



Reactions of selenium dichloride and dibromide with divinyl selenide: synthesis of novel selenium heterocycles and rearrangement of 2,6-dihalo-1,4-diselenanes

Vladimir A. Potapov*, Svetlana V. Amosova, Kaleria A. Volkova, Maxim V. Penzik, Alexander I. Albanov

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

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ABSTRACT

The synthesis of novel selenium heterocycles, 2,6-dihalo-1,4-diselenanes, 4-halo-2-halomethyl-1,3-diselenolanes and 2-halomethyl-1,3-diselenoles, based on the reactions of selenium dichloride and dibromide with divinyl selenide is described. The spontaneous rearrangement of 2,6-dihalo-1,4-diselenanes to 4-halo-2-halomethyl-1,3-diselenolanes is observed. Distillation of 4-chloro-2-chloromethyl-1,3-diselenolane leads to regioselective dehydrochlorination and the formation of 2-chloromethyl-1,3-diselenole.

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Vinyl selenides are versatile reagents and synthons for organic synthesis.^{1–5} The vinylseleno group is able to undergo addition of electrophilic and radical reagents.^{1–10} Divinyl selenide is a prospective starting material for the preparation of functionalized organoselenium compounds.^{6–16} The addition of thiols to divinyl selenide afforded functionalized diorganyl selenides.¹⁰

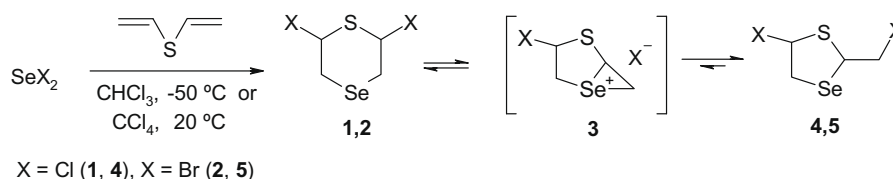
Selenium dichloride and dibromide are promising reagents for organic synthesis, however, in solution, they exist in equilibrium. The equilibrium of selenium dichloride includes Se_2Cl_2 and SeCl_4 , whereas selenium dibromide is in equilibrium with Se_2Br_2 and bromine.^{17–20} Nevertheless, freshly prepared selenium dichloride and dibromide are practically pure compounds and can take part in various reactions to give products of selenium dihalides rather than products of disproportionation. Selenium dichloride was used for the preparation of compounds not containing a carbon–selenium bond.^{21–25} The addition of selenium dihalides to dimethyl diethynyl silane represented the first synthesis of organoselenium compounds using SeCl_2 and SeBr_2 .^{26,27} Later, reports on reactions of SeCl_2 with organic compounds were published.^{28–34}

Organolithium and organomagnesium reagents have been used in reactions with selenium dichloride to afford diaryl selenides.²⁸ Functionalized divinyl selenides are obtained by the addition of

selenium dichloride to propargylic alcohols.²⁹ We carried out the reaction of selenium halides with various diorganyl diethynyl silanes and germanes and obtained previously unknown 1,4-selenasila- and selenagermafulvenes.^{26,27,30–34}

We have also studied the reactions of selenium dichloride and dibromide with divinyl sulfide.^{6–10} 2,6-Dihalo-1,4-thiaselenanes (**1**, **2**) were obtained, and underwent spontaneous rearrangement to 5-halo-2-halomethyl-1,3-thiaselenolanes (**4**, **5**) upon standing at room temperature in chloroform solution (Scheme 1).^{6,7} This simple rearrangement was attributed to the anchimeric assistance effect^{35–37} of the selenium atom which increased considerably the ease of loss of the halogen atoms. Selenirane species **3** is assumed to be an intermediate in the rearrangement (Scheme 1).^{6,7} Thiaselenanes **1** and **2** are regarded as kinetic products, which are converted into the more stable thermodynamic products, thiaselenolanes **4** and **5**.

