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Regioselective One-Pot Synthesis of Novel Functionalized Organoselenium Compound by Bis-Alkoxyselenenylation of Alkenes with Selenium Dibromide and Alcohols

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Abstract: The one-pot efficient synthesis of novel functionalized organoselenium compound by bis-alkoxyselenenylation of alkenes with selenium dibromide and alcohols was developed. The reaction of the selenium dibromide with cyclopentene or cyclohexene in the system alcohol/sodium bicarbonate/methylene chloride at room temperature afforded bis(2-alkoxycycloalkyl) selenides in 90–99% yields. The regioselective and efficient method for bis-alkoxylation of terminal alkenes was developed based on the addition of selenium dibromide with 1-alkenes in acetonitrile followed by refluxing of addition products in alcohols in the presence of traces of sulfuric acid. This method made it possible to selectively obtain bis(2-alkoxyalkyl) selenides in 94–98% yields.

Keywords: alcohols; alkenes; selenium dibromide; alkoxyselenenylation; selenium dihalides; cycloalkenes

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1. Introduction

Functionalized organoselenium compounds exhibit various types of biological activities, including antibacterial, antitumor, antifungal, anti-inflammatory, neuroprotective and glutathione peroxidase-like actions [1–17]. The development of regioselective and efficient methods for functionalization plays an important role in modern organoselenium chemistry [18–23]. The application of novel selenium-containing reagents that make it possible to carry out functionalization reactions in an efficient and regioselective fashion is an important task.

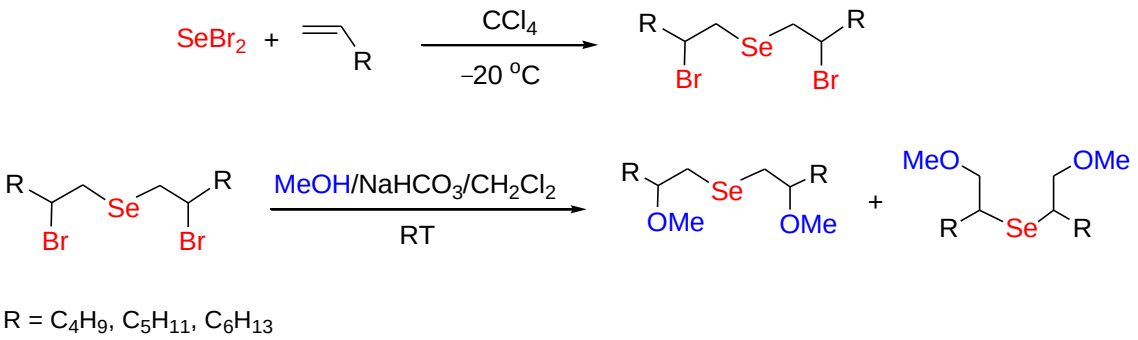
In the beginning of this century, we successfully applied selenium dihalides for the synthesis of organoselenium compounds [24–27]. Selenium dichloride can be easily obtained from elemental selenium and sulfuryl chloride. We showed the possibility of the selenium dibromide generation from elemental selenium and bromine [24]. Although selenium dichloride and dibromide undergo slow disproportionation in solutions, it has been demonstrated that these reagents, involved in reactions in situ immediately after the generation, can be successfully applied for regio- and stereoselective introduction of the selenium atom into organic molecules [25–46].

It has been found that the reactions of selenium dichloride and dibromide with acetylene proceed in a stereoselective fashion as *anti*-addition affording bis(*E*-2-halovinyl) selenides [28]. The addition of selenium dihalides to terminal acetylenes occurs in a regio- and stereoselective mode giving anti-Markovnikov adducts with (*E*)-configuration [30].

The addition of selenium dichloride and dibromide to double bonds was studied in the reactions with linear terminal 1-alkenes giving bis(2-haloalkyl) selenides [39,40] and divinylic substrates affording novel selenium heterocyclic compounds [31–34]. The stereochemistry of the addition of selenium dihalides to the double bond in these reactions was not examined.

The transannular addition of selenium dihalides to cis,cis-1,5-cyclooctadiene afforded 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes in high yields [41–43]. 2,6-Dichloro-9-selenabicyclo[3.3.1] nonane was used for studying the anchimeric assistance effect of selenium in comparison with the effect of sulfur and nitrogen atoms. It has been established that the anchimeric assistance effect of the selenium atom is more than two orders of magnitude greater than the effect of the sulfur and nitrogen atoms [41]. These results showed that β-halogen leaving groups are strongly activated by the selenium atom and can easily be replaced by other groups in nucleophilic substitution reactions to form functionalized organoselenium compounds. Examples of regio- and stereoselective chemistry of selenium dihalides have recently been shown [44–46].

Previously, we studied the methanolysis reaction of the selenium dibromide adducts with linear terminal alkenes (1-hexene, 1-heptene, and 1-octene). It was found that nucleophilic substitution of bromine in bis(2-bromoalkyl) selenides by methanol in the system $MeOH/NaHCO_3/CH_2Cl_2$ (or $CHCl_3$) at room temperature led to a mixture of Markovnikov-type bis(2-methoxyalkyl) selenides and anti-Markovnikov bis(1-methoxyalk-2-yl) selenides (Scheme 1) [39,40]. The latter were the minor products (17–28% yields) and the Markovnikov-type adducts were the major products (51–55% yields). These products, bis-(2-methoxyalkyl) selenides and bis-(1-methoxyalk-2-yl) selenides, were isolated by column chromatography and their spectral characteristics were described [39,40].



Scheme 1. The methanolysis reaction of the selenium dibromide adducts with linear terminal alkenes (1-hexene, 1-heptene, and 1-octene) in the system $MeOH/NaHCO_3/CH_2Cl_2$.

In the last few decades, the methods of functionalization based on selenium reagents have acquired particular importance as valuable tools for modern organic synthesis and have been widely explored [18–23,47–63].

