Tetrahedron Letters 51 (2010) 5258–5261

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Reactions of selenium dichloride and dibromide with divinyl sulfone: synthesis of novel four- and five-membered selenium heterocycles

Vladimir A. Potapov *, Evgeny O. Kurkutov, Maxim V. Musalov, Svetlana V. Amosova

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Division of the Russian Academy of Sciences, 1 Favorsky Str., Irkutsk 664033, Russian Federation

ARTICLE INFO

Article history:
Received 11 May 2010
Revised 12 July 2010
Accepted 23 July 2010
Available online 30 July 2010

ABSTRACT

The reactions of selenium dichloride and dibromide with divinyl sulfone leading to novel selenium heterocycles, 2,4-bis(halomethyl)-1,3-thiaselenetane-1,1-diones and 5-halo-2-halomethyl-1,3-thiaselenolane-1,1-diones, have been studied. Under the action of silica gel or pyridine, 5-halo-2-halomethyl-1,3-thiaselenolane-1,1-diones undergo facile regioselective dehydrohalogenation into 5-halo-2-methylene-1,3-thiaselenolane-1,1-diones.

Vinylic chalcogenides[1] serve as versatile precursors and synthons for organic synthesis and as potential starting materials for the preparation of functionalized organochalcogen compounds.[2] Promising reagents are divinyl chalcogenides,[3–5] bearing two vinylchalcogeno groups which are able to form heterocyclic compounds[6] by reactions with bifunctional reagents. Earlier, we elaborated efficient methods for the preparation of divinyl sulfide,[3] divinyl selenide,[3b,4] and their derivatives.[5] Divinyl sulfide is highly reactive in electrophilic and radical additions.[3] Oxidation of divinyl sulfide leads to divinyl sulfone, the properties of which differ essentially from those of divinyl sulfide. The sulfonyl group exhibits a pronounced electron-withdrawing effect and vinyl sulfones[2a] have revealed high reactivity with respect to nucleophilic reagents. The addition of bifunctional nucleophiles to divinyl sulfone afforded novel heterocycles.[6d] However, little is known about the synthesis of heterocyclic compounds by electrophilic addition to divinyl sulfone. This is not surprising since the double bonds of vinylic sulfones are deactivated with respect to electrophilic reagents.

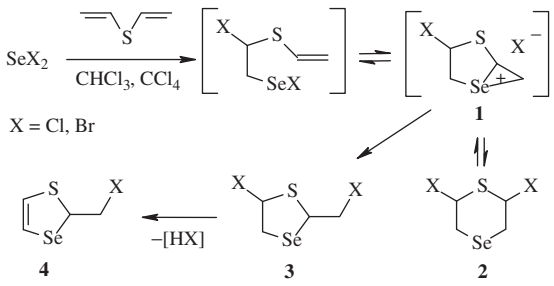
Previously, we studied the reactions of novel electrophilic reagents, selenium dichloride and dibromide, with various unsaturated compounds.[7–10] The reactions of selenium dichloride and dibromide with dimethyl diethynyl silane leading to 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes[7] were the first synthesis of organoselenium compounds using selenium dihalides. The addition of selenium dichloride and dibromide to divinyl sulfide[8] and divinyl selenide[9] afforded novel selenium heterocycles.

It is known that selenium dichloride and dibromide exist in equilibrium with other selenium species.[11] The equilibrium of selenium dichloride includes Se_2Cl_2 and $SeCl_4$, whereas selenium dibromide is in equilibrium with Se_2Br_2 and Br_2.[11] Nevertheless, we found that freshly prepared selenium dichloride and dibromide are practically pure reagents, which can take part in reactions[7–10] with various substrates to give adducts of selenium dihalides rather than products of disproportionation.

According to the literature,[12] addition of selenenyl halides to terminal alkenes under kinetically controlled conditions gives anti-Markovnikov products (steric effects determine the regioselectivity), whereas under thermodynamic control the reactions lead to Markovnikov products (polar effects determine the regioselectivity). However, these trends may differ in the case of the formation of heterocyclic compounds in the addition reactions of selenium dihalides; for example, heterocycles which represent anti-Markovnikov products may be energetically preferable compared to the isomeric Markovnikov heterocyclic products.

Recently, we studied the reactions of selenium dichloride and dibromide with divinyl sulfide affording novel selenium heterocycles.[8] The reaction in carbon tetrachloride gave the Markovnikov products, 2,6-dihalo-1,4-thiaselenanes (**2**), in high yield (Scheme 1).

At room temperature in chloroform, thiaselenanes **2** underwent rearrangement to 5-halo-2-halomethyl-1,3-thiaselenolanes (**3**).[8] It was assumed that the rearrangement was accelerated by anchimeric assistance involving the selenium atom, which increased sufficiently the ability of the halogen atoms to act as leaving



Scheme 1.

