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Reactions of selenium dichloride and dibromide with unsaturated ethers. Annulation of 2,3-dihydro-1,4-oxaselenine to the benzene ring

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ABSTRACT

Highly chemo-, regio-, and stereoselective syntheses of novel organoselenium compounds from selenium dichloride or dibromide and unsaturated ethers are described. The reactions of selenium dichloride with allyl and propargyl phenyl ethers afford either annulated products or bis-adducts depending on the conditions. The first examples of annulation of 3-chloromethyl- and 3-chloromethylene-2,3-dihydro-1,4-oxaselenine to the benzene ring are reported.

Selenium was considered a poison for many years, until Schwarz and Foltz identified it as a micronutrient for mammals and bacteria.[1] Since then, there has been growing interest in the synthesis of organoselenium compounds[2,3] due to their use in bioorganic chemistry, enzymology, and medicine. These compounds exhibit various types of biological activities[3] including antitumor, anti-inflammatory, antibacterial, and antifungal. Antioxidative and glutathione peroxidase-like[3] actions are among the most important. Many selenium-containing compounds, which possess biological activity, are heterocycles.[3] The selenium-containing heterocyclic compound, abselen has demonstrated high glutathione peroxidase-like activity.[3] The synthesis of novel selenium-containing compounds and especially heterocycles, possessing promising biologically active properties, represents an important challenge for organoselenium chemists.

Electrophilic selenium reagents play an important role in modern organic synthesis.[4] Recently, we studied reactions of the novel electrophilic reagents,[5–10] selenium dichloride and dibromide, with compounds bearing double[5–7] or triple bonds.[8,9] Although the presence of selenium dichloride and dibromide in the gas phase and in solutions was demonstrated in the literature, none of the selenium dihalides has been isolated as a pure compound. It was shown that in solution, selenium dichloride underwent disproportionation to Se_2Cl_2 and $SeCl_4$, whereas selenium dibromide was converted into Se_2Br_2 and bromine.[11] Nevertheless, we found that freshly prepared selenium dichloride and dibromide could be used in situ for selective synthesis of organoselenium compounds[5–10] including heterocycles.[5–8] The reactions of selenium dichloride and dibromide with dimethyl diethynyl silane leading to 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes represented the first syntheses of organoselenium compounds using selenium dihalides.[8] Efficient syntheses of novel 4-, 5-, and 6-membered selenium heterocycles via the addition of selenium dichloride and dibromide to divinyl sulfide,[5] divinyl selenide,[6] and divinyl sulfone[7] were elaborated.

The reaction of selenium dichloride with methoxybenzene afforded bis(4-methoxyphenyl)selenide.[10a] This reaction was the first example of aromatic electrophilic substitution with selenium dihalides. Although the methoxy group activated the benzene ring with respect to electrophilic substitution, heating the reaction mixture (reflux of a chloroform solution) was necessary to obtain a high yield (91%) of bis(4-methoxyphenyl)selenide.

Since selenium dichloride is able to participate in both electrophilic substitution and addition, this opens the possibility to combine two types of reactions in one molecule. In this work, we report our studies on the reactions of selenium dichloride and dibromide with propargyl phenyl, allyl phenyl, and vinyl organyl ethers. A novel approach to annulation of selenium heterocycles, which is based on the combination of addition and electrophilic substitution with selenium dichloride, is proposed. Selenium dichloride was prepared from selenium and sulfuryl chloride in carbon

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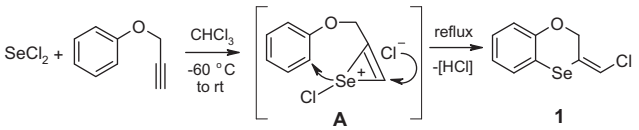
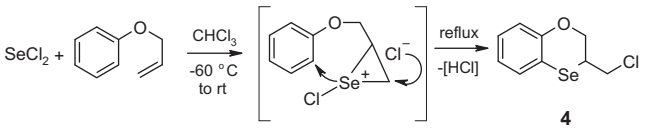


Scheme 1.



Scheme 3.

tetrachloride or chloroform, and selenium dibromide was obtained from selenium and bromine in the same solvents. The selenium dihalides were used in reactions immediately after their preparation.

