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# Thermal and photochemical reactions of phenylethynyltris-(trimethylsilyl)germane

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#### ABSTRACT

The thermal and photochemical behavior of phenylethynyltris(trimethylsilyl)germane (1) has been reported. The thermolysis of 1 in the absence of a trapping agent in a sealed glass tube at 240 °C for 6 h gave 1,3-bis(trimethylsilyl)-1-tris(trimethylsilyl)germyl-1-germaindene (2) in 18% yield, together with phenyl(trimethylsilyl)acetylene in 60% yield. Similar thermolysis of 1 in the presence of 2,3dimethylbutadiene afforded 3,4-dimethyl-1,1-bis(trimethylsilyl)-1-germacyclopent-3-ene (3) in 62% yield, along with phenyl(trimethylsilyl)acetylene. When 1 was irradiated with a low-pressure mercury lamp in the presence of a large excess of 2,3-dimethylbutadiene at room temperature for 10 min, compound **3** was obtained in 11% yield, in addition to 17% of phenyl(trimethylsilyl)acetylene and 31% of the starting compound 1. The photolysis of 1 in the absence of a trapping agent under the same conditions afforded phenyl(trimethylsilyl)acetylene as the sole volatile product. The DFT calculations were carried out to investigate the reaction mechanisms for the thermal reaction of 1 leading to the germaindene 2.

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#### 1. Introduction

The chemistry of germenes constitutes one of the most active areas of current research [1], and many papers dealing with the synthesis and reactions of the germenes, including stable ones have been published to date [2]. The synthetic methods reported for the germenes so far mainly involve the following routes: reaction of germylene with carbenes [2b,h], Peterson-type reaction [3], cycloreversion of four-membered reactions [2i,4], and defluorosilylation [2g] or defluorolithiation [2a,2c–f]. The synthetic methods for the germenes are rather limited, compared with those of the silenes. In fact, the photolysis of acylpoly(silyl)silanes offers a convenient route to the silenes, but similar photolysis of acylpoly(silyl)germanes affords no germenes [5].

We have found that the thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)germane, like many types of the acylpolysilanes, readily produces the respective germenes, and the germenes thus formed react with butadienes [6], methyl vinyl ketone, and acrolein [7] to give formal [2+4] cycloadducts in good yields.

In order to learn more about the similarity and dissimilarity of germyl compounds to silvl compounds, we have investigated the thermolysis and photolysis of phenylethynyltris(trimethylsilyl)germane. Previously, we have reported that irradiation of phenylethynylpolysilanes with a low-pressure mercury lamp produces two types of the reactive species, silacyclopropenes and silapropadienes, via a 1,2- and 1,3-silyl shift of the trimethylsilyl group on a central silicon atom, respectively [8]. The silacyclopropenes thus formed undergo a wide variety of the reactions, depending on the substituents on the silacyclopropene ring [9].



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In this paper, we report the thermolysis and photolysis of phenylethynyltris(trimethylsilyl)germane (1) in the presence or absence of 2,3-dimethylbutadiene. To our knowledge, only paper concerning the reactivity of 1 has been reported by Baumgartner and his coworkers [10]. They have found that the reaction of 1 with zirconocene dichloride/magnesium in THF produces the zirconacyclopropene derivative. experiments at 500 MHz are also consistent with the structure proposed for **2**. Thus, irradiation of a signal at 7.37 ppm, due to the olefinic proton on the C2 carbon in the germaindene ring reveals a strong enhancement of the signal at 0.17 ppm, attributed to the trimethylsilyl protons on the germanium atom, and the signal at 0.29 ppm, due to the trimethylsilyl protons on the C3 carbon. These results are wholly consistent with the structure proposed for **2**.



#### 2. Results and discussion

#### 2.1. Synthesis of compound 1

Phenylethynyltris(trimethylsilyl)germane (1) was prepared using the method reported by Brook et al. [5] and Marschner et al. [11], as shown in Scheme 1. Thus, the hydrolysis of (Me<sub>3</sub>Si)<sub>3</sub>GeK, obtained by the reaction of (Me<sub>3</sub>Si)<sub>4</sub>Ge with *tert*-BuOK, with dilute hydrochloric acid, followed by treatment of the resulting (Me<sub>3</sub>Si)<sub>3</sub>GeH with CCl<sub>4</sub> gave (Me<sub>3</sub>Si)<sub>3</sub>GeCl [5]. The reaction of the chlorogermane with phenylethynyllithium afforded compound 1, whose spectral data were identical with those reported by Baumgartner et al., as colorless viscous liquid [10].

