



## Note

## Quantum chemical studies of the reaction of selenium dichloride with divinyl sulfide and comparison with experimental results

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## ABSTRACT

Quantum chemical studies of the reaction of selenium dichloride with divinyl sulfide have been carried out. The major reaction route (2,6-dichloro-1,4-thiaselenane  $\rightarrow$  5-chloro-2-chloromethyl-1,3-thiaselenolane  $\rightarrow$  2-chloromethyl-1,3-thiaselenole) and main trends of the reaction (a rearrangement of 2,6-dichloro-1,4-thiaselenane, facile selective dehydrochlorination of 5-chloro-2-chloromethyl-1,3-thiaselenolane), which have been determined by the quantum chemical studies, are in excellent agreement with experimental data.

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## 1. Introduction

We have earlier reported the addition reaction of selenium dichloride and dibromide to dimethyl diethynyl silane to give unsaturated 5-membered heterocycles [1,2]. The reaction was performed with various diorganyl diethynyl silanes and -germanes and provided previously unknown 1-selena-4-silafulvenes and 1-selena-4-germafulvenes [3–8].

It has been shown that in solutions selenium dichloride exists in equilibrium with  $\text{Se}_2\text{Cl}_2$  and  $\text{SeCl}_4$ , whereas the equilibrium of selenium dibromide involves  $\text{Se}_2\text{Br}_2$  and bromine [9–12]. In spite of the fact, that selenium dichloride and dibromide exist in equilibrium with other selenium species, these reagents can be used in reactions to give organoselenium compounds with good selectivity and in high yield [1–8].

As part of our continued investigations of reactions of selenium halides with organic compounds [1–8,13] we have recently studied the addition reaction of selenium dichloride (2) to divinyl sulfide (1) [14]. We found that the reaction at  $-50^\circ\text{C}$  in chloroform afforded 2,6-dichloro-1,4-thiaselenane (3), in virtually quantitative yield (Scheme 1).

At room temperature in chloroform solution, thiaselenane 3 underwent spontaneous rearrangement to 5-chloro-2-chloromethyl-1,3-thiaselenolane (4). A mechanism of the rearrangement was supposed to involve seleniranium cation [14]. We suggested

that thiaselenane 3 was the kinetic product and thiaselenolane 4 was the thermodynamic product. The complete conversion of thiaselenane 3 to thiaselenolane 4 occurred when the chloroform solution of the former was allowed to stand at room temperature for 7 days. However, along with thiaselenolane 4, the formation of 2-chloromethyl-1,3-thiaselenole (5) was also observed in this case (Scheme 1) [14]. We have found that upon standing at room temperature in chloroform solution, thiaselenolane 4 underwent slow dehydrochlorination to thiaselenole 5. The same reaction occurred faster when the solution was warmed on a water bath. Vacuum distillation of thiaselenolane 4 led to thiaselenole 5 in 30% yield [14].

In this work we wish to present results of quantum chemical studies of the reaction of selenium dichloride with divinyl sulfide, which exhibit excellent agreement with the experimental results.

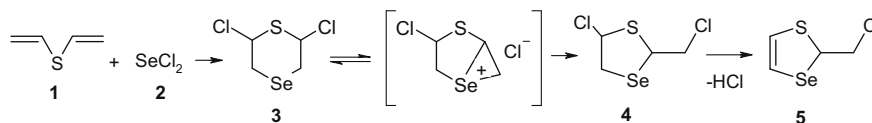
## 2. Results and discussion

We carried out quantum chemical calculations of the reaction routes, which can be potentially envisaged for the interaction of 2 with 1, using the program complex Gaussian [15]. Probability of the formation of products 3–8 and intermediates A (the product of the addition of 2 to the  $\text{C}_\beta$  atom of one double bond of 1) and B (the product of the addition of 2 to the  $\text{C}_\alpha$  atom of one double bond of 1) has been analyzed. Scheme 2 illustrates the results obtained.

