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Photochemical Reactions of Vinyl-, Styryl-, and Benzyl-Substituted Digermanes

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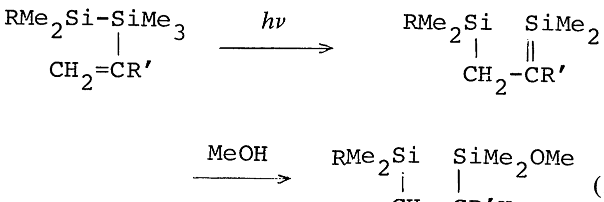
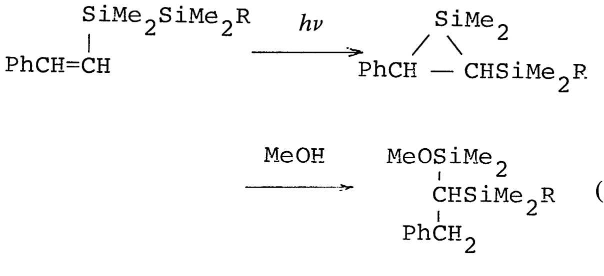
Photochemical reactions of vinyl-, styryl-, and benzyl-substituted digermanes were investigated by chemical trapping experiments. Photolysis of vinylpentamethyldigermane afforded 1-trimethyl-2-(pentamethyldigermyl)ethane as a major product, and styrylpentamethyldigermanes gave mainly styryltrimethylgermane. On the other hand, photolysis of benzyl-substituted digermanes (benzylpentamethyldigermane and 1,2-dibenzyltetramethyldigermane) gave hydrogermanes and hydrodigermanes as main products, respectively. These products were derived from germyl radicals generated by photoinduced homolysis of the germanium–germanium bond. In carbon tetrachloride (CCl_4), these germyl radicals were converted to the corresponding chlorogermanes by abstraction of a chlorine atom. Germylene species were also to be evolved from such photolyses.

Recently, the photochemistry of organosilicon compounds having σ(Si–Si)–π(C–C) conjugated systems has been investigated extensively. However, the photochemical behavior of germanium analogues is particularly intriguing from the view of group 14 element chemistry.[1] Previously, we reported the generation of germyl radicals on photolysis of phenyl-substituted digermanes.[2,3] We herein describe the photoreactions of σ(Ge–Ge)–π(C–C) conjugated vinyl- and styryl-substituted digermanes, and benzyl-substituted digermanes as a further extension of our studies.

The photolyses of vinyldisilanes have been reported to induce 1,3-silyl migration to give the corresponding silaethenes as highly reactive intermediates, which were proved by trapping experiments with methanol (Eq. 1).[4]


(1)

Similarly, styryldisilanes undergo 1,2-silyl migration to give the corresponding silacyclopropanes as reactive intermediates, which were also evidenced by trapping experiments (Eq. 2).[5]


(2)

On the other hand, the irradiation of benzyldisilanes gives a pair of organosilyl radicals by homolysis of the silicon-silicon σ bond (Eq. 3).[6]

$$PhCH_2Me_2Si\text{-}SiMe_3 \xrightarrow{h\nu} PhCH_2Me_2Si\cdot + \cdot SiMe_3 \quad (3)$$

The purpose of the studies described here is to clarify the photochemical behavior of digermanes and to compare their reactivities with thoes of the analogous vinyl-, styryl-, and benzyl-substituted disilanes.