* Corresponding author. Tel.: +7 3952 424954; fax: +7 3952 419346.
E-mail address: v_a_potapov@irioch.irk.ru (V.A. Potapov).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.07.133

groups. Thiaselenanes **2** were regarded as kinetic products, which were converted into the more stable thermodynamic products, thiaselenolanes **3**. Selenirane species **1** were assumed to be the intermediates of the rearrangement (Scheme 1).[8] With pyridine, thiaselenolanes **3** underwent dehydrohalogenation to form thiaselenoles **4**. The same reaction was observed during chromatography of thiaselenolanes **3** on silica gel. The dehydrohalogenation reaction occurred selectively and led to formation of the endocyclic double bond (Scheme 1).[8]

In this Letter, we report our studies on the reactions of selenium dichloride and dibromide with divinyl sulfone. Selenium dichloride was prepared from selenium and sulfuryl chloride in chloroform, carbon tetrachloride, or acetonitrile, while selenium dibromide was obtained from selenium and bromine in the same solvents. The selenium dihalides were used in reactions immediately after their preparation.

We found that the reaction of selenium dichloride with divinyl sulfone at room temperature in carbon tetrachloride afforded the novel heterocycles, 2,4-bis(chloromethyl)-1,3-thiaselenetane-1,1-dione[13] (**5**) in 85% yield and 5-chloro-2-chloromethyl-1,3-thiaselenolane-1,1-dione[14] (**6**) in 15% yield (yields were calculated based on consumed divinyl sulfone, the conversion of divinyl sulfone was 58%) (Scheme 2).

Compound **5** consisted of two diastereomers (cis- and trans-isomers) in a 5:3 ratio (NMR data). The major diastereomer of compound **5** was isolated by column chromatography and its crystals were studied by X-ray analysis.[15] It was found that both chloromethyl groups were disposed on one side of the four-membered ring and therefore the major product was the cis-diastereomer (Fig. 1). The diastereomeric ratio of heterocycle **6** was found to be 3:1.

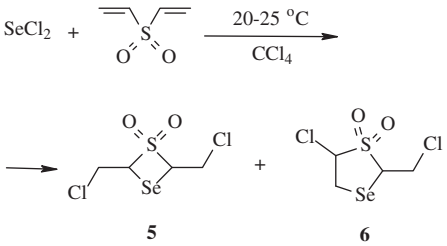
Carrying out the reaction in chloroform increased the conversion of divinyl sulfone up to 74%. The yield of heterocycle **6** increased to 32% (the yield of compound **5** was 68%). Since chloroform is a more polar solvent than carbon tetrachloride, we supposed that increasing the polarity of the solvent would lead to an improved yield of heterocycle **6**. Indeed, carrying out the reaction in acetonitrile increased the yield of heterocycle **6** up to 45% as well as the conversion of divinyl sulfone (82%).[16]

The reaction of selenium dibromide with divinyl sulfone at room temperature in chloroform proceeded with high regioselectivity affording 2,4-bis(bromomethyl)-1,3-thiaselenetane-1,1-dione[17] (**7**) in near quantitative yield (the conversion of divinyl sulfone was 28%) (Scheme 3). Compound **7** consisted of two diastereomers in a 7:1 ratio.

When the reaction was carried out in acetonitrile, along with compound **7** (78% yield, 20:1 diastereomeric ratio), the five-membered heterocycle 5-bromo-2-bromomethyl-1,3-thiaselenolane-1,1-dione[18] (**8**) was formed in 22% yield (9:1 diastereomeric ratio) (Scheme 4).[19] The conversion of divinyl sulfone increased to 79%.

The high stereoselectivity of this reaction in acetonitrile is noteworthy: the amounts of major diastereomers of heterocycles **7** and **8** considerably overweighed those of the minor diastereomers.

Thus, whereas the addition of the electrophile 'Se^{2+}' to the vinylthio group[20] occurred at the β-carbon atom, the reaction of



5 6

Scheme 2.

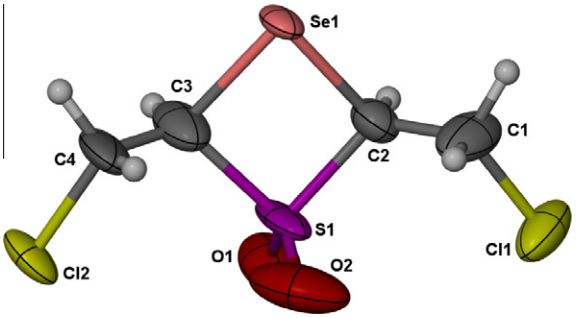
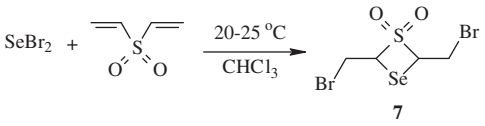
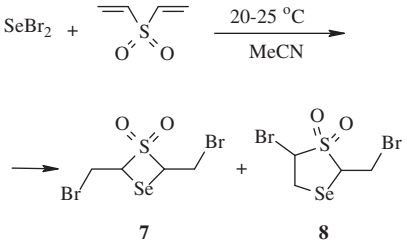


Fig. 1. ORTEP drawing of the *cis*-diastereomer of thiaselenetane **5**.



