ISSN 1070-4280, Russian Journal of Organic Chemistry, 2017, Vol. 53, No. 12, pp. 1809–1814. © Pleiades Publishing, Ltd., 2017. Original Russian Text © M.V. Musalov, E.O. Kurkutov, V.A. Potapov, A.G. Khabibulina, A.I. Albanov, S.V. Amosova, 2017, published in Zhurnal Organicheskoi Khimii, 2017, Vol. 53, No. 12, pp. 1774–1779.

Synthesis of Bis(2-haloalkyl) Selanes and Selenides Based on Selenium Dioxide and Terminal Alkenes

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Received August 15, 2017

Abstract—Selenium tetrahalides generated from selenium dioxide and hydrogen halides (HCl, HBr) reacted with hex-1-ene, hept-1-ene, and oct-1-ene at a SeO₂–alkene molar ratio of 1:2 to give mixtures of dihalobis-(2-haloalkyl)- λ^4 -selanes (yield 80–90%) and bis(2-haloalkyl) selenides (yield 5–12%). Halogenation of the resulting mixtures afforded 85–93% (calculated on the initial SeO₂) of the corresponding dihalobis(2-haloalkyl)- λ^4 -selanes, and the reduction of the same mixtures with Na₂S₂O₅ gave bis(2-haloalkyl) selenides in 80–86% yield. In the reaction with a SeO₂–alkene ratio of 5:8, pure dihalobis(2-haloalkyl)- λ^4 -selanes were formed in 84–93% yield. Dichlorobis(2-chloro-2-phenylethyl)- λ^4 -selane was obtained in 72% yield in the reaction of SeO₂–HCl with styrene.

DOI: 10.1134/S1070428017120041

There are a few published data on the addition reactions of selenium tetrahalides with terminal alkenes, and no NMR spectra of the addition products were given in these publications [1, 2]. Instead of using solid selenium tetrahalides that are poorly soluble in most organic solvents, they are generated in situ from SeO_2 and hydrogen halides [2–4]. The reactions of ethylene, hex-1-ene, and styrene with a mixture of SeO_2 and HX (X = Cl, Br) afforded dihalobis(2-haloethyl)- λ^4 -selanes, dichlorobis(2-chlorohexyl)- λ^4 selane, and dihalobis(2-halo-2-phenylethyl)- λ^4 -selanes, respectively [2]. However, Migalina et al. [3] studied the reactions of SeO_2 -HX (X = Cl, Br) with styrene and its derivatives and obtained products of halogen addition to the double bond, whereas no selenium tetrahalide adducts to the double bond were formed.

The use of new electrophilic reagents, selenium dihalides, opens new prospects in the synthesis of organoselenium compounds [5–15]. The addition of selenium dibromide to terminal alkenes leads to the formation of bis(2-bromoalkyl)selanes in 95–100% yield [13, 14]. Selenium dibromide reacted with hex-1ene and oct-1-ene to give kinetically controlled anti-Markovnikov intermediates, bis(1-bromoalkan-2-yl) selenides, which underwent fast rearrangement (presumably, through seleniranium intermediates) to thermodynamically stable Markovnikov adducts [13]. Halogenation of bis(2-haloalkyl) selenides afforded 95–98% of dihalobis(2-haloalkyl)- λ^4 -selanes [14].

Reactions of selenium tetrahalides with alkenes require further detailed studies with the aid of NMR spectroscopy to determine the structure of interme-



 $1-3, 7-9, X = Cl; 4-6, 10-12, X = Br; 1, 4, 7, 10, R = C_4H_9; 2, 5, 8, 11, R = C_5H_{11}; 3, 6, 9, 12, R = C_6H_{13}$



13–15, X = Cl; **16–18**, X = Br; **13**, **16**, R = C₄H₉; **14**, **17**, R = C₆H₁₃; **15**, **18**, R = C₅H₁₁.

diates and reaction products. In this work we studied the addition of selenium tetrahalides generated from SeO₂ and hydrogen halides to terminal alkenes (hex-1-ene, hept-1-ene, and oct-1-ene) at a SeO₂-alkene ratio of 1:2. These reactions led to the formation of mixtures of dihalobis(2-haloalkyl)- λ^4 -selanes **1–6** and bis(2-haloalkyl) selenides **7–12** in 80–90 and 5–12% yields, respectively (according to the NMR data; Scheme 1).