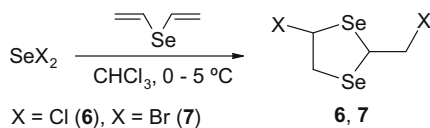
In a non-polar solvent such as CCl_4 , the rearrangement proceeded very slowly and thiaselenanes **1** and **2** were obtained in near quantitative yields when the reactions were carried out at room temperature. Chloro-containing thiaselenane **1** was isolated in pure form whereas bromo-containing thiaselenane **2** was registered only by NMR in solution, and the rearrangement of



Scheme 1.

* Corresponding author.

E-mail address: v.a.potapov@mail.ru (V.A. Potapov).



Scheme 2.

thiaselenane **2** to thiaselenolane **5** occurred even on concentration of solutions of compound **2** in vacuo.^{6,7} The ease of the rearrangement in the case of thiaselenane **2** was due to the better leaving ability of the bromine atom compared to the chlorine atom in thiaselenane **1**.

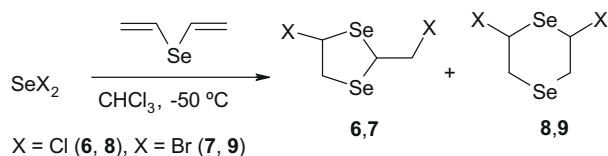
In this work, we report our studies on the reactions of selenium dichloride and dibromide with divinyl selenide. Selenium dichloride was prepared from selenium and sulfur chloride in chloroform or carbon tetrachloride and selenium dibromide was obtained from selenium and bromine in the same solvents. The selenium halides were used in reactions immediately after their preparation.

The reactions of selenium dichloride and dibromide with divinyl selenide at 0–5 °C in chloroform afforded novel five-membered heterocycles, 4-halo-2-halomethyl-1,3-diselenolanes **6** and **7**, in 85% and 80% yield, respectively (Scheme 2).^{38,39}

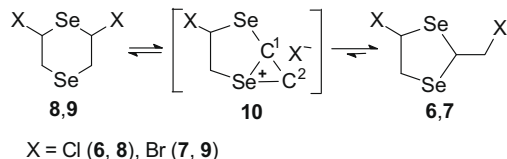
Compounds **6** and **7** consisted of two diastereomers (*cis*- and *trans*-isomers) in the ratios 4:1 (compound **6**) and 3:2 (diselenolane **7**). The ratios were determined by integration of the relevant signals in the ¹H NMR spectra. The assignment of the *cis*- and *trans*-isomers of diselenolanes **6** and **7** was made using homonuclear NOESY ¹H–¹H 2D NMR.

When the reaction of selenium dichloride with divinyl selenide was performed in chloroform at –50 °C, a mixture of diselenolane **6** and 2,6-dichloro-1,4-diselenane⁴⁰ (**8**) was obtained in a 3:2 ratio. The reaction of selenium dibromide with divinyl selenide under the same conditions gave diselenolane **7** and 2,6-dibromo-1,4-diselenane⁴¹ (**9**) in the ratio 2:1 (Scheme 3). The total yields were near quantitative in both reactions (Scheme 3).

When we continued stirring the reaction mixtures at –50 °C temperature, the ratios of the compounds changed: a decrease in the amount of diselenane **8** or **9** was observed along with a concomitant increase of diselenolane **6** or **7** (NMR data). For example, on standing at room temperature in chloroform solution for 24 h, the ratio of compounds **6** and **8** changed from 3:2 to 6:1. Complete conversion of diselenane **8** into diselenolane **6** was observed in 48 h. Thus, as with thiaselenanes **1** and **2**, diselenanes **8** and **9** underwent spontaneous rearrangement to diselenolanes **6** and **7** (Scheme 4). Selenirane species **10** is assumed to be an intermediate in the rearrangement.



Scheme 3.



Scheme 4.

Earlier we found that in a non-polar solvent such as CCl₄, the rearrangement proceeded very slowly and thiaselenanes **1** and **2** were obtained in near quantitative yields when the reactions were carried out at room temperature. To increase the quantity of diselenane **9**, the reaction of selenium dibromide with divinyl selenide was carried out in carbon tetrachloride at –20 °C. Indeed, in this case, the amount of diselenane **9** increased and the ratio of compounds **7** and **9** changed from 2:1 (chloroform, –50 °C) to 1:1. However, the conversion of divinyl selenide was about 50% (NMR data). When we performed the same reaction in carbon tetrachloride at room temperature, the complete conversion of divinyl selenide was observed and the ratio of compounds **7** and **9** was 6:5.

