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Addition of selenium dibromide to divinyl sulfide: spontaneous rearrangement of 2,6-dibromo-1,4-thiaselenane to 5-bromo-2-bromomethyl-1,3-thiaselenolane

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ABSTRACT

Synthesis of the novel selenium heterocycles **1**, 2, and **3** based on the addition reaction of selenium dibromide to divinyl sulfide is described. The reaction proceeded in CCl_4 at room temperature to give the thiaselenane **1**. Even at low temperature in chloroform solution, the 6-membered thiaselenane**1**underwent spontaneous rearrangement to the 5-membered thiaselenolane **2**. In turn, the thiaselenolane **2** underwent spontaneous dehydrobromination to the thiaselenole **3** in chloroform.

There are few data in the literature on reactions of selenium dichloride and dibromide. Solutions of the selenium halides were studied by various spectral methods including ^{77}Se NMR.[1–4] Although the presence of selenium dichloride and dibromide in the gas phase and in solutions has been demonstrated, none of the selenium dihalides were isolated as pure compounds.[1–4] It has been shown that in solution, selenium dichloride exists in equilibrium with Se_2Cl_2 and $SeCl_4$, whereas the equilibrium of selenium dibromide includes Se_2Br_2 and bromine (Scheme 1).[1–4] Chemical shifts for the selenium dihalides and equilibrium constants (Scheme 1) have been determined in various solvents from ^{77}Se NMR spectra.[3]

Selenium dichloride was used for the preparation of several compounds not containing a carbon-selenium bond.[5–9] In the reaction with *N*,*N*-bis(trimethylsilyl)-2,6-diisopropylaniline, selenium dichloride underwent disproportionation to Se_2Cl_2 and selenium tetrachloride, which was involved in the electrophilic aromatic substitution reaction.[10]

We reported previously the synthesis of an organoselenium compound using $SeCl_2$ and $SeBr_2$ via the addition of the selenium dihalide to dimethyl diethynyl silane.[11,12] Various diorganyl diethynyl silanes and -germanes were involved in this reaction

$$3\ SeCl_2 \rightleftharpoons Se_2Cl_2 + SeCl_4$$

$$2\ SeBr_2 \rightleftharpoons Se_2Br_2 + Br_2$$

Scheme 1.

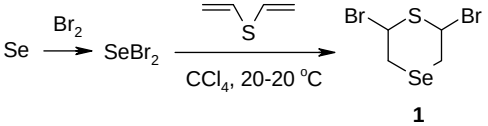
affording novel unsaturated 5-membered heterocycles, 1,4-selenasilafulvenes and 1,4-selenagermafulvenes.[13–19]

Recently, the reaction of selenium dichloride with organolithium and organomagnesium reagents[20] and the addition of selenium dichloride to propargylic alcohols[21] have been reported.

Divinyl sulfide is a versatile starting material for the synthesis of a variety of sulfur-containing heterocycles.[22–24] The addition of selenium electrophiles to divinyl sulfide has not been described in the literature. In this work, we report studies on the addition reaction of selenium dibromide to divinyl sulfide.[25]

The formation of 5-membered fulvenes rather then 6-membered heterocycles in our previous work[13–19] was suggested to be a result of the higher stability of 5-membered heterocycles. However, the reaction of selenium dibromide with divinyl sulfide in carbon tetrachloride at room temperature led to the 6-membered heterocyclic compound, 2,6-dibromo-1,4-thiaselenane (**1**), in near quantitative yield (Scheme 2).[26] Selenium dibromide was prepared from selenium and bromine in carbon tetrachloride.

Compound **1** was analyzed by ^1H, ^{13}C, and ^{77}Se NMR in the CCl_4 solution of the reaction mixture without isolation. The thiaselenane **1** was stable for several days at −20 °C in CCl_4 solution. We found that thiaselenane **1** underwent spontaneous rearrangement to the 5-membered isomer, 5-bromo-2-bromomethyl-1,3-thiaselenolane (**2**) (Scheme 3). When the carbon tetrachloride was



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Scheme 2.

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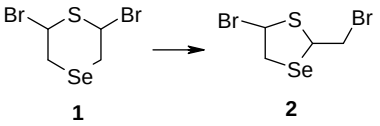
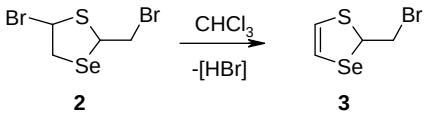


Scheme 3.



Scheme 5.

evaporated from the reaction mixture, the NMR spectrum of the residue showed thiaselenolane **2** as the only product. Thus, the rearrangement of the thiaselenane **1** to the thiaselenolane **2** occurred spontaneously even under concentration in vacuo. This approach is convenient for the preparation of thiaselenolane **2** in near quantitative yield.[26]

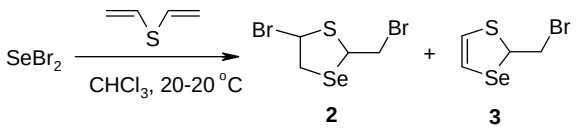
We have found that the nature of the solvent is very important for the reaction of selenium dibromide with divinyl sulfide. At room temperature in chloroform, the formation of the thiaselenolane **2** (78% yield) and 2-bromomethyl-1,3-thiaselenole (**3**)[27] (17% yield) was observed (Scheme 4).