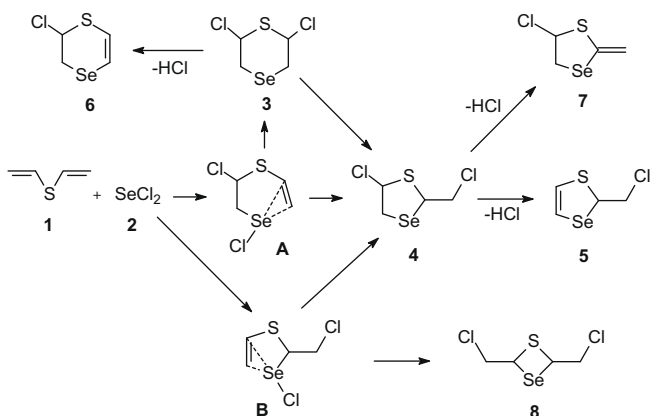
The interaction of selenium dichloride with divinyl sulfide was studied using two rotamers of divinyl sulfide, which are equally possible from a thermodynamic viewpoint: plane *trans-trans* 1a

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Scheme 1.



Scheme 2.

and *trans-cis* **1b** (Fig. 1 and Table 1). The values of the torsion angles of the vinylic fragments in respect to the plane of the backbone are  $15.1^\circ$  and  $144.9^\circ$  in **1a**. The stabilization energy of the pre-reaction system **1** + **2** was estimated as a difference of total energies of optimal states of these reactants and of their bimolecular complex and valued 12.1 and 11.3 kJ/mol for **1a** and **1b**, respectively.

The contacts of the selenium atom with the carbon atoms  $C_\alpha$  or  $C_\beta$  of the vinyl groups were regarded as the main reaction coordinate of interaction of compounds **1** and **2**. As shown by the potential energy surface (PES) analysis, either concerted or stepwise routes can be envisaged. Transition states **TS1** and **TS2** are related to stepwise routes which include the formation of intermediates **A** and **B**, and transition state **TS3** corresponds to one of concerted routes leading to thiaselenane **3** (Fig. 1 and Table 1). In the case of the concerted reaction, the selenium and halogen atoms simultaneously attack both vinyl fragments of sulfide **1** and transition state **TS3** leads to thiaselenane **3**. Rotamer **1b** is the most probable partner of compound **2** in this route. Unlike the concerted route, the stepwise cyclization proceeds with the formation of relatively stable intermediates **A** and **B** (Fig. 1). The first step is the limiting one. The transition states (**TS1** and **TS2**) and the values of the activation barriers for the formation of intermediates **A** and **B** are presented in Figs. 1 and 2 and Table 1. From the values of activation parameters, it is apparent that the route leading to the intermediate **A** is the more favorable. The routes involving transition states **TS2** and **TS3** are approximately equally probable and are less favorable by about 20 kJ/mol compared to the route leading to intermediate **A** (Fig. 2 and Table 1). The exothermicity of the formation of intermediates **A** and **B** are 16.4 and 15.9 kJ/mol, respectively. Intermediates **A** and **B** lie in potential wells with heights of 64.7 and 79.6 kJ/mol, respectively. The distance between selenium and carbon atoms ( $Se-C_\beta$ ) is the principal component of the reaction coordinate in the cyclization of intermediate **A**. The initiator of the cyclization of intermediate **B** is the intramolecular 1,4-migration of the chlorine atom followed by rearrangement with the formation of the covalent bond  $Se-C_\beta$ . The data obtained indicate the prevalence of the route **1** + **2**  $\rightarrow$  **TS1**  $\rightarrow$  **A**  $\rightarrow$  **3**. The conversion of intermediate **A** to thiaselenane **3** is more favorable than the forma-

