilyl radical and trimethylsilyl radical via disproportionation could not be detected. When **2** was photolyzed in the presence of *t*-butanol, no *t*-butoxygermane was detected in the photolysate. Thus, germyl radicals did not undergo a disproportionation, unlike silyl radicals, under the present reaction conditions. The formation of trimethylgermane in photolysis of **2** with alcohol may be ascribed to hydrogen abstraction of the germyl radical from proton sources such as solvents, alcohol and methyl group of **2**.

On the other hand, the presence of $2\text{-C}_4\text{H}_3\text{OSiMe}_3$ and $2\text{-C}_4\text{H}_3\text{OGeMe}_3$ in the photolysate implies that dimethylsilylene and dimethylgermylene should be generated on the photolysis of **1** and **2** under a variety of irradiation conditions. This is supported by the following trapping experiments. In cyclohexane containing a large excess of triethylsilane, which is a good trapping agent for silylene [11], the photolysis of **1** gave triethylsilyldimethylsilane (2%) together with trimethylsilane (35%) and 2-(trimethylsilyl)furan (1%). However, on photolysis of **2** in the presence of germylene trapping agents [12], 2,3-dimethylbutadiene and 2-methylbutadiene, no 1,1-dimethyl-1-germacyclopentadiene derivatives were detected in the photolysate even by means of GC-MS. It is known that photoinduced dimethylgermylene cannot be efficiently trapped by diene [5–7].

The origin of the oxygen atom involved in the siloxanes and the germoxanes is not certain at this stage. In

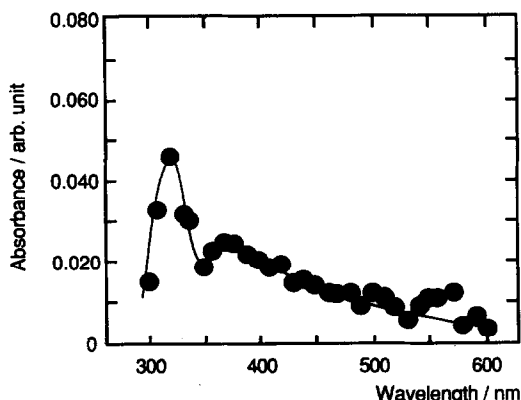


Fig. 1. Transient absorption spectrum at 200 ns after photoexcitation of 2-(pentamethyldisilanyl)furan in degassed cyclohexane solution.

spite of efforts to minimize moisture and air, the siloxanes and the germoxanes were still obtained in appreciable amounts.

2.2. Laser flash-photolysis of disilanyl- and digermanyl-furans

Nanosecond transient absorption spectra measurements were performed on degassed solutions containing **1** and **2** at 293 K using the fourth harmonic pulse of a Nd:YAG laser as an exciting light source.

The time dependence of absorbance of the transient absorption $A(t)$ was measured with **1** and **2** in cyclohexane in the wavelength region of 300–700 nm. Time resolution of the apparatus was about 10 ns [13].

Using the $A(t)$ curves at various wavelengths, the time-resolved absorption spectra of **1** and **2** were obtained at 200 ns after laser excitation, and are shown in Figs. 1 and 2. Two well-separated transient peaks are observed at 310–320 nm and 370–380 nm for both **1** and **2**. The signals show a fast rise and subsequent decay.

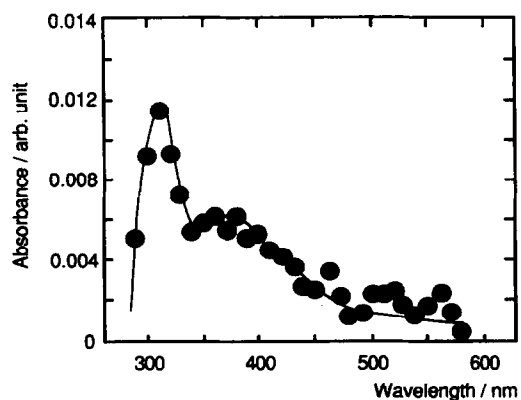


Fig. 2. Transient absorption spectrum at 200 ns after photoexcitation of 2-(pentamethyldigermanyl)furan in degassed cyclohexane solution.

