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Research Article

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Photochemical reactions of polygermanes by steady-state and matrix isolation

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ABSTRACT

Photochemical reactions of substituted tris(trimethylgermyl)germanes I-III in cyclohexane has been studied by steady-state and matrix isolation techniques. Photolysis of trigermanes I-III involved both extrusion of (trimethylgermyl) germylenes and formation of germyl radicals via homolytic fission of germanium-germanium bond. The reaction of trigermanes I-III with CHCl₃ and 2,3-dimethyl-1,3-butadiene as trapping agents gave the corresponding 1-germacyclopent-3-enes. The UV absorption bands of germylenes in matrix at 77 K were also observed. A possible suitable mechanism has been suggested to account for the identified products.

Keywords: photolysis; polygermanes; matrix isolation; (trimethylgermyl) germylenes.

INTRODUCTION

The study of σ -conjugated Group 14 element compounds has attracted considerable interest in recent years because of their unique chemical and physical properties arising from electronic delocalization in the Group 14 element-Group 14 element σ -bond. However, the study of germanium–germanium bond is very much limited as compared with that of silicon-silicon σ -bond[1]. The related tris (trimethylsilyl)germyl moiety, where germanium occupies only the central position, was introduced by Mochida et al. [2] more than 20 years ago in an attempt to obtain germens via photolytic rearrangements. Previously, it was reported that photolysis of permethylated linear polygermanes proceeds by both the contraction of the chain with loss of germylene and the homolytic scission of germanium-germanium σ -bond[3-5]. In continuation of our interest in photochemistry of germanium-germanium σ bond, we have done the photoreactions of the three substituted tris(trimethylgermyl)germanes: (Me₃Ge)₄Ge I, PhGe(GeMe₃)₃II and MeGe(GeMe₃)₃ III by chemical trapping experiments and matrix isolation. The trigermanes I-III involved both extrusion of germylenes and formation of the germyl radicals and digermyl radicals.

EXPERIMENTAL SECTION

General Data:¹H-NMR spectra were recorded on Varian unity-Inova 400 MHz instrument. GC-MS spectra were obtained with JEOL-JMS-DX 303 mass spectrometer. Mass spectra were obtained on a JEOL-JMS-DX 303 GC-MS using electron impact ionization at 70 eV. Gas chromatography was carried out on a Shimadzu GC 8A with 1cm 20% SE 30 and 30% Apiezon L columns. Elementary analyses were carried using a Heraeus Vario Elementar EL apparatus. The UV and UV-vis spectra were measured on a Shimadzu UV-2200 spectrometer. All melting points were uncorrected.

Materials: Chloroform, 2,3-dimethyl-1.3-butadiene, 1,1,2,2-tetrachloroethane and carbon tetrachloride were commercially available. Lithium was used as wire with sodium content between 0.5% and 1%. Hexamethyldigermane Me_6Ge_2 ; b.p. 138°C[6], hexamethyldigermoxane (Me_3Ge_2); b.p. 135°C [7], and chlorotrimethylgermane Me_3GeCl ; b.p. 98°C [8]were prepared as described in the literature.

Solvents: Cyclohexane was distilled from sodium/benzophenone under argon. Pentane was deolefinized with concentrated sulfuric acid, dried with anhydrous magnesium sulfate, and distilled from either CaH_2 or LiAlH₄. Hexamethylphosphoramide (HMPA) was distilled over anhydrous BaO and stored over 3A molecular sieves. 3-Methylpentane (3-MP) was dried over calcium chloride and distilled under argon. Tetrahydrofuran (THF) was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use.

Reported yields are based on unrecovered germalyenes precursor and were determined by gas chromatography with the aid of an inert internal standard, error limits were estimated to be 10%.

Moreover, conversion yields were estimated by decrease of initial GC peak area after irradiation.

Preparation of tetrakis(trimethylgermyl)germaneI

To a solution containing germanium tetrachloride 14.8 g (0.069 mole) in 50 ml THF and chlorotrimethylgermane 36.7 g (0.24 mole) in 100 ml THF was added lithium metal 3.36 g (0.48 mole) cut into small chunks. The solution was allowed to stirring at room temperature for 12 h and then refluxed for an additional 6 h, at which time GC analysis indicated the reaction to be complete. The solution was filtered to remove unreacted lithium and insoluble salts. Next, the filtrate evaporated in vacuo. The remaining residue gave a brown oil which was chromatographed on neutral alumina. Elution with petroleum ether (60-80°C) gave colourless oil.