The ring-opening reactions of epoxides with selenium nucleophiles, which gave impetus to the use of chalcogens in the nucleophilic ring-opening reactions, continue to be of great synthetic importance. A series of methods has been developed for transformation of strained heterocycles into functionalized organoselenium compounds [52–57]. The nucleophilic ring-opening reactions of epoxides and aziridines were proved to be a method of choice for the synthesis of β-hydroxy- and β-aminoorganylselenides. The selenium-mediated ring-opening reactions are widely used in organic synthesis including the total synthesis of (−)-galanthamine [58], (−)-morphine [58], lycorine [59], and plumisclerin [60].

The oxyselenenylation reactions of selenium-containing reagents with alkenes proceeding with the introduction of an oxy group (for example, the alkoxy function) and the selenium atom are also widely used in organic synthesis [48–51,61–63]. After transformations, the selenium atom can be removed from the molecule. Catalytic asymmetric oxyselenenylation–elimination reactions using chiral selenium compounds [61] and asymmetric oxyselenenylation–deselenenylation reactions of alkenes induced by camphor diselenide and ammonium persulfate with the formation of enantiomerically enriched allylic alcohols and ethers were developed [63].

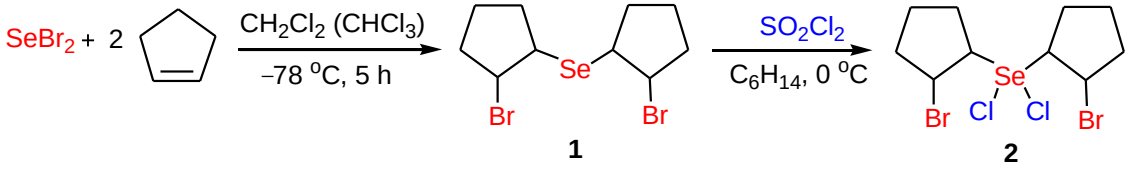
The application of selenium dihalides in alkoxyselenenylation reactions can provide the introduction of two functional groups simultaneously along with the selenium atom. However, opportunities of these bis-functionalization reactions have not yet been realized.

2. Results and Discussion

The aim of this work is to develop the selective bis-alkoxyselenenylation reactions for the simultaneous introduction of the selenium atom and two alkoxy functions in molecules of cycloalkenes (cyclopentene and cyclohexene) and terminal alkenes (1-hexene, 1-heptene, and 1-octene).

The reaction of selenium halides with acetylenes proceeded as *anti*-addition. To determine the stereochemistry of the addition of selenium halides to alkenes is more difficult. The stereochemistry can be defined based on X-ray analysis data if the products are crystalline compounds.

We succeeded in the synthesis of crystalline product, dichloro[bis(2-bromocyclopentyl)]-λ^4-selane (**2**), and its structural studying by X-ray diffraction analysis. The product **2** with the tetravalent selenium atom was prepared by the addition of selenium dibromide to cyclopentene followed by the halogenation reaction of the obtained adduct **1** with sulfuryl chloride (Scheme 2).



Scheme 2. Synthesis of dichloro[bis(2-bromocyclopentyl)]-λ^4-selane (**2**).

The data of X-ray diffraction analysis showed that compound **2** has *trans,trans*-configuration (Figure 1) and therefore the addition of selenium dibromide to the double bond proceeds as an *anti*-process. The selenium-chlorine bonds in compound **2** represent hypervalent bonds; the Se–Cl bond length is 1.2134 Å and the Cl–Se–Cl angle is approximately 174°.

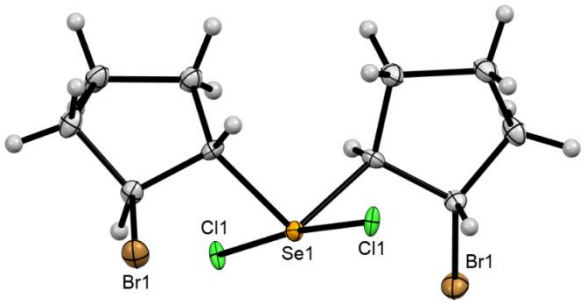
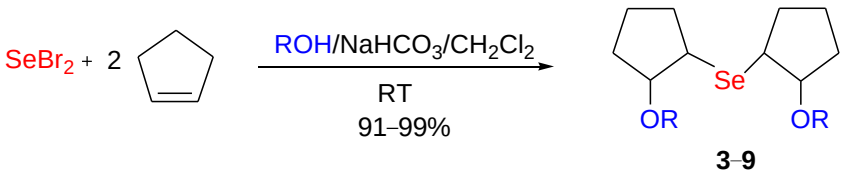


Figure 1. ORTEP molecular structure of *trans,trans*-dichloro[bis(2-bromocyclopentyl)]-λ^4-selane (**2**) at 50% thermal ellipsoid probability.

The efficient and convenient method for bis-alkoxyselenenylation of cycloalkenes was developed based on the reaction of selenium dibromide with cyclopentene and cyclohexene in the system alcohol/sodium bicarbonate/methylene chloride at room temperature (Scheme 3).



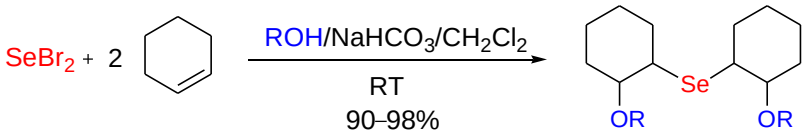
R = Me (**3**), Et (**4**), Pr (**5**), *i*-Pr (**6**), Bu (**7**), *i*-Bu (**8**), Hex (**9**)

Scheme 3. The synthesis of bis(2-alkoxycyclopentyl) selenides **3**–**9** from selenium dibromide, cyclopentene, and alcohols.

A solution of selenium dibromide, prepared from elemental selenium and bromine, was added to a mixture of methylene chloride and alcohol (a 5:1 volume ratio) containing sodium bicarbonate.