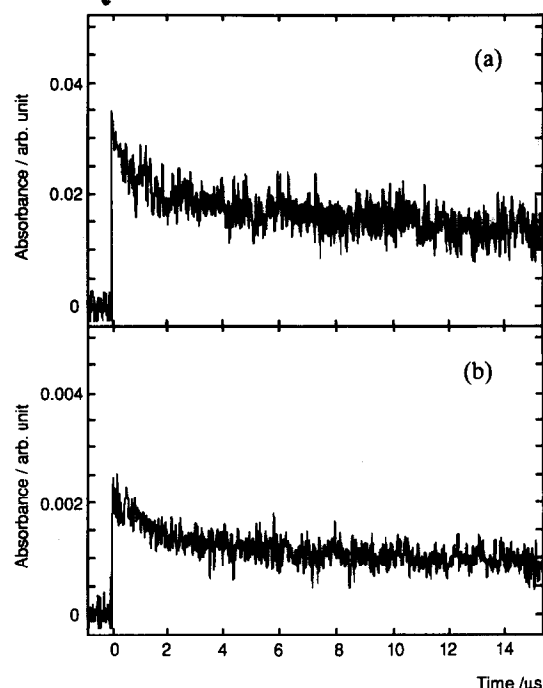


Fig. 3. Representative data from laser flash photolysis kinetic spectroscopy experiments: (a) Absorbance at 320 nm as a function of time upon irradiation of 2-(pentamethyldisilanyl)furan (0.1 M) in degassed cyclohexane solution. (b) Absorbance at 370 nm.

The $A(t)$ curves observed in **1** and **2** at 310–320 nm are shown in Figs. 3 and 4. Such curves can be computer analyzed regarding composition of two components (half times, $t_{1/2} = 2.3 \mu\text{s}$ and $t_{1/2} < 40 \mu\text{s}$ for **1**, and $t_{1/2} = 3.1 \mu\text{s}$ and $t_{1/2} < 40 \mu\text{s}$ for **2**). Both shorter-lived transients decay with pseudo first-order kinetics and are assigned to those of furyl-substituted silyl and germyl radicals from comparison of spectral characteristics and quenching velocities with those reported for similar silyl and germyl radicals. That the decay obeys pseudo first-order kinetics may suggest that silyl and germyl radicals generated by homolysis of the silicon–silicon bond and germanium–germanium bond of **1** and **2**, respectively, add to furylated compounds or react with solvents. The assignment of shorter-lived transients have been further substantiated by quenching experiments with carbon tetrachloride,

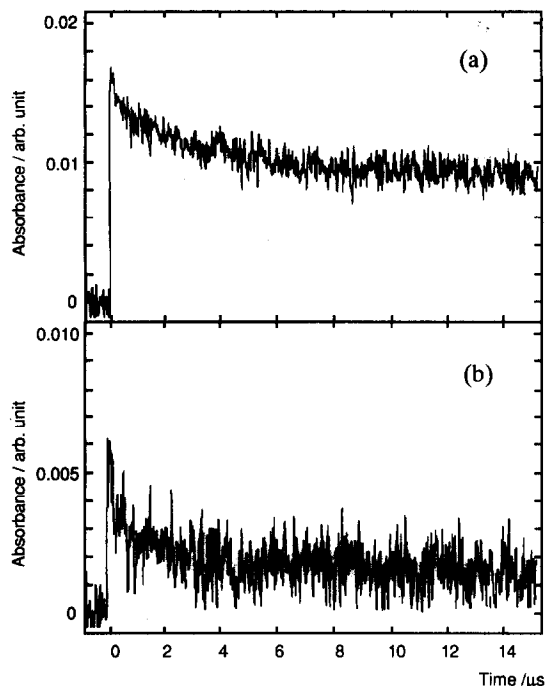


Fig. 4. Representative data displays from laser flash photolysis kinetic spectroscopy experiments: (a) Absorbance at 320 nm as a function of time upon irradiation of 2-(pentamethyldigermanyl)furan (69.6 mM) in degassed cyclohexane solution. (b) Absorbance at 380 nm.

oxygen, triethylsilane, ethanol and 2,3-dimethylbutadiene. Carbon tetrachloride, an effective Group 14 element-centred radical scavenger, quenched the transient absorptions with rates shown in Table 2. The quenching-rate constants observed agree with the values reported for silyl and germyl radicals [5–7,14]. Similarly, oxygen quenched the shorter-lived transients very quickly. The experimentally determined decay constants of these shorter-lived transient species are summarized in Table 2. What is the subsequent career of the longer-lived transient? Taking into account the unusually long life times and the positions of the absorption bands of these transients, the longer-lived transients may be assigned to photoproducts containing π -systems.

