Tetrahedron 68 (2012) 10567–10572

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Stereoselective synthesis of (*E*,*E*)-bis(2-halovinyl) selenides and its derivatives based on selenium halides and acetylene

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ARTICLE INFO

*Article history:*
Received 10 July 2012
Received in revised form 24 September 2012
Accepted 25 September 2012
Available online 29 September 2012

*Keywords:*
Acetylene
Selenium dihalides
Selenium monohalides
Selenium tetrahalides

ABSTRACT

Efficient stereoselective synthesis of (*E*,*E*)-bis(2-chlorovinyl) and (*E*,*E*)-bis(2-bromovinyl) selenides in 95–98% yield based on the reactions of selenium dihalides or monohalides with acetylene has been elaborated. Reactions of selenium tetrahalides with acetylene afford (*E*,*E*)-bis(2-halovinyl) selenides and (*E*)-2-halovinyl 1,2,2-trihaloethyl selenides. Convenient synthesis of (*E*,*E*)-bis(2-halovinyl) selenium dihalides in near quantitative yield has been developed. (*E*,*E*)-Bis(2-halovinyl) selenium dihalides undergo spontaneous rearrangement with the halogen migration from the selenium atom to the double bond. The previously described reactions of selenium monochloride and tetrabromide with acetylene have been reinvestigated.

## 1. Introduction

Selenium was considered a poison for many years, until Schwarz and Foltz identified it as an essential micronutrient for human beings.[1] Since then, there has been growing interest to organoselenium chemistry and compounds with various types of biological activity have been found.[2] Vinylic selenides play a special role in organoselenium chemistry serving as versatile precursors and synthons in organic synthesis.[3] The most general approach to vinylic selenides is the nucleophilic addition of selenium nucleophiles to alkynes.[4] The addition of selenium electrophiles to alkynes may be regarded as another efficient synthetic approach to vinylic selenides on condition that these reactions are regio- and stereoselective.[5]

Selenium tetrahalides are commonly used electrophilic reagents for organoselenium chemistry.[5] However, reactions of these reagents often lead to mixtures of products, e.g., diorganylselenium dihalides, diorganyl selenides and halogenated compounds.[5,6] It has been demonstrated that selenium dichloride and dibromide,[7–11] are more selective and efficient electrophilic reagents for preparation of diorganyl selenides compared with selenium tetrahalides. Although the presence of selenium dichloride and dibromide in the gas phase and in solutions has been demonstrated in the literature, none of the selenium dihalides was isolated as a pure compound.[12] It has been shown that in solution, selenium dichloride underwent disproportionation to $Se_2Cl_2$ and $SeCl_4$, whereas selenium dibromide converted to $Se_2Br_2$ and bromine.[12] Nevertheless, we found that freshly prepared selenium dichloride and dibromide can be used in situ for selective synthesis of organoselenium compounds including heterocycles.[7–11] The reaction of selenium dichloride and dibromide with dimethyl diethynyl silane leading to selenasilafulvene derivatives represented the first synthesis of an organoselenium compound using selenium dihalides.[7]

Recently we studied the reactions of selenium dichloride and dibromide with divinyl sulfide,[8] divinyl selenide[9] and divinyl sulfone[10] leading to novel four-, five- and six-membered selenium heterocycles. Efficient methods for preparation of divinyl sulfide[1a,13] and divinyl selenide[14] were earlier elaborated based on addition of sulfide and selenide anions to acetylene.

## 2. Results and discussion

The reactions with acetylene are important from both practical and theoretical viewpoints. In this work, we report a full account of our studies on reactions of selenium dihalides, tetrahalides and monohalides with acetylene including reinvestigations of previously described reactions of selenium monochloride and tetrabromide with acetylene. Preliminary results of these studies were published as short communications without experimental details.[15] Selenium dichloride was prepared from selenium and sulfuryl chloride in carbon tetrachloride, chloroform or methylene chloride, while selenium dibromide was obtained from selenium and bromine in the same solvents.