A broad range of alkanols from methanol to hexanol was involved in this reaction. The bicyclic products, bis(2-alkoxycyclopentyl) selenides **3**–**9**, were obtained in 90–98% yields. A slight decrease in the yield of products was observed with increasing the carbon chain length of the alcohols going from methanol (the most active nucleophile in this series, a 99% yield) to hexanol (a 91% yield). It is worthy to note that the reaction proceeded with high selectivity and compounds **3**–**9** did not require additional purification by column chromatography or by other methods.

The efficient and selective method for the preparation of bis(2-alkoxycyclohexyl) selenides **10**–**13** based on selenium dibromide, cyclohexene, and alcohols was developed (Scheme 4). The bis-alkoxyselenenylation reaction of selenium dibromide with cyclohexene was carried out in the system alcohol/sodium bicarbonate/methylene chloride at room temperature in a similar manner as the reaction of selenium dibromide with cyclopentene.



10–**13**

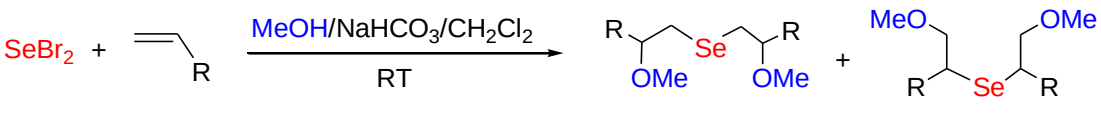
R = Me (**10**), Et (**11**), Pr (**12**), *i*-Bu (**13**)

Scheme 4. The synthesis of bis(2-alkoxycyclohexyl) selenides **10**–**13** from selenium dibromide, cyclohexene, and alcohols.

When going from methanol (a 98% yield of the product **10**) to isobutanol (a 90% yield of the product **13**), the slight decrease in the yield of products was also observed with an increase in the carbon chain length of the alcohols.

It is worthy to note that selenium dichloride can also be used in bis-alkoxyselenenylation reactions but yields of the desired products in this case are about half as low under the same conditions.

Terminal alkenes (1-hexene, 1-heptene, and 1-octene) were also involved in the bis-alkoxyselenenylation reaction. When the conditions for the reactions of cycloalkenes (Schemes 3 and 4) were used for bis-methoxyselenenylation of 1-alkenes, a mixture of addition products of Markovnikov (**14**–**16**) and anti-Markovnikov (**17**–**19**) types (a 5:2–3 ratio) was obtained in 84–90% total yields (Scheme 5). The same products, bis(2-methoxyalkyl) selenides **14**–**16** and bis(1-methoxyalk-2-yl) selenides **17**–**19**, were formed in the methanolysis reaction of the addition products of selenium dibromide to 1-alkenes (Scheme 1). The methanolysis reaction was studied in this laboratory previously and the Markovnikov **14**–**16** and anti-Markovnikov **17**–**19** types of products were isolated by column chromatography [39,40].

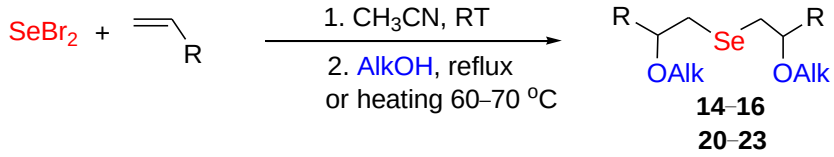


14–**16** **17**–**19**

R = C_4H_9 (**14**, **17**); C_5H_{11} (**15**, **18**); C_6H_{13} (**16**, **19**)

Scheme 5. The bis-methoxyselenenylation of 1-alkenes in the system alcohol/sodium bicarbonate/methylene chloride at room temperature.

The regioselective and efficient method for bis-alkoxyselenenylation of terminal alkenes was developed based on the reaction of the selenium dibromide with 1-alkenes in acetonitrile followed by the addition of alcohol and refluxing of the reaction mixture. The use of these conditions allows to direct the reaction to the formation of Markovnikov addition products and to obtain compounds **14**–**16** and ethoxy derivatives **20**–**22** in 88–94% yields (Scheme 6).



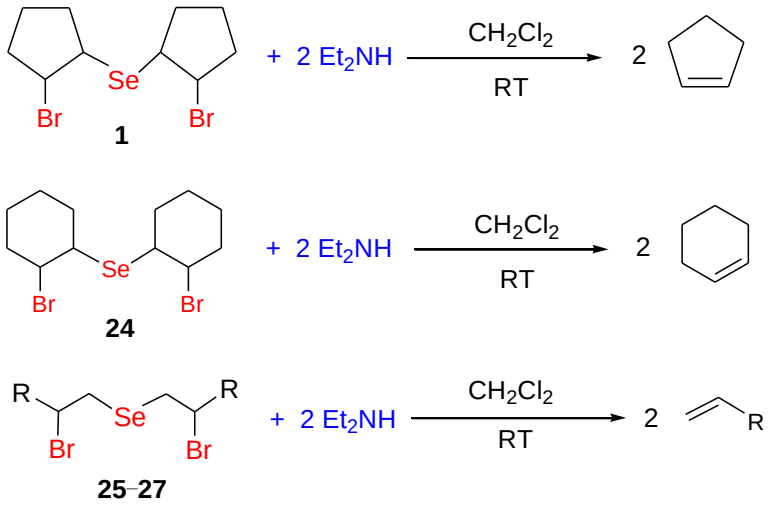
R = C_4H_9 (**14**, **20**); C_5H_{11} (**15**, **21, 23**); C_6H_{13} (**16**, **22**);
Alk = Me (**14-16**); Et (**20-22**); i-Bu (**23**)

Scheme 6. The selective synthesis of bis(2-alkoxyalkyl) selenides **14**–**16** and **20**–**23** from selenium dibromide, 1-alkenes and alcohols.

However, it was established that products **14**–**16** and ethoxy and isobutoxy derivatives **20**–**23,** which did not require additional purification, can be obtained in high yields by refluxing of the reaction mixture in methanol or heating in ethanol or isobutanol. It was also found that this reaction proceeded cleaner if the alcohol (methanol, ethanol or isobutanol) contained traces of an acid. According to this method, acetonitrile was removed from the reaction mixture on a rotary evaporator and alcohol containing traces of sulfuric acid was added followed by refluxing of the mixture in methanol or heating at 60–70 °C in the case of ethanol or isobutanol (Scheme 6). The use of this method made it possible to selectively obtain pure products **14**–**16** and ethoxy and isobutoxy derivatives **20**–**23** in 94–98% yields.