Vacuum distillation (b.p. 142-150°C, 0.5 mmHg) of this material yielded 12 g of **I** as colourless crystals (37% yield, m.p. 272-285°C (subl)). A representative example, by as described in literature as similar manner[9, 10].

¹H NMR (CDCl₃, 400 MHz): δ 0.38 (s, 36H, GeMe₃). ; ¹³C NMR (δ ppm): 2.8.; MS (70 eV): m/z, (%) 543 (22.2) (M⁺), 529 (92)(M⁺ -Me), 425.4 (100) (M⁺ -GeMe₃), 325.8 (83) (M⁺ -Ge(GeMe₃), 307.8 (50) (M⁺ -(GeMe₃)₂), 218.2 (64) (Ge₂Me₅⁺), 119 (94) (GeMe₃⁺). ; UV (pentane): λ_{max} = 212 nm (ε = 3.1 x 10⁴ [M⁻¹ cm⁻¹])⁺ Anal. Calcd for C₁₂H₃₆Ge₅ (543.4): C 26.52, H 6.68. Found: C 26.86, H 6.67.

Preparation of 2-phenyl-2-(trimethylgermyl)hexamethyltrigermane II

A 1-L, 4-necked flask, a mechanical stirrer, a reflux condenser, and an additional funnel were assembled under nitrogen. This was then charged with crushed Mg, (25g, 1.04 mol), 178.7 mL of Me₃GeCl (153.1g, 1mol), and 340 mL of dry HMPA. The mixture was heated to 95°C, and then phenyl trichlorogermane (59.5 mL, 79.1g, 0.31 mol) was added dropwise with moderate stirring. The reaction that ensued was slightly exothermic, and the flask needed to be cooled occasionally with an ice bath. After 2h, the addition was complete and the mixture was stirred at 95°C for 16 h. The reaction mixture was allowed to cool and, with rapid stirring , quenched with 200 mL of hexane followed by 120 mL of 7% HCl solution. After the solution was stirred for 1h, the hexane layer was separated and dry chromatographed over a silica gel column (60-220 mesh) with hexane as an eluent. The hexane was rotary evaporated to yield brown viscous oil. Vacuum distillation (127-135°C, 0.5 mmHg) of this material yielded 12 g of **II** as colourless liquid (25 % yield). As described in the literature as similar manner[11].

¹H NMR (CDCl₃, 400 MHz): δ 0.37 (s, 27 H, GeMe₃), 7.3-7.8 (m, 5H, Ar-H).; ¹³C NMR (δ, CDCl₃): 2.01 (CH₃, GeMe₃), 127.7 (CH, Ph), 136.6 (CH, Ph), 137.4 (CH, Ph).; MS (70 eV): m/z (%) 502.4 (20) (M⁺), 487.9 (10) (M⁺ - Me), 384.8 (12) (M⁺ -GeMe₃), 369.8 (18) (M⁺ -GeMe₄), 307 (65) (M⁺ -PhGeMe₃), 149.6 (50) (M⁺ -PhGe(GeMe₃)₂), 117.6 (100) (GeMe₃⁺).; UV (pentane): $\lambda_{max} = 235$ nm ($\epsilon = 1.1 \times 10^4$ [M⁻¹ cm⁻¹]).; Anal. Calcd for C₁₅H₃₂Ge₄ (502.4): C 35.83, H 6.37. Found: C 35.88, H 6.33.

Preparation of 2-methyl-2-(trimethylgermyl)hexamethyltrigermane III

As similar manner as mentioned above by using methyl trichlorogermane (45.2 mL,0.31 mol); as colourless liquid; b.p. 115-127, 0.5 mmHg (32 % yield)[11].

¹H NMR (CDCl₃, 400MHz): δ 0.32 (s, 30H, GeMe₃).; MS (70 eV): m/z (%) 440.4 (26) (M⁺), 425.4 (10) (M⁺ -Me), 322.8 (13)(M⁺ -GeMe₃), 307.8 (35) (M⁺ -GeMe₄), 236 (55) (M⁺ - MeGe(GeMe₃)), 117.6 (100) (GeMe₃⁺).; UV (pentane): $\lambda_{max} = 221$ nm ($\epsilon = 2.1 \text{ x } 10^4$ [M⁻¹ cm⁻¹]).; Anal. Calcd for C₁₀H₃₀Ge₄ (440.4): C 27.25, H 6.81. Found: C 27.29, H 6.78.

