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The halogen effect on the ring-opening of germacyclopropylidenoids to germaallenes

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Abstract: Density functional theory calculations were employed to explore the ring–opening reaction mechanisms of mono germanium analogues of cyclopropylidenoids *via* Doering–Moore–Skattebøl method. The theoretical findings revealed that the stepwise fashion with the intermediacy of a free germacyclopropylidene is operative for the structure with germanium atom on the carbenic position (**1**). Moreover, the cyclopropylidene analogue (**4**) of the title structures proceeds *via* concerted manner for the corresponding ring-opening reaction. The calculated overall energy barrier to trigger the stepwise ring-opening reaction for **1** is strongly higher than the concerted fashion for **4**. Additionally, the effect of halogens (X = F, Cl, Br) on the reaction mechanism were also investigated. The energy barriers for chlorine substituted precursors are found to be lower than the fluorine and bromine substituted forms.

Keywords: Germaallene; reaction mechanism; DFT; germanoid; germylene.

1. Introduction

Organogermanium compounds have aroused the interest of experimental and theoretical chemists due to their biologic activity [1]. Germylenoids, R_2GeMX (M = alkali metal, X = halogen), are important active intermediates in organometallic reactions [2,3]. In 1991, Gaspar and Lei postulated that a kind of germylenoid was formed in the reaction of substituted butadiene with dichlorodimethylgermane [4]. Similar to carbenoid [5], silylenoid [6], and germylenoid, germacyclopropylidenoid is the complex formed between free germacyclopropylidene and inorganic salt. For the first time, the structural isomers of germacyclopropylidenoidshave been investigated by Azizoglu et al [7]. The theoretical calculations indicated that germacyclopropylidenoids could have two stationary structures, germanoidal (**G**) and inverted (**I**). It is obtained no tetrahedral structure (**T**) was observed for the studied germacyclopropylidenoids (Scheme 1).

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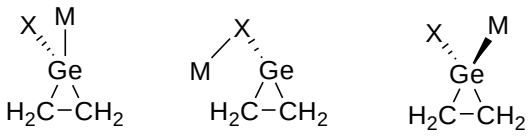
Likewise, it is necessary to conduct systematic experimental and theoretical studies on the germacyclopropylidenoids to understand their structures, properties, and especially the reactions. However, due to their high reactivity, to best of our knowledge, currently, there is no method available in the literature to prepare stable germacyclopropylidenoids. Hence, computational studies appear to be the only means of investigating these compounds. In this study, ring–opening mechanism of germacyclopropylidenoids to form the corresponding germaallenes is reported.

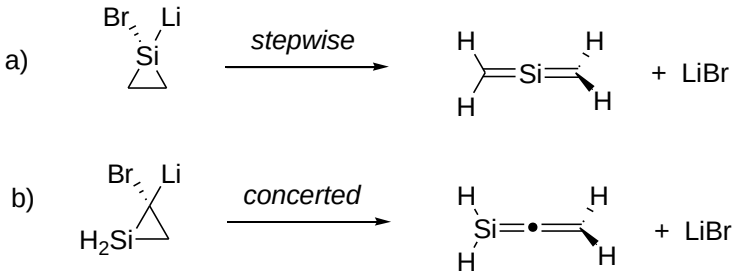


(**G**) (**I**) (**T**)

Scheme 1. Germanoidal (**G**), inverted (**I**), and tetrahedral (**T**) forms of germacyclopropylidenoid

2. Background

Recently, our groups employed a series of theoretical calculations to explore the potential formation mechanisms of 1- and 2-silaallenes based on Doering-Moore-Skattebøl reaction (Scheme 2) [8]. DFT results revealed that elimination of LiBr from the corresponding starting materials occurs in a concerted (for 1-silaallene) and stepwise (for 2-silaallene) manners. Additionally, the ring-opening mechanisms of trisilacyclopropylidenoid and disilacyclopropylidenoids were also investigated with the help of quantum chemical calculations [9]. In a similar fashion, the concerted and stepwise mechanisms are operative to produce the related silaallenes.