The reaction of selenium dichloride with propargyl phenyl ether proceeded in a chemo-, regio-, and stereoselective manner to afford the novel heterocycle, *E*-3-chloromethylene-2,3-dihydro-1,4-benzoxaselenine (**1**),[12,13] in 82% yield (Scheme 1). The regio- and stereoselectivities of the reaction can be rationalized by a probable formation of intermediate selenirenium cation **A** followed by electrophilic aromatic substitution.

The reaction was carried out in chloroform using equimolar amounts of the reagents. The best yield (82%) was achieved when selenium dichloride and a solution of the ether were added separately and simultaneously to a flask with chloroform cooled to −60 °C followed by stirring at room temperature and heating the reaction mixture to reflux. Since the addition of selenium dichloride to the triple bond proceeds more easily compared with the electrophilic substitution, we suppose that the addition occurred at the temperature from −60 to 20 °C, whereas the electrophilic aromatic substitution required heating. It is noteworthy that reflux was necessary to perform the electrophilic aromatic substitution of methoxybenzene with selenium dichloride in high yield.[10a]

When we used excess propargyl phenyl ether, the reaction of selenium dichloride afforded the *anti*-Markovnikov product, *E,E*-bis(3-phenoxy-1-chloro-1-propen-2-yl) selenide (**2**),[14,15] in 94% yield. Selenium dichloride was added to a solution of propargyl phenyl ether (twofold molar excess) in CCl_4 at −20 °C followed by stirring at room temperature (Scheme 2). Thus, the reaction of selenium dichloride with propargyl phenyl ether was directed selectively either to annulated product **1** or to bis-adduct **2** depending on the conditions.

Under the conditions for the formation of heterocycle **1**, selenium dibromide did not give an annulated product. We assume that selenium dibromide possesses lower reactivity with respect to electrophilic aromatic substitution than selenium dichloride. Indeed, we failed to obtain bis(4-methoxyphenyl)selenide from selenium dibromide and methoxybenzene under the conditions for the preparation of this compound from selenium dichloride.[10a] However, when we used excess propargyl phenyl ether, the reaction with selenium dibromide led to the *anti*-Markovnikov product, *E,E*-bis(3-phenoxy-1-bromo-1-propen-2-yl) selenide (**3**)[14,16] in 96% yield (Scheme 2).

It should be emphasized that the reactions of selenium dihalides with propargyl phenyl ether are highly chemo-, regio-, and stereoselective and give the products **1**–**3** bearing a vinylseleno group in high yields. Vinylic selenides are powerful tools for organic synthesis serving as versatile precursors and synthons.[2,17] Besides the reactions of selenium electrophiles with alkynes, the addition of selenium nucleophiles to the triple bond, which often proceeds in a regio- and stereoselective manner, represents another general synthetic approach to vinylic selenides.[18]

The chemo- and regioselective synthesis of the novel annulated heterocycle, 3-chloromethyl-2,3-dihydro-1,4-benzoxaselenine (**4**),[12,19] in 90% yield was elaborated based on the reaction of selenium dichloride with allyl phenyl ether (Scheme 3).

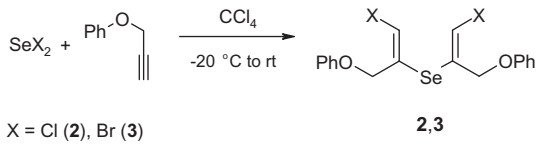
A solution of selenium dichloride and a solution of an equimolar amount of allyl phenyl ether in chloroform were added separately and simultaneously to a flask at low temperature (−60 °C) followed by stirring at room temperature and heating the reaction mixture to reflux to carry out the electrophilic aromatic substitution reaction.

Unlike the reaction of selenium dichloride with excess propargyl phenyl ether leading to *anti*-Markovnikov product **2**, selenium dichloride reacted with excess allyl phenyl ether to afford the Markovnikov product, bis(3-phenoxy-2-chloropropyl) selenide (**5**)[14,20] in 98% yield (Scheme 4).