TABLE 2. Rate constants for disappearance in photolysis of **1** and **2** in cyclohexane (ca. 0.1 M) at 293 K

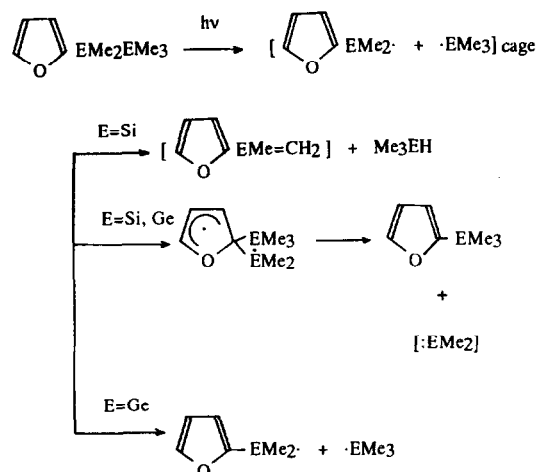
Dimetal	λ_{max} (nm)	k (10^6 s^{-1})	rate constant/ $10^6 \text{ s}^{-1} \text{ M}^{-1}$				
			O_2	CCl_4	Et_3SiH	EtOH	diene
1	320	0.44	3.1×10^3	1.6×10^2	2.2×10	^a	
	370	0.63	2.5×10^3	^a	1.7×10	^a	
2	310	0.36		9.4×10			^b
	380	1–1.5		^b			^b

^a Not quenched. ^b The transient was too weak for rate constants to be determined.

On the other hand, the transients at longer wavelength (Figs. 1 and 2) also consist of two components (half times, $t_{1/2} = 1.6 \mu\text{s}$ and $t_{1/2} < 40 \mu\text{s}$ for **1**, and $t_{1/2} = 0.8 \mu\text{s}$ and $t_{1/2} < 40 \mu\text{s}$ for **2**) by computer analysis. The shorter-lived transients at longer wavelength may be assigned to those of dimethylsilylene and dimethylgermylene by comparing chemical and spectral properties with those reported. Until now, the absorption bands of dimethylsilylene and dimethylgermylene have been reported to appear in the region of 420–450 nm [15,16]. The bands observed in this study are blue-shifted compared with those previously reported of dimethylsilylene and dimethylgermylene. The observed blue shifts for dimethylsilylene and dimethylgermylene are probably due to the diorganosilylene and -germylene complexes with furan **1** and **2** [17–20].

To confirm the stability of dimethylsilylene and dimethylgermylene complexes with furan, matrix isolation studies at 77 K and laser flash-photolysis at 293 K were carried out. The known precursors of dimethylsilylene and dimethylgermylene ($(\text{Me}_2\text{Si})_6$, and $(\text{Me}_2\text{Ge})_6$ and $\text{Me}(\text{Me}_2\text{Ge})_5\text{Me}$, respectively) in a matrix [3-MP-isopentane (IP), 3:2] containing furan were photolyzed with a 110 W low pressure Hg lamp at 77 K. The absorption band at 455 nm due to free Me_2Si : photogenerated from $(\text{Me}_2\text{Si})_6$ was blue shifted (455 nm to 345 nm) in the matrix (molar ratio of furan to $(\text{Me}_2\text{Si})_6 = 33:1$). Similar phenomena were observed in the absorption band of Me_2Ge : produced from $(\text{Me}_2\text{Ge})_6$ (from 430 to 365 nm). Laser flash-photolysis studies also showed dimethylgermylene complexes with furan. Thus, the transient absorption at 440 nm due to free Me_2Ge : photogenerated from $\text{Me}(\text{Me}_2\text{Ge})_5\text{Me}$ was blue-shifted (from 440 to 370 nm) in the presence of large excess amounts of furan (molar ratio of furan to $\text{Me}(\text{Me}_2\text{Ge})_5\text{Me} = 100:1$).