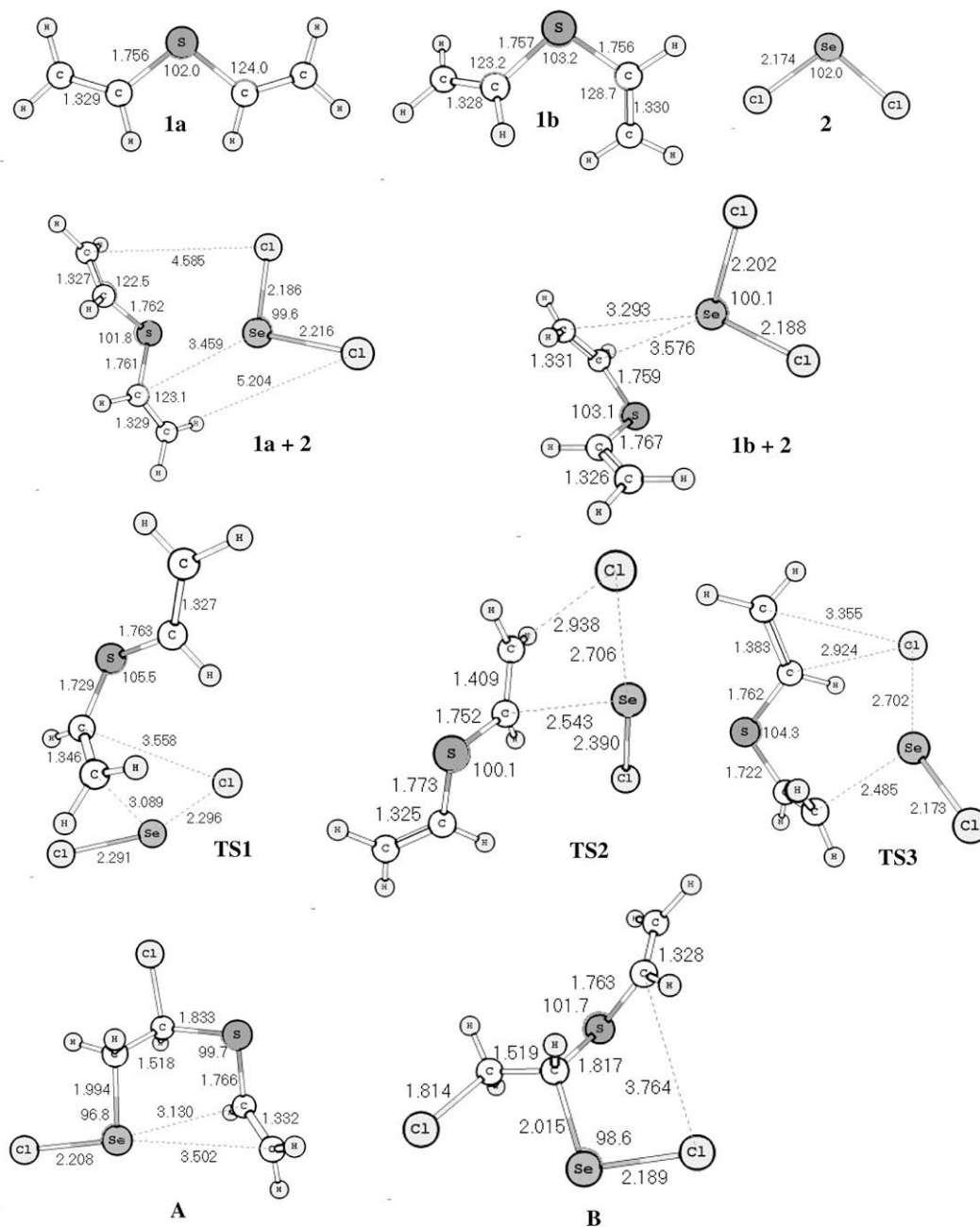
tion of thiaselenolane **4** from intermediate **A** (Fig. 2 and Table 1). On the other hand, the conversion of intermediate **B** to thiaselenolane **4** is more favorable than the formation of 4-membered compound **8** from intermediate **B** (Fig. 2). The values of the dipole moments of the transition states **TS1**, **TS2** and **TS3** (7.17, 6.23 and 5.14 D) indicate the higher degree of charge separation in **TS1** in comparison to **TS2** and **TS3** (Table 1).