When the reaction was carried out in chloroform at −55 °C, thiaselenane **1** was detected as the only product at the beginning of the process.[28] The course of the reaction was monitored by ^{1}H NMR spectroscopy. Solutions of selenium dibromide and divinyl sulfide in $CHCl_3$ were added simultaneously with stirring to a flask containing $CHCl_3$ at −55 °C. To avoid the rearrangement, which occurred during evaporation of the solvent, $CDCl_3$ was added to the samples of the reaction mixture and these samples were analyzed by ^{1}H NMR. After about half of each reagent had been added (10 min from the start of the addition), $CDCl_3$ was added to a sample of the reaction mixture and this sample was analyzed by ^{1}H NMR spectroscopy (Table 1, entry 1) revealing thiaselenane **1** as the only product. The appearance of thiaselenolane **2** and a simultaneous decrease in the amount of thiaselenane **1** were observed as the reaction progressed. The rearrangement occurred in chloroform even at low temperature to give thiaselenolane **2** (Table 1, entries 2–5).

Another interesting observation was spontaneous dehydrobromination of thiaselenolane **2** (Scheme 5). On standing at room temperature in chloroform, compound **2** underwent slow dehydrobromination to the thiaselenole **3**.

This reaction proceeded slowly even at low temperature (Table 1, entries 4 and 5).

Pure thiaselenolane **2** was obtained when the carbon tetrachloride was evaporated in vacuo from the reaction mixture containing thiaselenane **1** (Scheme 2). The thiaselenolane **2** consisted of two



Scheme 4.

Table 1
The effect of the reaction time on the yield of products **1**, **2**, and **3** in the reaction mixture ($CHCl_3$, −55 °C)[28]

Entry	Reaction time (min)	Amount of products **1**, **2**, and **3** (%)		
		1	**2**	**3**
1	10	95	0	0
2	70	55	40	0
3	130	40	55	0
4	190	22	70	3
5	250	7	82	6

diastereomers in the ratio 3:2. The ratio can be determined from the signals of the protons of the SCHBr group, which appeared as a doublet of doublets at 6.10 ppm (major diastereomer) and 5.91 ppm (minor diastereomer).

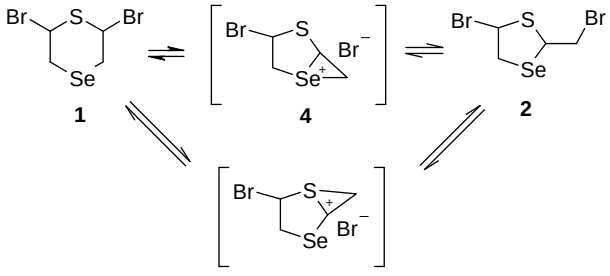
Like thiaselenolane **2**, thiaselenane **1** could exist as two diastereomers. However, we found the content of the minor diastereomer of thiaselenane **1** to be too low to make the assignment possible. In the ^{1}H NMR spectrum of compound **1** the protons of the CH_2Se group of the major diastereomer were not equivalent and each of the protons appeared as a doublet of doublets at 3.31 ppm and 3.48 ppm with a geminal coupling constant ^2J = 12.7 Hz. The proton of the SCHBr fragment of the major diastereomer was revealed as a doublet of doublets at 5.58 ppm.

In carbon tetrachloride, the rearrangement and dehydrobromination proceeded considerably slower. Therefore, the rate of the rearrangement depends on the polarity of the solvent. The rate is low in non-polar solvents such as carbon tetrachloride and increases with higher polarity of the solvent.

We suggest that compound **1** is the kinetic product and compound **2** is the thermodynamic product. The formation of thiaselenane **1** proceeds faster but the formation of the thiaselenolane **2** is favorable from the thermodynamic viewpoint. The conversion of compound **1**–**2** is assumed to proceed via the intermediate **4**. The rearrangement proceeds considerably faster in chloroform than in carbon tetrachloride. The effect of the polarity of the solvent supports the ionic nature of the postulated intermediate **4**.

The driving force for the rearrangement may be due to anchimeric assistance,[29–31] which causes high mobility of the bromine atom. This effect is important for the stabilization of cation **4**, the assumed intermediate. The halogen atom in 2-haloethyl sulfides and selenides is known to be strongly activated by the anchimeric assistance effect with participation of the sulfur or selenium atom.[29–31] Replacement of halogen atoms by a nucleophile in 2-haloethyl sulfides and selenides proceeds exceptionally easily. The formation of 3-membered thiirane and selenirane intermediates has been suggested to explain the considerable increase of the rate in nucleophilic substitution reactions. We suggest that in this case, not only the selenium atom but the sulfur atom as well can participate in stabilization of the intermediates, which include the selenirane and thiirane fragments (Scheme 6).