Thiaselenane **1** was stable enough to be isolated in pure form. In the case of heterocycles **8** and **9**, all attempts to isolate these compounds failed due to their tendency to rearrange. The rearrangement occurred on silica gel and we obtained only diselenolanes **6** or **7** in attempts to separate the mixtures of compounds **6** and **8** or **7** and **9** by column chromatography. NMR data indicated that the rearrangement of diselenanes **8** and **9** proceeded faster compared with sulfur analogs **1** and **2**.

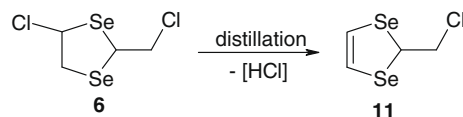
Previously, we found that the rearrangement of bromo-containing thiaselenane **2** occurred faster in comparison with chloro-containing thiaselenane **1**.^{6,7} Similar trends were observed in the case of diselenanes **8** and **9**: the rearrangement of bromo derivative **9** was faster than that of chloro derivative **8**. The greater ease of the rearrangement in the case of diselenane **9** was attributed to the better leaving ability of the bromine atom compared to the chlorine atom in diselenane **8**. As with the rearrangement of sulfur analogs **1** and **2**, the rearrangement of diselenanes **8** and **9** proceeded faster in polar (chloroform) than in non-polar solvents (CCl₄) indicating the ionic character of the intermediates.

The reasons for the faster rearrangement of diselenanes **8** and **9** compared with the sulfur analogs **1** and **2** are not clear. According to the literature, a sulfur atom is able to stabilize an adjacent positive charge better than a selenium atom.⁴² On the other hand, attack of the halide anion at the carbon atom C-2 affords rearrangement products whereas attack at C-1 leads to initial diselenanes **8** or **9**. The bulky selenium atom decreases the possibility of attack at C-1 due to steric hindrance and therefore increases the share of the halide anions attacking at C-2. Therefore, in the case of species **10**, the halide anions attack preferentially at C-2 to give the products of rearrangement.

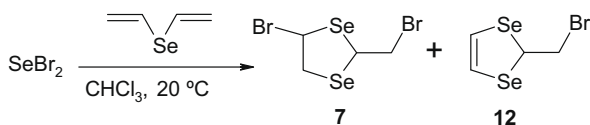
Surprisingly, distillation of diselenolane **6** led to dehydrochlorination and the formation of previously unknown 2-chloromethyl-1,3-diselenole⁴³ (**11**) in 58% yield (Scheme 5).

It is noteworthy that the elimination reaction was highly regioselective: the dehydrochlorination occurred only with the SeCHCl fragment and did not involve the CH₂Cl group. Diselenole **11** was also obtained by distillation of the mixture of compounds **6** and **8**. In this case the rearrangement of diselenane **8** to diselenolane **6** was accompanied by dehydrochlorination of diselenolane **6**. Unlike diselenolane **6**, the distillation of bromo-containing diselenolane **7** resulted in decomposition and the formation of tars.

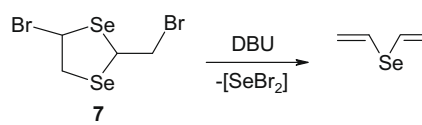
2-Bromomethyl-1,3-diselenole⁴⁴ (**12**) was obtained in 20% yield along with diselenolane **7** (60% yield) in the reaction of selenium dibromide with divinyl selenide in chloroform at room temperature (Scheme 6). We found that the dehydrobromination occurred spontaneously upon standing of diselenolane **7** in chloroform



Scheme 5.



Scheme 6.



