

Photochemical Generation of Chlorine-substituted Digermenes and Their Rearrangement to Germylgermylenes

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Photolysis of *cis,trans*-1,2,3-trichloro-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermane and *trans*-1,2-dichloro-3-methyl-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermane in the presence of triethylsilane yielded products arising from a germylgermylene, which is formed by the 1,2-chlorine migration on digermenes.

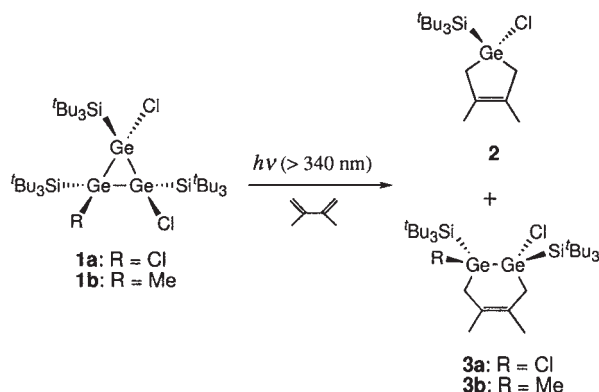
The chemistry of small ring systems consisting of heavier group 14 elements has attracted considerable interest owing to the inherent ring strain and resulting high reactivity.¹ Recently, we reported the synthesis of *cis,trans*-1,2,3-trichloro-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermane (**1a**) by the reaction of $\text{GeCl}_2 \cdot \text{dioxane}$ with tri-*tert*-butylsilylsodium.² The thermal or photochemical conversion of cyclotrigermenes into germynes and digermenes is well established, however almost all of the intensively studied cyclotrigermenes are of the type $(\text{R}_2\text{Ge})_3$ (R = bulky aryl or alkyl group).¹ We presumed that the thermolysis and photolysis of **1** should be quite interesting, as it may generate halogen-substituted germynes and digermenes with unique properties.^{3,4} We herein report the generation of chlorine-substituted digermenes by photolysis of **1** that involves 1,2-chlorine migration in a chlorine-substituted digermene to a germylgermylene.

First, we have examined thermolysis of **1a** at 100 °C in toluene in the presence of 2,3-dimethyl-1,3-butadiene to produce chloro(tri-*tert*-butyl)silane and unidentified polymeric compounds. No evidence was obtained for the cycloelimination to generate the corresponding germylene and digermene. In contrast to the thermal reaction, the photochemical reaction of **1a** cleanly resulted in cycloelimination to produce the expected germylene **4** and digermene **5a**. Thus, irradiation of a hexane solution of **1a** with light having a wavelength greater than 340 nm for 1 h at room temperature in the presence of 2,3-dimethyl-1,3-butadiene resulted in the formation of the germacyclopent-3-ene derivative **2**⁵ (39%) and the 1,2-digermacyclohex-4-ene derivative **3a**⁶ (56%), arising from the trapping of chloro(tri-*tert*-butylsilyl)ger-

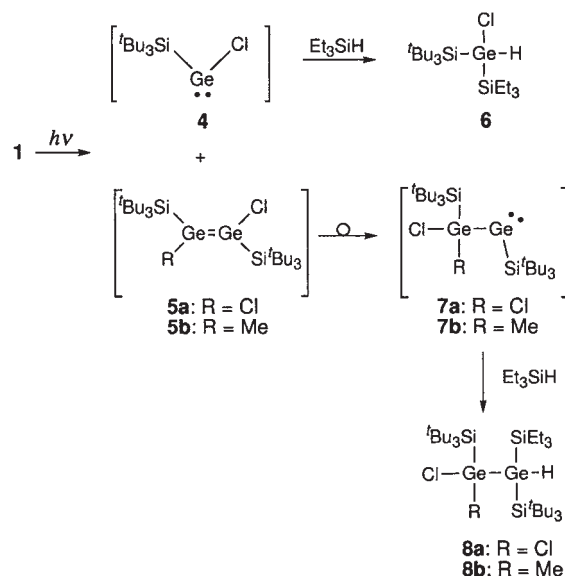
mylene (**4**) and *trans*-1,2-dichloro-1,2-bis(tri-*tert*-butylsilyl)digermene (**5a**) (Scheme 1 and 2).⁷ None of the *cis*-isomer of **3a** was found. We have also performed photolysis of **1a** in the presence of triethylsilane, which can react exclusively with divalent species. Photolysis of **1a** in the presence of excess triethylsilane for 1.5 h at room temperature yielded chloro(tri-*tert*-butylsilyl)(triethylsilyl)germane (**6**)⁸ in 50% yield and 1,1-dichloro-1,2-bis(tri-*tert*-butylsilyl)-2-triethylsilyldigermene (**8a**) in 26% yield (Scheme 2). The structure of **8a** was determined by all spectral data⁹ and finally confirmed by X-ray analysis.¹⁰