Scheme 2. Ring-openings of 1-bromo-1-lithiosilirane and 2-bromo-2-lithiosilirane to 2-silallene and 1-silaallene, respectively.

3. Experimental

The computational details were described in detail elsewhere [10]. Gaussian 09W and Gaussview 5 programs were used for the quantum chemical calculations [11]. The optimizations of the title structures were performed at WB97XD/6-31+G(d,p) level. The characters of the optimized structures were determined considering their obtained imaginary frequencies. The ΔG energies are in kcal/mol. The proposed transition states were confirmed by the Intrinsic Reaction Coordinate (IRC) calculations [12].

4. Present Study

In order to obtain 1- and 2-germaallenes, two different pathways were proposed *via* intramolecular rearrangements of germacyclopropylidenoids. One is the stepwise fashion, and the other is the concerted manner as given in Figure 1.

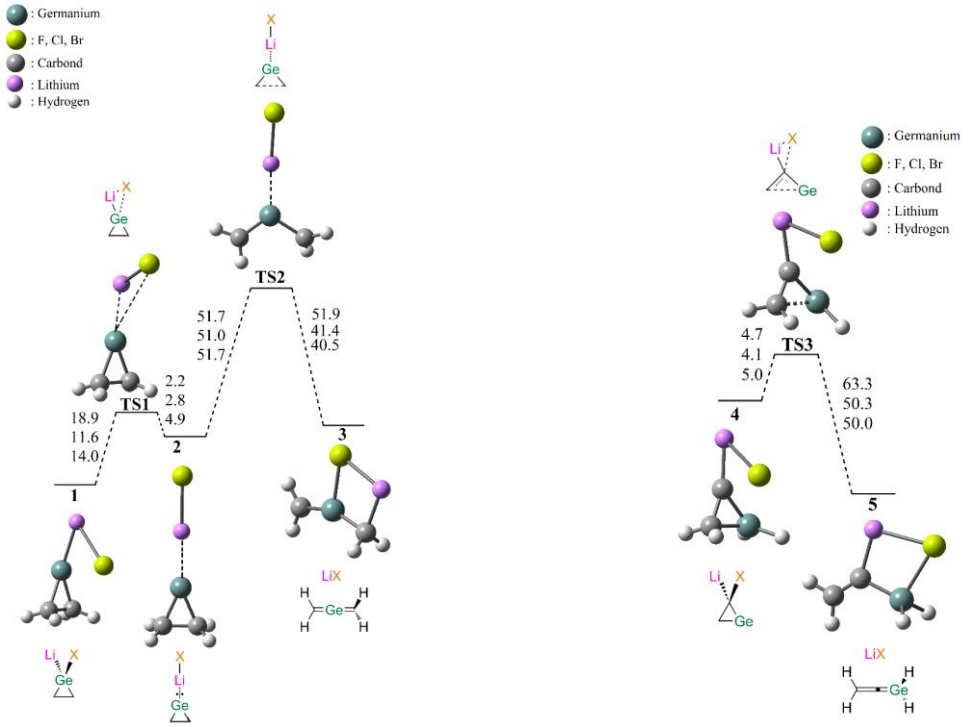


Figure 1. The proposed stepwise (left) and concerted (right) ring-opening mechanism of **1→3** and **4→5** at the WB97XD/6–31+G(d,p) level of theory, respectively. (Energy values for F, Cl, and Br, respectively; X = F, Cl, Br).