### 2.2. Thermolysis of 1

We first carried out the thermolysis of 1 in the absence of a trapping agent. Thus the thermolysis of **1** in a sealed glass tube at 240 °C for 6 h produced 1,3-bis(trimethylsilyl)-1tris(trimethylsilyl)germyl-1-germaindene (2) in 18% yield, along with phenyl(trimethylsilyl)acetylene in 60% yield. No other volatile products were detected in the reaction mixture, after treatment of the resulting mixture with column chromatography. Compound 2 is stable toward atmospheric oxygen and can be handled in air without decomposition. The structure of **2** was confirmed by mass and,  ${}^{1}$ H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectrometric analysis. In fact, mass spectrometric analysis for **2** indicates the presence of a molecular ion at m/z 614, corresponding to the calculated molecular weight for C<sub>23</sub>H<sub>50</sub>Si<sub>5</sub>Ge<sub>2</sub>. The  ${}^{13}C$  NMR spectrum for **2** shows three signals at -0.50, 0.17, and 3.08 ppm, due to Me<sub>3</sub>Si carbons, and eight signals attributed to the sp<sup>2</sup> carbons. The <sup>29</sup>Si NMR spectrum reveals three signals at -8.5, -6.0, -3.3 ppm, due to three different kinds of the silicon atoms. Furthermore, the results obtained from NOE-DIF difference To learn more about the mechanism for the formation of **2**, we investigated the reaction of **1** in the presence of 2,3-dimethylbutadiene as a trapping agent under the same reaction conditions. The reaction of **1** with 4.5 equiv of 2,3-dimethylbutadiene gave 3,4-dimethyl-1,1-bis(trimethylsilyl)-1-germacyclopent-3-ene (**3**), arising from [1 + 4] cycloaddition of bis(trimethylsilyl)germylene (**C**) to the butadiene in 62% yield, along with 69% of phenyl (trimethylsilyl)acetylene.

The formation of compound **2** may be best understood in terms of a series of the reactions shown in Schemes 2 and 3. Addition of bis(trimethylsilyl)germylene **C**, which produced by the thermolysis of 1,1,2-tris(trimethylsilyl)-3-phenyl-1-germacyclopropene (**B**) once formed from the starting compound **1**, to 3-phenyl-1,1,3tris(trimethylsilyl)-1-germapropadiene (**A**) generated simultaneously from **1** affords 3-phenyl(trimethylsilyl)methylene-1,1,2,2tetrakis(trimethylsilyl)-1,2-digermacyclopropane (**D**). The opening of the digermacyclopropane ring in **D** produces 1-tris(trimethylsilyl)germyl-1-germapropadiene (**E**). The hydrogen shift from the ortho position of the phenyl ring to the internal carbon in **E**, to give a diradical intermediate (**F**), and then intramolecular coupling of the resulting phenyl radical with the germyl radical produces compound **2**. Unfortunately, at present, evidence for the presence of **D**, and also intermediates, **B**, **E**, and **F**, has not yet been obtained.

In the silicon chemistry, it has been reported that the reaction of a silapropadiene derivative with silylene gives the disilacyclopropane derivative, arising from addition of silylene to a silicon—carbon double bond in the silapropadiene [8c], and also reported that addition of silylene to a silene produces the disilacyclopropane derivative [12].

Germylene **C** may be considered to be produced from two different routes, that is, the direct formation from **1** and the thermal decomposition of germacyclopropane **B** once formed from **1**, as shown in Scheme 2. To clarify whether or not the direct formation



Scheme 1. Synthesis of the starting compound 1.



Scheme 2. Route from compound 1 to germapropadiene A and germylene C.

of the germylene **C** is involved in the present reaction, we have carried out the theoretical investigation for the thermal reaction of **1**, as described below.