Photolysis of trigermanes I-III

A mixture of trigermanes (ca. 100 mg) and n-eicosane as an internal standard in 3 ml of cyclohexane was placed in a quartz photolysis cell. The cell was degassed in a vacuum and replaced with argon. The samples were irradiated with a 110 W low-pressure Hg arc lamp at room temperature for 1-3 h. After irradiation, the photoproducts were

identified by GC-MS spectra and also were verified by comparing the retention times with those of authentic samples via GC spectra. Quantitative analysis by GC shows the formation of the products as cited in Table 1.

Photolysis of trigermanes I-III in the presence of chloroform

A mixture of trigermanes **I-III** (ca. 100 mg) and n-eicosane in 3 ml cyclohexane containing chloroform (4.01 mmol) for 1 h. The photoproducts were determined by GC and GC-MS spectra as shown in Table 1.





^t The yield of Me₃GeCl could not determined. The retention time of Me₃GeCl of GLC partially overlapped with that of CHCl₃ and cyclohexane.

Photolysis of trigermanes I-III in the presence of 2,3-dimethyl-1,3-butadiene.

A cyclohexane solution of trigermanes **I-III** (100 mg), n-eicosane, and 2,3-dimethyl-1,3-butadiene (4.02 mmol) was irradiated for 1 h at room temperature. The photoproducts were identified by GC and GC-MS spectra. Also, the formation of the corresponding 1-germacyclopenta-3-ene can rationalized by the reaction of the corresponding germylene precursors with 2,3-dimethyl-1,3-butadiene[12].

Matrix isolation of the trigermanes I-III at 77K

The trigermanes **I-III** (ca. 1×10^{-2} mM) was dissolved in 3 ml of 3-MP, then was added to a quartz UV cell. The samples were degassed with replaced argon. The cell was placed into quartz windowed Dewar filled with liquid nitrogen. The resulting matrix was cooled to 77 K and was irradiated for 15-60 minutes with a 110-W low-pressure Hg arc lamp. The electronic absorptions were taken at periodic intervals and were recorded on a Schmidzu UV 2200 spectrometer as shown in Figures 1-3 and Table 2.

Precursors	λ max/nm	Reference
(Me ₃ Ge) ₄ Ge	410, 320	this work
Ι		
PhGe(Me ₃ Ge) ₃	420, 570	this work
II		[13, 25]
MeGe(Me ₃ Ge) ₃	400, 290	this work
III		

Table 2. UV Data Generated by Photolysis of I-III in 3-MP Matrix at 77 K

Photolysis of trigermanes I-III in a 3-MP Matrix Containing 2,3-Dimethyl-1,3-butadiene

A mixture of trigermanes I-III (1x10⁻² mM), 2,3-dimethyl-1,3-butadiene (140 mg, 1.71 mmol), and 3-MP (5 ml) was placed in a quartz cell and degassed by three freeze-pump-thaw cycles. The mixture was cooled to 77 K, and the resulting matrix was irradiated with a low pressure mercury lamp. The electronic absorptions were taken at periodic intervals. Two absorption bands at λ_{max} 250-270 and 400-410 nm appear for trigermanes I, III, in addition to absorption band at λ_{max} 570 nm for sample II and grew on irradiation. On annealing the matrix, the 400-410 band and 570 nm band for II immediately disappeared and the 250-270 nm band was unchanged. Volatile materials were distilled under reduced pressure, and the analysis of the mixture by GC and GC-MS showed the corresponding 1-germa-cyclopent-3-enes as follow:

1,1-Bis(trimehylgermyl)-3,4-dimethyl-1-germacyclopent-3-ene MS (70 eV): m/e 394 (M⁺, 0.5), 322 (38), 275 (2), 203 (12), 119 (base, 100), 89 (6).; 1-Phenyl-1-(trimethylgermyl)-

3,4-dimethyl-1-germacyclopent-3-ene

MS (70 eV): m/e 352 (M⁺, 2), 270 (8), 234 (12), 181 (base, 100), 151 (18), 119 (38), 89 (19).

1-Trimethylgermyl-1,3,4-trimethyl-1-germacyclopent-3-ene

MS (70 eV): m/e 290 (M⁺, 3), 261 (8), 207 (44), 171 (5), 119 (base, 100), 89 (27).