7

Scheme 3.

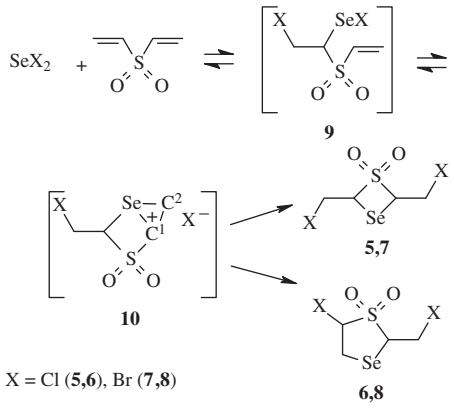


7 8

Scheme 4.

selenium dihalides with divinyl sulfone proceeded preferentially at the α-carbon atom giving mainly anti-Markovnikov products. On enhancing the solvent polarity, the proportion of five-membered heterocycles **6** and **8** increased. Earlier, we observed that the analogs of heterocycles **6** and **8**, thiaselenanes **2**, underwent rearrangement to thiaselenolanes **3** in polar solvents (Scheme 1).[8] We suggest that the formation of five-membered heterocycles **6** and **8** could be the result of isomerization of heterocycles **5** and **7** analogous to the conversion of thiaselenanes **2** into thiaselenolanes **3**. However, we were not able to obtain heterocycles **6** and **8** from compounds **5** and **7** in acetonitrile or chloroform. We suppose that the formation of heterocycles **6** and **8** was not the result of isomerization, but probably occurred from the same intermediate **10** as for heterocycles **5** and **7** (Scheme 5). In the first stage, addition proceeds at the α-carbon atom of the vinylsulfonyl group leading to intermediate **9**, the anti-Markovnikov product. In the second stage, the formation of four-membered heterocycles **5** and **7** or thiaselenolanes **6** and **8** is determined by the attack of the halide anions on intermediate **10**. Attack of the halide anions at the terminal carbon atom (C-2) affords four-membered heterocycles **5** and **7**, whereas attack at C-1 leads to five-membered **6** or **8**. We assume that there is some strain in the four-membered heterocycles **5** and **7** and the formation of five-membered heterocycles **6** and **8** is preferable from a thermodynamic viewpoint. On the other hand, attack of halide anions at the terminal carbon atom (C-2) of intermediate **10** is sterically favorable.

It is worth noting the higher yield of five-membered chloro-containing heterocycle **6** compared with bromo analog **8**. Scheme 5 explains this trend: the larger size of the bromine atom makes the attack by the bromine anion at C-1 less probable than the attack at C-2. Therefore, in the case of bromine derivatives, the

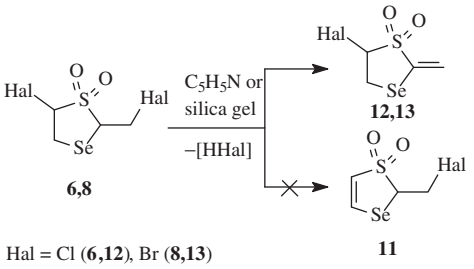


Scheme 5.

bromide anion attacks predominantly at C-2 to give mainly the four-membered heterocycle **7**. We assume that intermediate **10**, bearing condensed four- and three-membered rings, is less stable compared with species **2** (Scheme 1), and the formation of thiaselenetanes **5** and **7** from intermediate **10** is an irreversible process (on the contrary, the formation of compounds **2** from species **1** is a reversible process in the reaction of selenium dichloride or dibromide with divinyl sulfide).

Compounds **5**–**8** were purified using column chromatography on silica gel. During chromatography, along with compounds **5**–**8**, five-membered unsaturated heterocycles were isolated. The formation of these unsaturated heterocycles was the result of dehydrohalogenation of compounds **5** and **7**. Previously, we observed dehydrohalogenation of thiaselenolanes **3** during chromatography on silica gel with the formation of thiaselenoles **4** (Scheme 1). Based on this analogy, we anticipated that the isolated compounds could be 2-halomethyl-1,3-thiaselenole-1,1-dioxides **11**. However, NMR analysis revealed that the isolated compounds were isomeric 5-halo-2-methylene-1,3-thiaselenolane-1,1-diones **12** and **13** (Scheme 6).[21,22]

Heterocycles **12** and **13** were also obtained in high yields by the action of pyridine on compounds **6** and **8**. It is noteworthy that the elimination reaction affording compounds **12** and **13** was highly regioselective: dehydrohalogenation led to the formation of only the product containing an exocyclic double bond. In the case of compounds **3**, the dehydrohalogenation was also regioselective but led to the formation of only the endocyclic double bond-containing product. This is an interesting example of a drastic change in the pathway of dehydrohalogenation reactions. It is important to mention that the sulfur atom is able to stabilize the adjacent positive charge in contrast to the sulfonic group. In the case of heterocycles **6** and **8**, the electron-withdrawing sulfonyl group increased the acidity of the α-CH protons, and hence the dehydrohalogenation leading to the exocyclic double bond became more preferable compared with the elimination reaction affording compound **4**.