#### 2.3. Photolysis of 1

Next, we investigated the photolysis of **1** in the absence of a trapping agent. In contrast to the reaction of the corresponding silyl derivative, phenylethynyltris(trimethylsilyl)silane, in which 3-phenyl-1,1,2-tris(trimethylsilyl)-1-silacyclopropene was readily isolated [8b], germyl compound **1** afforded no isolable germacyclopropene **B**. Thus, compound **1** was irradiated with a low-pressure mercury lamp bearing a Vycor filter in  $C_6D_6$  at room temperature, and the reaction was followed by <sup>1</sup>H NMR spectrometry. The result showed that the resonance at 0.28 ppm attributable to the

trimethylsilyl protons of **1** decreased gradually with the elapse of time, and was replaced by the resonance due to the trimethylsilyl protons of phenyl(trimethylsilyl)acetylene. Furthermore, the broad resonances were also observed in the methylsilyl region. However, when a hexane solution of **1** in the presence of a large excess of 2,3-dimethylbutadiene was photolyzed under the same conditions for 10 min, compound **3** derived from addition of bis(silyl)germylene **C** to 2,3-dimethylbutadiene was obtained in 11% yield, along with 17% of phenyl(trimethylsilyl)acetylene and 31% of the starting compound **1**. No other volatile products were detected in the reaction mixture. Compound **3** was identified by comparison of the spectral data with those reported by Apeloig et al. [13], and also with those of the sample obtained from the thermal reaction. In both photolyses, no germacyclopropene derivatives such as **B**, **D**, and **D**' were detected by spectrometric analysis (Scheme 4).



Scheme 3. Formation of compound 2.



Scheme 4. Thermolysis and photolysis of compound 1 in the presence of 2,3-dimethyl-1,3-butadiene.

#### 2.4. Theoretical calculations

The reaction mechanisms shown in Schemes 2 and 3 were investigated by the Density Functional Theory calculations. Whole reaction was divided into several elementary steps, in which the transition state (TS) was characterized, and the Intrinsic Reaction Coordinate (IRC) analysis [14] was carried out at each TS for the both directions, i.e., reactant and product. The IRC analysis was limited rather in the neighborhood of TS, and full optimization was followed at the end points of IRC analysis. Finally we confirmed that the reaction path was connected from the reactant to the product via the TS. The standard Becke-three-parameter-Lee–Yang–Parr hybrid method [15] implemented in the Gaussian 03 program [16] was used with the 6-31(d) basis set.



Fig. 1. Structures of LMs and TSs locating between 1 and A along a 1,3-shift of the trimethylsilyl group (Route a). The number in parentheses for TS structures indicates the weight of the internal parameter (such as bond length) in direction of the reaction coordinate.



Fig. 2. Structures of LMs and TSs locating between 1 and the product (C + PhCCSiMe<sub>3</sub>) in the stepwise manner, a 1,2-shift of the trimethylsilyl group, followed by degradation of germacyclopropane B (Route b). See caption of Fig. 1 for numbers in parentheses.

Fig. 1 shows the local minima (LMs) and transition states (TSs) locating between the starting compound **1** and germapropadiene **A** (Route a). The formation of **A** involves a 1,3-shift of a trimethylsilyl group from a germanium atom onto a phenyl-substituted ethynyl carbon atom in **1**. In detail, the potential energy surface shown in Fig. 7 indicates that a trimethylsilyl group on the germanium atom migrates to the germyl-substituted ethynyl carbon, and then phenyl-substituted ethynyl carbon through a twice-consecutive 1,2-silyl shift. LMa-1 is the product arising from the initial 1,2-shift of the trimethylsilyl group. However, the energy change from TSa-1, LMa-1 to TSa-2 is very small, and the reaction essentially proceeds with a 1,3-silyl shift.

Two routes are considered for the formation of germylene **C** from the starting compound **1**. One involves the degradation of the germacyclopropane **B** formed from **1** (Route b), and the other is the formation of germylene **C** and phenyl(trimethylsilyl)acetylene from **1** in the concerted manner (Route c). Figs. 2 and 3 show the LMs and TSs locating along the reaction from **1** to the products, germylene **C** and phenyl(trimethylsilyl)acetylene. The germacyclopropane **B** is a rather stable, and the energy is higher than that of **1** only by 66 kJ mol<sup>-1</sup>. However, as shown in Fig. 2, the energies for TSs (TSb-2, TSb-3) and LMs (LMb-2, LMb-3) in the subsequent reaction of germacyclopropane **B** to the final product, germylene **C** and phenyl(trimethylsilyl)acetylene are higher than that of **B** by more



Fig. 3. Structures of LMs and TSs locating between 1 and the product (C + PhCCSiMe<sub>3</sub>) in the concerted manner (Route c). See caption of Fig. 1 for numbers in parentheses.

than 200 kJ mol<sup>-1</sup>. Fig. 3 shows the structures and energy changes along the route involving no germacyclopropene structure (Route c). The potential energy surface is still higher than that of the route with the germacyclopropene ring (Route b). In both cases, the potential energy surface is up-hill, and the product is more unstable than the reactant by 251 kJ mol<sup>-1</sup>.