Increase of the amount of selenium dioxide relative to the stoichiometric SeO₂-alkene ratio (1:2) resulted in increase of the yield of **1–6** and proportional decrease of the yield of **7–12** (calculated on the initial alkene). When the SeO₂-alkene ratio was 5:8, the fraction of selenides **7–12** was reduced to 1–3%, and almost pure λ^4 -selanes **1–3** (yield 84–88%) and **4–6** (90–93%) were obtained.

The reactions with HBr were faster (30 min), whereas approximately 7 h was required to attain high yields in the reactions with HCl. In the reactions of alkenes with SeO₂-HCl unsymmetrical dichloro-(1-chloroalkan-2-yl)(2-chloroalkyl)- λ^4 -selanes **13–15** were formed; after 30 min, their content in mixtures with selanes **1–3** was about 35–45% (Scheme 2). Compounds **13–15** were characterized by ¹H and ¹³C NMR spectra. They were converted to **1–3** in a hour at room temperature in chloroform. This transformation is useful for the preparation of pure selanes **1–3**. If after 7 h the reaction mixture contained some amount of **13–15**, the mixture was dissolved in chloroform and stirred for 1 h. Presumably, compounds **13–** **15** are formed as intermediate products which readily rearrange to more stable Markovnikov adducts 1-3 (Scheme 2). This rearrangement is analogous to the transformation of bis(1-haloalkan-2-yl) selenides to bis-(2-haloalkyl) selenides described by us previously [13].

The rearrangement of analogous bromo derivatives **16–18** was considerably faster, and the corresponding Markovnikov adducts **4–6** were formed even in 30 min (in this case, the addition of chloroform was not necessary). The higher rate of the rearrangement of bis(1-bromoalkan-2-yl) selenides to bis(2-bromoalkyl) selenides in comparison to chloro-substituted analogs was observed by us previously [13]. Presumably, the rearrangement involves λ^4 -seleniranium intermediates (Scheme 2) like those proposed in the reactions of selenium tetrachloride with (*Z*)- and (*E*)-but-2-enes, which were responsible for the stereo-selective *anti*-addition [16].

 λ^4 -Selanes 1–6 formed in the reactions of alkenes with SeO₂–HX (SeO₂–alkene ratio 1:2) can be separated from the corresponding selenides 7–12 by reprecipitation or recrystallization from hexane or carbon tetrachloride; however, in this case a part of the product is lost. It is advisable to convert selenides 7–12 to 1– 6 by halogenation of the product mixture (Scheme 3). For this purpose, halogenating agent (sulfuryl chloride or bromine) should be added in an amount corresponding to the content of 7–12 in the product mixture. The yield of 1–6 in two stages was 85–93% calculated on SeO₂. Selanes 1–6 can readily be reduced to selenides 7–12 (Scheme 3). By treatment of mixtures of 1–6 and



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7–12 with an aqueous solution of sodium metabisulfite we obtained pure selenides 7–12 in 80-86% yield (calculated on the initial SeO₂).

Styrene reacted with SeO₂–HBr to give (1,2-dibromoethyl)benzene in ~90% yield, while its reaction with SeO₂–HCl afforded dichlorobis(2-chloro-2phenylethyl)- λ^4 -selane (**19**) as the major product (yield 72%) and (1,2-dichloroethyl)benzene as minor one (20%) (Scheme 4). Analogous selenium(II) derivatives, bis(2-chloro-2-phenylethyl) and bis(2-bromo-2phenylethyl) selenides, were formed in the reaction of selenium dihalides with styrene [15]. These compounds were characterized by ¹H and ¹³C NMR spectra but were not isolated since they slowly decomposed at room temperature.