Structure **3** can be stabilized as a chair or distorted boat with *cis*- or *trans*-orientated chlorine atoms. Conformers **3a,b** represent the *cis*- isomer and conformers **3c,d** correspond to the *trans*- isomer of thiaselenane **3** (Fig. 3). The exothermicity of the reaction is in the range 40–60 kJ/mol depending on the isomer and conformer formed, the chair conformers **3a,c** of each isomer being the most stable (Fig. 2 and Table 1). The yields of *cis*- and *trans*-isomers are controlled by the steric conditions of the reaction. The activation barrier of the interconversion chair (**3a**) – boat (**3b**) is 15.3 kJ/mol. The transition state **TS4** for this interconversion is presented in Fig. 3. The chair conformation is thermodynamically much more favorable than the boat conformation and the proportion of chair conformer **3a** is considerably more than that of the boat conformer **3b** in the equilibrium mixture.

The formation of thiaselenane **3** occurs faster than that of thiaselenolane **4**. However, thiaselenolane **4** is thermodynamically more stable than thiaselenane **3** (Fig. 2 and Table 1). As a consequence, thiaselenane **3** tends to convert to the more stable thiaselenolane **4** via a rearrangement. The activation barrier for the intramolecular rearrangement **3a**  $\rightarrow$  **4b** is 200.5 kJ/mol (Fig. 4 and Table 1). The structure of the transition state **TS10** of the rearrangement is depicted in Fig. 3. The rearrangement can be facilitated by participation of a mediator. An electrophilic reagent able to coordinate with the chlorine atom can play the role of the mediator, e.g., selenium dichloride or hydrogen chloride (Scheme 3), which is present in the reaction mixture due to hydrolysis of selenium dichloride by traces of water. The participation of the mediator is able to decrease significantly the activation barrier to 125–144 kJ/mol.

The HCl elimination can occur competitively with the rearrangement **3**  $\rightarrow$  **4** (Fig. 4). According to the PES analysis, the transition state **TS9** in the HCl elimination reaction of compound **3a** corresponds to an activation barrier of 151.7 kJ/mol (Fig. 4 and Table 1). The structures of the transition state **TS9** and products **6** + HCl are presented in Fig. 5. The activation barrier of the transition of **4b** to thiaselenole **5** (**4b**  $\rightarrow$  **TS11**  $\rightarrow$  **5** + HCl, Figs. 4 and 5) is 158.2 kJ/mol. The HCl elimination with the formation of compound **7** (**4b**  $\rightarrow$  **TS12**  $\rightarrow$  **7** + HCl) deals with higher energetic expenses (Fig. 4 and Table 1). This is in good agreement with the experimental results: the selective HCl elimination reaction of thiaselenolane **4** with the formation of thiaselenole **5** rather than compound **7** has been observed in experiments [14].

The possibility of cyclization of intermediate **B** with the formation of 4-membered heterocycles *cis*- and *trans*-2,4-dichloromethyl-1,3-thiaselenetanes (**8a** and **b**) was considered. The exothermicity of the conversion **B**  $\rightarrow$  **8a** (**8b**) is 13.7 (13.0) kJ/mol, and the activation energy (**TS8**) is 190.8 kJ/mol (Fig. 2 and Table 1). The lower prevalence of this route compared with the cyclization of intermediate **B** to thiaselenolane **4** is obvious. Indeed, the formation of 4-membered heterocycles has not been observed in experiments.



**Fig. 1.** Molecular structures and basic geometrical parameters of starting compounds **1** and **2**, their bimolecular complex (**1 + 2**), the transition states (**TS1–TS3**) and intermediates (**A** and **B**) according to the B3LYP/6-311+G(3df) data (bond lengths are in Å, valence angles are in grad).

### 3. Conclusions

Quantum chemical studies of the reaction of selenium dichloride with divinyl sulfide have been carried out. The major reaction route (**1 + 2** → **A** → **3** → **4** → **5**) and main trends of the reaction (a rearrangement of 2,6-dichloro-1,4-thiaselenane, facile selective dehydrochlorination of 5-chloro-2-chloromethyl-1,3-thiaselenolane), which have been determined by the quantum chemical studies, are in excellent agreement with experimental data. The sequences **1 + 2** → **A** → **4**, **1 + 2** → **B** → **4**, **A** → **3** → **6** and **A** → **4** → **7** corresponds to the minor reaction routes.