Next, we carried out theoretical treatment for addition of germylene **C** to a C–Ge double bond in germapropadiene **A**, leading to the final product **2**, as shown in Scheme 3. The structures of LMs and TSs between digermacyclopropane **D** and 1,3-bis(silyl)-1germyl-1-germapropadiene **E**, and between **E** and the product **2** are shown in Figs. 4 and 5, respectively. The relative energies from **D** to **2** are shown in Fig. 8 (Route d), where the sum of energies of **A** and **C** is adopted as the reference. The formation of digermacyclopropane **D** is strongly exothermic more than 300 kJ mol<sup>-1</sup>. 1,3-Bis(silyl)-1-germyl-1-germapropadiene **E** is more stable than **D** by 40 kJ mol<sup>-1</sup>, but **F** is more unstable by 168 kJ mol<sup>-1</sup>. **D**–**E**(TS1) and **D**–**E**(TS2) correspond to migration of the trimethylsilyl group and scission of the C–Ge bond, respectively. The highest energy point on the reaction path is the TS between **F** and **2**, **F**–**2**(TS), whereas it is below zero, and still more stable than those of the isolated **A** and **C**. As expected from Scheme 3, **F** has a biradical character, and the electronic structures for **E**–**F**(TS), **F**, and **F**–**2**(TS) are evaluated by the broken symmetry solution, i.e., the spin polarized singlet state.



 $\mathbf{E}: \Delta \mathbf{E} = -359.6 \text{ kJ mol}^{-1}$ 

Fig. 4. Structures of LMs and TSs locating between D and E in the reaction of A with C (Route d). See caption of Fig. 1 for numbers in parentheses.



Fig. 5. Structures of LMs and TSs locating between E and 2 (common with Routes d and e). See caption of Fig. 1 for numbers in parentheses.

For the formation of **E**, there is another possible route (Route e) from **1** and germylene **C**, via tris(trimethylsilyl)germyl-substituted germacyclopropene **D'** as illustrated in Scheme 3. The structure and energy changes along this route are shown in Figs. 6 and 8. There are two TSs, i.e., **D'**–**E**(TS1) and **D'**–**E**(TS2), and this situation is similar to Route d. The energy of **D'** is only by 8 kJ mol<sup>-1</sup> lower than **D**. Although the energy of reactant (**1** + **C**) is lower than that of (**A** + **C**), the potential energy surface lies higher than that of Route d. Especially, **D'**–**E**(TS2) is unstable probably due to the migration of the bulky tris(trimethylsilyl)germyl group.

In whole reactions, the formation of germylene C is the most endothermic reaction. Once germylene C is produced, the reaction of C with A to give the product 2 proceeds within the attractive potential energy region.

In conclusion, the thermolysis of **1** at 240 °C for 6 h in a sealed glass tube gave 1,3-bis(trimethylsilyl)-1-tris(trimethylsilyl)germyl-1-germaindene **2**. Compound **2** would be produced by the reaction of the germapropadiene **A** with germylene **C**, generated thermally from

**1**. Addition of germylene **C** to germapropadiene **A** would produce the reactive digermacyclopropane intermediate **D**, and the digermacyclopropane derivative thus formed isomerizes, to give the final product, germaindene **2**. On the other hand, irradiation of **1** in the presence of 2,3-dimethylbutadiene with a low-pressure mercury lamp gave 3,4-dimethyl-1,1-bis(trimethylsilyl)-1-germacyclopent-3ene **3**, arising from [1 + 4] cycloaddition of germylene **C** to the butadiene, as the volatile product. All the LMs and TSs locating on the reaction paths were characterized by the DFT calculations. The formation of **C** was the most endothermic process. However, if **C** is once formed, the latter half reactions proceed on the down-hill potentials.