The structure of compounds 1-12 and 19 was confirmed by ¹H and ¹³C NMR spectra and elemental analyses. Unsymmetrical λ^4 -selanes 13–15 were identified by ¹H and ¹³C NMR in mixtures with compounds 1-3. The isolated compounds were mixtures of two diastereoisomers (dl and meso) at a ratio of $\sim 1:1$. The SeCH₂ and CHX carbon signals in the ¹³C NMR spectra of 1–15, as well as the selenium signals in their ⁷⁷Se NMR spectra, were doubled due to the presence of two diastereoisomers. The C-Se coupling constant of the CH₂ carbon nuclei in the ¹³C NMR spectra was 59-70 Hz, which corresponds to direct coupling $({}^{1}J_{C-Se})$ and indicates formation of Markovnikov adducts. The selenium signals of chloroalkyl (8, 9) and bromoalkyl selenides (11, 12) were located at δ_{Se} 163–169 and 199–204 ppm, respectively, and the selenium nucleus in λ^4 -selanes resonated in a downfield region (2, 3: δ_{se} 523–528 ppm, Cl₂SeCH₂; **(5, 6**: δ_{Se} 495–499 ppm).

Thus, we have developed efficient methods for the synthesis of intermediate products for organoelement chemistry on the basis of reactions of selenium tetrahalides with terminal alkenes and styrene. The procedure for the synthesis of selenides 7-12 via reduction of selanes 1-6 seems less convenient than the one-step synthesis of bis(2-haloalkyl) selenides via addition of selenium dihalides to alkenes [13, 14]; however, it is also sufficiently effective, and it can be regarded as an alternative method with the use of SeO₂.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 (¹H), 100.61 (¹³C), and 76.30 MHz (⁷⁷Se) using CDCl₃ as solvent; the chemical shifts were measured relative to hexamethyldisiloxane (¹H, ¹³C) and Me₂Se (⁷⁷Se). The solvents used were preliminarily dried and distilled. The elemental analyses were obtained on a Thermo Flash EA1112 analyzer.

Dihalobis(2-haloalkyl)- λ^4 -selanes 1–6 (general procedure). a. A solution of 8 mmol of terminal alkene in 15 mL of diethyl ether was cooled to 0°C and added to a solution of 0.555 g (5 mmol) of SeO₂ in 5 mL of 36% aqueous HCl (or 46% aqueous HBr), and the mixture was vigorously stirred for 7 h (0.5 h in the reaction with HBr) at room temperature. The organic layer was separated, and the aqueous layer was extracted with 10 mL of diethyl ether. The organic phase was dried over CaCl₂, and the solvent was distilled off. For the synthesis of chloro derivatives 1-3, the residue was dissolved in 15 mL of chloroform, the solution was stirred for 1 h (to convert compounds 13-15 to 1-3), the solvent was distilled off, and the residue was dried under reduced pressure. Yield of 1-3 84-88%, and of 4-6, 90-93% (calculated on the initial terminal alkene).

b. The reactions of SeO₂–HCl (HBr) with alkenes at a SeO₂–alkene ratio of 1:2 were carried out in a similar way. The resulting mixtures of **1–6** (yield 80– 90%) and **7–12** (5–12%) were then subjected to halogenation and reduction. The reaction of styrene with SeO₂–HCl gave 72% of dichlorobis(2-chloro-2phenylethyl)- λ^4 -selane (**19**) and 20% of (1,2-dichloroethyl)benzene.

c. A mixture of selane 1-6 and selenide 7-12obtained in the reaction of alkenes with SeO₂-HCl (HBr) was dissolved in 20 mL of carbon tetrachloride, the solution was cooled to 0°C, and a cold (0°C) solution of sulfuryl chloride (or bromine) in 10 mL of carbon tetrachloride was added (the amount of the halogenating agent corresponded to the content of 7-12 in the mixture). The mixture was stirred for 1 h at 0°C, the cooling bath was removed, and the mixture was stirred for 1 h to allow it to warm up to room temperature. The solvent was distilled off, and the residue was dried under reduced pressure.

Dichlorobis(2-chlorohexyl)- λ^4 -selane (1). Yield 88%, colorless crystals, mp 43–45°C. ¹H NMR spectrum, δ, ppm: 0.94 t (6H, CH₃), 1.48–1.56 m (8H, CH₂), 2.12–2.20 m (2H, CH₂), 2.24–2.32 m (2H, CH₂), 4.12–4.24 m (4H, CHSe), 4.64–4.72 m (2H, CHCl). ¹³C NMR spectrum, δ_C , ppm: 14.12 (CH₃), 21.92 (CH₂), 30.56 (CH₂), 37.35 (CH₂), 56.76 (CHCl), 68.65 (CH₂Se), 68.72 (CH₂Se). Found, %: C 37.29; H 6.40; Cl 36.23; Se 19.98. C₁₂H₂₄Cl₄Se. Calculated, %: C 37.04; H 6.22; Cl 36.45; Se 20.29.