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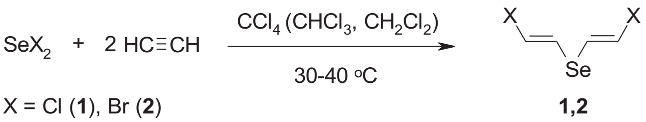
http://dx.doi.org/10.1016/j.tet.2012.09.099

Several examples[16] of reactions of acetylene with selenium monochloride,[16a] tetrachloride[16b] and tetrabromide[16c,d] were previously described in the literature. The addition of selenium tetrachloride to acetylene (diethyl ether at −78 °C) afforded bis(2-chlorovinyl)selenium dichloride in 9% yield.[16b] The spectral characteristics and stereochemistry of this product were not presented. Bis(2-bromovinyl)selenium dibromide was obtained from acetylene and selenium tetrabromide, which was generated from selenium dioxide and hydrobromic acid.[16c] However, the yield and stereochemistry of the product were not reported.

We studied the reactions of selenium dichloride and dibromide with acetylene under the pressure in an autoclave as well as under ambient conditions. The reaction afforded (*E*,*E*)-bis(2-chlorovinyl) selenide (**1**) and (*E*,*E*)-bis(2-bromovinyl) selenide (**2**) in many solvents, such as $CCl_4$, chloroform, methylene chloride, acetonitrile and diethyl ether. However, carbon tetrachloride was the best among studied solvents in respect to chemo- and stereoselectivity. In this solvent, the reaction proceeded in chemo- and stereoselective manner to afford selenides **1** and **2** as the only products (Scheme 1). The highest yields (95–98%) of selenides **1** and **2** were achieved under the pressure of acetylene (an autoclave, 10–12 atm, 30–40 °C).



**Scheme 1.** Reactions of selenium dihalides with acetylene.

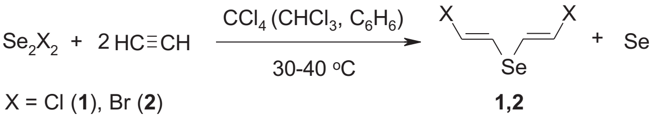
Although the reactions proceeded faster in polar solvent (acetonitrile, diethyl ether), the yields in these solvents are lower than in $CCl_4$ due to the formation of by-products. Along with carbon tetrachloride, chloroform and methylene chloride were found to be suitable solvents for the preparation of selenides **1** and **2** in high yield (80–90%).

First experiments under ambient conditions were carried out by bubbling acetylene into solutions of selenium dichloride or dibromide in carbon tetrachloride, chloroform or methylene chloride. These experiments gave selenides **1** and **2**, which were contaminated with by-products. Apparently, initially formed selenides **1** and **2** underwent further reactions to give mixtures of compounds. However, satisfactory results were obtained when solutions of selenium dichloride or dibromide were added to a chloroform solution saturated with acetylene followed by bubbling acetylene into this solution. These conditions permitted to obtain selenides **1** and **2** in 30–33% yield with good selectivity. Although these yields were lower than in experiments under the pressure of acetylene, the synthetic procedures with the use of acetylene under atmospheric pressure are very valuable since they make selenides **1** and **2** easy accessible.

The structural assignments of compounds **1** and **2** were made with $^1$H, $^{13}$C, $^{77}$Se NMR spectroscopy and GC–MS. (*E*)-Stereochemistry of selenides **1** and **2** was assigned based on the value of the coupling constant $^3J_{HH}$ (13.3 Hz), which corresponds to the trans-position of the protons in 2-halovinyl selenides. It is known that the coupling constant $^3J_{HH}$ for (*Z*)-2-halovinyl selenides is about 6.3 Hz.[15c] Molecular ions of compounds **1** and **2** were observed in the mass spectra.

The reaction of selenium monochloride, $Se_2Cl_2$, with acetylene was described previously.[16a] It is known[17] that arsenic trichloride reacts with acetylene to afford lewisite, $Cl_2AsCH{=}CHCl$. In a similar manner, according to the Ref. 16a, selenium monochloride reacts with acetylene to give (*E*)-2-chlorovinylselenenyl chloride, $ClCH{=}CHSeCl$. Spectral data for proving the structure of this compound are absent in the Ref. 16a; authors presented only analytical data (the contents of selenium and chlorine).