The proposed stepwise reaction mechanism for the ring-opening of **1** to is given in Figure 1. The lowest energy barriers were found for the chlorine substituted forms. Thus, the results of the chlorine substituted germacyclopropylidene structures were considered for discussion. The first step of the mechanism was considered to be related to the Ge-X bond breaking *via* **TS1** to give the intermediate **2** by an energy barrier of $\Delta G^{\neq}$ =11.6 kcal/mol for X = Cl. Subsequently, the ring-opening of the three–membered ring **2** took place *via* **TS2**. This step required a considerable high energy barrier of $\Delta G^{\neq}$ = 51.0 kcal/mol for X = Cl at WB97XD/6–31+G(d,p) level of the theory. The calculated overall pathway for **3** was determined to be heavily endergonic by ΔG = 18.4 kcal/mol (X = Cl). In the case of constitutional isomer **4**, the formation of 1–germaallene **5** was only operative *via* the concerted manner. Similar to the ring-opening mechanism of **1**, the chlorine substituted structure **4** was found to be more suitable for the ring-opening mechanism as compared to X = F and Br cases in terms of energy of the reaction. The corresponding transition state **TS3** required an energy barrier of $\Delta G^{\neq}$ = 4.1 kcal/ mol (X = Cl) to form 1-germaallene (Figure 1). The formation energy of **5** was calculated to be heavily exergonic by ΔG = -46.2 kcal/mol at the WB97XD/6–31+G(d,p) level.

Alternative pathways to produce 1- and 2-germaallenes were suggested through the ring-openings of the corresponding germacyclopropylidenes (**6** and **7**). In a similar fashion with the germylenoid analogue **1**, the required energy barrier to arrive at **TS4** to give **7** was determined to be very high by $\Delta G^{\neq}$ = 54.1 kcal/mol (Figure 2). Moreover, the overall reaction for **7** is strongly endergonic by ΔG = 28.5 kcal/mol. It is interesting to note that the singlet state of **8** could not be located as minima on its potential energy surface. Instead, the triplet state of **8** was optimized as a minimum. Then, the ring opening reaction for 1-germaallene **9** was proposed from the triplet state of **8**. The predicted energy barrier for **TS5** was observed to be very low by $\Delta G^{\neq}$ = 1.2 kcal/mol, so that the overall pathway for the final product **9** is heavily exergonic by ΔG = -30.9 kcal/mol.

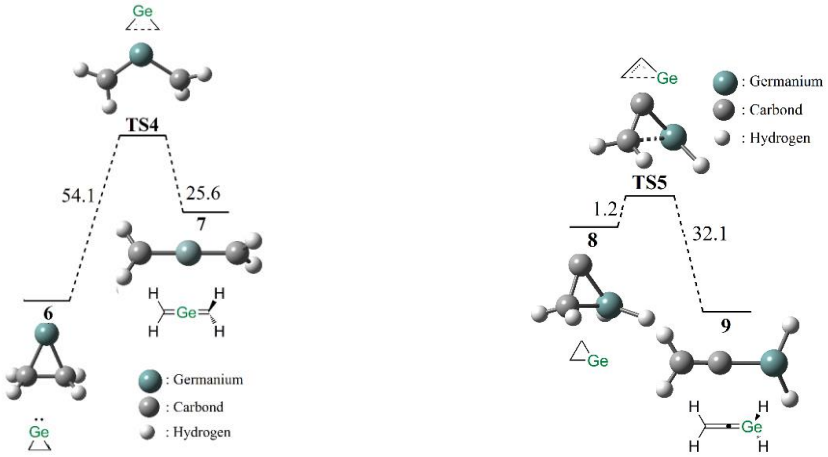


Figure 2. The proposed ring-opening mechanisms for **6**→**7** (Left) and **8**→**9** (Right) at the WB97XD/6–31+G(d,p) level.

5. Conclusion

Effect of halogen on energies of the proposed ring–opening reactions of **1** and **4** to **3** and **5** were investigated, respectively. In all cases, the stepwise mechanism is operative for **1** to generate the complex 2–germaallene **3**, whereas the formation of the complex 1–germaallene **5** was suggested *via* the concerted ring-opening of **4**. The lowest energy barrier was found for chlorine substituted forms. Moreover, the considerable endergonic character of the intramolecular ring opening of **1** was calculated to be ΔG = 19.3 kcal/mol despite the exergonicity of **5** by ΔG = -46.2 kcal/mol. Thus, the ring–opening reaction for **4** is thermodynamically more favorable than the ring–opening of **1**. Intramolecular rearrangement of **6** and **8** also gives the free germaallenes **7** and **9**, respectively. It is clear that the formation of 2-germaallene **8** is more likely to appear with the observed lower energy barrier and strong exergonic character as in the case of **4**.

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Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/organic-communications

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