Results and Discussion

Photochemical Reactions of Vinylpentamethyldigermane. Vinylpentamethyldigermane, CH_2=$CHMe_2Ge$-$GeMe_3$ (**1**) in cyclohexane (ca. 0.2 M, 1 M=1 mol dm^{-3}) was irradiated with a 110 W low-pressure Hg arc lamp (a spiral type) at room temperature under argon for 10 h. In addition to a large excess of an unidentified high-boiling product, 1-trimethylgermyl-2-(pentamethyldigermyl)ethane ($Me_3GeCH_2CH_2Ge_2Me_5$, 8% yield) was obtained as a main product together with trace amounts of trimethylgermane (Me_3GeH), vinyldimethylgermane (CH_2=$CHGeMe_2H$), pentamethyldigermane (Me_5Ge_2H), vinyltrimethylgermane (CH_2=$CHGeMe_3$), hexamethyldigermane (Me_6Ge_2), and 1,2-bis(pentamethyldigermyl)ethane ($Me_5Ge_2CH_2$-$CH_2Ge_2Me_5$). Along with hydrogermanes (Me_3GeH and CH_2=$CHMe_2GeH$), formation of digermane (Me_6-Ge_2) indicated the intermediacy of germyl radicals. Since organogermyl radicals abstract a chlorine atom from CCl_4 effectively and rapidly to trap these germyl radical intermediates,[7] the photolysis of compound **1** was carried out in cyclohexane containing CCl_4. As expected, the corresponding chlorogermanes (CH_2=CH-Me_2GeCl and Me_3GeCl) and hexachloroethane were obtained along with (2-chloroethyl)pentamethyldigermane ($ClCH_2CH_2Ge_2Me_5$), pentamethylchlorodigermane (Me_5Ge_2Cl), and CH_2=$CHGeMe_3$. The formation of Me_5Ge_2H also implied that digermyl radicals and vinyl radicals were generated by homolysis of the carbon–germanium bond along with the germanium–germanium bond. This was further substantiated by the formation of Me_5Ge_2Cl from the photolysis of **1** in the presence of CCl_4. The expected $CH_2{=}CH_2$ and $CH_2{=}CHCl$ were not detected with and without CCl_4, respectively, due to their high degree of volatility. The formation of $ClCH_2CH_2Ge_2Me_5$ could be explained as follows. Addition of a chlorine radical generated by photolysis of CCl_4 to gave the 1-(pentamethyldigermyl)-2-chloroethyl radical ($ClCH_2\dot{C}HGe_2Me_5$), followed by abstraction a hydrogen atom from solvents to produce $ClCH_2CH_2Ge_2Me_5$.

A trace amount of dimethyldichlorogermane (Me_2GeCl_2) was detected in the photolysate. The formation of Me_2GeCl_2 may be accounted for by thermal decomposition of (trichloromethyl)dimethylchlorogermane (CCl_3Me_2GeCl), which is produced by insertion of photochemically generated dimethylgermylene into the C–Cl bond of CCl_4,[8] or chlorine abstraction from CCl_4 stepwise by dimethylgermylene as shown in the silicon cases.[9]

The material balance and yields of the chlorogermanes were poor.

Radical Pair Processes (Main Path).

$$(CH_2{=}CH)Me_2Ge{-}GeMe_3$$

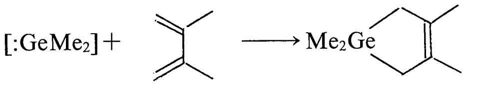
$$\xrightarrow{h\nu}\begin{cases}\xrightarrow{CCl_4}(CH_2{=}CH)Me_2GeCl + Me_3GeCl\\ \xrightarrow{CCl_4} CH_2{=}CHCl + ClMe_2GeGeMe_3\end{cases} \qquad (4)$$

On the other hand, the presence of $CH_2{=}CHGeMe_3$ in the photolysate implied that dimethylgermylene was generated on the photolysis of **1** under a variety of irradiation conditions. This was supported by the following trapping experiments. In cyclohexane containing a large excess of 2,3-dimethyl-1,3-butadiene as a germylene trapping agent,[10] the photolysis of **1** gave 1,1-dimethylgermacyclopent-3-ene (3% yield).

Germylene Formation Process (Minor Path).

$$(CH_2{=}CH)Me_2Ge{-}GeMe_3$$

$$\xrightarrow{h\nu} CH_2{=}CHGeMe_3 + [:GeMe_2] \qquad (5)$$



(6)

In the photolysis of vinyldisilanes, 1,2-disilylethenes were formed as important intermediates.[4] The germanium–carbon double-bonded species (germenes) are known to react quite effectively with methanol to give the corresponding methoxygermanes.[11] Hence, to confirm the formation of germenes, the photolysis of **1** was examined in cyclohexane containing a large excess of methanol. As a result, no methoxygermanes were detected in the photolysate. Thus, this meant that no germanium–carbon double-bonded species (germenes) were formed as reactive intermediates in the photolysis of vinyl-substituted digermanes (**1**).