Thiaselenane **3** is the kinetic product and its formation occurs faster than that of thiaselenolane **4**. However, thiaselenolane **4** is thermodynamically more stable than thiaselenane **3**. As a consequence, thiaselenane **3** undergoes conversion to thiaselenolane **4**

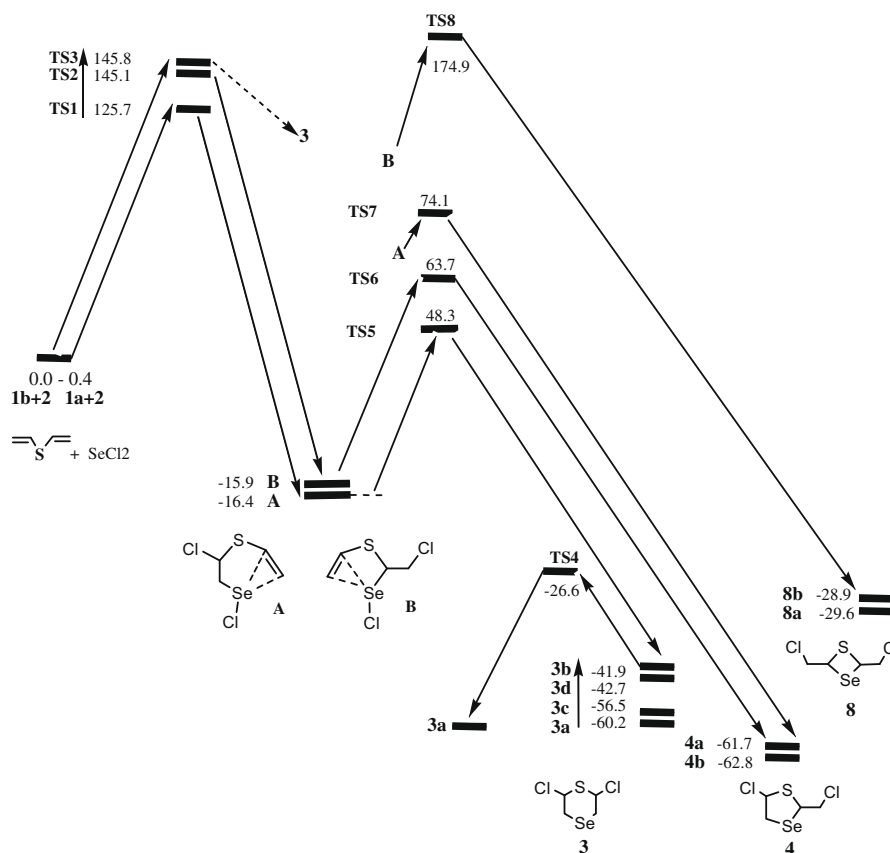
via the intramolecular rearrangement. The participation of electrophilic species (hydrogen chloride and selenium dichloride) as a mediator is able to decrease significantly the activation barrier of the rearrangement.