Scheme 8.

solution. It is notable that the reaction of selenium dibromide with divinyl sulfide in chloroform at room temperature afforded 2-bromomethyl-1,3-thiaselenole along with thiaselenolane **5** (Scheme 6).⁶

The structural assignments of compounds **6–9**, **11** and **12** were made with ^1H , ^{13}C , ^{77}Se NMR spectroscopy and GC–MS. Homonuclear and heteronuclear 2D NMR spectra were also used.

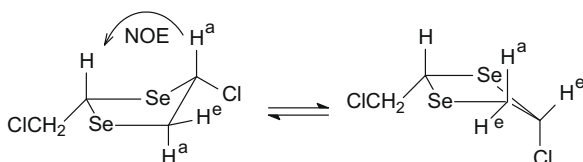
In the NOESY spectrum of diselenolane **6**, cross peaks were observed for the major diastereomer. The cross peaks revealed a dipole–dipole interaction between the methine proton of the SeCHSe fragment with the methine proton of the ClCHSe group and indicated the *cis*-arrangement of the substituents on the five-membered ring (Scheme 7). The same trends were found in the NOESY spectrum of diselenolane **7**. Therefore, the major diastereomers of diselenolanes **6** and **7** were *cis*-isomers and the minor diastereomers had *trans*-stereochemistry.

A comparison of the ^1H NMR spectra of diselenolane **6** and diselenolane **8** revealed that the coupling constants of the vicinal protons of the $\text{HalCHCH}_2\text{Se}$ group in diselenolane **8** ($^3J = 2.0$, $^3J = 8.1$, major diastereomer) and diselenolane **6** ($^3J = 4.0$, $^3J = 4.0$, major diastereomer) were quite different. This can be explained by facile interconversion of the conformations of the five-membered ring that leads to an averaging of the values of the coupling constants. The interconversion of two envelope conformations of the *cis*-isomer of diselenolane **6** is presented in Scheme 7. Similar trends were observed for diselenolane **7** (Scheme 7).

It is noteworthy that the conformationally averaged coupling constants between all the vicinal pairs of protons have been measured in cyclopentane.⁴⁵ It is known that cyclopentane exists as a mixture of numerous conformations which interconvert by pseudorotation so that each carbon atom can assume any position in the envelope and half-chair forms.⁴⁵ We assume that similar trends take place in the case of diselenolanes **6** and **7**.

A considerable difference (236 ppm) in the chemical shifts of the selenium atoms in the ^{77}Se NMR spectrum of diselenolane **6** was attributed to the presence of the chlorine atom at the α -carbon of one selenium atom. It is known that the introduction of chlorine atoms to the α -carbon in dialkyl selenides leads to deshielding of selenium atoms and may increase significantly the chemical shifts of the selenium atoms.⁴⁶

The halogen atoms in compounds **6–9**, **11** and **12** are highly efficient leaving groups since they are activated by anchimeric assistance by the selenium atoms. We regard the anchimeric assistance effect^{35–37} as the driving force for the rearrangement of diselenolanes **8** and **9** to diselenolanes **6** and **7** (Scheme 4). The synthesized compounds can find application in the preparation of organoselenium compounds via nucleophilic substitution and dehydrohalogenation reactions. Compounds **6,7**, **11** and **12** can



Scheme 7.

be regarded as precursors of 1,4-diselenafulvene, which in turn, represents a precursor for the synthesis of tetraselenafulvalene.⁴⁷ The latter compound has been intensively studied due to the unique conductive properties of its complexes.⁴⁸

One of most useful dehydrohalogenation reagents is 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).^{49,50} In our attempts to carry out the dehydrobromination we observed an unexpected reaction which led to the formation of divinyl selenide (66% yield) rather than to dehydrobrominated products. The elimination of selenium dibromide instead of hydrogen bromide occurred under the action of DBU on diselenolane **7** in carbon tetrachloride at room temperature (Scheme 8).

We envisage that the behavior of diselenolane **7** is due to the presence of intermediate **10** in equilibrium with **7** (Scheme 4). There is a positive charge on the selenium atom in intermediate **10** and attack of the nitrogen atom of DBU on the charged selenium atom starts the reaction leading to the elimination of selenium dibromide and the formation of divinyl selenide.