These photochemical results are summarized in Table 1.

Photochemical Reactions of Styrylpentamethyldigermane. Styrylpentamethyldigermane ($PhCH{=}CHMe_2GeGeMe_3$) (**2**) in cyclohexane (ca. 0.1 M) was similarly irradiated with a 110 W low-pressure Hg arc lamp at room temperature under argon for 6 h. Together with a large amount of unidentified polymeric compounds containing germanium atoms, styryltrimethylgermane ($PhCH{=}CHGeMe_3$, 15% yield) as a major product and trace amounts of Me_3GeH and Me_5Ge_2H were obtained. The presence of $PhCH{=}CHGeMe_3$ in the photolysate implied the generation of dimethylgermylene under these reaction conditions. To trap this dimethylgermylene, the photolysis of **2** in cyclohexane solution containing a large excess of 2,3-dimethyl-1,3-butadiene[10] was carried out. As expected, 1,1-dimethylgermacyclopent-3-ene (5% yield) was produced. These trapping results suggested that 2,3-dimethyl-1,3-butadiene did not effectively trap photoinduced dimethylgermylene.[12] Dimethylgermylene may have similarly arisen from a simple extrusion process as observed in the vinyldigermane.

$$PhCH{=}CHGeMe_2GeMe_3$$

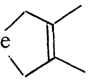
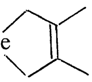
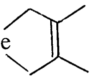
$$\xrightarrow{h\nu} PhCH{=}CHGeMe_3 + [:GeMe_2] \qquad (7)$$

Formation of trace amounts of hydrogermanes (Me_3GeH and Me_5Ge_2H) indicated the intermediate involvement of germyl radicals. This was confirmed by the formation of the corresponding chlorogermanes ($PhCH{=}CHMe_2GeCl$ and Me_3GeCl) in the presence of CCl_4.[7] Me_5Ge_2Cl and $PhCH{=}CHCl$ were also detected in the photolysate. These chlorides indicated the presence of digermyl radicals and styryl radicals, which were generated by homolysis of the germanium–carbon bond. Under these conditions, neither digermanes nor hydrogermanes were detected in the photolysate.

Interestingly, in the photolysis of **2**, a small amount of styrylheptamethyltrigermane ($PhCH{=}CHMe_2GeMe_2GeGeMe_3$) was detected. This implied that dimethylgermylene is able to insert into a germanium–germanium bond under these reaction conditions.[3]

In the photolysis of styryldisilanes, silacyclopropanes have been reported to be key reactive species.[5] Germacyclopropanes were effectively trapped with methanol to give 1,1-digermyl-2-phenylethanes.[13] Therefore, to examine the possibility of germacyclopropanes as reactive intermediates, the photolysis of **2** in cyclohexane with methanol was carried out. However,

Table 1. Photoproducts and Yields from the Photolysis of the Vinyl-, Styryl-, and Benzyl-Substituted Digermanes **1**—**4** in Cyclohexane