Scheme 6.

The structural assignments of heterocycles **5**–**8** were made using ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. X-ray studies showed that the major diastereomer of thiaselenetane **5** exhibited cis-stereochemistry. Taking into account similarities in the NMR data of four-membered chloro- and bromo-containing heterocycles **5** and **7**, we assume that the major diastereomer of compound **7** was also the cis-isomer. The NMR spectra of five-membered heterocycles **6** and **8** showed that both the CH_2- and CH-groups revealed direct coupling of the carbon atoms with the selenium atom indicating that the selenium atom was bonded to both CH_2- and CH-groups.

It is worth emphasizing that data on thiaselenetanes are very scarce in the literature.[23–25] Whereas many derivatives of dithietanes[26] and diselenetanes[27] have been described, thiaselenetanes represent a relatively novel class of compounds. Previously, we reported the synthesis of thiaselenetane **7** from selenium dibromide and divinyl sulfone without experimental details.[23] Compound **7** was also obtained from divinyl sulfone and selenium tetrabromide. However, the reported spectral data did not permit an unequivocal assignment (^{1}H NMR, IR spectroscopy, and elemental analysis were used to prove the structure) and the diastereomeric composition was not determined.[24] Recently, the syntheses of 1,3-thiaselenetane-1-one and 1,3-thiaselenetane-1,1-dione were described.[25]

In conclusion, syntheses of novel selenium heterocycles **5**–**8**, **12** and **13** based on the reactions of selenium dichloride and dibromide with divinyl sulfone have been developed. A drastic change in the dehydrohalogenation reaction pathway was found. We hope that further studies on the reactions of thiaselenetanes **5** and **7** (dehydrohalogenation, nucleophilic substitution, etc.) will lead to an increase in the number of representatives of this novel class of compounds.

Acknowledgment

Financial support from the Russian Foundation for Basic Research (Grants No. 10-03-00543 and 10-03-92666) is gratefully acknowledged.

References and notes

1. (a) Perin, G.; Lenardão, E. J.; Jacob, R. G.; Panatieri, R. B. *Chem. Rev.* **2009**, *109*, 1277; (b) Silveira, C. C.; Santos, P. C. S.; Mendes, S. R.; Braga, A. L. *J. Organomet. Chem.* **2008**, *693*, 3787; (c) Potapov, V. A.; Amosova, S. V. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *79*, 277; (d) Potapov, V. A.; Amosova, S. V.; Shestakova, V. Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *136–138*, 205; (e) Potapov, V. A.; Amosova, S. V.; Petrov, B. V. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *136–138*, 587; (f) Potapov, V. A.; Petrov, P. A.; Amosova, S. V. *Russ. Chem. Bull. Int. Ed.* **1993**, *42*, 210; (g) Potapov, V. A.; Amosova, S. V.; Denisov, A. L. *Zh. Org. Khim.* **1989**, *25*, 1112; (h) Potapov, V. A.; Amosova, S. V.; Dremin, O. L.; Keiko, V. V. *Zh. Org. Khim.* **1990**, *26*, 2224.
2. (a) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951; (b) Stein, A. L.; Alves, D.; da Rocha, J. T.; Nogueira, C. W.; Zeni, G. *Org. Lett.* **2008**, *10*, 4983; (c) Potapov, V. A.; Amosova, S. V. *Russ. J. Org. Chem.* **1996**, *32*, 1142; (d) Martynov, A. V.; Potapov, V. A.; Amosova, S. V.; Makhaeva, N. A.; Beletskaya, I. P.; Hevesi, L. *J. Organomet. Chem.* **2003**, *674*, 101; (e) Potapov, V. A.; Amosova, S. V.; Dudareva, G. N.; Shestakova, V. Y.; Zhnikin, A. R.; Petrov, B. V.; Aksamentova, T. N. *Rec. Trav. Chim.* **1996**, *115*, 443; (f) Potapov, V. A.; Amosova, S. V.; Beletskaya, I. P.; Starkova, A. A.; Hevesi, L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *136–138*, 591; (g) Martynov, A. V.; Potapov, V. A.; Amosova, S. V.; Albanov, A. I. *Russ. J. Gen. Chem.* **2003**, *73*, 1398.
3. (a) Trofimov, B. A.; Amosova, S. V. *Sulfur Rep.* **1984**, *3*, 323; (b) Trofimov, B. A.; Amosova, S. V.; Gusarova, N. K.; Potapov, V. A.; Tatarinova, A. A. *Sulfur Lett.* **1983**, *1*, 151; (c) Trofimov, B. A.; Potapov, V. A.; Gusarova, N. K.; Amosova, S. V.; Sinegovskaya, L. M.; Vitkovsky, V. Y. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1983**, *35*, 205; (d) Potapov, V. A.; Gusarova, N. K.; Amosova, S. V.; Turchaninova, L. P.; Sinegovskaya, L. M.; Krivdin, L. B.; Trofimov, B. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 639.
4. (a) Potapov, V. A.; Gusarova, N. K.; Amosova, S. V.; Kashik, A. S.; Trofimov, B. A. *Zh. Org. Khim.* **1986**, *22*, 276; (b) Amosova, S. V.; Potapov, V. A.; Gusarova, N. K.; Trofimov, B. A. *Zh. Org. Khim.* **1989**, *25*, 2283; (c) Gusarova, N. K.; Potapov, V. A.; Amosova, S. V.; Kashik, A. S.; Trofimov, B. A. *Zh. Org. Khim.* **1983**, *19*, 2477; (d) Martynov, A. V.; Ivanov, A. V.; Amosova, S. V.; Potapov, V. A. *Russ. J. Org. Chem.* **2006**, *42*, 1083.
5. (a) Amosova, S. V.; Gostevskaya, V. I.; Gavrilova, G. M.; Afonin, A. V.; Potapov, V. A. *Zh. Org. Khim.* **1990**, *26*, 1131; (b) Amosova, S. V.; Gostevskaya, V. I.;