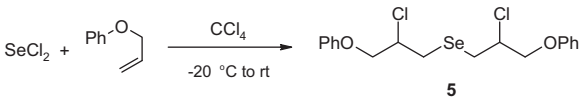
The question arose as to why the addition of selenium dichloride to excess allyl phenyl ether occurred at the terminal carbon atom of the allyl group to give Markovnikov product **5**, whereas formation of the annulated product **4** was accompanied by the addition of selenium dichloride to the central carbon atom of the allyl group? Assuming the formation of the final products is determined by two main factors: (a) the thermodynamic stability of the product and (b) the reversibility of the addition reaction, the addition of selenium dichloride to the double bond is reversible and this makes possible the interconversion of Markovnikov and *anti*-Markovnikov products. The addition of selenium dichloride to excess allyl phenyl ether gives the Markovnikov product since it is thermodynamically more stable. However, in the case of the annulation reaction, the addition occurs to the central carbon atom of the allyl group since six-membered oxaselenine **4** is thermodynamically preferred over the hypothetical seven-membered heterocycle, which could be formed if the addition takes place to the terminal carbon atom of the allyl group.

Similar to the reaction of selenium dibromide with propargyl phenyl ether, selenium dibromide reacted with allyl phenyl ether to give bis-adducts rather than an annulated product. However, the formation of both Markovnikov and *anti*-Markovnikov products **6** and **7** in a 1:2 ratio (92% total yield) was observed in the reaction of selenium dibromide with excess allyl phenyl ether (Scheme 5).[14,21]

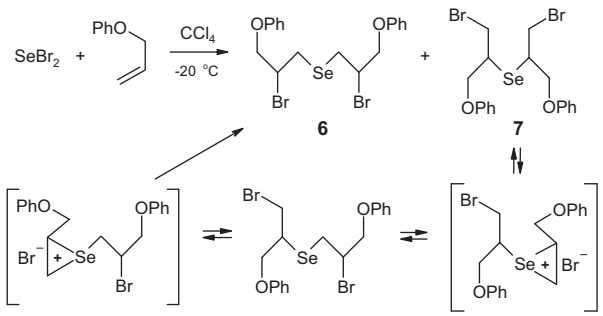
The bromine atom is larger than a chlorine atom and, therefore, steric hindrance is a more important factor for the addition of the bromide anion to the intermediate seleniranium cation. Attack by the bromine anion at the terminal unhindered carbon atom of the intermediate seleniranium cation leads to *anti*-Markovnikov product **7**, the alternative pathway leading to Markovnikov product **6** is less probable (Scheme 5). From this viewpoint, the probability of *anti*-Markovnikov products is higher for selenium



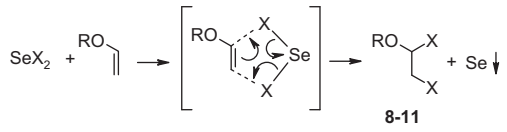
Scheme 2.



Scheme 4.



Scheme 5.



X = Cl (**8**,**10**), Br (**9**,**11**); R = Ph (**8**,**9**), CH=CH$_2$ (**10**,**11**)

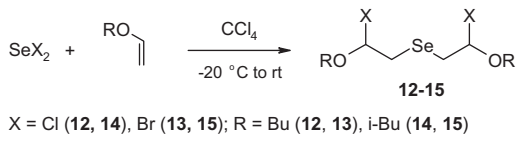
Scheme 6.

dibromide compared with selenium dichloride. We found that heating the mixture of products **6** and **7** led to conversion of *anti*-Markovnikov product **7** into Markovnikov product **6**. Refluxing a CCl_4 solution for 5 h led to a change in the ratio of products **6** and **7** from 1:2 to 5:1 (Scheme 5).

These data can be explained by the possible reversibility of the addition of selenium dibromide to allyl phenyl ether (Scheme 5). *Anti*-Markovnikov selenide **7** is a kinetic product, which is converted into the more stable thermodynamic Markovnikov product **6** upon heating.

Apart from allyl and propargyl phenyl ethers, we regarded vinyl phenyl ether as a probable candidate for the annulation reaction with selenium dichloride. This compound contains a highly reactive double bond along with the benzene ring activated with respect to electrophilic aromatic substitution. In spite of the fact that vinyl ethers are among the most reactive compounds in electrophilic addition, there are no data in the literature on reactions of selenium halides with vinyl ethers. We attempted the annulation of vinyl phenyl ether with selenium dichloride under the conditions for the synthesis of heterocycles **1** and **4**. However, the reaction gave predominantly products of halogenation of the vinyloxy group, 1,2-dihaloethyloxybenzenes **8** and **9**, rather than selenation products (Scheme 6).