The shorter-lived transient species generated from **1** and **2** decay with pseudo-first order kinetics, suggesting that addition of such divalent species to **1** and **2**, or to solvents, or disproportionation into silenes and germenenes is occurring [21]. This was affirmed by quenching experiments with divalent species trapping agents. The transient from **1** decayed in the presence of large excesses of the triethylsilane and oxygen with pseudo first-order kinetics. It is known that the rate constants of dimethylsilylene photogenerated from the π -system of arylated precursors are different from those of free dimethylsilylene produced from $(\text{Me}_2\text{Si})_6$ [22,23]. Unexpectedly, this transient species was not quenched with carbon tetrachloride and ethanol under these experimental conditions. These facts may be explained by the low reactivity of dimethylsilylene resulting from strong interaction of dimethylsilylene with the



Scheme 1.

furan ring in **1**. The transient from **2** was quenched by carbon tetrachloride and 2,3-dimethylbutadiene, but was too weak for rate constants to be determined. Representative data from laser flash photolysis experiments are given in Table 2. What is the longer-lived transient at the longer wavelengths? At present, we may temporarily assign it to high molecular weights of silicon and germanium compounds produced by repeated addition of silyl and germly radicals to furyl groups.

2.3. Photoreaction mechanism of furylated Group 14 catenates

The results of photochemical reactions and laser flash photolysis studies on **1** and **2** imply that Group 14 element-centred radicals are generated from photo-induced homolysis of Si–Si and Ge–Ge bonds as described in Scheme 1. A similar mechanism has been proposed for the photolysis of the germanium analogue, aryldigermane [5–7].

At first, photolysis of furylated Group 14 element catenates **1** and **2** causes cleavage of the bond between two Group 14 elements to yield a pair of group 14 element-centred radicals. In CCl_4 these radicals abstract a chlorine atom to give the corresponding chlorides. Considering the formation of the chlorides and the results of laser flash photolysis, the Group 14 element-centred radical pair appears to be a key intermediate in these photo-reactions.

Relatively large amounts of hydrosilanes were obtained together with the corresponding chloride, but no hydrogermanes, in the reaction with CCl_4 . Group 14 element-centred radicals are expected to undergo disproportionation to give Group 14 element–carbon double bonded species (silenes and germenenes) and Group 14 element hydrides (monosilanes and mono-germanes). The results in Table 1 show that this dis-

proportionation route is favoured in the case of silyl radicals. This is in contrast to the germyl radical pairs. This fact may be explained by $(2p-3p)\pi$ conjugation being energetically more stable than $(2p-4p)\pi$ conjugation. The silenes formed by disproportionation are trapped by alcohol to give alkoxysilanes.

On the other hand, the germyl radical pair, whose disproportionation path is unfavourable, abstracts a hydrogen atom from solvents and from **2** to yield hydrogermanes, or couple at the *ipso*-position to give the corresponding diradical as a main path. The diradical produces a germylene as shown in Scheme 1. Competitively, the diradical may undergo further intramolecular 1,2-migration of the germyl radical to produce a germanium-carbon double bonded intermediate. However, we have no concrete evidence for the occurrence of such a 1,3-germyl migration (Table 1). The formation of germylene and germylene elimination products from the coupling products of germyl radicals (diradicals) is thermodynamically more favourable than the formation of germyl migration products.

From the low yields and the poor material balance of photo-products, other processes (addition reactions of silyl and germyl radicals to **1** and **2**, 1,2-furyl group shift of **1** and **2**, and so on) may compete with radical pair processes as indicated by Scheme 1.

3. Experimental section

^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 Shimadzu 2200 UV spectrometer. Gas chromatography was performed on a Shimadzu GC-6A and 8A with 1 m 20% SE30 and 1 m 20% Apiezon L columns.

3.1. Materials

2-Methylbutadiene, 2,3-dimethylbutadiene, CCl_4 , CHCl_3 , EtOH, $^i\text{BuOH}$, and Et_3SiH were commercially obtained. Me_3SiH [24], Me_3SiCl [25], $(\text{Me}_3\text{Si})_2\text{O}$ [26], $\text{Et}_3\text{SiMe}_2\text{SiH}$ [11], $2\text{-C}_4\text{H}_3\text{OSiMe}_3$ [27], Me_3GeH [28], Me_3GeCl [28], $(\text{Me}_3\text{Ge})_2\text{O}$ [29], $\text{ClMe}_2\text{GeGeMe}_3$ [30] and $2\text{-C}_4\text{H}_3\text{OGeMe}_3$ [31] were prepared as described in the cited references. The solvents cyclohexane, tridecane and pentadecane were distilled from sodium/benzophenone under argon.