Taking into account high reactivity of organylselenenyl chlorides, we questioned the formation of (*E*)-2-chlorovinylselenenyl chloride as the product in the reaction of selenium monochloride with acetylene,[16a] although this compound can be an intermediate in this reaction. We studied the reaction of selenium monochloride with acetylene under the conditions, which were indicated in the Ref. 16a (benzene, 2–4 °C). We found that the reaction led to selenide **1** (30% yield) rather than to (*E*)-2-chlorovinylselenenyl chloride (Scheme 2). The best yield (95%) of selenide **1** was reached when the reaction was carried out under the pressure of acetylene in an autoclave (10–12 atm, 30–40 °C) using carbon tetrachloride as a solvent. The process was concomitant with the precipitation of elemental selenium.



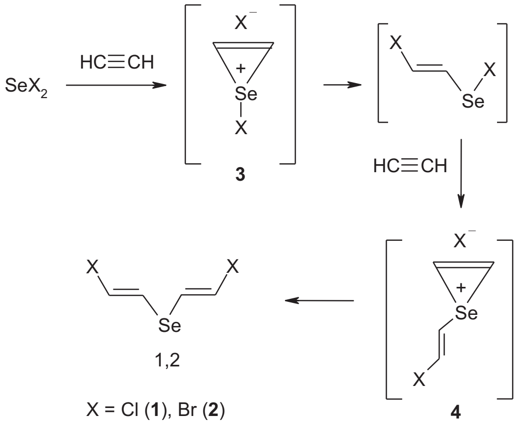
**Scheme 2.** Reactions of selenium monohalides with acetylene.

Thus, we suppose that the statement[16a] concerning the formation of (*E*)-2-chlorovinylselenenyl chloride as the only product of the reaction of selenium monochloride with acetylene is a mistake. To correct these data[16a] are important since they were cited in reviews[5a,b] and this may create a wrong notion about the reactivity of acetylene and selenium halides.

Like selenium monochloride, selenium monobromide reacted with acetylene in carbon tetrachloride or chloroform to afford selenide **2** in high yield (93%). The precipitation of equimolar amount of elemental selenium was observed. The reactions of selenium monochloride and monobromide were carried out in an autoclave under the pressure of acetylene (10–12 atm) at 30–40 °C (Scheme 2). The reactions of selenium monochloride and monobromide with acetylene are also suitable for the preparation of selenides **1** and **2** under atmospheric pressure.

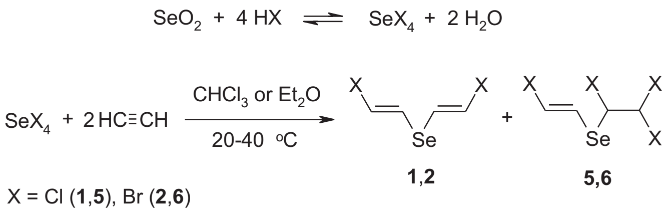
The reaction of selenium dihalides with acetylene represents efficient atom-economic synthesis of selenides **1** and **2**, whereas a half amount of selenium is lost as precipitate in the case of selenium monohalides.

The stereochemistry of the addition of selenium dihalides to acetylene can be explained by assuming the formation of intermediate selenirenium cations **3** and **4** (Scheme 3). The formation of selenirenium species as intermediates in the reactions of organylselenenyl halides with alkynes is well known.[3]



**Scheme 3.** A supposed mechanism of the *anti*-addition of selenium dihalides to acetylene.

We studied the reactions of selenium tetrahalides with acetylene under the pressure in an autoclave as well as under ambient conditions. In both cases the reactions led to selenides **1** and **2** (45–70% yield) and (*E*)-2-halovinyl 1,2,2-trihaloethyl selenides (**5**, **6**) (15–32% yield) as the main products (Scheme 4). Selenides **5** and **6** were isolated by column chromatography on silica gel (eluent: hexane).



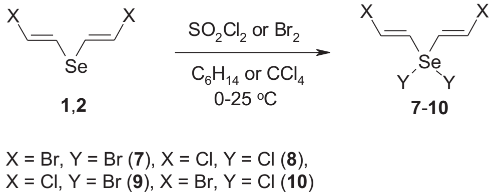
**Scheme 4.** Reactions of selenium tetrahalides with acetylene.