A similar reaction took place in the case of divinyl ether: selenium dihalides acted as halogenation reagents to form products **10** and **11**. Surprisingly, in contrast to divinyl and vinyl phenyl ethers, alkyl vinyl ethers reacted with selenium dichloride and dibromide to produce selenation products. The addition of selenium dihalides to alkyl vinyl ether afforded bis(2-alkoxy-2-haloethyl) selenides **12**–**15**[22–25] in 80–98% yields (Scheme 7). The reaction of selenium dibromide proceeded with high selectivity to give selenides **13** and **15** in 98% and 93% yields, whereas the formation of some by-products was observed in the reaction with selenium dichloride. These reactions represent the first examples of selenation of vinylic ethers with selenium halides.



X = Cl (**12, 14**), Br (**13, 15**); R = Bu (**12**, **13**), i-Bu (**14**, **15**)

Scheme 7.

Why halogenation of the double bond predominates over the selenation for phenyl vinyl and divinyl ethers, whereas alkyl vinyl ethers give bis-adducts **12**–**15**, is not clear. The second substituent (phenyl, vinyl, or alkyl groups) imparts a considerable influence on the reactivity of vinyl organyl ethers in reactions with selenium dihalides. An unshared electron pair on the oxygen atom is able to stabilize the adjacent positive charge in the intermediate cation, which is formed by addition of selenium dihalides to the vinyloxy group. However, the vinyl group or the phenyl moiety is capable of conjugation with the unshared electron pair of the oxygen and thus decrease the ability of the oxygen atom to stabilize the adjacent positive charge. On the contrary, electron-donating alkyl groups increase the stabilization of the adjacent cation center. We suppose that the selenation proceeds as an electrophilic process via seleniranium intermediates, whereas concurrent halogenation by selenium dihalides is a molecular reaction (e.g., cycloaddition). Phenyl vinyl and divinyl ethers, which possess a conjugated electron system, react with selenium dihalides to form halogenated products and elemental selenium via probable [3+2] cycloaddition (Scheme 6). Examples of increasing the rate of cycloaddition reactions with an increase of conjugation are well known for the Diels–Alder reaction.[26] It is noteworthy that the reactivity of vinyl phenyl ether in the Diels–Alder reaction is considerably higher than alkyl vinyl ethers.[26b] It is relevant to mention that styrene, which possesses a double bond in conjugation with a phenyl ring, also reacted with selenium dihalides to form halogenation products.[27]

The structural assignments of novel compounds **1**–**7** and **12**–**15** were made using ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy including NOESY. The regiochemistry of the addition was defined by estimation of the values of the spin-spin coupling constants $^1J_{C-Se}$. Values within 50–150 Hz[28] correspond to direct coupling constants $^1J_{C-Se}$, and, therefore, this carbon atom is regarded as bonding with the selenium atom. For example, the carbon atom of the CH-group as well as the aromatic carbon atom not bearing protons revealed direct coupling constants $^1J_{C-Se}$ (68 and 104 Hz) in the ^{13}C NMR spectra of heterocycle **4**.[19] Therefore, the selenium atom is bonded with the central carbon atom of the allyl group and with the carbon atom of the benzene ring in heterocycle **4**. The ^{13}C NMR spectrum of compound **5** showed a direct coupling constant $^1J_{C-Se}$ (65 Hz) with the carbon atom of the CH_2-group.[20] This means that the addition takes place at the terminal carbon atom of the allyl group to afford the Markovnikov product. In the case of compounds **2**,[15] and **3**,[16] direct coupling constants $^1J_{C-Se}$ (115 and 117 Hz) with carbon atoms not bearing protons were observed. Thus, the addition takes place at the central carbon atom of the propargyl group to afford *anti*-Markovnikov products. The stereochemistry of compounds **1**–**3** was assigned based on the NOESY spectra. The selenides **5**–**7** and **12**–**15**, as compounds with two chiral carbon atoms, consist of two diastereomers (*d,l* and *meso*-forms) in a 1:1 ratio. The fragments $SeCH_2CHX$ of selenides **5**–**7** and **12**–**15** revealed different signals for each of the two diastereomers in the NMR spectra.