The formation of products **6** and **8a** clearly shows the formation of intermediate germynes **4** and **7a** during the photolysis of **1a**. Digermene **5a** is inert toward triethylsilane, but instead undergoes a 1,2-chlorine shift to give a germylgermylene isomer **7a**, which is subsequently trapped by the triethylsilane to give compound **8a**.

We have also examined photolysis of *trans*-1,2-dichloro-3-methyl-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermane **1b**. Photolysis of **1b** in the presence of 2,3-dimethyl-1,3-butadiene at room temperature yielded compounds **2** (66%) and **3b**¹¹ (52%), from the trapping of the germylene **4** and 1-chloro-2-methyl-1,2-bis(tri-*tert*-butylsilyl)digermene (**5b**). Interestingly, the absence of any trapping products from the methyl(tri-*tert*-butylsilyl)germylene and the digermene **5a** indicates that photochemical decomposition of **1b** proceeded regioselectively. Photolysis of **1b** in the presence of triethylsilane gave compound **6** (25%) and a mixture of diastereomers **8b**¹¹ (38%) (Scheme 2). Compound **8b** appears to be derived from the insertion of germylgermylene **7b** into the Si-H bond of triethylsilane.

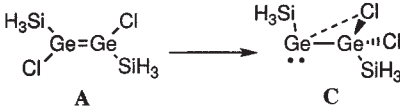
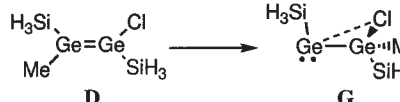


Scheme 1.



Scheme 2.

Table 1. Relative energies (in kcal/mol) of the digermenes, the corresponding germylene isomers, and the transition states (TS) at the B3LYP and MP2 (in parentheses) levels

Reaction	Digermene A, D	Germylgermylene C, G	TS of Cl shift [B], [E]	TS of Me shift [F]
 A → C	0.0 (0.0)	-1.4 (-2.7)	5.0 (5.4)	—
 D → G	0.0 (0.0)	-2.9 (-2.5)	8.0 (10.2)	15.6 (15.5)

Previously, Baines et al. reported the facile digermene-to-germylgermylene and gemasilene-to-silylgermylene rearrangement by the 1,2-mesityl shift of tetramesityldigermene and tetramesitylgermasilene, respectively.¹² Quite recently, we also reported the ring contraction reaction of 1,2-digermacyclohexa-1,4-diene to (germacyclopent-3-enyl)germylene.¹³ Since the rearrangement of the present system involves a unique 1,2-halogen migration on digermene, we have performed mechanistic studies from the theoretical viewpoint.