### 4. Experimental

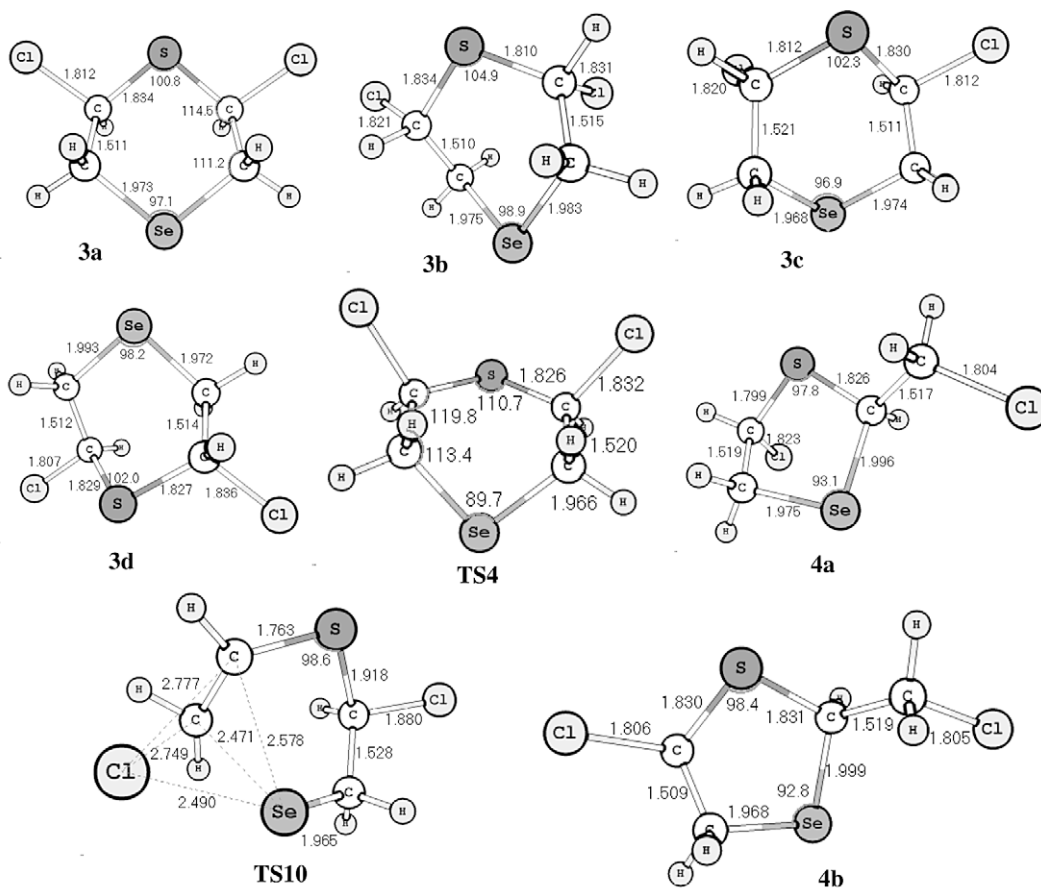
All calculations were realized in the framework of the program complex GAUSSIAN-98 [15]. The search of critical points and gradient routes connecting these points was carried out using density functional theory (DFT) with the 3-parameter function [16–18]. Taking into account the character of the electron orbital of the heteroatoms, the basis sets LANL2DZ and 6-311+G(3df) were applied. The former was used for express analysis of the potential energy

**Table 1**  
Total energies ( $-E_{\text{tot}}$ , a.u.), zero-point harmonic vibration energies (ZPVE, a.u.), relative energies ( $\Delta E$ ,  $\text{kJ/mol}^{-1}$ ), lowest harmonic frequencies ( $i\omega/\omega_1$ ,  $\text{cm}^{-1}$ ) and dipole moments ( $\mu$ , D) according to the B3LYP/6-311+G(3df) data (the relative energy  $\Delta E$  ( $E_{\text{tot}} + E_{\text{ZPVE}}$ ) of the bimolecular system **1a** + **2** was taken as zero; 1 a.u. = 2622.987 kJ/mol).