In conclusion, syntheses of novel selenium heterocycles based on the reactions of selenium dichloride and dibromide with divinyl selenide have been developed. A previously unknown rearrangement, which proceeded spontaneously even at low temperature, was observed. The driving force for the rearrangement is suggested to be due to anchimeric assistance^{35–37} with participation of the selenium atom. This effect is important for stabilization of cation **10**, which is assumed to be the intermediate in the rearrangement. Distillation of diselenolane **6** led to regioselective dehydrochlorination and formation of diselenole **11**.

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38. **4-Chloro-2-chloromethyl-1,3-diselenolane (6)**: A solution of sulfonyl chloride (2.4 g, 18 mmol) in chloroform (10 ml) was added to a mixture of selenium (1.4 g, 18 mmol) and chloroform (5 ml) and the resulting mixture was stirred overnight at room temperature. The solution of selenium dichloride thus prepared was cooled in an ice bath and a solution of divinyl selenide (3.0 g, 23 mmol) in chloroform (15 ml) was added dropwise over 40 min with stirring. The mixture was stirred overnight at room temperature. The mixture was filtered and the solvent was evaporated at room temperature. Chromatography of the residue through a thin layer of silica gel gave diselenolane **6** in 85% yield (4.4 g) as a pale yellow liquid. The *cis/trans* isomer ratio was 4:1. *cis*-Isomer of diselenolane **6**, ^1H NMR (400 MHz, CCl_4): δ 3.83 (dd, 1H, CH_2Cl , $^2J = 11.0$, $^3J = 8.5$ Hz), 3.85 (d, 2H, CH_2Se , $^2J = 4.0$ Hz), 3.94 (dd, 1H, CH_2Cl , $^2J = 11.0$, $^3J = 7.0$ Hz), 5.14 (dd, 1H, SeCHSe , $^3J = 7.0$, $^3J = 8.5$ Hz), 6.35 (t, 1H, SeCHCl , $^3J = 4.0$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 38.66 (SeCHSe), 44.41 (CH_2Se), 50.50 (CH_2Cl), 65.73 (ClCHSe). ^{77}Se NMR (76.3 MHz, CDCl_3): δ 401 (m, CH_2Se , $^2J_{\text{SeH}} = 34.8$, $^2J_{\text{SeH}} = 23.2$ Hz), 637 (m, ClCHSe , $^2J_{\text{SeH}} = 22.8$ Hz). *trans*-Isomer of diselenolane **6**, ^1H NMR (400 MHz, CCl_4): δ 3.90 (d, 2H, CH_2Se , $^3J = 4.5$ Hz), 4.05 (dd, 1H, CH_2Cl , $^2J = 11.8$, $^3J = 7.9$ Hz), 4.08 (dd, 1H, CH_2Cl , $^2J = 11.8$, $^3J = 7.7$ Hz), 5.05 (dd, 1H, SeCHSe , $^3J = 7.9$, $^3J = 7.7$ Hz), 6.18 (t, 1H, SeCHCl , $^3J = 4.5$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 38.83 (SeCHSe), 44.82 (CH_2Se), 50.80 (CH_2Cl), 63.68 (ClCHSe). ^{77}Se NMR (76.3 MHz, CDCl_3): δ 398 (m, CH_2Se), 622 (m, ClCHSe). GC-MS: *m/z* (rel. intensity) 284 [$\text{M}]^+$ (100), 235 (34), 222 (57), 199 (20), 187 (18), 169 (23), 160 (90), 142 (28), 133 (19), 107 (58), 93 (20), 80 (23), 27 (65). Anal. Calcd for $\text{C}_4\text{H}_6\text{Cl}_2\text{Se}_2$: C, 16.98; H, 2.14; Cl, 25.04; Se, 55.84. Found: C, 17.23; H, 2.29; Cl, 24.54; Se, 56.38.