We attempted to use unsaturated alcohols, allylic and propargylic alcohols, in the bis-alkoxyselenenylation reaction. Under the conditions similar to the above processes (Schemes 3, 4 and 6), the reactions with allylic and propargylic alcohols proceeded in a special way with the formation of a mixture of products. The formation of the expected products, analogues of compounds **3**–**16**, was not observed in appreciable amounts.

We also started studying the possibility of carrying out the aminoselenenylation reaction of alkenes with selenium dibromide and amines. Preliminary experiments were conducted using diethylamine. The analysis showed the formation of starting alkenes and cycloalkenes in high yields (85–92%) along with a selenium-containing residue as a result of the reactions of adducts **1** and **24**–**27** with diethylamine both in the presence of $NaHCO_3$ and in the absence of a base (Scheme 7). The same results were obtained by carrying out the reactions of adducts **1** and **24**–**27** with diethylamine in $CDCl_3$ or CD_2Cl_2 followed by the ^{1}H- and ^{13}C-NMR analysis.



R = C_4H_9 (**25**); C_5H_{11} (**26**); C_6H_{13} (**27**)

Scheme 7. The reactions of adducts **1** and **24**–**27** with diethylamine.

The structural assignments of the synthesized compounds were made using ^{1}H- and ^{13}C-NMR spectroscopy, including the ^{13}C-NMR *J*mod method, and were confirmed by

elemental analysis. The obtained products consist of two diastereomers (*dl* and *meso* forms) approximately in an equimolar ratio. Two diastereomers manifest themselves in the NMR spectra. Two closely spaced signals of the carbon atoms of the $SeCH_2CHOR$ and SeCHCHOR groups, which correspond to two diastereomers, are observed in the ^{13}C-NMR spectra of the synthesized compounds**.**

The obtained products represent a novel family of organoselenium compounds with promising biological activity.

3. Materials and Methods

3.1. General Information

X-ray diffraction experiments were carried out on a Bruker D8 Venture Photon 100 CMOS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). X-Ray crystallographic data for compound **2** (CCDC 2207651) are shown in Supplementary Info. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (accessed on 1 October 2022).

^1H (400.1 MHz) and ^{13}C (100.6 MHz) NMR spectra (the spectra can be found in Supplementary Materials) were recorded on a Bruker DPX-400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) in 5–10% solution in $CDCl_3$. ^1H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm), relative to the residual solvent peak of $CDCl_3$ (δ = 7.27 and 77.16 ppm in ^1H and ^{13}C-NMR, respectively).

Elemental analysis was performed on a Thermo Scientific Flash 2000 Elemental Analyzer (Thermo Fisher Scientific Inc., Milan, Italy).

The organic solvents were dried and distilled according to standard procedures.

3.2. The Synthesis of Compound **2**

trans,trans-Dichloro[bis(2-bromocyclopentyl)]-λ^4-selane (**2**). A solution of selenium dibromide (2 mmol) was prepared from selenium (0.16 g, 2 mmol) and bromine (0.32 g, 2 mmol) in methylene chloride (2 mL). The obtained solution of selenium dibromide (2 mmol) was added dropwise to a stirred solution of cyclopentene (0.3 g, 4.4 mmol) in methylene chloride (15 mL) at −78 °C. A cooling bath was removed and the mixture was stirred for 5 h at room temperature. The solvent was removed on a rotary evaporator and the residue was dissolved in hexane (10 mL). A solution of sulfuryl chloride (0.27 g, 2 mmol) in hexane (2 mL) was added dropwise to a cooled to −0 °C solution of obtained bis(2-bromocyclopentyl) selenide **1** in hexane (10 mL) and the mixture was stirred at −0 °C (an ice bath) for 4 h and then left overnight (16 h) in the refrigerator at 4 °C. Next day, the formed precipitate was filtered off, washed with cold hexane and dried in a vacuum to give the product **2** as a white-yellow powder, mp = 112–114 °C (decomp.). Yield: 0.723 g (81%). Crystals suitable for X-ray studies were obtained by recrystallization from chloroform. X-ray analysis data for the product **2** (CCDC 2207651) are given in Supplementary Materials.

3.3. The Synthesis of Bis(2-alkoxycyclopentyl) Selenides **3**–**9**

Bis(2-methoxycyclopentyl) selenide (**3**). A solution of selenium dibromide (1.5 mmol) was prepared from selenium (0.12 g, 1.5 mmol) and bromine (0.24 g, 1.5 mmol) in methylene chloride (2 mL). The obtained solution of selenium dibromide (1.5 mmol) was added dropwise to a stirred solution of cyclopentene (0.24 g, 3.5 mmol) in methylene chloride (10 mL). The mixture was stirred for 6 h at room temperature and then methanol (2 mL) and $NaHCO_3$ (0.3 g, 3.6 mmol) were added. The mixture was stirred overnight (14 h) at room temperature. The mixture was filtered in order to remove sodium bicarbonate, which was rinsed with methylene chloride (3 mL). Solvents were removed from the filtrate on a rotary evaporator and the residue was dried in a vacuum to give the product as a light-yellow oil. Yield: 0.412 g (99%).

^1H NMR (400 MHz, $CDCl_3$): 1.60–1.75 (m, 8H, CH_2), 1.92–1.99 (m, 2H, CH_2), 2.16–2.25 (m, 2H, CH_2), 3.29–3.37 (m, 2H, CHSe), 3.32 (s, 6H, CH_3), 3.77–3.82 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$): 22.7 (CH_2), 22.8 (CH_2), 30.4 (CH_2), 30.5 (CH_2), 32.0 (CH_2), 32.3 (CH_2), 42.2 (CHSe, J^1_{Se-C} = 66.9 Hz), 42.3 (CHSe, J^1_{Se-C} = 67.2 Hz), 56.5 (CH_3O), 56.5 (CH_3O), 88.9 (CHO), 89.1 (CHO).