In conclusion, efficient syntheses of novel compounds **1**–**7** and **12**–**15**, which are potential candidates with respect to biological activity and as intermediates for preparation of functionalized organoselenium compounds, have been elaborated. A convenient approach to annulation of 2,3-dihydro-1,4-oxaselenine to the benzene ring by the reactions of selenium dichloride with allyl and propargyl phenyl ethers is proposed. Depending on the conditions, the reactions can be directed selectively either to annulation or to the formation of bis-adducts. The first examples of selenation of vinylic ethers with selenium halides are also described.

Acknowledgments

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12. *Typical procedure for the preparation of annulated products **1** and **4**.* A solution of $SeCl_2$ was prepared from Se (0.79 g, 10 mmol) and SO_2Cl_2 (1.35 g, 10 mmol) in $CHCl_3$ (20 ml). The solution of $SeCl_2$ thus prepared and a solution of allyl phenyl ether (1.34 g, 10 mmol) in $CHCl_3$ (20 ml) were added separately and simultaneously with stirring over 1 h to a flask containing $CHCl_3$ (80 ml) cooled to −60 °C. The cooling bath was removed and the mixture was allowed to warm to room temperature with stirring and then heated at reflux for 5 h. The solvent was evaporated and the crude product was purified by chromatography on a short column of silica gel (eluent: hexane) to give heterocycle **4** (2.21 g, 90% yield) as a yellow oil.
13. *E*-3-chloromethylene-2,3-dihydro-1,4-benzoxaselenine (**1**), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39 (s, 2H, CH_2O), 6.30 (s, 1H, =CHCl), 6.86–7.12 (m, 4H, C_6H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 66.87 (OCH_2), 113.97 (=CHCl), 115.01 (C_6H_4, SeC, $^1J_{SeC}$ = 65 Hz), 119.25 (C_6H_4), 123.57 (C_6H_4), 126.94 (C_6H_4), 128.49 (C_6H_4), 131.40 (SeC=, $^1J_{SeC}$ = 100 Hz), 154.65 (C_6H_4,CO). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 495. GC-MS: *m/z* (rel. intensity) 246 (66) $[M]^{+\cdot}$, 211 (28) $[M-Cl]^+$, 183 (10) $[M-C_2H_4Cl]^+$, 166 (84) $[M-Se]^{+\cdot}$, 144 (70) $[M-OSeH_2]^{+\cdot}$, 131 (100) $[OSeCl]^+$, 118 (35) $[SeC_3H_2]^{+\cdot}$, 91 (12) $[PhCH_2]^+$, 63 (92) $[C_2H_4Cl]^+$, 50 (25) $[CH_3Cl]^{+\cdot}$. Anal. Calcd for C_9H_7OClSe: C, 44.02; H, 2.87; Cl, 14.44; Se 32.15. Found: C, 43.67; H, 2.69; Cl, 14.82; Se, 31.87.
14. *Typical procedure for the preparation of selenides **2**,**3** and **5**–**7**.* A solution of $SeBr_2$ was prepared from Se (0.395 g, 5 mmol) and Br_2 (0.8 g, 5 mmol) in CCl_4 (20 ml). The solution of $SeBr_2$ thus prepared was added dropwise over 1 h to a solution of propargyl phenyl ether (1.32 g, 10 mmol) in CCl_4 (50 ml) cooled to −20 °C. After stirring for 2 h at −20 °C, the cooling bath was removed and the mixture was allowed to warm and stirred at room temperature for 1 h. The solvent was evaporated and the crude product was purified by chromatography on a short column of silica gel (eluent:hexane) to give selenide **3** (2.43 g, 96% yield) as a yellow oil.