The relative energies of the model compounds, digermenes (**A** and **D**), corresponding germylgermylenes (**C** and **G**) and their isomerization transition states (**B**, **E** and **F**) are given in Table 1.¹⁴ Several theoretical calculations reported so far have concluded that prototype digermene to germylgermylene isomerizations are slightly endothermic (2.0–4.6 kcal/mol).^{13,15} However, in the present system, germylgermylene isomers (**C** and **G**) are more favorable than the corresponding digermenes (**A** and **D**) by 1.4 (B3LYP), 2.7 (MP2) kcal/mol and 2.9 (B3LYP), 2.5 (MP2) kcal/mol, respectively. Focusing on the structures of germylgermylenes, we found an additional bonding interaction between one of the chlorine atoms and germylene center by coordination of a lone pair of Cl to the vacant p orbital of germylene (2.648 Å for **C**, 2.656 Å for **G**; ca. 30% shorter than the sum of the van der Waals radii), which is probably one of the reasons for the exothermic rearrangements of **A** to **C** and **D** to **G**. Transition state energies of chlorine migration, relative to the corresponding digermenes, are 5.0 kcal/mol and 8.0 kcal/mol for **B** and **E**, respectively. These relatively small barriers are likely to be surmountable at ambient temperature with a considerable rate, which is consistent with the present experimental results.¹⁶ An alternative pathway from **D** to **G** involves a methyl group migration (via **F**). However, the transition state energy of this path is almost twice as high (15.6 kcal/mol), due to the poor migratory aptitude of the alkyl group relative to that of the Cl atom. Therefore, in the digermene **5b**, only the chlorine atom undergoes a 1,2-migration to give the germylgermylene **7b**.

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- Spectral data for **2**: a colorless oil; ¹H NMR (C₆D₆, δ) 1.18 (s, 27 H), 1.66 (s, 6 H), 2.14 (d, *J* = 17 Hz, 2 H), 2.25 (d, *J* = 17 Hz, 2 H); ¹³C NMR (C₆D₆, δ) 19.1, 24.2, 31.1, 36.7, 130.3; ²⁹Si NMR (C₆D₆, δ) 18.6; HRMS *m/z*: M⁺ calcd for C₁₈H₃₇ClGeSi 390.1564, found 390.1565.
- For the spectral data and crystal structure of **3a**, see the supporting information in Ref. 2.
- The digermene **5a** could be independently generated by β-elimination of ^tBu₃SiGe(Cl₂)Ge(Cl)(Na)Si^tBu₃ in the presence of 2,3-dimethyl-1,3-butadiene to give **3a**, see Ref. 2.
- Spectral data for **6**: a colorless oil; ¹H NMR (C₆D₆, δ) 1.22 (s, 27 H), 1.00–1.09 (m, 15 H), 5.60 (s, 1 H); ¹³C NMR (C₆D₆, δ) 5.0, 8.2, 24.6, 31.3; ²⁹Si NMR (C₆D₆, δ) 8.8, 24.7; HRMS *m/z*: M⁺ calcd for C₁₈H₄₃ClGeSi₂, 424.1803; found, 424.1801.
- Spectral data for **8a**: Mp 86–90 °C (dec); ¹H NMR (C₆D₆, δ) 1.27 (s, 27 H), 1.39 (s, 27 H), 1.10–1.22 (m, 15 H), 4.16 (s, 1 H); ¹³C NMR (C₆D₆, δ) 8.3, 8.7, 24.6, 26.9, 32.0, 32.3; ²⁹Si NMR (C₆D₆, δ) 15.1, 38.9, 45.3; Anal. Calcd for C₃₀H₇₀Cl₂Ge₂Si₃: C, 49.28; H, 9.65%. Found: C, 49.58; H, 9.44%.
- Crystal data for **8a**·(C₇H₈)_{0.5} at 120 K: C₃₀H₇₀Cl₂Ge₂Si₃·(C₇H₈)_{0.5}, fw = 777.28, monoclinic, space group = P2₁/n, *a* = 14.1060(6), *b* = 15.4440(7), *c* = 19.4150(6) Å, β = 93.544(3)°, *V* = 4221.5(3) Å³, *Z* = 4, *d*_{calc} = 1.223 g·cm⁻³. The final *R* factor was 0.0500 (*R*_w = 0.1401 for all data) for 8701 reflections with *I* > 2σ(*I*). GOF = 1.047.
- All the new products obtained here showed the satisfactory spectral data.
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- All calculations were performed with the Gaussian 98W programs. All structures were fully optimized at B3LYP and MP2 levels with the LANL2DZ basis set.
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