Dichlorobis(2-chloroheptyl)-λ⁴-selane (2). Yield 87%, colorless crystals, mp 65–67°C. ¹H NMR spectrum, δ, ppm: 0.90 t (6H, CH₃), 1.23–1.40 m (8H, CH₂), 1.44–1.66 m (4H, CH₂), 1.81–2.95 m (4H, CH₂), 4.11–4.31 m (4H, CH₂Se), 4.75–4.82 m (2H, CHCl). ¹³C NMR spectrum, δ_{C} , ppm: 13.97 (CH₃), 22.42 (CH₂), 26.02 (CH₂), 31.02 (CH₂), 37.59 (CH₂), 56.74 (CHCl), 68.77 and (CH₂Se), 68.88 (CH₂Se). ⁷⁷Se NMR spectrum, δ_{Se} , ppm: 523.1, 525.2. Found, %: C 40.12; H 6.62; Cl 34.27; Se 18.68. C₁₄H₂₈Cl₄Se. Calculated, %: C 40.31; H 6.77; Cl 34.00; Se 18.93.

Dichlorobis(2-chlorooctyl)-λ⁴-selane (3). Yield 84%, colorless crystals, mp 67–69°C. ¹H NMR spectrum, δ, ppm: 0.80 t (6H, CH₃), 1.16–1.27 m (12H, CH₂), 1.33–1.45 m (4H, CH₂), 1.46–1.54 m (2H, CH₂), 1.73–1.84 m (2H, CH₂), 4.07–4.18 m (4H, CH₂Se), 4.62–4.70 m (2H, CHCl). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 14.24 (CH₃), 22.62 (CH₂), 26.37 (CH₂), 28.66 (CH₂), 31.66 (CH₂), 37.69 (CH₂), 56.84 (CHCl), 68.78 (CH₂Se, ¹J_{C-Se} = 60 Hz), 68.85 (CH₂Se, ¹J_{C-Se} = 59 Hz). ⁷⁷Se NMR spectrum, $\delta_{\rm Se}$, ppm: 526.3, 528.3. Found, %: C 42.94; H 7.42; Cl 32.12; Se 18.04. C₁₆H₃₂Cl₄Se. Calculated, %: C 43.17; H 7.24; Cl 31.85; Se 17.74.

Dibromobis(2-bromohexyl)- λ^4 -selane (4). Yield 93%, yellowish crystals, mp 61–63°C. ¹H NMR spectrum, δ , ppm: 0.95 t (6H, CH₃), 1.46–1.54 m (8H, CH₂), 1.96–2.03 m (2H, CH₂), 2.06–2.13 m (2H, CH₂), 4.08–4.20 m (4H, CHSe), 4.57–4.66 m (2H, CHBr). ¹³C NMR spectrum, δ_C , ppm: 13.91 (CH₃), 18.98 (CH₂), 30.83 (CH₂), 36.89 (CH₂), 48.02 (CHBr), 66.72 (CH₂Se). Found, %: C 25.17; H 4.09; Br 56.06; Se 14.27. C₁₂H₂₄Br₄Se. Calculated, %: C 25.42; H 4.27; Br 56.38; Se 13.93.

Dibromobis(2-bromoheptyl)- λ^4 -selane (5). Yield 92%, yellowish crystals, mp 64–67°C. ¹H NMR spectrum, δ , ppm: 0.88 t (6H, CH₃), 1.32–1.42 m (8H, CH₂), 1.43–1.53 m (2H, CH₂), 1.57–1.67 m (2H, CH₂),

1.86–1.98 m (4H, CH₂), 4.24–4.39 m (4H, CH₂Se), 4.85–4.96 m (2H, CHBr). ¹³C NMR spectrum, δ_{C} , ppm: 14.07 (CH₃), 22.45 (CH₂), 27.30 (CH₂), 30.88 (CH₂), 38.05 (CH₂), 48.52 (CHBr), 66.31 (CH₂Se), 66.35 (CH₂Se). ⁷⁷Se NMR spectrum, δ_{Se} , ppm: 495.6, 497.7. Found, %: C 27.98; H 4.56; Br 54.09; Se 13.51. C₁₄H₂₈Br₄Se. Calculated, %: C 28.26; H 4.74; Br 53.72; Se 13.27.

