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Mechanism of the cyclization of dimethyl diethynyl silane with selenium tetrabromide: Computational and structural studies, and monitoring

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Abstract

The structure of 2,4-dibromo-2-dibromomethyl-3,3-dimethyl-1-selena-3-silacyclopentene-4, formed by regioselective electrophilic addition of $SeBr_4$ to dimethyl diethynyl silane, has been determined using X-ray analysis technique. Quantum chemistry methods were used to study elementary stages of the reaction. It was found that the first stage consisted of $SeBr_4$ conversion into bimolecular complex $Br_2\cdot\cdot SeBr_2$, initiated by dimethyl diethynyl silane. Possible formation of five-membered and six-membered heterocycles involves different cyclization mechanisms. The formation of only five-membered heterocycle is explained by kinetically preferable ring closure through four-center transition state. The conclusions obtained by calculations were confirmed by monitoring of the reaction using ^1H NMR method.

Keywords: Chalcogens; Five-membered unsaturated heterocycles; Reaction mechanisms; NMR spectroscopy; X-ray diffraction

1. Introduction

Saturated sulfur-silicon containing heterocycles [1] including five-membered ones are known from the literature [2a,2b,2c]. Previously we have briefly reported on the synthesis of unsaturated five-membered selenium-silicon containing heterocycle of cyclopentene [3a] structure by the reaction of dimethyl diethynyl silane **1** with selenium tetrabromide. Also this reaction was studied on a series of diethynyl silanes [3b]. But the conclusion about structure of the heterocycle formed was made only on the basis of ^1H, ^{13}C and ^{77}Se NMR methods and GC–MS. At the same time this reaction may involve the cyclization not only into five-membered **2**, but also six-membered heterocycle **4** (Scheme 1). In addition we have found that along with the main reaction product – heterocycle **2**, isolated from the reaction mixture as a crystalline compound, the reaction led to the formation of 3,6-dibromo-4,4-dimethyl-1,4-selenasilafulvene **3** as *Z*- and *E*-isomers (Scheme 1). These heterofulvenes were shown earlier to be the products of the reaction of silane **1** with $SeBr_2$ [4]. The present work deals with the mechanism of new reaction of $SeBr_4$ with silane **1**, which affords the heterocycle **2**. We are going to determine also if the heterofulvene **3** is an intermediate during the formation of heterocycle **2**.

2. Results and discussion

2.1. XRD analysis

The structure of the main product, formed in the reaction of diethynyl silane **1** with $SeBr_4$, was identified by X-ray analysis of the crystalline compound obtained by slow

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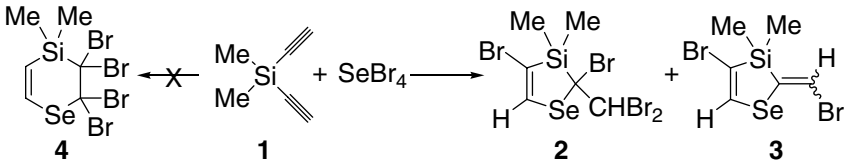

Scheme 1.

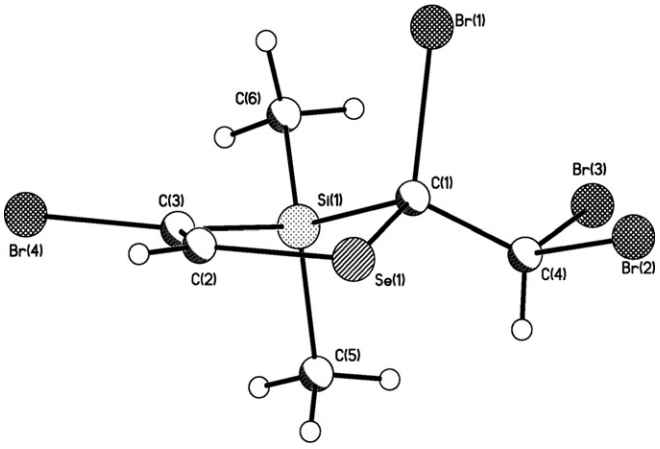

Fig. 1. Molecular structure of heterocycle **2**.

crystallization from chloroform. It was shown that this product is 2,4-dibromo-2-dibromomethyl-3,3-dimethyl-1-selena-3-silacyclopentene-4 (**2**).

The principal geometrical parameters in heterocycle **2** (Fig. 1) are listed in Table 1. Although the direct comparison of bond lengths in **2** is impossible since it is a first structurally characterized compound with 1-selen-3-silacyclopentene-4 fragment we can mention that lengths of endocyclic Se–C bonds in **2** are close to literature data for diselenium analogue [5].