Dimetal	Trapping agent	Photoproducts[a] (yield/%)
$CH_2=CHGe_2Me_5$ **1**	None	Me_3GeH (20), $Me_3GeCH_2CH_2Ge_2Me_5$ (8), $Me_5Ge_2CH_2CH_2Ge_2Me_5$ (1), $(c\text{-}C_6H_{11})_2$ (1)
	CCl_4	$CH_2=CHMe_2GeCl$ (9), Me_5Ge_2Cl (13), $ClCH_2CH_2Ge_2Me_5$ (60), C_2Cl_6 (61), Me_3GeCl (trace), $CH_2=CHGeMe_3$ (trace)
	MeOH	$Me_3GeCH_2CH_2Ge_2Me_5$ (2), $Me_5Ge_2CH_2CH_2Ge_2Me_5$ (1)
	Diene	Me_3GeH (6), Me_2Ge  (3)
$PhCH=CHGe_2Me_5$ **2**	None	$PhCH=CHGeMe_3$ (15), $(c\text{-}C_6H_{11})_2$ (8)
	CCl_4	Me_5Ge_2Cl (51), $PhCH=CHGeMe_3$ (3), C_2Cl_6 (54)
	Diene	$PhCH=CHGeMe_3$ (25), Me_2Ge  (5)
$PhCH_2Ge_2Me_5$ **3**	None	Me_3GeH (12), Me_5Ge_2H (5), $(PhCH_2Me_2Ge)_2O$ (1), Me_8Ge_3 (2), $PhCH_2Ge_3Me_7$ (1), $(PhCH_2)_2$ (5)
	CCl_4	$PhCH_2Me_2GeCl$ (21), Me_5Ge_2Cl (29), C_2Cl_6 (50)
	MeOH	$(PhCH_2Me_2Ge)_2O$ (1), $(PhCH_2)_2$ (11)
	Diene	Me_5Ge_2H (1), Me_2Ge  (3)
$(PhCH_2Me_2Ge)_2$ **4**	None	$PhCH_2Me_2GeH$ (7), $(PhCH_2)_2GeMe_2$ (2), $PhCH_2Me_2GeMe_2GeH$ (7), $(PhCH_2)_2$ (7)
	CCl_4	$PhCH_2Me_2GeCl$ (39), $PhCH_2Me_2GeMe_2GeCl$ (23), C_2Cl_6 (45)
	MeOH	$PhCH_2Me_2GeMe_2GeH$ (10), $(PhCH_2)_2$ (10)
	Diene	$(PhCH_2)_2GeMe_2$ (1), $PhCh_2Me_2GeMe_2GeH$ (1), $(PhCH_2)_2$ (3)

a) Ttace amounts of other products were obtained.

no methoxy-substituted compounds were detected in the photolysate. Thus, this result strongly indicated either no formation of germacyclopropanes as reactive intermediates in the photochemical reaction of **2** or that the life time of the germacyclopropane was too fast to be trapped chemically under these conditions.

The results of these photochemical reactions of **2** are also included in Table 1.

Photochemical Reactions of Benzyl-Substituted Digermanes. Benzylpentamethyldigermane ($PhCH_2Me_2GeGeMe_3$) (**3**) and 1,2-dibenzyltetramethyldigermane ($PhCH_2Me_2GeGeMe_2CH_2Ph$) (**4**) in cyclohexane (each 0.1 M) were irradiated with a 110 W low-pressure Hg arc lamp at room temperature under argon for 3—4 h. Many photoproducts were formed in low yields. Among with a large amount of polymeric materials, photolysis of **3** in cyclohexane gave Me_3GeH (12% yield), Me_5Ge_2H (5% yield), and bibenzyl (5% yield) as major products and trace amounts of benzyldimethylgermane ($PhCH_2Me_2GeH$), benzyltrimethylgermane ($PhCH_2GeMe_3$), Me_6Ge_2, dibenzyldigermanoxane ($(PhCH_2Me_2Ge)_2O$), bis(pentamethyldigermyl)oxide ($(Me_5Ge_2)_2O$), octamethyltrigermane (Me_8Ge_3), and 1-benzylheptamethyltrigermane ($PhCH_2Me_7Ge_3$) were also detected. On the other hand, photolysis of **4** in cyclohexane afforded $PhCH_2Me_2GeH$ (7% yield), dibenzyldimethylgermane ($(PhCH_2)_2GeMe_2$) (2% yield), $PhCH_2Me_2GeGeMe_2H$ (7% yield), and $(PhCH_2)_2$ (7% yield).