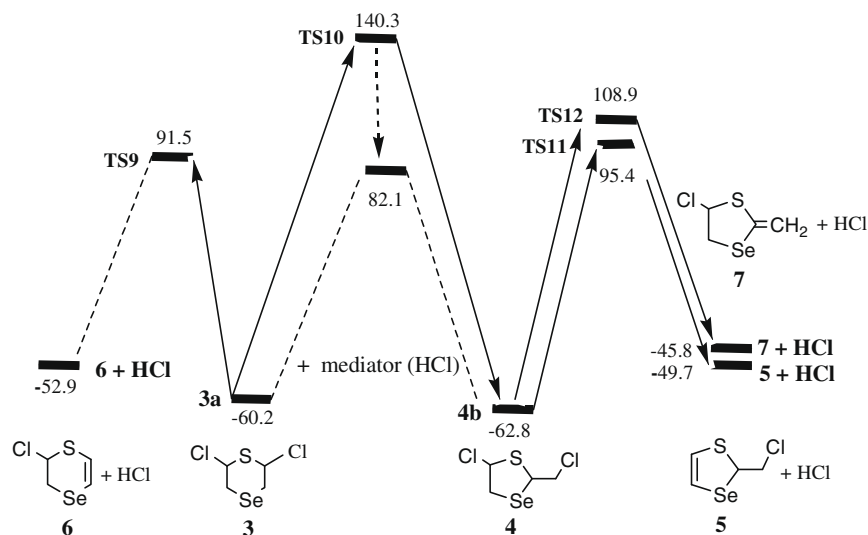
Structure	$-E_{\text{tot}}$	ZPVE	$\Delta E$	$i\omega/\omega_1$	$\mu$
<b>1a</b>	554.25641	0.08492	–	77	1.06
<b>1b</b>	554.25694	0.08584	–	88	0.89
<b>2</b>	3322.02281	0.00219	–	156	1.08
<b>1a</b> + <b>2</b>	3876.28508	0.08836	0.0	21	3.99
<b>1b</b> + <b>2</b>	3876.28489	0.08831	0.4	25	2.07
<b>TS1</b>	3876.24043	0.09164	125.7	i196	7.17
<b>TS2</b>	3876.23325	0.09187	145.1	i273	6.23
<b>TS3</b>	3876.23294	0.09179	145.8	i261	5.14
<b>A</b>	3876.29462	0.09165	–16.4	26	1.93
<b>B</b>	3876.29440	0.09162	–15.9	26	2.59
<b>3a</b>	3876.31439	0.09471	–60.2	77	2.28
<b>3b</b>	3876.30748	0.09477	–41.9	28	2.30
<b>3c</b>	3876.31294	0.09468	–56.5	60	2.12
<b>3d</b>	3876.30773	0.09474	–42.7	23	2.18
<b>4a</b>	3876.31495	0.09471	–61.7	25	2.53
<b>4b</b>	3876.31517	0.09450	–62.8	16	0.77
<b>TS4</b>	3876.30197	0.09512	–26.6	i311	7.56
<b>TS5</b>	3876.27049	0.09219	48.3	i378	2.91
<b>TS6</b>	3876.26458	0.09215	63.7	i243	3.17
<b>TS7</b>	3876.26657	0.09223	74.1	i383	2.96
<b>TS8</b>	3876.22311	0.09307	174.9	i483	4.09
<b>TS9</b>	3876.25708	0.09523	91.5	i417	3.57
<b>TS10</b>	3876.23685	0.09361	140.3	i198	8.20
<b>TS11</b>	3876.25547	0.09511	95.4	i213	1.89
<b>TS12</b>	3876.25038	0.09517	108.9	i215	1.96
<b>5</b>	3415.46349	0.08024	–	65	1.86
<b>6</b>	3415.46082	0.08045	–	48	1.42
<b>7</b>	3415.46176	0.07994	–	48	1.86
<b>5</b> + <b>HCl</b>	3876.30211	0.08643	–49.7	11	1.43
<b>6</b> + <b>HCl</b>	3876.30304	0.08611	–52.9	17	1.62
<b>7</b> + <b>HCl</b>	3876.29631	0.08825	–45.8	9	2.90
<b>8a</b>	3876.30257	0.09457	–29.6	33	0.32
<b>8b</b>	3876.30227	0.09452	–28.9	28	2.27



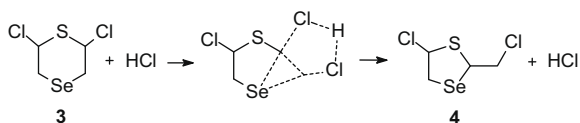
**Fig. 2.** Schematic energy profile for the reaction routes leading to compounds **3**, **4** and **8** according to the B3LYP/6-311+G(3df) data (unit: kJ/mol).



**Fig. 3.** Molecular structures and principal geometric characteristics of compounds **3**, **4** and the transition states **TS4**, **TS10** and according to the B3LYP/6-311+G(3df) data (bond lengths are in Å, valence angles are in grad).