Gavrilova, G. M.; Afonin, A. V.; Romanenko, L. S.; Potapov, V. A. *Zh. Org. Khim.* **1991**, *27*, 1618; (c) Amosova, S. V.; Gostevskaya, V. I.; Gavrilova, G. M.; Afonin, A. V.; Romanenko, L. S.; Potapov, V. A. *Zh. Org. Khim.* **1992**, *28*, 306; (d) Amosova, S. V.; Gostevskaya, V. I.; Gavrilova, G. M.; Afonin, A. V.; Potapov, V. A. *Zh. Org. Khim.* **1990**, *26*, 2056; (e) Amosova, S. V.; Gostevskaya, V. I.; Gavrilova, G. M.; Potapov, V. A.; Afonin, A. V.; Modonov, V. B. *Zh. Org. Khim.* **1989**, *25*, 1631; (f) Potapov, V. A.; Amosova, S. V.; Rakhmatulina, T. N.; Antonova, E. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1988**, *37*, 823.

6. (a) Amosova, S. V.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Russ. Chem. Bull. Int. Ed.* **2007**, *56*, 2513; (b) Amosova, S. V.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Russ. J. Gen. Chem.* **2008**, *78*, 503; (c) Amosova, S. V.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Russ. J. Org. Chem.* **2007**, *43*, 1087; (d) Potapov, V. A.; Amosova, S. V.; Doron'kina, I. V.; Korsun, O. V. *J. Organomet. Chem.* **2003**, *674*, 104.
7. (a) Potapov, V. A.; Amosova, S. V.; Belozerova, O. V.; Albanov, A. I.; Yarosh, O. G.; Voronkov, M. G. *Chem. Heterocycl. Compd.* **2003**, *39*, 549; (b) Potapov, V. A.; Amosova, S. V. *Russ. J. Org. Chem.* **2003**, *39*, 1373.
8. (a) Amosova, S. V.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Tetrahedron Lett.* **2009**, *50*, 306; (b) Amosova, S. V.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *J. Organomet. Chem.* **2009**, *694*, 3369; (c) Potapov, V. A.; Shagun, V. A.; Penzik, M. V.; Amosova, S. V. *J. Organomet. Chem.* **2010**, *695*, 1603.
9. (a) Potapov, V. A.; Amosova, S. V.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I. *Tetrahedron Lett.* **2010**, *51*, 89; (b) Potapov, V. A.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I.; Amosova, S. V. *Russ. J. Gen. Chem.* **2009**, *79*, 1225; (c) Potapov, V. A.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I.; Amosova, S. V. *Russ. J. Org. Chem.* **2008**, *44*, 1556; (d) Potapov, V. A.; Volkova, K. A.; Penzik, M. V.; Albanov, A. I.; Amosova, S. V. *Russ. J. Gen. Chem.* **2008**, *78*, 1990.
10. (a) Amosova, S. V.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Russ. J. Gen. Chem.* **2009**, *79*, 161; (b) Amosova, S. V.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Russ. J. Org. Chem.* **2009**, *45*, 1271; (c) Potapov, V. A.; Khuriganova, O. I.; Amosova, S. V. *Russ. J. Org. Chem.* **2009**, *45*, 1569; (d) Potapov, V. A.; Volkova, K. A.; Amosova, S. V. *Russ. J. Gen. Chem.* **2009**, *79*, 1758; (e) Amosova, S. V.; Penzik, M. V.; Albanov, A. I.; Potapov, V. A. *Russ. Chem. Bull. Int. Ed.* **2008**, 1323; (f) Amosova, S. V.; Abramova, E. V.; Potapov, V. A. *Russ. J. Gen. Chem.* **2008**, *78*, 1463; (g) Klyba, L. V.; Amosova, S. V.; Belozerova, O. V.; Potapov, V. A.; Zhanchipova, E. P.; Yarosh, O. G.; Voronkov, M. G. *Russ. Chem. Bull. Int. Ed.* **2005**, *54*, 650; (h) Potapov, V. A.; Amosova, S. V.; Belozerova, O. V.; Albanov, A. I.; Yarosh, O. G.; Voronkov, M. G. *Chem. Heterocycl. Compd.* **2003**, *39*, 551.
11. (a) Nagy-Felsobuki, E.; Peel, J. B. *Chem. Phys.* **1980**, *45*, 189; (b) Milne, J. *Polyhedron* **1985**, *4*, 65; (c) Lamoureux, M.; Milne, J. *Polyhedron* **1990**, *9*, 589; (d) Steudel, R.; Jensen, D.; Baumgart, F. *Polyhedron* **1990**, *9*, 1199.
12. (a) Back, T. G.. In *Organoselenium chemistry*; Liotta, D., Ed.; John Wiley & Sons: New York, 1987; Vol. 1, (b) Raucher, S. *J. Org. Chem.* **1977**, *42*, 2950.