According to the Ref. 16c, the reaction of acetylene with selenium tetrabromide, which was generated in the system $SeO_2$/HBr/$Et_2O$, led to bis(2-bromovinyl)selenium dibromide (**7**) as a mixture of (*E*,*E*)- and (*Z*,*Z*)-isomers (a 1:1.15 ratio) in 54% yield. The authors reported that they failed to divide (*E*,*E*)- and (*Z*,*Z*)-isomers on a column with silica gel ($R_f$ was indicated for the mixture of the isomers, i.e., both isomers had the same $R_f$). Only analytical and NMR $^1$H data were presented for structural assignment. NMR $^{13}$C data were not given.[16c]

We studied the reaction of selenium tetrabromide with acetylene under the conditions, which were indicated in the Ref. 16c (a solution of $SeO_2$ in concentrated HBr was added to a solution of acetylene in ether at −78 °C). Selenides **2** and **6** were obtained in 45% and 32% yields, respectively. The spectral characteristics of compound **6** were generally the same as those of product **7**.[16c] Noteworthy, compounds **6** and **7** have the same composition and analytical data coincide.

Thus, we suppose that the compound, which was described[16c] as a mixture of (*E*,*E*)- and (*Z*,*Z*)-isomers of compound **7** was, in fact, selenide **6**. Indeed, the values of the coupling constant ($^3J_{HH}$) are about 13.3 Hz for (*E*)-2-halovinyl selenides and 6.3 Hz for (*Z*)-2-halovinyl selenides. The value of the coupling constant (3.8 Hz), which was indicated for compound **7**,[16c] is too low to be regarded as $^3J_{HH}$ for olefinic protons. It became clear why both isomers had the same $R_f$ and the authors failed to divide them.

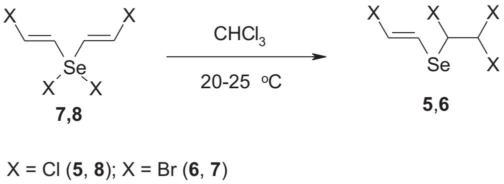
We found that compounds **7**–**10** can be obtained in almost quantitative yield by halogenation of selenides **1** and **2**. When we added a solution of bromine or sulfuryl chloride to a solution of selenides **1** and **2** in hexane or $CCl_4$, the precipitation of compounds **7**–**10** was observed (Scheme 5). Previously unknown compounds **9** and **10** containing different halogen atoms are also accessible by this approach.



**Scheme 5.** Preparation of compounds **7**–**10**.

It is known that divinyl selenide reacted with bromine to give the bromination product of the double bond.[18] In contrast to divinyl selenide, compounds **1** and **2** underwent the addition of bromine to the selenium atom (Scheme 5). Thus, going from divinyl selenide to its dihalo derivatives **1** and **2**, the complete change in the direction of the halogenation reaction is observed. The addition of halogens to the chalcogen atom of unsaturated chalcogenides rather than to the unsaturated C–C bond is typical for unsaturated tellurides.[19]

Upon standing for several days at room temperature in chloroform solutions, the compounds **7** and **8** underwent spontaneous rearrangement to selenides **5** and **6** (Scheme 6). The rearrangement consists of the halogen migration from the selenium atom to the carbon atoms of the double bond. The reaction can be monitored by NMR technique.



**Scheme 6.** The rearrangement of compounds **7** and **8**.

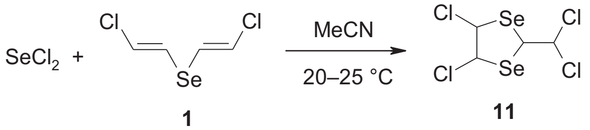
Based on this observation (Scheme 6), we suppose that the reactions of selenium tetrahalides with acetylene (Scheme 4) primarily led to bis(2-halovinyl)selenium dihalides, which underwent rearrangement to selenides **5** and **6**. It is worthy to note that the reaction of tellurium tetrachloride with acetylene proceeded in similar manner as *anti*-addition to afford (*E*,*E*)-bis(2-chlorovinyl) tellurium dichloride.[20]

The compounds **7** and **8** are solids, whereas selenides **5** and **6** are oils. Interestingly, the rearrangement reactions also occurred when the crystalline compounds **7** and **8** were allowed to stand on open air at room temperature. The crystals began 'weeping' when the conversion of solids **7** and **8** into oils **5** and **6** proceeded.

The similar rearrangements with compounds **9** and **10** bearing different halogen atoms were also observed. However, these reactions were concomitant with the formation of by-products and complex mixtures were formed.