Anal. calcd for $C_{12}H_{22}O_2Se$ (277.26): C 51.98, H 8.00, Se 28.48%. Found: C 52.07, H 8.05, Se 28.61%.

Bis(2-ethoxycyclopentyl) selenide (**4**) was obtained in a 98% yield under similar conditions as the product **3**.

^{1}H NMR (400 MHz, $CDCl_3$): 1.19 (t, 6H, CH_3, *J* = 7.0 Hz), 1.58–1.79 (m, 8H, CH_2), 1.93–2.01 (m, 2H, CH_2), 2.17–2.27 (m, 2H, CH_2), 3.29–3.34 (m, 2H, CHSe), 3.46–3.53 (m, 4H, CH_2O), 3.86–3.91 (m, 2H, CHO).

^{13}C NMR (100 MHz,$CDCl_3$):15.7 (CH_3), 15.7 (CH_3), 23.1 (CH_2), 23.2 (CH_2), 31.3 (CH_2), 3!.4 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 43.0 (CHSe, J^1_{Se-C} = 67.0 Hz), 64.6 (CH_2O), 64.7 (CH_2O), 87.5 (CHO), 87.7 (CHO).

Anal. calcd for $C_{14}H_{26}O_2Se$ (305.31): C 55.08, H 8.58, Se 25.86%. Found: C 54.98, H 8.57, Se 26.14%.

Bis(2-propoxycyclopentyl) selenide (**5**) was obtained in a 96% yield under similar conditions as the product **3**.

H NMR (400 MHz, $CDCl_3$): 0.89 (t, 6H, CH_3, *J* = 7.3 Hz), 1.50–1.59 (m, 4H, CH_2), 1.61–1.76 (m, 8H, CH_2), 1.90–2.00 (m, 2H, CH_2), 2.15–2.23 (m, 2H, CH_2), 3.27–3.32 (m, 2H, CHSe), 3.34–3.42 (m, 4H, CH_2O), 3.82–3.88 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$):10.6 (CH_3), 23.0 (CH_2), 23.1 (CH_2), 23.3 (CH_2), 31.1 (CH_2), 3!.3 (CH_2), 32.3 (CH_2), 32.6 (CH_2), 42.9 (CHSe, J^1_{Se-C} = 66.3 Hz), 71.0 (CH_2O), 71.1 (CH_2O), 87.5 (CHO), 87.7 (CHO).

Anal. calcd for $C_{16}H_{30}O_2Se$ (333.37): C 57.65, H 9.07, Se 23.69%. Found: C 57.58, H 9.02, Se 23.65%.

Bis(2-isopropoxycyclopentyl) selenide (**6**) was obtained in a 91% yield under similar conditions as the product **3**.

^{1}H NMR (400 MHz, $CDCl_3$): 1.13–1.16 (m, 12H, CH_3), 1.56–1.78 (m, 8H, CH_2), 1.92–2.01 (m, 2H, CH_2), 2.18–2.25 (m, 2H, CH_2), 3.23–3.28 (m, 2H, CHSe), 3.62–3.70 (m, 2H, CH_2O), 3.91–3.98 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$):22.9 (CH_3), 22.9 (CH_3), 23.0 (CH_2), 23.1 (CH_2), 3!.9 (CH_2), 32.1 (CH_2), 32.4 (CH_2), 32.6 (CH_2), 43.6 (CHSe, J^1_{Se-C} = 68.0 Hz), 43.7 (CHSe, J^1_{Se-C} = 67.7 Hz), 69.9 ($CH_3\underline{C}HO$), 70.2 ($CH_3\underline{C}HO$), 84.9 ($CH_2\underline{C}HO$), 85.1 ($CH_2\underline{C}HO$).

Anal. calcd for $C_{16}H_{30}O_2Se$ (333.37): C 57.65, H 9.07, Se 23.69%. Found: C 57.61, H 9.05, Se 23.76%.

Bis(2-butoxycyclopentyl) selenide (**7**) was obtained in a 95% yield under similar conditions as the product **3**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.91 (t, 6H, CH_3, *J* = 7.1 Hz), 1.31–1.41 (m, 4H, CH_2), 1.48–1.57 (m, 4H, CH_2), 1.59–1.78 (m, 8H, CH_2), 1.92–2.00 (m, 2H, CH_2), 2.16–2.26 (m, 2H, CH_2), 3.29–3.33 (m, 2H, CHSe), 3.40–3.45 (m, 4H, CH_2O), 3.83–3.90 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$):14.0 (CH_3), 19.5 (CH_2), 23.0 (CH_2), 23.1 (CH_2) 31.1 (CH_2), 3!.3 (CH_2), 32.2 (CH_2), 32.3 (CH_2), 32.6 (CH_2), 42.9 (CHSe, J^1_{Se-C} = 66.5 Hz), 42.9 (CHSe, J^1_{Se-C} = 66.5 Hz), 69.1 (CH_2O), 69.1 (CH_2O), 87.5 (CHO), 87.8 (CHO).

Anal. calcd for $C_{18}H_{34}O_2Se$ (361.42): C 59.82, H 9.48, Se 21.85%. Found: C 59.85, H 9.51, Se 22.10%.

Bis(2-isobutoxycyclopentyl) selenide (**8**) was obtained in a 93% yield under similar conditions as the product **3**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (d, 12H, CH_3, *J* = 6.7 Hz), 1.58–1.76 (m, 8H, CH_2), 1.76–1.85 (m, 2H, $C\underline{H}CH_3$), 1.93–1.99 (m, 2H, CH_2), 2.16–2.25 (m, 2H, CH_2), 3.14–3.21 (m, 4H, CH_2O), 3.28–3.33 (m, 2H, CHSe), 3.82–3.87 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$):19.4 (CH_3), 19.4 (CH_3), 22.8 (CH_2), 28.6 ($\underline{C}HCH_3$), 28.6 ($\underline{C}HCH_3$), 30.8 (CH_2), 31.0 (CH_2), 32.0 (CH_2), 32.3 (CH_2), 42.6 (CHSe, J^1_{Se-C} = 66.7 Hz), 42.7 (CHSe, J^1_{Se-C} = 66.8 Hz), 76.0 (CH_2O), 76.0 (CH_2O), 87.5 (CHO), 87.7 (CHO).