13. Thiaselenetane **5**, colorless crystals, mp 76–77 °C (dr = 5:3). Major *cis*-diastereomer of thiaselenetane **5**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (dd, 2H, CH_2Cl, ^2J = 11.8, ^3J = 7.1 Hz), 4.27 (dd, 2H, CH_2Cl, ^2J = 11.8, ^3J = 7.1 Hz), 5.52 (dd, 2H, CHSe, ^3J = 7.1, ^3J = 7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 41.39 (CH_2Cl), 69.36 (CHSe). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 193. Minor *trans*-diastereomer of thiaselenetane **5**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (dd, 2H, CH_2Cl, ^2J = 11.9, ^3J = 7.7 Hz), 4.31 (dd, 2H, CH_2Cl, ^2J = 11.9, ^3J = 7.9 Hz), 5.54 (dd, 2H, CHSe, ^3J = 7.7, ^3J = 7.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 41.63 (CH_2Cl), 70.03 (CHSe). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 200. GC–MS: *m*/*z* (rel. int., %) 268 $[M]^{+\cdot}$ (29), 204 (12), 169 (100), 142 (56), 133 (34), 107 (82), 93 (24), 81 (13), 61 (19), 53 (21). Anal. Calcd for $C_4H_6O_2Cl_2SSe$: C, 17.93; H, 2.26; Cl, 26.46. Found: C, 17.69; H, 2.21; Cl, 26.30.
14. Thiaselenolane **6**, colorless crystals, mp 87–88 °C (dr = 3:1). Major diastereomer of thiaselenolane **6**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.22 (dd, 1H, CH_2Se, ^2J = 11.3, ^3J = 7.1 Hz), 3.50 (dd, 1H, CH_2Se, ^2J = 11.3, ^3J = 5.1 Hz), 3.88 (dd, 1H, CH_2Cl, ^2J = 11.6, ^3J = 9.7 Hz), 4.29 (dd, 1H, CH_2Cl, ^2J = 11.6, ^3J = 5.7 Hz), 4.47 (dd, 1H, $SeCHSO_2$, ^3J = 5.7, ^3J = 9.7 Hz), 4.47 (dd, 1H, $ClCHSO_2$, ^3J = 5.1, ^3J = 7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.46 (CH_2Se, $^1J_{C-Se}$ = 56.8 Hz), 43.84 (CH_2Cl), 50.47 ($SeCHSO_2$, $^1J_{C-Se}$ = 82.9 Hz), 72.89 ($ClCHSO_2$). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 270. Minor diastereomer of thiaselenolane **6**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (dd, 1H, CH_2Se, ^2J = 11.3, ^3J = 6.7 Hz), 3.54 (dd, 1H, CH_2Se, ^2J = 11.3, ^3J = 5.0), 3.55 (dd, 1H, CH_2Cl, ^2J = 11.7, ^3J = 8.2 Hz), 3.82 (dd, 1H, CH_2Cl, ^2J = 11.7, ^3J = 6.3 Hz), 4.63 (dd, 1H, $SeCHSO_2$, ^3J = 6.3, ^3J = 8.2 Hz), 5.11 (dd, 1H, $ClCHSO_2$, ^3J = 5.0, ^3J = 6.7 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.42 (CH_2Se), 42.20 (CH_2Cl), 48.59 ($SeCHSO_2$), 70.58 ($ClCHSO_2$). GC–MS: *m*/*z* (rel. int., %) 268 $[M]^{+\cdot}$ (14), 142 (100), 107 (26), 93 (11), 62 (12). Anal. Calcd for $C_4H_6O_2Cl_2SSe$: C, 17.93; H, 2.26; Cl, 26.46. Found: C, 17.87; H, 2.16; Cl, 26.65.
15. CCDC contains the supplementary crystallographic data for the *cis*-diastereomer of compound **5** (CCDC 775446). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
16. *Typical procedure for the synthesis of compounds **5**, **6**, and **12***. A solution of selenium dichloride was prepared by stirring a mixture of selenium (1.6 g, 20 mmol) and sulfuryl chloride (2.7 g, 20 mmol) in MeCN (15 ml) at room temperature. To the solution of selenium dichloride was added dropwise a solution of divinyl sulfone (2.36 g, 20 mmol) in MeCN (10 ml) over 5 min with stirring. The mixture was stirred overnight at room temperature. The solvent was evaporated in vacuo at room temperature. According to NMR data, the residue (4.29 g) contained 10% (0.43 g, 82% conversion) of divinyl sulfone, 49% (2.12 g, 55% yield) of thiaselenetane **5**, and 41% (1.74 g, 45% yield) of thiaselenolane **6**. Column chromatography of the residue on silica gel (benzene/hexane 3:1) gave thiaselenetane **5** (1.92 g, 50% yield), thiaselenolane **6**, (0.89 g, 23% yield), and thiaselenolane **12** (0.62 g, 80% yield based on consumed thiaselenolane **6**).
17. Thiaselenetane **7**, colorless crystals, mp 113–114 °C (dr = 7:1). Major diastereomer of thiaselenetane **7**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (dd, 2H, CH_2Br, ^2J = 10.8, ^3J = 7.6 Hz), 4.10 (dd, 2H, CH_2Br, ^2J = 10.8, ^3J = 8.1 Hz), 5.56 (dd, 2H, CHSe, ^3J = 7.6, ^3J = 8.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 27.21 (CH_2Br), 68.41 (CH, $^1J_{SeC}$ = 51.0 Hz). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 244 (m, $^2J_{SeH}$ = 9.5 Hz). GC–MS: *m*/*z* (rel. int., %) 276 $[M-HBr]^{+\cdot}$ (14), 133 (5), 106 (100), 80 (13), 57 (8), 48 (12), 28 (16), 27 (50), 18 (19). Minor diastereomer of thiaselenetane **7**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (dd, 2H, CH_2Br, ^2J = 11.0, ^3J = 7.7 Hz), 4.14 (dd, 2H, CH_2Br, ^2J = 11.0, ^3J = 7.9 Hz), 5.54 (dd, 2H, CHSe, ^3J = 7.7, ^3J = 7.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 27.74 (CH_2Br), 69.28 (CH). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 251 (m, $^2J_{SeH}$ = 10.0 Hz). GC–MS: *m*/*z* (rel. int., %) 276 $[M-HBr]^{+\cdot}$ (17), 106 (100), 80 (16), 57 (13), 48 (12), 28 (54), 27 (55), 18 (95). Anal. Calcd for $C_4H_6O_2Br_2SSe$: C, 13.46; H, 1.69; Br, 44.77. Found: C, 13.21; H, 1.82; Br, 44.89.