15. *E,E*-bis(3-phenoxy-1-chloro-1-propen-2-yl) selenide (**2**), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.71 (s, 4H, OCH_2), 6.43 (s, 2H, =CHCl), 6.78 (m, 4H, C_6H_5), 6.85 (m, 2H, C_6H_5), 7.13 (m, 4H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 66.25 (OCH_2), 114.88 (C_6H_5, *ortho*), 121.49 (C_6H_5, *para*), 123.55 (=CHCl), 128.95 (SeC, $^1J_{SeC}$ = 115 Hz), 129.54 (C_6H_5, *meta*), 157.95 (C_6H_5, *ipso*). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 416. Anal. Calcd for $C_{18}H_{16}O_2Cl_2Se$: C, 52.20; H, 3.89; Cl, 17.12; Se 19.06. Found: C, 51.96; H, 3.94; Cl, 16.93; Se, 19.35.
16. *E,E*-bis(3-phenoxy-1-bromo-1-propen-2-yl) selenide (**3**), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (s, 4H, OCH_2), 6.59 (s, 2H, =CHCl), 6.77 (m, 4H, C_6H_5), 6.84 (m, 2H, C_6H_5), 7.13 (m, 4H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 68.54 (OCH_2), 111.40 (=CHBr), 114.94 (C_6H_5, *ortho*), 121.55 (C_6H_5, *para*), 129.56 (C_6H_5, *meta*), 130.61 (SeC, $^1J_{SeC}$ = 117 Hz), 157.89 (C_6H_5, *ipso*). Anal. Calcd for $C_{18}H_{16}O_2Br_2Se$: C, 42.97; H, 3.21; Br, 31.77; Se 15.70. Found: C, 43.14; H, 3.09; Br, 32.02; Se, 15.43.
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19. 3-Chloromethyl-2,3-dihydro-1,4-benzoxaselenine (**4**), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.50 (m, 1H, CHSe), 3.75 (dd, 1H, CH_2Cl, ^2J = 10.9, ^3J = 4.6 Hz), 3.92 (dd, 1H, CH_2Cl, ^2J = 10.9, ^3J = 11.2 Hz), 4.10 (dd, 1H, CH_2O, ^2J = 12.1, ^3J = 1.0 Hz), 4.65 (dd, 1H, CH_2O, ^2J = 12.1, ^3J = 3.1 Hz), 6.85 (m, 2H, C_6H_4) 6.95 (m, 1H, C_6H_4), 7.07 (m, 1H, C_6H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 35.54 (CHSe, $^1J_{C-Se}$ 68 Hz), 44.61 (CH_2Cl), 65.85 (CH_2O), 114.81 (C_6H_4, CSe, $^1J_{C-Se}$ 104 Hz), 119.48 (C_6H_4), 122.98 (C_6H_4), 126.56 (C_6H_4), 129.37 (C_6H_4), 154.07 (C_6H_4, CO). ^{77}Se NMR (76.3 MHz, $CDCl_3$): δ 279. GC–MS: *m/z* (rel intensity) 248 (86) $[M]^{+\cdot}$, 199 (22) $[M-CH_2Cl]^+$, 172 (38) $[C_6H_7OSe]^{+\cdot}$, 144 (90) $[C_2H_5ClSe]^{+\cdot}$, 63 (60) $[COCl]^+$, 39 (100) $[C_3H_3]^{+\cdot}$. Anal. Calcd for C_9H_9OClSe: C, 43.66; H, 3.66; Cl, 14.32; Se 31.89. Found: C, 43.34; H, 3.85; Cl, 13.98; Se, 32.24.
20. Bis(3-phenyloxy-2-chloropropyl) selenide (**5**), yellow oil (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (m, 2H, CH_2Se), 3.27 (m, 2H, CH_2Se), 4.21–4.40 (m, 6H, CH_2O, CHCl), 6.84 (m, 4H, C_6H_5), 6.91 (m, 2H, C_6H_5), 7.21 (m, 4H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 29.71, 29.75 (CH_2Se, $^1J_{C-Se}$ 65 Hz), 58.13, 58.20 (CHCl), 69.96, 70.02 (CH_2O), 114.79 (C_6H_5, *ortho*), 121.59 (C_6H_5, *para*), 129.55 (C_6H_5, *meta*), 158.02 (C_6H_5, *ipso*). Anal. Calcd for $C_{18}H_{20}O_2Cl_2Se$: C, 51.69; H, 4.82; Cl, 16.95; Se 18.88. Found: C, 51.46; H, 4.97; Cl, 17.14; Se, 19.07.