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

Along with hydrogermanes (Me_3GeH and $PhCH_2GeMe_2H$ for **3** and $PhCH_2GeMe_2H$ for **4**, respectively), formation of digermanes (Me_6Ge_2 for **3** and $(PhCH_2Me_2Ge)_2$ for **4**, respectively) indicated intermediary germyl radicals. To trap such germyl radical intermediates as the corresponding chlorides, the photolyses of **3** and **4** were carried out in cyclohexane containing CCl_4.[8] The corresponding chlorogermanes were obtained and neither digermanes nor hydrogermanes were detected as shown in Table 1. The formation of benzyldimethylchlorogermane ($PhCH_2Me_2GeCl$) and Me_5Ge_2Cl for **3**, and benzyltetramethyldigermyl chloride ($PhCH_2Me_2GeMe_2GeCl$) for **4**, also implied that homolysis of the germanium–carbon bond of benzyl-substituted digermanes **3** and **4** occured along with the homolysis of the germanium–germanium bond.

Radical Pair Processes (Main Path).

$$PhCH_2\text{–}Me_2Ge\text{–}GeMe_2R \quad \xrightarrow{h\nu} \begin{cases} \xrightarrow{CCl_4} PhCH_2Me_2GeCl + RMe_2GeCl \\ \xrightarrow{CCl_4} PhCH_2Cl + ClMe_2GeGeMe_2R \end{cases} \tag{8}$$

R=Me, $PhCH_2$

On the other hand, the formation of $PhCH_2GeMe_3$ for **3** and $(PhCH_2)_2GeMe_2$ for **4**, respectively, with and without CCl_4 implied that dimethylgermylene was generated under a variety of irradiation conditions. 1,1-Dimethylgermacyclopent-3-ene (3% yield and trace amounts for **3** and **4**, respectively) was formed in the photolysis of **3** and **4** in cyclohexane with a large excess of 2,3-dimethyl-1,3-butadiene.10)

Germylene Formation Process (Minor Path).

$$\begin{array}{l} \mathrm{PhCH_2Me_2GeGeMe_2R} \\ \xrightarrow{h\nu} \mathrm{PhCH_2GeMe_2R} + [:\mathrm{GeMe_2}] \qquad (9) \\ \qquad \mathrm{R{=}Me,\ PhCH_2} \end{array}$$

The photochemical behavior of benzyl-substituted digermanes was similar to that of the silicon analogues. However, no formation of silylenes has been reported so far.6)

The photochemical results of benzyl-substituted digermanes (**3** and **4**) are also summarized in Table 1.

Mechanism of Photochemical Reactions of Vinyl-, Styryl-, and Benzyl-Substituted Digermanes. The results obtained from the analysis of the photoproducts were best rationalized on basis of a pair of radicals generated from the photoinduced homolysis of the germaium–germanium and germanium–carbon bonds (Eqs. 4 and 8) as a main path, and of simple extrusion of dimethylgermylene (Eqs. 5, 7, and 9) as a minor path.

Photolysis of digermanes **1**—**4** caused germanium–germanium and germanium–carbon bond cleavage to yield the corresponding pairs of radicals. In CCl_4 the photogenerated germyl-centered radicals and carbon-centered radicals abstracted a chlorine atom effectively to give the corresponding chlorides.8,14) Thus, in contrast to the silicon analogues, both germyl radicals and carbon radicals appeared to act as reactive intermediates in these photoreactions.

In addition to the homolysis, the extrusion of dimethylgermylene to yield the corresponding monogermanes also occured. Dimethylgermylene arising from a simple extrusion process was also a reactive intermediate independent of the homolytic process.

Thus, the photoproducts isolated here were rationalized to arise from either the radical pair generated from photoinduced homolytic fission of the germanium–germanium and germanium–carbon bonds or extrusion of dimethylgermylene from the starting digermanes. We obtained no evidence for the formation of a germanium–carbon double-bonded species (germene) or germacyclopropane derived from 1,3- and 1,2-germyl migration. On irradiation, however, the silicon analogues underwent 1,3- and/or 1-2-silyl migration to give the corresponding silicon–carbon double-bonded species (silene) and/or silacyclopropane; these could be rationalized also to have arisen by way of the radical pair generated from the photoinduced homolysis of the silicon–silicon bond.