Selenides **1** and **2** are novel prospective synthons for organic synthesis and starting materials for the preparation of organoselenium functionalized and heterocyclic compounds. It is known that vinylic selenides are used for stereoselective synthesis of ethenes by cross-coupling reactions.[3] Compounds with the 2-halovinylselanyl moiety are capable to the nucleophilic substitution[21] of halogen atoms, which are activated by the selenium atom via anchimeric assistance.[22]

We found that the addition of selenium dichloride to selenide **1** affords novel five-membered heterocycle, 4,5-dichloro-2-dichloromethyl-1,3-diselenolane (**11**), in 80% yield (Scheme 7).



**Scheme 7.** The heterocyclization of selenide **1**.

This is the first example of heterocyclization of bis(2-halovinyl) selenides, which demonstrates possibilities of application of selenide **1** in synthesis of heterocyclic compounds.

## 3. Conclusion

In conclusion, efficient stereoselective syntheses of compounds **1**,**2** and **5**–**10** based on the reactions of selenium dihalides or monohalides with acetylene have been elaborated. The procedures are based on cheap and available chemicals (acetylene, selenium, sulfuryl chloride, bromine), and the products can find application as starting materials in synthesis of selenium heterocyclic compounds. Thus, the efficient synthesis of novel heterocycle **11** has been developed from selenide **1** and selenium dichloride. The previously described reactions of selenium monochloride and tetrabromide with acetylene have been reinvestigated. The addition of $Se_2Cl_2$ to acetylene led to selenide **1** rather than to 2-chlorovinylselenenyl chloride. Reactions of selenium tetrachloride or tetrabromide with acetylene afforded compounds **1** and **5** or **2** and **6**. Convenient synthesis of compounds **7**–**10** in near quantitative yield from selenides **1** and **2** has been developed. Compounds **7**–**10** were found to undergo spontaneous rearrangement with the migration of the halogens from the selenium atom to the double bond.

## 4. Experimental section

### 4.1. General

The solvents ($CCl_4$, $CHCl_3$, $CH_2Cl_2$, $C_6H_6$, hexane) were dried and purified according the literature procedures.[23] Column chromatographic purifications were performed with Macherey–Nagel silica gel (MN Kieselgel 60, 70–230 mesh). Elemental analysis was performed on a Thermo Finnigan EA 1112 elemental analyzer. Melting points were determined on a Boetius melting point apparatus (PHMK 05 VEB Wagetechnik Rapido, Radebeul, Germany).

The $^1H$, $^{13}C$ and $^{77}Se$ NMR spectra were recorded at 400.13, 100.61 and 76.30 MHz, respectively, on a Bruker DPX-400 spectrometer using HMDS as internal standards ($^1H$ and $^{13}C$) and $Me_2Se$ as an external standard ($^{77}Se$). Mass spectra were recorded with a Shimadzu GC–MS-QP5050A (electronic impact at 70 eV).

Precaution: acetylene can react explosively when combined with oxygen or other oxidizers. Standard safety measures should be taken in the working area. Provide adequate explosion-proof mechanical ventilation to ensure acetylene does not accumulate and reach its lower explosive limit of 2.5%.

### 4.2. Reactions of selenium dihalides with acetylene under a pressure. Typical procedure

*4.2.1. (E,E)-Bis(2-chlorovinyl) selenide (**1**).* A solution of sulfuryl chloride (2.7 g, 20 mmol) in $CCl_4$ (1 mL) was added dropwise to selenium (1.58 g, 20 mmol) with stirring and the mixture was stirred at ambient temperature until the solid disappeared. This usually takes from 30 to 60 min. Then the mixture was stirred for 15 min and the additional amount of $CCl_4$ (140 mL) was added. The obtained solution of selenium dichloride (20 mmol) was heated (30–40 °C) in a 1 L rotating autoclave for 5 h under the pressure of acetylene (10–12 atm). The mixture was filtered and the solvent was evaporated in vacuo to give the crude product (3.96 g, 98% yield) as a dark oil. The product **1** (3.64 g, 90% yield) of high purity (~99%) was obtained as a yellowish oil by purification by column chromatography on silica gel (eluent: hexane); [Found: C, 23.51; H, 2.17; Cl, 35.59; Se, 39.57. $C_4H_4Cl_2Se$ requires: C, 23.79; H, 2.00; Cl, 35.11; Se, 39.10]; $\delta_H$ (400 MHz $CDCl_3$) 6.31 (2H, d, =CHCl, $^3J$ 13.3 Hz), 6.63 (2H, d, =CHSe, $^3J$ 13.3 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 117.31 (=CHCl), 121.56 (=CHSe); $\delta_{Se}$ (76.3 MHz, $CDCl_3$) 336; *m/z* (EI) 202 $[M]^+$ (89), 167 (100), 141 (67), 131 (64), 115 (35), 106 (60), 87 (69), 80 (39), 61 (67), 51 (65%).