39. **4-Bromo-2-bromomethyl-1,3-diselenolane (7)** was obtained in 80% yield under similar conditions to diselenolane **6**. The *cis/trans* isomer ratio was 3:2. *cis*-Isomer of diselenolane **7**, ^1H NMR (400 MHz, CCl_4): δ 3.85 (dd, 1H, CH_2Br , $^2J = 10.0$, $^3J = 8.1$ Hz), 3.92 (dd, 1H, CH_2Br , $^2J = 10.0$, $^3J = 7.6$ Hz), 3.98 (dd, 1H, CH_2Se , $^2J = 10.8$, $^3J = 5.5$ Hz), 4.05 (dd, 1H, CH_2Se , $^2J = 10.8$, $^3J = 3.8$ Hz), 5.29 (t, 1H, SeCHSe , $^3J = 8.1$ Hz), 6.15 (dd, 1H, SeCHBr , $^3J = 3.8$, $^3J = 5.5$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 39.24 (SeCHSe), 39.48 (CH_2Se), 45.36 (CH_2Br), 49.98 (BrCHSe). ^{77}Se NMR (76.3 MHz, CDCl_3): δ 428 (m, CH_2Se), 634 (m, BrCHSe). *trans*-Isomer of diselenolane **7**, ^1H NMR (400 MHz, CCl_4): δ 3.94 (dd, 1H, CH_2Se , $^2J = 10.8$, $^3J = 4.1$ Hz), 4.02 (dd, 1H, CH_2Se , $^2J = 10.8$, $^3J = 7.4$ Hz), 4.03 (dd, 1H, BrCH_2 , $^2J = 10.1$, $^3J = 8.1$ Hz), 4.10 (dd, 1H, BrCH_2 , $^2J = 10.1$, $^3J = 11.5$ Hz), 5.18 (t, 1H, SeCHSe , $^3J = 8.1$ Hz), 5.91 (dd, 1H, SeCHBr , $^3J = 4.1$, $^3J = 7.4$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 39.24 (SeCHSe), 39.32 (CH_2Se), 44.04 (CH_2Br), 47.74 (BrCHSe). ^{77}Se NMR (76.3 MHz, CDCl_3): δ 429 (m, CH_2Se), 617 (m, BrCHSe). GC-MS: *m/z* (rel. intensity) 292 [$\text{M}-\text{Br}]^+$ (78), 213 (62), 199 (100), 160 (24), 133 (90), 106 (54), 93 (28), 80 (38), 53 (78), 27 (47). Anal. Calcd for $\text{C}_4\text{H}_6\text{Br}_2\text{Se}_2$: C, 12.92; H, 1.63; Br, 42.98; Se, 42.47. Found: C, 13.10; H, 1.78; Br, 42.78; Se, 42.22.
40. **2,6-Dichloro-1,4-diselenane (8)**: A solution of sulfonyl chloride (0.8 g, 6 mmol) in chloroform (10 ml) was added to a mixture of selenium (0.47 g, 6 mmol) and chloroform (15 ml) and the resulting mixture was stirred overnight at room temperature. The solution of selenium dichloride thus prepared, and a solution of divinyl selenide (0.8 g, 6 mmol) in chloroform (15 ml) were added separately with stirring over 40 min to a flask containing chloroform (20 ml) cooled to -50°C . In order to monitor the course of the reaction, CDCl_3 was added to a sample of the reaction mixture and the sample was analyzed by ^1H and ^{13}C NMR spectroscopy. The NMR analysis showed the presence of diselenolane **6** and diselenane **8** in a 3:2 ratio. The total yield was near quantitative. Diselenane **8** consisted of two diastereomers in the ratio 5:4. Further NMR analysis revealed an increase in the amount of diselenolane **6** accompanied by a simultaneous decrease of the content of diselenane **8**. Major diastereomer of diselenane **8**, ^1H NMR (400 MHz, CDCl_3): δ 3.29 (dd, 2H, CH_2SeCH_2 , $^2J = 13.0$, $^3J = 2.0$ Hz), 3.46 (dd, 2H, CH_2SeCH_2 , $^2J = 13.0$, $^3J = 8.1$ Hz), 5.65 (dd, 2H, CHCl , $^3J = 2.0$, $^3J = 8.1$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 29.91 (CH_2Se), 50.38 (SeCHCl). Minor diastereomer of diselenane **8**, ^1H NMR (400 MHz, CDCl_3): δ 3.57 (dd, 2H, CH_2SeCH_2 , $^2J = 12.7$, $^3J = 2.9$ Hz), 3.70 (dd, 2H, CH_2SeCH_2 , $^2J = 12.7$, $^3J = 9.7$ Hz), 5.44 (dd, 2H, CHCl , $^3J = 2.9$, $^3J = 9.7$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 28.54 (CH_2Se), 49.24 (SeCHCl).