Anal. calcd for $C_{18}H_{34}O_2Se$ (361.42): C 59.82, H 9.48, Se 21.85%. Found: C 59.89, H 9.50, Se 22.03%.

Bis(2-hexylcyclopentyl) selenide (**9**) was obtained in a 91% yield under similar conditions as the product **3**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.89 (t, 6H, CH_3, J = 6.7 Hz), 1.25–1.37 (m, 12H, CH_2), 1.51–1.58 (m, 4H, CH_2), 1.60–1.79 (m, 8H, CH_2), 1.94–2.01 (m, 2H, CH_2), 2.14–2.25 (m, 2H, CH_2), 3.27–3.55 (m, 2H, CHSe), 3.38–3.44 (m, 4H, CH_2O), 3.84–3.92 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$):14.2 (CH_3), 22.8 (CH_2), 23.1 (CH_2), 26.1 (CH_2), 30.1 (CH_2), 30.2 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 31.8 (CH_2), 32.4 (CH_2), 32.6 (CH_2), 42.9 (CHSe), 69.4 (CH_2O), 69.5 (CH_2O), 87.5 (CHO), 87.8 (CHO).

Anal. calcd for $C_{22}H_{42}O_2Se$ (417.53): C 63.29, H 10.14, Se 18.91%. Found: C 63.32, H 10.17, Se 19.20%.

3.4. The Synthesis of Bis(2-alkoxycyclohexyl) Selenides **10**–**13**

Bis(2-methoxycyclohexyl) selenide (**10**). A solution of selenium dibromide (1 mmol) was prepared from selenium (0.079 g, 1 mmol) and bromine (0.16 g, 1 mmol) in methylene chloride (1 mL). The obtained solution of selenium dibromide (1 mmol) was added dropwise to a stirred solution of cyclohexene (0.18 g, 2.2 mmol) in methylene chloride (10 mL). The mixture was stirred for 8 h at room temperature and then methanol (2 mL) and $NaHCO_3$ (0.25 g, 3 mmol) were added. The mixture was stirred overnight (14 h) at room temperature. The mixture was filtered in order to remove sodium bicarbonate, which was rinsed with methylene chloride (2 mL). Solvents were removed from the filtrate on a rotary evaporator and the residue was dried in a vacuum to give the product as a light-yellow oil. Yield: 0.299 g (98%).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.07–1.20 (m, 3H, CH_2), 1.29–1.39 (m, 1H, CH_2), 1.40–1.48 (m, 1H, CH_2), 1.49–1.57 (m, 1H, CH_2), 1.82–1.92 (m, 1H, CH_2), 1.93–2.03 (m, 1H, CH_2), 2.90–2.98 (m, 1H, CHSe), 2.99–3.07 (m, 1H, CHO), 3.19 (m, 3H, CH_3O).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.58, 22.73 (CH_2), 24.83, 25.02 (CH_2), 29.41 (CH_2), 31.11, 31.34 (CH_2), 41.97 (CHSe, $^1J_{CSe}$ 67 Hz), 42.31 (CHSe, $^1J_{CSe}$ 67 Hz), 55.84, 55.99 (CH_3O), 82.97, 83.08 (CHO).

Anal. calcd for $C_{14}H_{26}O_2Se$ (305.31): C 55.08, H 8.58, Se 25.86%. Found: C 54.79, H 8.75, Se 26.07%.

Bis(2-ethoxycyclohexyl) selenide (**11**) was obtained in a 95% yield under similar conditions as the product **10**.

^{1}H NMR (400 MHz, $CDCl_3$): 1.17–1.22 (m, 6H, CH_3), 1.25–1.36 (m, 6H, CH_2CH_2), 1.45–1.50 (m, 2H, CH_2CH_2), 1.58–1.74 (m, 4H, CH_2CH_2), 1.98–2.20 (m, 4H, C$\underline{H}_2$CH), 3.07–3.18 (m, 2H, CHSe), 3.21–3.29 (m, 2H, CHO), 3.43–3.66 (m, 4H, CH_2O).

^{13}C NMR (100 MHz,$CDCl_3$): 15.8 (CH_3), 15.9 (CH_3), 23.6 (CH_2), 23.8 (CH_2), 25.7 (CH_2), 26.0 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 32.2 (CH_2), 32.4 (CH_2), 42.8 (CHSe, $J^1_{Se\text{-}C}$ = 67.2 Hz), 43.9 (CHSe, $J^1_{Se\text{-}C}$ = 65.6 Hz), 64.3 (CH_2O), 64.5 (CH_2O), 82.4 (CHO), 82.9 (CHO).

Anal. calcd for $C_{16}H_{30}O_2Se$ (333.37): C 57.65, H 9.07, Se 23.69%. Found: C 57.72, H 9.09, Se 23.88%.

Bis(2-propoxycyclohexyl) selenide (**12**) was obtained in a 93% yield under similar conditions as the product **10**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.84–0.89 (m, 6H, CH_3), 1.18–1.30 (m, 6H, C$\underline{H}_2CH_2CH$), 1.39–1.67 (m, 10H, C$\underline{H}_2CH_2CH$, C$\underline{H}_2CH$, C$\underline{H}_2CH_3$), 1.92–2.10 (m, 4H, C$\underline{H}_2CH$), 3.03–3.14 (m, 2H, CHSe), 3.15–3.23 (m, 2H, CHO), 3.29–3.49 (m, 4H, CH_2O).