*4.2.2. (E,E)-Bis(2-bromovinyl) selenide (**2**).* Selenide **2** was obtained in 95% yield from $SeBr_2$ and acetylene under the similar conditions as above; [Found: C, 16.92; H, 1.54; Br, 54.51; Se, 26.89. $C_4H_4Br_2Se$ requires: C, 16.52; H, 1.39; Br, 54.95; Se, 27.15]; $\delta_H$ (400 MHz $CDCl_3$) 6.43 (2H, d, =CHBr, $^3J$ 13.3 Hz), 6.91 (2H, d, =CHSe, $^3J$ 13.3 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 108.68 (=CHBr), 120.23 (=CHSe); $\delta_{Se}$ (76.3 MHz, $CDCl_3$) 388; *m/z* (EI) 292 $[M]^+$ (32), 211 (23), 185 (20), 132 (100), 105 (56), 84 (33), 49 (69%).

### 4.3. Reactions of selenium dihalides with acetylene under atmospheric pressure. Typical procedure

A solution of acetylene in $CHCl_3$ was obtained by bubbling acetylene into $CHCl_3$ (100 mL) for 2 h at 0–5 °C (cooling with an ice bath). A solution of selenium dichloride was prepared by stirring a mixture of selenium (1.58 g, 20 mmol) and sulfuryl chloride (2.7 g, 20 mmol) in $CHCl_3$ (1 mL) at ambient temperature until the solid disappeared. This usually takes from 30 to 60 min. Then the mixture was stirred for 15 min and the additional amount of $CHCl_3$ (100 mL) was added. The obtained solution of selenium dichloride (20 mmol) in $CHCl_3$ was added dropwise for 1 h to the solution of $CHCl_3$ saturated with acetylene at 0–5 °C (cooling with an ice bath). During the addition, bubbling of acetylene was continued. After addition, acetylene was bubbled into the reaction mixture for 3 h at 0–5 °C and for 2 h at room temperature. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (eluent: hexane) to give selenide **1** (1.33 g, 33% yield) as a yellowish oil. Selenide **2** was obtained from $SeBr_2$ and acetylene under the similar conditions in 30% yield.

### 4.4. Reactions of selenium monohalides with acetylene under a pressure. Typical procedure

A solution of bromine (1.6 g, 10 mmol) in $CHCl_3$ (50 mL) was added dropwise to a stirred mixture of selenium (1.58 g, 20 mmol) and $CHCl_3$ (50 mL) and the resulted mixture was stirred at ambient temperature until the solid disappeared. This usually takes from 1 to 2 h. Then the mixture was stirred for 15 min. The obtained solution of selenium monobromide (10 mmol) in $CHCl_3$ (100 mL) was heated (30–40 °C) in a 1 L rotating autoclave for 5 h under the pressure of acetylene (10–12 atm). Precipitated selenium (0.79 g) was filtered off. The solvent was evaporated in vacuo to give the crude product (2.81 g, 97% yield) as a dark oil. The product **2** (2.70 g, 93% yield) of high purity (~99%) was obtained as a yellow oil by purification by column chromatography on silica gel (eluent: hexane). Selenide **1** was obtained from $Se_2Cl_2$ and acetylene under the similar conditions in 95% yield.