18. Thiaselenolane **8**, colorless crystals, mp 133–134 °C (dr = 19:1). Major diastereomer of thiaselenolane **8**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (dd, 2H, $SeCH_2$, ^3J = 10.1, ^3J = 5.6 Hz), 3.73 (dd, 1H, CH_2Br, ^2J = 10.6, ^3J = 9.1 Hz); 4.15 (dd, 1H, CH_2Br, ^2J = 10.6, ^3J = 6.4 Hz), 4.61 (dd, 1H, SO_2CHSe, ^3J = 6.4, ^3J = 9.1 Hz), 5.20 (dd, 1H, SO_2CHBr, ^3J = 10.1, ^3J = 5.6 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 21.19 ($SeCH_2$, $^1J_{Se-C}$ = 55.6 Hz), 28.57 (CH_2Br), 49.36 (SCHSe, $^1J_{Se-C}$ = 80.7 Hz), 59.51 (SCHBr). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 287. GC–MS: *m*/*z* (rel. int., %) 276 $[M-HBr]^{+\cdot}$, 108 (42), 106 (100), 104 (94), 102 (38), 80 (14), 48 (14). Anal. Calcd for $C_4H_6O_2Br_2SSe$: C, 13.46; H, 1.69; Br, 44.77. Found: C, 13.28; H, 1.75; Br, 44.37. The amount of the minor diastereomer of thiaselenetane **8** was too low to permit the spectral characteristics to be determined.
19. *Typical procedure for the synthesis of compounds **7**, **8**, and **13***. A solution of selenium dibromide was prepared by stirring a mixture of selenium (1.6 g, 20 mmol) and bromine (3.2 g, 20 mmol) in MeCN (40 ml) at room temperature. To the solution of selenium dibromide was added dropwise a solution of divinyl sulfone (2.36 g, 20 mmol) in MeCN (20 ml) over 1 h with stirring. The mixture was stirred overnight at room temperature. The solvent was evaporated in vacuo at room temperature. According to NMR data, the residue (6.19 g) contained 8% (0.49 g, 79% conversion) of divinyl sulfone, 72% (4.47 g, 78% yield) of thiaselenetane **7**, and 20% (1.24 g, 22% yield) of thiaselenolane **8**. Column chromatography of the residue on silica gel (benzene/hexane 3:1) gave thiaselenetane **7** (2.40 g, 42% yield), thiaselenolane **8** (0.57 g, 10% yield), and thiaselenolane **13** (0.33 g, 62% yield based on consumed thiaselenolane **8**).
20. Besides the reaction of selenium dihalides with divinyl sulfide,[8] we carried out the addition of selenium dichloride to phenyl vinyl sulfide leading to the Markovnikov product, bis(2-chloro-2-phenylsulfanylethyl) selenide. These results will be published elsewhere.
21. Thiaselenolane **12**, colorless crystals, mp 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.30 (dd, 1H, $SeCH_2$, ^2J = 11.3, ^3J = 5.9 Hz), 3.67 (dd, 1H, $SeCH_2$, ^2J = 11.3, ^3J = 5.0 Hz), 4.96 (dd, 1H, $ClCHSO_2$, ^3J = 5.0, ^3J = 5.9 Hz), 6.01 (d, 1H, $=CH_2$, ^2J = 3.2 Hz), 6.57 (d, 1H, $=CH_2$, ^2J = 3.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.37 ($SeCH_2$, $^1J_{CSe}$ = 53.1 Hz), 66.19 ($ClCHSO_2$), 120.18 ($=CH_2$), 132.62 ($SeCSO_2$). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 263. GC–MS: *m*/*z* (rel. int., %) 232 $[M]^{+\cdot}$ (12), 106 (100), 104 (50), 80 (14), 62 (8), 48 (9). Anal. Calcd for $C_4H_5O_2ClSSe$: C, 20.75; H, 2.18; Cl, 15.31. Found: C, 20.98; H, 2.37; Cl, 15.07.
22. Thiaselenolane **13**, colorless crystals, mp 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (dd, 1H, $SeCH_2$, ^2J = 10.9, ^3J = 8.3 Hz), 3.64 (dd, 1H, $SeCH_2$, ^2J = 10.9, ^3J = 5.3 Hz), 4.98 (dd, 1H, $BrCHSO_2$, ^3J = 5.3, ^3J = 8.3 Hz), 6.02 (d, 1H, $=CH_2$, ^2J = 3.2 Hz), 6.61 (d, 1H, $=CH_2$, ^2J = 3.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.12 ($SeCH_2$, $^1J_{CSe}$ = 52.0 Hz), 55.23 ($BrCHSO_2$), 119.62 ($=CH_2$), 133.66 ($SeCSO_2$). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 288. GC–MS: *m*/*z* (rel. int., %) 276 $[M]^{+\cdot}$ (38), 108 (42), 106 (100), 104 (94), 102 (38), 80 (14), 48 (14). Anal. Calcd for $C_4H_5O_2BrSSe$: C, 17.41; H, 1.83; Br, 28.95. Found: C, 17.21; H, 1.97; Br, 28.87.