RESULTS AND DISCUSSION

Photolysis of trigermanes, $(Me_3Ge)_4Ge I$, PhGe(GeMe₃)₃II, and MeGe(GeMe₃)₃III in cyclohexane through a quartz tube with a low-pressure Hg arc lamp under argon at room temperature for 1-3 h resulted in the formation of digermane (Me₃Ge)₂ inmoderate yields as shown in Table 1 and a very small amounts of digermoxane (Me₃Ge)₂O together with unidentified high boiling products containing germanium. The formation of digermoxane may explained through an accidental oxidation of germyl radical by oxygen which could not be excluded completely during photolysis[13].

In order to obtain more information on possible reactive intermediates in photochemical reaction of **I-III**, trapping techniques was made.

A cyclohexane solution containing ca.20 molar equiv of 2,3-dimethyl-1,3-butadiene was similarly irradiated to produce digermane in 16%, 15%, and 13%, respectively and expected products of the corresponding 1-germacyclopenta-3-enes in low yields based on the amount of **I-III** consumed. The low yields of the corresponding 1-germacyclopenta-3-enes may be attributed to easily decompose of 1-germa- cyclopenta-3-enes to give polymers under photochemical conditions[14,15].3-Butenylgermyl derivatives were also detected as minor products by GC-MS spectra. The formation of germacyclopent-3-enes suggests the intermediacy of germylenes[16] as shown in Scheme 1.



Similar photolysis of **I-III** in cyclohexane containing chloroform (ca. 10 times) afforded digermane, chlorotrimethylgermane together with 1,1,2,2-tetrachloro- ethane. The observed yields are shown in Table 1. The

formation of chlorotrimethylgermane indicates formation of the germyl radicals produced by germaniumgermanium bond homolysis of **I-III**. Moreover, photogeneration trimethylgermyl radicals abstract a chlorine atom from chloroform to give chlorotrimethylgermane and dichloromethylene radical[17]. The dichloromethylene radicals dimerize to form 1,1,2,2-tetrachloroethane. No dichlorogermane, were formed in the photolysis **I-III** in the presence of chloroform [18] as shown in GC-MS and in Scheme 2.



The photochemical results are summarized in Table 1.

In order to obtain more information on the reactive intermediates and primary photochemical processes, matrix isolation at 77 K of **I-III** was also carried out.



Electronic Absorption of trigermanes I-III in 3-Methylpentane (3-MP) at 77 K

The matrix isolation technique has been widely used in the observation of reactive species [5]. Irradiation of trigermanes **I-III** in rigid 3-methyl- pentane (3-MP) at 77 K with a 110-W low pressure Hg arc lamp produced yellow glass for **I** and **III** and purple glass for **II** as shown in Table 2. Two absorption bands were obtained at λ_{max} 290-410 nm for all trigermanes **I-III** beside absorption band at λ_{max} 570 nm for **II** (Figures 1-3). The 3-MP glass was annealed for few seconds, the bands 400-410 nm and 570 nm for **II** rapidly disappeared, whereas the 250-270 nm remain unchanged. The absorption band 250-270 nm was assigned to the digermane (Me₃Ge)₂ according to the spectral characteristic with those of digermane previously reported [5,19]. The yellow and purple species with λ_{max} at 400-410 nm and 570 nm, respectively, obtained in this study can be assigned to the corresponding germylenes

from comparison of spectral characteristics with those of similar germylenes reported previously [17,20]. This result almost contrasts with that of silysilylenes and related germylenes [20-22]. Convincing evidence for identification of the germylenes is provided by trapping experiment when irradiation of trigermanes **I-III** in 3-MP containing 2,3-dimethyl-1,3-butadiene at 77 K [23,24]. Analysis of the photolysate by GC-MS showed that the corresponding 1-germacyclopent-3-enes has been formed (see experimental section). UV data for the germylenes observed are listed in Table 2.



Mechanism of Germylenes Formation

Various trapping experiments and matrix isolation studies showed the photoreaction of trigermanes **I-III** to give germylenes and germyl radicals. Germylenes might arise from a simple extrusion process as deduced from the results obtained in this study as a similar manner was reported earlier [5]as shown in Scheme 3.



Scheme 3

CONCLUSION

Irradiation of substituted trigermanes **I-III** in solution leads to the formation of predominant elimination of digermanes (Me₃Ge)₂ and forming new germylenes by the homolysis of germanium-germinium bond as a major process. Trapping agents; CHCl₃ and 2,3-dimethyl-1,3-butadiene was used to obtain more information of primary photoproducts. Matrix isolation studies of **I-III** showed two absorption bands at λ_{max} 250-270 nm and 400-410 nm were also observed.

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