In conclusion, the novel selenium heterocycles **1**, **2**, and **3** have been synthesized via the reaction of selenium dibromide with divinyl sulfide. A novel rearrangement, which proceeded in chloroform even at low temperature, has been described. The ease of the rearrangement may be explained by the anchimeric assistance effect.



Scheme 6.

Acknowledgment

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26. The reaction in CCl_4 at room temperature. A solution of bromine (4.8 g, 30 mmol) in CCl_4 (50 ml) was added to a mixture of selenium (2.37 g, 30 mmol) and CCl_4 (50 mL) and the resulting mixture was stirred overnight at room temperature. Solutions of selenium dibromide and divinyl sulfide (2.58 g, 30 mmol) both in CCl_4 (10 ml) were added simultaneously with stirring to a flask containing CCl_4 (50 ml) at 20–25 °C. The resulting mixture was stirred for 2 h and the product thiaselenane **1** was analyzed by ^1H, ^{13}C, and ^{77}Se NMR of an aliquot of the CCl_4 solution of the reaction mixture without isolation. The yield of the thiaselenane **1** was near quantitative. The major diastereomer of the thiaselenane **1**, ^1H NMR (400 MHz, CCl_4): δ 5.58 (dd, 2H, SCHBr, ^3J = 2.2, ^3J = 7.8 Hz), 3.48 (dd, 2H, CH_2SeCH_2, ^3J = 2.2, ^2J = 12.7 Hz), 3.31 (dd, 2H, CH_2SeCH_2, ^3J = 7.8, ^2J = 12.7 Hz). ^{13}C NMR (100.6 MHz, CCl_4): δ 29.21 (CH_2Se), 48.67 (CHBr). ^{77}Se NMR (76.3 MHz, CCl_4): δ 203. The solvent was distilled off in vacuo and the residue was analyzed by NMR. The NMR analysis showed that the residue (10.26 g) contained the thiaselenolane **2** (the purity was about 95%, the yield was near quantitative). The thiaselenolane **2** consisted of two diastereomers in the ratio 3:2. The major diastereomer of the thiaselenolane **2**. ^1H NMR (400 MHz, CCl_4): δ 3.86 (m, 1H, CH_2Br), 3.79–3.84 (m, 2H, CH_2Se), 3.99 (dd, 1H, CH_2Br, ^2J = 9.4, ^3J = 8.0 Hz), 5.03 (t, 1H, SCHSe, ^3J = 8.0 Hz), 6.10 (dd, 1H, SCHBr, ^3J = 3.3, ^3J = 3.4 Hz). ^3C NMR (100.61 Hz, CCl_4): δ 38.47 (CH_2Br), 45.97 (CH_2Se), 48.18 (SCHSe), 59.69 (SCHBr). ^{77}Se NMR (76.3 MHz, CCl_4): δ 410. The minor diastereomer of the thiaselenolane **2**. ^1H NMR (400 MHz, CCl_4): δ 3.69–3.73 (m, 2H, CH_2Br), 3.70 (m, 1H, CH_2Se), 3.89 (m, 1H, CH_2Se), 5.05 (t, 1H, SCHSe, ^3J = 7.9 Hz), 5.91 (dd, 1H, SCHBr, ^3J = 4.1, ^3J = 4.3 Hz). ^3C NMR (100.61 Hz, CCl_4): δ 37.50 (CH_2Br), 44.39 (CH_2Se), 47.27 (SCHSe), 58.36 (SCHBr). ^{77}Se NMR (76.3 MHz, CCl_4): δ 415. Anal. Calcd for $C_4H_6Br_2SSe$: C, 14.79; H, 1.86; Br, 49.18. Found: C, 14.63; H, 1.89; Br, 48.94.
27. 2-Bromomethyl-1,3-thiaselenole (**3**). ^1H NMR (400 MHz, CCl_4): δ 6.62 (d, 1H, SeCH, ^3J = 6.1 Hz), 6.40 (d, 1H, SCH, ^3J = 6.1 Hz), 4.94 (t, 1H, SCHSe, ^3J = 7.8 Hz) 3.48 (m, 2H, CH_2Br, ^3J = 7.8 Hz). ^{77}Se NMR (76.3 MHz, CCl_4): δ 519.
28. The reaction in $CHCl_3$ at −55 °C. A solution of bromine (4.8 g, 30 mmol) in $CHCl_3$ (50 ml) was added to a mixture of selenium (2.37 g, 30 mmol) and $CHCl_3$ (50 mL) and the resulting mixture was stirred overnight at room temperature. Solutions of selenium dibromide and divinyl sulfide (2.58 g, 30 mmol) both in $CHCl_3$ (10 ml) were added simultaneously with stirring to a flask containing $CHCl_3$ (50 ml) at −55 °C. When about half of each reagent had been added (10 min from the start of the addition), $CDCl_3$ was added to a sample of the reaction mixture and this sample was analyzed by ^1H NMR (Table 1). Further samples were taken every hour and analyzed by ^1H NMR (Table 1).
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