These differences in the photoreactions between the two 14 group metal compounds may be attributed to the difference in the energy of the bond cleaved, namely, germanium–germanium and germanium–carbon bonds are weaker than those of the corresponding silicon–silicon and silicon–carbon bonds. The difference in the thermodynamic stability of germyl and silyl radicals may also contribute to prefential formation of radical products in the photolysis of the digermanes. The strong radical nature of the reaction intermediates may suffer some deterioration of product yields and the material balance of the photolysis.

Experimental

^{1}H 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 peaks are shown. Infrared spectra were recorded on a Shimadzu FT IR 4200 spectrometer. UV and visible 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 20% Apiezon L columns.

Materials. 2,3-Dimethyl-1,3-butadiene, CCl_4, and MeOH were commerically available and distilled prior to use. $CH_2{=}CHMe_2Ge{-}GeMe_3$,15) Me_3GeH,16) $CH_2{=}CHGeMe_3$,17) Me_5Ge_2Cl,15) 1,1-dimethylgermacyclopent-3-ene,18) Me_5Ge_2H,19) $PhCH_2Me_2GeCl$,20) Me_8Ge_3,21) Me_6Ge_2,22) and $Me_2GeCl_2$16) were prepared as described in the cited references.

Solvent. Cyclohexane was distilled from benzophenone/sodium under argon.

Preparation of Styrylpentamethyldigermane ($PhCH{=}CHGe_2Me_5$). Styrylmagnesium bromide was prepared from 4.8 g (26 mmol) of styryl bromide and 0.63 g (26 mmol) of magnesium in 40 ml of THF. To this Grignard reagent, 3.4 g (13 mmol) of pentamethylchlorodigermane dissolved in 40 ml of THF was added and refluxed gently for 4 h. After hydrolysis with water, reaction mixtures were extracted with ether, and the organic layer was dried over anhydrous sodium sulfate. After the solvent was removed, fractional distillation gave styrylpentamethyldigermane (3.6 g, 85% yield), bp 119—131 °C/31 mmHg (1 mmHg=133.322 Pa). Pure digermane was isolated by preparative GLC (SE30 20% 2 m column). ^{1}H NMR (CCl_4) δ=0.25 (s, 9H), 0.35 (s, 6H), 6.65 (m, 2H), and 7.22 (m, 5H); MS (70 eV) *m/z* 324 (6), 207 (100), 119 (26), and 105 (48); UV (in cyclohexane) λ_{max} 266.3 nm (ε 19000); IR (neat) 795m 825, 1665, 1703, 2930, and 2980 cm^{-1}. Found: C, 48.50; H, 6.56%. Calcd for $C_{13}H_{22}Ge_2$: C, 48.27; H, 6.86%.

Preparation of Benzylpentamethyldigermane ($PhCH_2Ge_2Me_5$). Benzylmagnesium chloride was prepared from 2.5 g (20 mmol) of benzyl chloride and 0.5 g (21 mmol) of magnesium in dry ether (30 ml). To this Grignard reagent, 2.0 g (7.8 mmol) of pentamethylchlorodigermane dissolved in dry ether (30 ml) was added. The reaction mixture was stirred with refluxing for 1 h. After hydrolysis with dilute HCl, the reaction mixture was extracted with ether and the organic layer was washed with water. The organic layer was dried over calcium chloride. After removal of the solvent, fractional distillation gave benzylpentamethyldigermane (1.8 g, 75% yield). The digermane was purified by preparative GLC. ^{1}H NMR (CCl_4) δ=0.17 (s, 15H), 2.27 (s, 2H), and 6.89—6.97 (m, 5H); MS (70 eV) m/z 312 (9), 221 (52), 119 (100), and 91 (60); UV (in cyclohexane) λ_{max} 288.8 (ε 12500); IR (neat) 690, 744, 1490, 1595, 2900, 2960, and 3070 cm^{-1}. Found: C, 46.42; H, 7.36%. Calcd for $C_{12}H_{22}Ge_2$: C, 46.27; H, 7.12%.