#### 3. Experimental

#### 3.1. General procedures

Thermal reactions were carried out in a degassed sealed tube (1.0 cm  $\phi \times$  15 cm). Yields of the products were calculated on the

 $D: \Delta E=-327.4 \text{ kJ mol}^{-1}$ 

D'-E(LM):  $\Delta E=-195.2 \text{ kJ mol}^{-1}$ 

D'-E(TS2): ΔE=-50.4 kJ mol<sup>-1</sup>

Fig. 6. Structures of LMs and TSs locating between D' and E in the reaction of 1 with C (Route e). See caption of Fig. 1 for numbers in parentheses.

basis of the isolated products. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Lowresolution mass spectra were measured on a JEOL Model JMS-700 instrument. Column chromatography was performed by using Wakogel C-300 (WAKO).

#### 3.2. Materials

Compound **1** was prepared by the method reported by Baumgartner et al. [10].

#### 3.3. Thermolysis of 1 at 240 °C

0.1347 g (0.343 mmol) of **1** in a sealed glass tube was heated at 240 °C for 6 h. The reaction mixture was chromatographed on a silica gel column, eluting with hexane to give 0.0191 g (18% yield) of **2** and 0.0356 g (60% yield) of phenyl(trimethylsilyl)acetylene. Data for **2**: Calcd for C<sub>23</sub>H<sub>50</sub>Si<sub>5</sub>Ge<sub>2</sub>: C, 45.12; H, 8.23. Found: C, 45.00; H, 8.01. MS *m*/*z* 614 (M<sup>+</sup>); <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>) 0.10 (s, 9H, Me<sub>3</sub>Si), 0.17 (s, 27H, Me<sub>3</sub>Si), 0.29 (s, 9H, Me<sub>3</sub>Si), 7.12 (t, 1H, ring proton, *J* = 7.5 Hz), 7.26 (t, 1H, ring proton, *J* = 7.5 Hz), 7.37 (s, 1H,



Fig. 7. Relative energies for LMs and TSs locating between 1 and the product ( $C + PhCCSiMe_3$ ).



Fig. 8. Relative energies for LMs and TSs locating between A + C or 1 + C and 2.

ring proton), 7.56 (d, 1H, ring proton, I = 7.5 Hz), 7.62 (d, 1H, ring proton, I = 7.5 Hz); <sup>13</sup>C NMR  $\delta$  (CDCl<sub>3</sub>) -0.50, 0.17, 3.08 (Me<sub>3</sub>Si), 124.65, 125.88, 126.81, 133.26, 148.24, 151.41, 152.48, 159.14 (ring carbons); <sup>29</sup>Si NMR δ (CDCl<sub>3</sub>) -8.5, -6.0, -3.3.

3.4. Thermolysis of 1 at 240 °C in the presence of 2,3-dimethyl-1,3butadiene

A mixture of 0.1081 g (0.275 mmol) of 1 and 0.1019 g (1.24 mmol) of 2,3-dimethylbutadiene in a sealed glass tube was heated at 240 °C for 6 h. After evaporation of the reaction mixture, the residue was chromatographed on a silica gel column, eluting with hexane to give 0.0515 g (62% yield) of **3** and 0.0331 g (69% yield) of phenyl(trimethylsilyl)acetylene. Data for 3: Calcd for C<sub>12</sub>H<sub>28</sub>Si<sub>2</sub>Ge: C, 47.86; H, 9.37. Found: C, 47.80; H, 9.01. MS *m*/*z* 302  $(M^+)$ ; <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>) 0.15 (s, 18H, Me<sub>3</sub>Si), 1.68 (s, 6H, CH<sub>3</sub>), 1.73 (s, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR  $\delta$  (CDCl<sub>3</sub>) –0.24 (Me<sub>3</sub>Si), 19.39 (CH<sub>2</sub>), 21.98 (CH<sub>3</sub>), 131.63 (ring carbons); <sup>29</sup>Si NMR  $\delta$  (C<sub>6</sub>D<sub>6</sub>) –9.0.

### 3.5. Photolysis of 1 in the presence of 2,3-dimethyl-1,3-butadiene

A mixture of 0.1250 g (0.318 mmol) of **1** and 0.2767 g (3.37 mmol) of 2,3-dimethylbutadiene in 50 mL of hexane was irradiated for 10 min internally with a 6 W low-pressure mercury lamp bearing a Vycor filter. The solvent was evaporated, and the residue was chromatographed on a silica gel column with hexane as a eluent to give the product **3** (0.0110 g, 11% yield), phenyl(trimethylsilyl)acetylene (0.0094 g, 17% yield), and the starting compound 1 (0.0384 g). All spectral data for 3 were identical with those of the authentic sample.

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