### 4.5. Reactions of selenium monohalides with acetylene under atmospheric pressure. Typical procedure

A solution of acetylene in $CHCl_3$ was obtained by bubbling acetylene into $CHCl_3$ (100 mL) for 2 h at 0–5 °C (cooling with an ice bath). A solution of sulfuryl chloride (1.35 g, 10 mmol) in $CCl_4$ (1 mL) was added dropwise to selenium (1.58 g, 20 mmol) with stirring and the mixture was stirred at ambient temperature until the solid disappeared. This usually takes from 1 to 2 h. Then the mixture was stirred for 15 min and the additional amount of $CHCl_3$ (100 mL) was added. The obtained solution of selenium monochloride (10 mmol) in $CHCl_3$ was added dropwise for 1 h to the solution of $CHCl_3$ saturated with acetylene at 0–5 °C (cooling with an ice bath). During the addition, bubbling of acetylene was continued. After addition, acetylene was bubbled into the reaction mixture for 3 h at 0–5 °C and for 3 h at room temperature. Precipitated selenium was filtered off. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (eluent: hexane) to give selenide **1** (0.69 g, 34% yield) as a yellowish oil. Selenide **2** was obtained from $Se_2Br_2$ and acetylene under similar conditions in 32% yield.

### 4.6. Reactions of selenium tetrahalides with acetylene. Typical procedure

*4.6.1. (E)-2-Chlorovinyl 1,2,2-trichloroethyl selenide (**5**).* Selenide **5** as a yellow oil was obtained in 25% yield along with selenide **1** (71% yield) from $SeCl_4$ and acetylene under the same conditions as those for selenide **6**; [Found: C, 17.23; H, 1.65; Cl, 51.47; Se, 29.41. $C_4H_4Cl_4Se$ requires: C, 17.61; H, 1.48; Cl, 51.97; Se, 28.94]; $\delta_H$ (400 MHz $CDCl_3$) 5.32 (1H, d, $^3J$ 3.4 Hz), 6.03 (1H, d, $^3J$ 3.4 Hz), 6.67 (1H, d, $^3J$ 13.3 Hz), 6.88 (1H, d, $^3J$ 13.3 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 62.96 (CHCl), 75.29 ($CHCl_2$), 121.34 (=CHCl), 127.76 (=CHSe).

*4.6.2. (E)-2-Bromovinyl 1,2,2-tribromoethyl selenide (**6**).* A solution of bromine (3.2 g, 20 mmol) in $CHCl_3$ (50 mL) was added dropwise to a stirred mixture of selenium (0.79 g, 10 mmol) and $CHCl_3$ (50 mL) and the resulted mixture was stirred at ambient temperature until the solid disappeared. This usually takes from 40 to 60 min. Then the mixture was stirred for 15 min. The obtained solution of selenium tetrabromide (0.79 g, 10 mmol) in $CHCl_3$ was heated (30–40 °C) in a 1 L rotating autoclave for 5 h under the pressure of acetylene (10–12 atm). After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (eluent: hexane) to give selenide **2** (1.92 g, 66% yield) and the product **6** (1.44 g, 32% yield) as a dark yellow oil; [Found: C, 10.24; H, 0.94; Br, 71.31; Se, 17.28. $C_4H_4Br_4Se$ requires: C, 10.66; H, 0.89; Br, 70.92; Se, 17.52]; $\delta_H$ (400 MHz $CDCl_3$) 5.50 (1H, d, $^3J$ 3 Hz), 6.06 (1H, d, $^3J$ 3 Hz), 6.82 (1H, d, $^3J$ 14 Hz), 7.11 (1H, d, $^3J$ 14 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 41.78 (CHBr), 51.42 ($CHBr_2$), 116.43 (=CHBr), 125.23 (=CHSe).

### 4.7. (*E*,*E*)-Bis(2-halovinyl)selenium dihalides (7–10)

*4.7.1. (E,E)-Bis(2-bromovinyl)selenium dibromide (**7**).* A solution of bromine (1.6 g, 10 mmol) in hexane (10 mL) was added dropwise to a stirred solution of selenide **2** (2.91 g, 10 mmol) in hexane (10 mL) at 0–2 °C (an ice bath) for 10 min. The reaction mixture was stirred for 30 min at 0–2 °C and for 1 h at room temperature. The precipitate was filtered off, washed with cold hexane and dried in vacuo to give the product **7** as an orange-yellow powder (4.33 g, 96% yield); [Found: C, 10.28; H, 0.84; Br, 71.22; Se, 17.27. $C_4H_4Br_4Se$ requires: C, 10.66; H, 0.89; Br, 70.92; Se, 17.52]; $\delta_H$ (400 MHz $CDCl_3$) 6.73 (2H, d, =CHBr, $^3J$ 13.6 Hz), 7.32 (2H, d, =CHSe, $^3J$ 13.6 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 106.61 (=CHBr), 121.58 (=CHSe).