Preparation of 1,2-Dibenzyltetramethyldigermane (($PhCH_2Me_2Ge)_2$). Dibenzyltetramethyldigermane was prepared from lithium metal (0.21 g, 30 mmol) and benzyldimethylchlorogermane (6.8 g, 30 mmol) in THF (15 nl). The reaction mixture was gently refluxed for 8 h. After completion of this reaction, the reaction mixture was hydrolyzed with diute HCl and extracted with ether. The organic layer was washed with water and dried over sodium sulfate. After removal of the solvent, fractional distillation gave digermane (1.8 g, 31% yield), bp 129—138 °C/3 mmHg. The digermane was purified by preparative GLC. ^{1}H NMR (CCl_4) δ=0.10 (s, 12H), 2.17 (s, 4H), and 6.67—6.90 (m, 10H); MS (70 eV) m/z 373 (1), 297 (34), 195 (34), and 91 (100); UV (in cyclohexane) λ_{max} 238.4 nm (ε 14000); IR (neat) 695, 746, 790, 1490, 1605, 2920, 2970, and 3030 cm^{-1}. Found: C, 55.80; H, 7.90%. Calcd for $C_{18}H_{26}Ge_2$: C, 55.78; H, 6.76%.

Identification of the Photoproducts. These compounds were separated by preparative GLC and the structures were assigned by comparing the NMR and GC data of similar compounds reported.

1-Trimethyl-2-(pentamethyldigermyl)ethane: MS (70 eV) m/z 366 (15), 323 (25), 247 (20), 221 (95), 207 (14), 119 (100), 104 (7), and 89 (18); ^{1}H NMR ($CDCl_3$) δ=0.10 (s, 9H), 0.17 (s, 6H), 0.22 (s, 9H), 0.64—0.73 (m, 2H), and 0.70—0.90 (m, 2H).

Chloroethylpentamethyldigermane: MS (70 eV) m/z 288; ^{1}H NMR ($CDCl_3$) δ=0.26 (s, 6H), 0.27 (s, 9H), 1.23—1.29 (m, 2H), and 2.60—2.66 (m, 2H).

Trace amounts of photoproducts were very carefully identified by comparing the GC data of similar compounds reported.

Vinyldimethylchlorogermane: MS (70 eV) m/z 166 (100), 129 (78), 94 (31), and 59 (9).

Vinyldimethylgermane: MS (70 eV) m/z 131 (100), 113 (5), 105 (40), 97 (8), 89 (10), and 70 (8).

Bis(pentamethyldigermyl)ethane: MS (70 eV) m/z 470 (6), 425 (9), 323 (19), 221 (100), 206 (19), 119 (97), and 89 (9).

Styryltrimethylgermane: MS (70 eV) m/z 222 (9), 207 (100), 191 (14), 151 (10), 117 (10), 105 (73), 89 (23), 77 (5).

1-Styrylheptamethyltrigermane: MS (70 eV) m/z 428 (1), 413 (8), 325 (36), 293 (12), 221 (64), 207 (40), 119 (100), 105 (16), and 89 (12).

Benzyldimethyldigermanoxane: MS (70 eV) m/z 402 (6), 387 (6), 285 (100), 219 (6), 194 (15), and 119 (19).

1-Benzyltetramethylchlorodigermane: MS (70 eV) m/z 332 (9), 297 (9), 241 (59), 195 (86), 119 (6), 195 (100).

Dibenzyldimethylgermane: MS (70 eV) m/z 286 (6), 195 (100), 165 (9), and 91 (90).

1-Benzyl-1,1,2,2-tetramethyldigermane: MS (70 eV) m/z 283 (8), 207 (82), 195 (40), 165 (38), 119 (100), 105 (20), and 91 (80).

Photochemical Reactions of Vinyl-, Styryl-, and Benzyl-Substituted Digermanes. A typical photochemical experiment was as follows: The digermane (ca. 200 mg) was dissolved in dry cyclohexane (6 ml) in a quartz tube. The tube was degassed under vacuum and the atmosphere was replaced with argon. The sample was irradiated with a 110 W low-pressure Hg arc lamp (Sen Tokushu Kogen Co. Ltd.) at room temperature. After irradiation, the photoproducts were identified by comparing the retention times and GC-MS with those of authentic samples.

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