41. **2,6-Dibromo-1,4-diselenane (9)**: A solution of bromine (1.6 g, 20 mmol) in CCl_4 (10 ml) was added to a mixture of selenium (0.8 g, 10 mmol) and CCl_4 (30 ml) and the resulting mixture was stirred overnight at room temperature. To the solution of selenium dibromide thus prepared, a solution of divinyl selenide (2.0 g, 15 mmol) in CCl_4 (20 ml) was added with stirring over 45 min at room temperature. The mixture was stirred for 90 min at room temperature and analyzed by ^1H and ^{13}C NMR spectroscopy. The NMR analysis showed the presence of compounds **7** and **9** in a 6:5 ratio. The conversion of divinyl selenide was complete and the total yield was virtually quantitative. Major diastereomer of diselenane **9**, ^1H NMR (400 MHz, CCl_4): δ 3.51 (dd, 2H, CH_2SeCH_2 , $^2J = 13.0$, $^3J = 2.6$ Hz), 3.51 (dd, 2H, CH_2SeCH_2 , $^2J = 13.0$, $^3J = 8.1$ Hz), 5.64 (dd, 2H, CHBr , $^2J = 2.6$, $^3J = 8.1$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3): δ 30.96 (CH_2Se), 38.21 (SeCHBr). The amount of the minor diastereomer of diselenane **9** was too low to make assignment possible. The mixture was filtered, and the solvent was distilled in vacuo. NMR analysis showed that the residue (3.93 g) contained diselenolane **7** (the purity was about 95%, the yield was virtually quantitative). The *cis/trans* isomer ratio was 2:1.
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43. **2-Chloromethyl-1,3-diselenole (11)** was obtained in 58% yield as a pale yellow liquid by distillation of diselenolane **6**. Bp $91-93^\circ\text{C}$ (1 mmHg). ^1H NMR (400 MHz, CDCl_3): δ 3.80 (d, 2H, CH_2Cl , $^3J = 7.7$ Hz), 5.10 (t, 1H, SeCHSe , $^3J = 7.7$ Hz), 7.04 (s, 2H, $\text{CH}=\text{CH}$). ^{13}C NMR (100.6 MHz, CDCl_3): δ 38.84 (SeCHSe), 48.88 (CH_2Cl), 117.52 ($\text{CH}=\text{CH}$). ^{77}Se NMR (76.3 MHz, CDCl_3): δ 521. GC-MS: *m/z* (rel. intensity) 248 [$\text{M}]^+$ (42), 199 (100), 160 (18), 133 (10), 106 (22), 80 (16), 53 (12), 27 (20). Anal. Calcd for $\text{C}_4\text{H}_5\text{ClSe}_2$: C, 19.49; H, 2.04; Cl, 14.39. Found: C, 19.89; H, 1.87; Cl, 13.98.
44. **2-Bromomethyl-1,3-diselenole (12)** was obtained in 20% yield in a mixture with diselenolane **7**. ^1H NMR (400 MHz, CDCl_3): δ 3.74 (d, 2H, CH_2Br , $^3J = 8.1$ Hz), 5.15 (t, 1H, SeCHSe , $^3J = 8.1$ Hz), 7.05 (s, 2H, $\text{CH}=\text{CH}$). ^{13}C NMR (100.6 MHz, CDCl_3): δ 38.59 (CH_2Br), 39.35 (SeCHSe), 117.90 ($\text{CH}=\text{CH}$). ^{77}Se NMR (76.3 MHz, CDCl_3): δ 539.
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