Dibromobis(2-bromooctyl)-λ⁴-selane (6). Yield 90%, yellowish crystals, mp 69–71°C. ¹H NMR spectrum, δ, ppm: 0.79 m (6H, CH₃), 1.13–1.26 m (12H, CH₂), 1.38–1.47 m (2H, CH₂), 1.55–1.64 m (2H, CH₂), 1.81–1.90 m (4H, CH₂), 4.11–4.21 m (4H, CH₂Se), 4.73–4.80 m (2H, CHBr). ¹³C NMR spectrum, δ_C, ppm: 14.45 (CH₃), 22.84 (CH₂), 27.79 (CH₂), 28.64 (CH₂), 31.83 (CH₂), 38.09 (CH₂), 47.93 (CHBr), 66.82 (CH₂Se). ⁷⁷Se NMR spectrum, δ_{Se}, ppm: 497.1, 498.8. Found, %: C 31.09; H 5.29; Br 51.53; Se 12.46. C₁₆H₃₂Br₄Se. Calculated, %: C 30.85; H 5.18; Br 51.30; Se 12.67.

Bis(2-haloalkyl)selenides 7–12 (general procedure). A mixture of selane 1–6 and selenide 7–12 obtained in the reaction of alkenes with SeO₂–HCl (HBr) was dissolved in 20 mL benzene, the solution was cooled to 5°C, and a cold (5°C) solution of 3 g of sodium metabisulfite in 20 mL of water was added. The mixture was stirred for 1 h at 5°C, the cooling bath was removed, and the mixture was stirred for 1 h to allow it to warm up to room temperature. The organic layer was separated, and the aqueous layer was extracted with 10 mL of benzene. The organic phase was dried over CaCl₂, the solvent was distilled off, and the residue was dried under reduced pressure.

Bis(2-chlorohexyl) selenide (7). Yield 83%, colorless oil. ¹H NMR spectrum, δ, ppm: 0.95 t (6H, CH₃), 1.30–1.41 m (4H, CH₂), 1.48–1.59 m (4H, CH₂), 1.58–1.67 m (2H, CH₂), 1.91–1.99 m (2H, CH₂), 2.90–2.99 m (4H, CH₂Se), 3.94–4.03 m (2H, CHCl). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 13.91 (CH₃), 21.85 (CH₂), 29.06 (CH₂), 33.18 (CH₂Se, ¹*J*_{C-Se} = 68 Hz), 33.34 (CH₂Se, ¹*J*_{C-Se} = 68 Hz), 37.01 (CH₂), 61.72 (CHCl), 61.81 (CHCl). Found, %: C 45.57; H 7.42; Cl 22.56; Se 25.07. C₁₂H₂₄Cl₂Se. Calculated, %: C 45.30; H 7.60; Cl 22.28; Se 24.82.

Bis(2-chloroheptyl) selenide (8). Yield 82%, colorless oil. ¹H NMR spectrum, δ , ppm: 0.92 t (6H, CH₃), 1.29–1.42 m (10H, CH₂), 1.50–1.60 m (2H, CH₂), 1.61–1.70 m (2H, CH₂), 1.89–1.99 m (2H, CH₂), 2.87– 2.90 m (2H, CH₂Se), 2.98–3.07 m (2H, CH₂Se), 3.94– 4.03 m (2H, CHCl). ¹³C NMR spectrum, δ_{C} , ppm: 13.99 (CH₃), 22.41 (CH₂), 25.82 (CH₂), 31.13 (CH₂), 33.25 (CH₂Se, ${}^{1}J_{C-Se} = 69$ Hz), 33.40 (CH₂Se, ${}^{1}J_{C-Se} = 69$ Hz), 37.13 (CH₂), 61.75 (CHCl), 61.84 (CHCl). ⁷⁷Se NMR spectrum, δ_{Se} , ppm: 163.7, 164.8. Found, %: C 48.83; H 8.34; Cl 20.23; Se 23.12. C₁₄H₂₈Cl₂Se. Calculated, %: C 48.56; H 8.15; Cl 20.48; Se 22.81.