21. Bis(3-phenyloxy-2-bromopropyl) selenide (**6**) (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.21 (m, 2H, CH_2Se), 3.31 (m, 2H, CH_2Se), 3.82 (m, 2H, CHBr), 4.20 (m, 2H, CH_2O), 4.36 (m, 2H, CH_2O), 6.85 (m, 4H, C_6H_5), 6.91 (m, 2H, C_6H_5), 7.22 (m, 4H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 29.08, 29.14 (CH_2Se, $^1J_{C-Se}$ 66 Hz), 48.78, 48.82 (CHBr), 69.09, 69.17 (CH_2O), 113.92 (C_6H_5, *ortho*), 120.66 (C_6H_5, *para*), 128.67 (C_6H_5, *meta*), 156.93 (C_6H_5, *ipso*). Bis(3-phenyloxy-1-bromopropyl-2) selenide (**7**) (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.50 (m, 2H, CHSe), 3.91 (m, 4H, CH_2Br), 4.30 (m, 2H, CH_2O), 4.45 (m, 2H, CH_2O), 6.86 (m, 4H, C_6H_5), 6.92 (m, 2H, C_6H_5), 7.23 (m, 4H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 33.08, 33.15 (CH_2Br), 40.48, 40.71 (CHSe), 69.75, 69.81 (CH_2O), 113.85 (C_6H_5, *ortho*), 120.53 (C_6H_5, *para*), 128.67 (C_6H_5, *meta*), 157.16 (C_6H_5, *ipso*). Anal. Calcd for $C_{18}H_{20}O_2Br_2Se$: C, 42.63; H, 3.98; Br, 31.51; Se 15.57. Found: C, 42.44; H, 4.11; Br, 31.71; Se, 15.34. Attempted isolation of selenides **6** and **7** by chromatography on silica gel resulted in mixtures of products.
22. Bis(2-butoxy-2-chloroethyl) selenide (**12**), yield: 82% (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, 6H, CH_3, ^3J = 7.2 Hz), 1.43 (m, 4H, CH_2), 1.62 (m, 4H, CH_2), 3.05 (m, 2H, $SeCH_2$), 3.32 (m, 2H, $SeCH_2$), 3.50 (m, 2H, OCH_2), 3.90 (m, 2H, OCH_2), 5.64 (m, 2H, OCHCl). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.20 (CH_3), 19.16 (CH_2), 31.31 (CH_2), 33.01, 33.14 ($SeCH_2$, $^1J_{C-Se}$ 70 Hz), 70.98 (CH_2O), 98.01, 98.23 (OCHCl). Attempted purification of selenides **12**–**15** by chromatography on silica gel resulted in their decomposition.
23. Bis(2-butoxy-2-bromoethyl) selenide (**13**), yield: 98% (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, 6H, CH_3, ^3J = 7.2 Hz), 1.45 (m, 4H, CH_2), 1.65 (m, 4H, CH_2), 3.24 (m, 2H, $SeCH_2$), 3.50 (m, 2H, OCH_2), 3.64 (m, 2H, $SeCH_2$), 3.86 (m, 2H, OCH_2), 5.95 (m, 2H, OCHBr). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.94 (CH_3), 19.35 (CH_2), 30.77 (CH_2), 33.37, 33.68 ($SeCH_2$, $^1J_{C-Se}$ 70 Hz), 72.24 (CH_2O), 93.81, 94.12 (OCHBr).

24. Bis(2-isobutoxy-2-chloroethyl) selenide (**14**), yield: 80% (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, 12H, CH_3, ^{3}J = 6.2 Hz), 1.96 (m, 2H, CH), 3.30 (m, 2H, $SeCH_2$), 3.40 (m, 4H, OCH_2), 3.65 (m, 2H, $SeCH_2$), 5.63 (m, 2H, OCHCl). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 19.49 (CH_3), 28.12 (CH), 32.85 ($SeCH_2$, $^{1}J_{C-Se}$ 70 Hz), 76.92 (CH_2O), 97.80, 98.02 (OCHCl).
25. Bis(2-isobutoxy-2-bromoethyl) selenide (**15**), yield: 93% (dr = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, 12H, CH_3, ^{3}J = 6.2 Hz), 1.98 (m, 2H, CH), 3.29 (m, 2H, $SeCH_2$), 3.41 (m, 4H, OCH_2), 3.65 (m, 2H, $SeCH_2$), 5.94 (m, 2H, OCHBr). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 19.53 (CH_3), 27.94 (CH), 33.53, 33.63 ($SeCH_2$, $^{1}J_{C-Se}$ 70 Hz), 79.19 (CH_2O), 94.45, 94.75 (OCHCl).
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