23. Potapov, V. A.; Kurkutov, E. O.; Albanov, A. I.; Amosova, S. V. *Russ. J. Org. Chem.* **2008**, *44*, 1547.
24. Migalina, Y. V.; Lendel, V. G.; Koz'min, A. S.; Zefirov, N. S. *Chem. Heterocycl. Compd.* **1978**, 584.
25. Block, E.; Dikarev, E. V.; Glass, R. S.; Jin, J.; Li, B.; Li, X.; Zhang, S.-Z. *J. Am. Chem. Soc.* **2006**, *128*, 14949.
26. Pushkara Rao, V. *Sulfur Rep.* **1992**, *12*, 359.
27. (a) Holm, A.; Berg, C.; Bjerre, C.; Bak, B.; Swanholt, H. *J. Chem. Soc., Chem. Commun.* **1979**, 99; (b) Haas, A.; Spehr, M. *J. Fluorine Chem.* **1989**, *45*, 35; (c) Haas, A.; Limberg, C.; Sterlin, S. R. *J. Fluorine Chem.* **1991**, *53*, 71; (d) Okuma, K.; Kubota, T. *Tetrahedron Lett.* **2001**, *42*, 3881; (e) Amosova, S. V.; Elokhina, V. N.; Nakhmanovich, A. S.; Larina, L. I.; Martynov, A. V.; Steele, B. R.; Potapov, V. A. *Tetrahedron Lett.* **2008**, *49*, 974; (f) Potapov, V. A.; Elokhina, V. N.; Larina, L. I.; Yaroshenko, T. I.; Tatarinova, A. A.; Amosova, S. V. *J. Organomet. Chem.* **2009**, *694*, 3679.