^{13}C NMR (100 MHz, $CDCl_3$): 10.7 (CH_3), 10.7 (CH_3), 23.3 (CH_2), 23.4 ($\underline{C}H_2CH_3$), 23.5 (CH_2), 25.5 (CH_2), 25.8 (CH_2), 30.8 (CH_2), 31.0 (CH_2), 31.9 (CH_2), 32.1 (CH_2), 42.6 (CHSe, $J^1_{Se\text{-}C}$ = 69.2 Hz), 43.6 (CHSe, $J^1_{Se\text{-}C}$ = 64.8 Hz), 70.6 (CH_2O), 70.8 (CH_2O), 82.2 (CHO), 82.8 (CHO).

Anal. calcd for $C_{18}H_{34}O_2Se$ (361.42): C 59.82, H 9.48, Se 21.85%. Found: C 59.97, H 9.54, Se 22.04%.

Bis(2-isobutoxycyclohexyl) selenide (**13**) was obtained in a 90% yield under similar conditions as the product **10**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.88–0.94 (m, 12H, CH_3), 1.17–1.29 (m, 6H, CH_2CH_2), 1.39–1.67 (m, 6H, CH_2CH_2), 1.72–1.82 (m, 2H, C<u>H</u>CH_3), 1.89–2.02 (m, 4H, C<u>H</u>$_2$CHCH), 2.99–3.05 (m, 2H, CHSe), 3.09–3.31 (m, 6H, CHO, CH_2O).

^{13}C NMR (100 MHz,$CDCl_3$): 19.6 (CH_3), 19.6 (CH_3), 23.3 (CH_2), 23.5 (CH_2), 25.4 (CH_2), 25.7 (CH_2), 29.0 (<u>C</u>HCH_3), 29.0 (<u>C</u>HCH_3), 30.6 (CH_2), 30.8 (CH_2), 31.8 (CH_2), 32.1 (CH_2), 42.6 (CHSe, $J^1_{Se\text{-}C}$ = 66.4 Hz), 43.6 (CHSe, $J^1_{Se\text{-}C}$ = 67.4 Hz), 75.9 (CH_2O), 76.0 (CH_2O), 82.2 (CHO), 82.8 (CHO).

Anal. calcd for $C_{20}H_{38}O_2Se$ (389.47): C 61.68, H 9.83, Se 20.27%. Found: C 61.79, H 9.84, Se 20.68%.

3.5. The Synthesis of Bis(2-methoxyalkyl) Selenides **14**–**16**

Bis(2-methoxyhexyl) selenide (**14**)**.** A solution of selenium dibromide (1.5 mmol) was prepared from selenium (0.12 g, 1.5 mmol) and bromine (0.24 g, 1.5 mmol) in methylene chloride (2 mL). The obtained solution of selenium dibromide (1.5 mmol) was added dropwise to a stirred solution of 1-hexene (0.26 g, 3.1 mmol) in acetonitrile (10 mL) and the mixture was stirred for 5 h at room temperature. The solvents were removed from the mixture on a rotary evaporator. Methanol (6 mL), containing traces of sulfuric acid, was added and the mixture was refluxed for 3 h. Sodium bicarbonate (0.1 g) was added to neutralize the sulfuric acid. Methanol was removed from the mixture on a rotary evaporator. Methylene chloride (8 mL) was added to the residue. The solution was filtered and methylene chloride was removed on a rotary evaporator. The residue was dried in a vacuum to give the product as a light-yellow oil. Yield: 0.455 g (98%). The spectral characteristics of the product correspond to those of the sample previously obtained by us [50,51].

Bis(2-methoxyheptyl) selenide (**15**) was obtained in a 98% yield under similar conditions as the product **14**. The spectral characteristics of the product correspond to those of the sample previously obtained by us [50,51].

Bis(2-methoxyoctyl) selenide (**16**) was obtained in a 97% yield under similar conditions as the product **14**. The spectral characteristics of the product correspond to those of the sample previously obtained by us [50,51].

3.6. The Synthesis of Bis(2-alkoxyalkyl) Selenides **20**–**23**

Bis(2-ethoxyhexyl) selenide (**20**)**.** A solution of selenium dibromide (1 mmol) was prepared from selenium (0.079 g, 1 mmol) and bromine (0.16 g, 1 mmol) in methylene chloride (1 mL). The obtained solution of selenium dibromide (1 mmol) was added dropwise to a stirred solution of 1-hexene (0.18 g, 2.2 mmol) in acetonitrile (8 mL) and the mixture was stirred for 5 h at room temperature. The solvents were removed from the mixture on a rotary evaporator. Ethanol (5 mL), containing traces of sulfuric acid, was added and the mixture was heated at 60–70 °C for 3 h. Sodium bicarbonate (0.1 g) was added to neutralize the sulfuric acid. Ethanol was removed from the mixture on a rotary evaporator. Methylene chloride (8 mL) was added to the residue. The solution was filtered and methylene chloride was removed on a rotary evaporator. The residue was dried in a vacuum to give the product as a light-yellow oil. Yield: 0.324 g (96%).

^{1}H NMR (400 MHz, $CDCl_3$): 0.90 (t, 6H, <u>CH_3</u>CH_2CH_2, $J^3_{H\text{-}H}$ = 6.83 Hz), 1.19 (t, 6H, <u>CH_3</u>CH_2O, $J^3_{H\text{-}H}$ = 7.0 Hz), 1.25–1.43 (m, 8H, CH_2CH_2), 1.50–1.62 (m, 4H, C<u>H</u>$_2$CH), 2.65–2.79 (m, 4H, CH_2Se), 3.38–3.44 (m, 2H, CHO), 3.44–3.62 (m, 4H, CH_2O).

^{13}C NMR (100 MHz, $CDCl_3$): 14.2 (<u>C</u>$H_3CH_2CH_2$), 15.7 (<u>C</u>H_3CH_2O), 22.9 (CH_2), 27.8 (CH_2), 29.3 (CH_2Se, $J^1_{Se\text{-}C}$ = 65.7 Hz), 29.4 (CH_2Se, $J^1_{Se\text{-}C}$ = 65.5 Hz), 29.7 (CH_2), 34.3 (CH_2), 64.8 (CH_2O), 79.8 (CHO), 79.8 (CHO).