The silicon atom Si(1) is characterized by slightly distorted tetrahedral configuration with the decrease of endocyclic C(1)Si(1)C(3) angle to 95.6(2)° (Table 2). The five-membered ring is characterized by envelope conformation with the deviation of C(1) atom from the plane of Si(1), Se(1), C(2) and C(3) atoms by 0.54 Å. The analysis of crystal packing has revealed that molecules in crystal are assembled into centrosymmetric dimers by means of secondary Br(1)···Br(4)′ ($-x$, $1-y$, $1-z$) (3.544 Å) interactions (Fig. 2). Taking into account the specific directionality of this contact (angle C(1)Br(1)···Br(4′) is equal to 170.3°) as well as elongation of C(1)–Br(1) bond up to 1.971(5) Å we can assume that this contact corresponds to the charge transfer from the electron lone pair (n) of Br(4) atom to antibonding orbital (σ^*) of C(1)–Br(1) bond, i.e. n–σ^* interaction.

Table 1
Bond lengths (Å) in heterocycle **2**

Atom(1)–Atom(2)	Å	Atom(1)–Atom(2)	Å
Si(1)–C(5)	1.834(6)	Br(1)–C(1)	1.971(5)
Si(1)–C(6)	1.841(5)	Br(2)–C(4)	1.946(6)
Si(1)–C(3)	1.870(6)	Br(3)–C(4)	1.924(6)
Si(1)–C(1)	1.917(5)	Br(4)–C(3)	1.903(6)
Se(1)–C(2)	1.909(6)	C(1)–C(4)	1.501(7)
Se(1)–C(1)	1.960(5)	C(2)–C(3)	1.302(7)

2.2. Computational results

To elucidate the reaction mechanism and to explain the formation of only five-membered heterocycle **2** we have carried out quantum chemical computation of possible

Table 2
Valence angles (°) in heterocycle **2**

Angle	ω (°)	Angle	ω (°)
C(5)–Si(1)–C(6)	111.3(3)	C(4)–C(1)–Br(1)	109.5(4)
C(5)–Si(1)–C(3)	109.0(3)	Si(1)–C(1)–Br(1)	107.0(3)
C(6)–Si(1)–C(3)	113.6(2)	Se(1)–C(1)–Br(1)	109.8(2)
C(5)–Si(1)–C(1)	110.0(3)	C(3)–C(2)–Se(1)	118.5(5)
C(6)–Si(1)–C(1)	116.3(3)	C(2)–C(3)–Si(1)	118.5(4)
C(3)–Si(1)–C(1)	95.6(2)	C(2)–C(3)–Br(4)	120.1(4)
C(2)–Se(1)–C(1)	93.8(3)	Si(1)–C(3)–Br(4)	121.4(3)
C(4)–C(1)–Si(1)	115.5(4)	C(1)–C(4)–Br(3)	113.3(4)
C(4)–C(1)–Se(1)	108.6(4)	C(1)–C(4)–Br(2)	114.0(4)
Si(1)–C(1)–Se(1)	106.4(2)	Br(3)–C(4)–Br(2)	110.0(3)

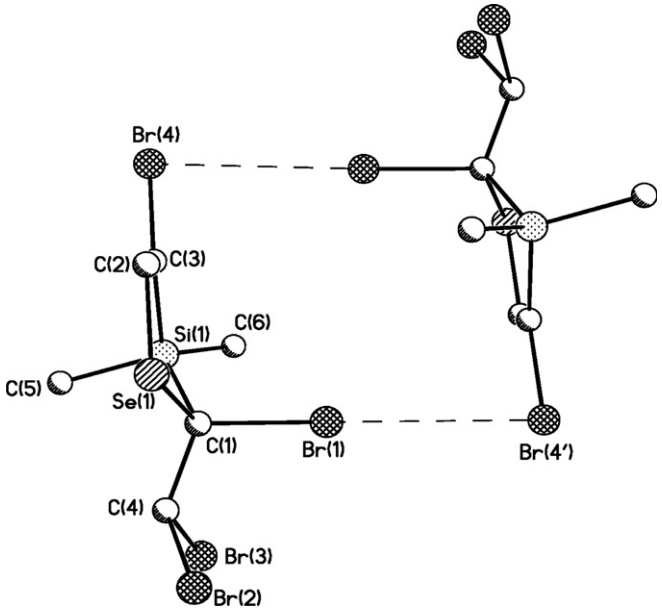

Fig. 2. The centrosymmetric dimers in crystal of **2** (H atoms omitted for clarity).