*4.7.2. (E,E)-Bis(2-chlorovinyl)selenium dichloride (**8**).* Compound **8** was obtained in 98% yield from selenide **1** and $SO_2Cl_2$ as a white powder under the same conditions as those for selenide **7**; [Found: C, 17.35; H, 1.61; Cl, 52.31; Se, 28.58. $C_4H_4Cl_4Se$ requires: C, 17.61; H, 1.48; Cl, 51.97; Se, 28.94]; $\delta_H$ (400 MHz $CDCl_3$) 6.62 (2H, d, =CHCl, $^3J$ 13.4 Hz), 7.04 (2H, d, =CHSe, $^3J$ 13.4 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 119.35, 119.79.

*4.7.3. (E,E)-Bis(2-chlorovinyl)selenium dibromide (**9**).* Compound **9** was obtained in 97% yield from selenide **1** and bromine as an orange-yellow powder under the same conditions as those for selenide **7**; [Found: C, 12.89; H, 0.97; Cl, 19.21; Br, 44.62; Se, 22.25. $C_4H_4Cl_2Br_2Se$ requires: C, 13.28; H, 1.11; Cl, 19.60; Br, 44.18; Se, 21.83]; $\delta_H$ (400 MHz $CDCl_3$) 6.56 (2H, d, =CHCl, $^3J$ 13.4 Hz), 7.00 (2H, d, =CHSe, $^3J$ 13.4 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 118.77, 119.34.

*4.7.4. (E,E)-Bis(2-bromovinyl)selenium dichloride (**10**).* Compound **10** was obtained in 98% yield from selenide **2** and $SO_2Cl_2$ as a white powder under the same conditions as those for selenide **7**; [Found: C, 13.41; H, 1.03; Cl, 19.87; Br, 43.98; Se, 22.17. $C_4H_4Cl_2Br_2Se$ requires: C, 13.28; H, 1.11; Cl, 19.60; Br, 44.18; Se, 21.83]; $\delta_H$ (400 MHz $CDCl_3$) 6.65 (2H, d, =CHBr, $^3J$ 13.7 Hz), 7.23 (2H, d, =CHSe, $^3J$ 13.7 Hz); $\delta_C$ (100.6 MHz, $CDCl_3$) 107.12 (=CHBr), 121.63 (=CHSe).

### 4.8. 2-Dichloromethyl-4,5-dichloro-1,3-diselenolane (11)

A solution of selenium dichloride was prepared by stirring a mixture of selenium (0.79 g, 10 mmol) and $SO_2Cl_2$ (1.35 g, 10 mmol) in acetonitrile (10 mL) at room temperature until the solid disappeared. This usually takes from 60 to 80 min. The obtained solution of selenium dichloride (10 mmol) was added dropwise to a solution of selenide **1** (2.02 g, 10 mmol) in acetonitrile (30 mL) and the mixture was stirred at room temperature for 20 h. The solvent was evaporated in vacuo. The residue was subjected to column chromatography on silica gel (eluent: hexane/ether 5:1) to give the product **11** (2.81 g, 80% yield) as a brown oil; [Found: C, 13.38; H, 1.28; Cl, 40.69; Se, 44.48. $C_4H_4Cl_4Se_2$ requires: C, 13.66; H, 1.15; Cl, 40.31; Se, 44.89]; $\delta_H$ (400 MHz $CDCl_3$) 6.13 (2H, s, 2SeCHCl); 5.98 (1H, d, *J* 8.1 Hz, $CHCl_2$); 5.63 (1H, d, *J* 8.1 Hz, SeCHSe); $\delta_C$ (100.6 MHz, $CDCl_3$) 75.51 ($CHCl_2$); 66.83 (SeCHCl); 46.82 (SeCHSe); $\delta_{Se}$ (76.3 MHz, $CDCl_3$) 589; *m*/*z* (EI) 352 $[M]^+$ (33), 269 (66), 256 (12), 221 (16), 195 (10), 173 (15), 160 (82), 141 (41), 115 (25), 106 (37), 93 (27), 80 (36), 61 (100), 36 (34%).

## Acknowledgements

Financial support of the Russian Academy of Sciences (Programs 5.1.8 and 8.16) and the Russian Foundation for Basic Research (Grants No. 10-03-00543, 11-03-00810 and 12-03-01098) is gratefully acknowledged.

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