Anal. calcd for $C_{16}H_{34}O_2Se$ (337.40): C 56.96, H 10.16, Se 23.40%. Found: C 57.02, H 10.15, Se 23.56%.

Bis(2-ethyloxyheptyl) selenide (**21**) was obtained in a 97% yield under similar conditions as the product **20**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.89 (t, 6H, $\underline{CH_3}CH_2CH_2$), 1.31 (t, 6H, $\underline{CH_3}CH_2O$ $J^3_{H\text{-}H}$ = 7.0 Hz), 1.40–1.52 (m, 12H, CH_2CH_2), 1.54–1.60 (m, 4H, $C\underline{H_2}CH$), 2.70–2.79 (m, 4H, CH_2Se), 3.38–3.44 (m, 2H, CHO), 3.44–3.52 (m, 2H, CH_2O), 3.54–3.59 (m, 2H, CH_2O).

^{13}C NMR (100 MHz,$CDCl_3$): 14.1 ($\underline{C}H_3CH_2CH_2$), 15.7 ($\underline{C}H_3CH_2O$), 22.7 (CH_2), 25.2 (CH_2), 29.2, 29.3 (CH_2Se), 32.0 (CH_2), 34.4 (CH_2), 64.8 (CH_2O), 79.8 (CHO), 79.8 (CHO).

Anal. Calcd for $C_{18}H_{38}O_2Se$: C 59.16, H 10.48, Se 21.61%. Found: C 58.86, H 9.95, Se 21.36%.

Bis(2-ethoxyoctyl) selenide (**22**) was obtained in a 96% yield under similar conditions as the product **20**.

^{1}H NMR (400 MHz, $CDCl_3$): 0.90 (t, 6H, $CH_3CH_2CH_2$, $J^3_{H\text{-}H}$ = 6.51 Hz), 1.19 (t, 6H, CH_3CH_2O, $J^3_{H\text{-}H}$ = 7.01 Hz), 1.26–1.43 (m, 16H, CH_2CH_2), 1.48–1.61 (m, 4H, $C\underline{H_2}CH$), 2.58–2.74 (m, 4H, CH_2Se), 3.33–3.39 (m, 2H, CHO), 3.41–3.61 (m, 4H, CH_2O).

^{13}C NMR (100 MHz, $CDCl_3$): 14.5 ($\underline{C}H_3CH_2CH_2$), 16.0 ($\underline{C}H_3CH_2O$), 23.0 (CH_2), 25.7 (CH_2), 25.7 (CH_2), 29.3 (CH_2Se), 29.4 (CH_2Se), 29.7 (CH_2), 32.2 (CH_2), 34.7 (CH_2), 64.8 (CH_2O), 80.0 (CHO), 80.0 (CHO).

Anal. calcd for $C_{20}H_{42}O_2Se$ (393.50): C 61.05, H 10.76, Se 20.07%. Found: C 61.07, H 10.75, Se 20.20%.

Bis(2-isobutoxyheptyl) selenide (**23**) was obtained in a 94% yield under similar conditions as the product **20** using isobutanol.

^{1}H NMR (400 MHz, $CDCl_3$): 0.87–0.94 (m, 18H, CH_3), 1.26–1.35 (m, 10H, CH_2CH_2), 1.39–1.48 (m, 2H, CH_2CH_2), 1.50–1.64 (m, 4H, $C\underline{H_2}CH$), 1.78–1.88 (m, 2H, $C\underline{H}CH_3$), 2.63–2.83 (m, 4H, CH_2Se), 3.13–3.32 (m, 4H, CH_2O), 3.35–3.41 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$): 14.2 ($\underline{C}H_3CH_2$), 19.7 ($\underline{C}H_3CH$), 19.7 ($\underline{C}H_3CH$), 22.8 (CH_2), 25.3 (CH_2), 29.1 ($\underline{C}HCH_3$), 29.3 (CH_2Se), 29.4 (CH_2Se), 32.1 (CH_2), 34.4 (CH_2), 76.6 (CH_2O), 80.1 (CHO), 80.2 (CHO).

Anal. calcd for $C_{22}H_{46}O_2Se$ (421.56): C 62.68, H 11.00, Se 18.73%. Found: C 62.64, H 10.97, Se 18.94%.

4. Conclusions

The application of selenium dihalides in functionalization reactions can provide the introduction of two functional groups simultaneously along with the selenium atom. However, opportunities of these bis-functionalization reactions of alkenes with selenium dihalides have not yet been realized.

The efficient and convenient method for bis-alkoxyselenenylation of cycloalkenes was developed based on the reaction of the selenium dibromide with cyclopentene and cyclohexene in the system alcohol/sodium bicarbonate/methylene chloride at room temperature.

The regioselective and efficient method for bis-alkoxyselenenylation of terminal alkenes was developed based on the reaction of the selenium dibromide with 1-alkenes in acetonitrile followed by the addition of alcohol and refluxing of the reaction mixture. It was established that products **14**–**16** and ethoxy and isobutoxy derivatives **20**–**23,** which did not require additional purification, can be obtained in high yields by refluxing of the reaction mixture in methanol, ethanol or isobutanol. It was also found that this reaction proceeded cleaner if the alcohol contained traces of an acid. According to this method, acetonitrile was removed from the reaction mixture on a rotary evaporator and alcohol containing traces of sulfuric acid was added followed by refluxing of the mixture. The use of this method made it possible to obtain pure products **14**–**16** and ethoxy and isobutoxy derivatives **20**–**23** in 94–98% yields.

Crystalline product, dichloro[bis(2-bromocyclopentyl)]-λ^4-selane (**2**) was obtained and studied by X-ray diffraction analysis (Figure 1).

The obtained products consist of two diastereomers (*dl* and *meso* forms), which manifest themselves in the NMR spectra, approximately in an equimolar ratio. They represent a novel family of organoselenium compounds with promising biological activity.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10120239/s1, the NMR spectra of the obtained compounds and X-ray crystallographic data for compound **2** [64–66].

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