3.2. Preparation of 2-furylated disilane and digermane

As a representative example, preparation of 2-(pentamethyldisilyl)-furan is described. Approximately 100

ml of anhydrous ether was distilled under nitrogen from sodium wire into a 300 ml three-necked flask fitted with a reflux condenser, dropping funnel, and mechanical stirrer. Furan (1.6 g, 24 mmol) was placed in this flask. $n\text{-BuLi}$ (16 ml, 1.5 N) was introduced and reaction allowed for 3 h at room temperature. To this mixture, chloropentamethyldisilane (3.4 g, 20 mmol) in ether (30 ml) was added with stirring for 3–4 h. The solution was distilled to yield 2-(pentamethyldisilanyl)-furan (3.1 g, 16 mmol, 76% yield), bp. $89^\circ\text{C}/33\text{ mmHg}$. NMR (δ , in CCl_4) 0.21 (s, 9H), 0.37 (s, 6H), 6.24–6.41 (m, 1H), 6.51–6.61 (m, 1H), 7.57–7.67 (m, 1H); IR (neat, cm^{-1}) 2950, 2900, 1250, 1200, 1150, 1100, 1000, 830, 800, 740; n_D^{25} 1.4708; MS m/z 198 (M^+). Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{Si}_2\text{O}$; C, 54.48; H, 9.14. Found: C, 54.62; H, 9.20%.

2-(Pentamethyldigermanyl)furan, bp. $43^\circ\text{C}/1\text{ mmHg}$, NMR (δ in CCl_4) 0.20 (s, 9H), 0.37 (s, 6H), 6.07–6.36 (m, 2H), 7.30–7.46 (m, 1H); IR (neat, cm^{-1}) 2980, 2900, 1410, 1235, 1200, 1140, 1090, 1000, 830, 800, 740, 600; n_D^{25} 1.5003; MS m/z 288 (M^+). Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{Ge}_2\text{O}$; C, 37.61; H, 6.31. Found: C, 37.90; H, 6.52%.

3.3. 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. 2-(Dimethylethoxysilyl)furan, $2\text{-C}_4\text{H}_3\text{OSi}(\text{CH}_3)_2(\text{OEt})$: NMR (δ in CCl_4) 0.37 (s, 6H), 1.15 (t, 3H), 3.69 (q, 2H), 6.35–6.44 (m, 1H), 6.69–6.77 (m, 1H), 7.60–7.67 (m, 1H). MS m/z (%): 170 (33), 155 (100), 143 (7), 125 (35), 111 (93), 99 (15), 75 (20), 59 (19). Monodeuterated 2-(dimethylethoxysilyl)furan, $2\text{-C}_4\text{H}_3\text{OSi}(\text{CH}_3)(\text{CH}_2\text{D})(\text{OEt})$: NMR (δ in CCl_4) 0.37 (s, 5H), 1.15 (t, 3H), 3.69 (q, 2H), 6.35–6.44 (m, 1H), 6.69–6.77 (m, 1H), 7.60–7.67 (m, 1H). MS m/z (%): 171 (38), 156 (96), 144 (5), 126 (35), 111 (100), 95 (23), 76 (23), 60 (12). 2-(Dimethyl-*t*-butoxysilyl)furan, $2\text{-C}_4\text{H}_3\text{OSi}(\text{CH}_3)_2(\text{t-OBu})$: MS m/z (%): 198 (18), 183 (56), 147 (27), 125 (100), 115 (13), 99 (11), 75 (78), 59 (15).

3.4. Photochemical reactions of the furylated Group 14 catenates

The catenate compound (*ca.* 40 mg) was dissolved in dry cyclohexane (2 cm^3) in a quartz tube. The tube was degassed *in vacuo* and replaced with argon. The sample was irradiated with a 110 W low-pressure Hg arc lamp ($\lambda = 189\text{ nm}$ and 254 nm) (Sen Tokushu Kogen Co. Ltd.) at room temperature for *ca.* 10 min and 3–4 h, respectively. After irradiation, the photo-products were identified by comparing the retention times on GLC and GC-MS with those of authentic samples.

3.5. 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-pump-thaw cycles. The concentrations of the catenate compounds were *ca.* 10^{-1} M. Laser flash-photolysis experiments were performed at room temperature by using the fourth harmonic ($\lambda = 266$ nm) of a Quanta-Ray DCR-1 Nd:YAG laser as an exciting light source. The laser pulse was about 5 ns, and the details of the laser photolysis apparatus have been published elsewhere [13]. 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 micro-computer.

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