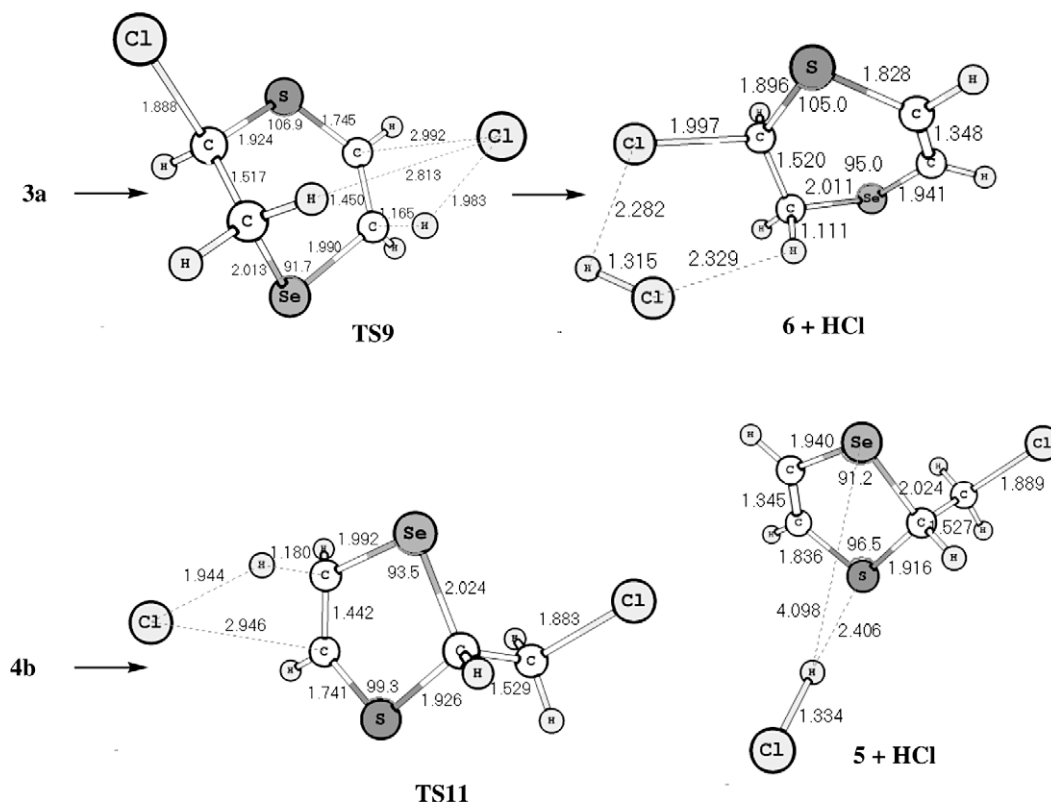


**Fig. 4.** Schematic energy profile for the reaction routes leading to compounds **4–7** according to the B3LYP/6-311+G(3df) data (unit: kJ/mol).



**Scheme 3.**

surface (PES) and preliminary survey of the reaction routes. The latter was used for studies of areas containing most important critical points and localization of gradient routes, which connected the critical points. The use of the basis set LANL2DZ on the first stage of calculations allows accelerating the work on analysis of gradient routes by the higher level basis set 6-311+G(3df).



**Fig. 5.** Molecular structures and principal geometric characteristics of the transition states **TS9** and **TS11** and the products (**6 + HCl**, **5 + HCl**) of the HCl elimination reaction according to the B3LYP/6-311+G(3df) data (bond lengths are in Å, valence angles are in grad).

The complete optimization of the molecular system geometry was performed to the value  $10^{-5}$  a.u./Bohr. The value of the gradient  $10^{-6}$  a.u. was taken for analysis of plane plots of the potential energy surface. Stationary points have been identified by analysis of the Hessian matrices. The search and localization of transition states was carried out by the methods QST2 and QST3 [19]. A method of the intrinsic reaction coordinate (IRC) has been used to fulfill the analysis of vibration frequencies in the saddle point and the correspondence of critical points to the gradient line connecting the points.

In those processes where two molecules comprise reactants or products, the systems were computed as bimolecular complexes, e.g., the stabilization energy of the pre-reaction system **1 + 2** was estimated as a difference of total energies of optimal states of these reactants and of their bimolecular complex.

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