Bis(2-chlorooctyl) selenide (9). Yield 80%, colorless oil. ¹H NMR spectrum, δ, ppm: 0.77 t (6H, CH₃), 1.12–1.26 m (14H, CH₂), 1.34–1.43 m (2H, CH₂), 1.45–1.54 m (2H, CH₂), 1.72–1.80 m (2H, CH₂), 2.77– 2.84 m (2H, CH₂Se), 2.87–2.93 m (2H, CH₂Se), 3.87– 3.94 m (2H, CHCl). ¹³C NMR spectrum, δ_{C} , ppm: 14.13 (CH₃), 22.54 (CH₂), 26.27 (CH₂), 28.59 (CH₂), 31.58 (CH₂), 33.38 (CH₂Se, ¹ $J_{C-Se} = 66$ Hz), 33.52 (CH₂Se, ¹ $J_{C-Se} = 66$ Hz), 37.37 (CH₂), 61.78, 61.87 (CHCl). ⁷⁷Se NMR spectrum, δ_{Se} , ppm: 167.6, 168.8. Found, %: C 51.08; H 8.43; Cl 19.23; Se 21.42. C₁₆H₃₂Cl₂Se. Calculated, %: C 51.34; H 8.62; Cl 18.94; Se 21.10.

Bis(2-bromohexyl) selenide (10). Yield 86%, light yellow oil. ¹H NMR spectrum, δ , ppm: 0.95 t (6H, CH₃), 1.39–1.56 m (8H, CH₂), 1.76 m (2H, CH₂), 2.03 m (2H, CH₂), 3.02–3.10 m (2H, CH₂Se), 3.17–3.22 m (2H, CH₂Se), 4.09 m (2H, CHBr). ¹³C NMR spectrum, δ_{C} , ppm: 13.91 (CH₃), 21.89 (CH₂), 29.29 (CH₂), 33.71 (SeCH₂, ¹*J*_{C-Se} = 69 Hz), 33.95 (SeCH₂, ¹*J*_{C-Se} = 69 Hz), 37.04 (CH₂), 54.25 (CHBr), 54.44 (CHBr). Found, %: C 35.67; H 6.09; Br 38.93; Se 19.18. C₁₂H₂₄Br₂Se. Calculated, %: C 35.40; H 5.94; Br 39.26; Se 19.40.

Bis(2-bromoheptyl) selenide (11). Yield 85%, light yellow oil. ¹H NMR spectrum, δ , ppm: 0.92 t (6H, CH₃), 1.35 m (10H, CH₂), 1.58 m (2H, CH₂), 1.75 m (2H, CH₂), 2.01 m (2H, CH₂), 3.06 m (2H, CH₂Se), 3.21 m (2H, CH₂Se), 4.09 m (2H, CHBr). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 13.89 (CH₃), 22.29 (CH₂), 26.76 (CH₂), 30.89 (CH₂), 33.68 (CH₂Se, ¹*J*_{C-Se} = 70 Hz), 33.90 (CH₂Se, ¹*J*_{C-Se} = 70 Hz), 37.30 (CH₂), 54.48 (CHBr). ⁷⁷Se NMR spectrum, $\delta_{\rm Se}$, ppm: 199.4, 201.1. Found, %: C 38.37; H 6.31; Br 36.59; Se 18.39. C₁₄H₂₈Br₂Se. Calculated, %: C 38.64; H 6.49; Br 36.73; Se 18.15.

Bis(2-bromooctyl) selenide (12). Yield 84%, light yellow oil. ¹H NMR spectrum, δ , ppm: 0.86 t (6H, CH₃), 1.22–1.34 m (6H, CH₂), 1.36–1.42 m (2H, CH₂), 1.48–1.56 m (2H, CH₂), 1.69–1.78 m (2H, CH₂), 1.95–2.03 m (2H, CH₂), 3.02–3.11 m (2H, CH₂Se), 3.18–3.23 m (2H, CH₂Se), 4.10–4.18 m (2H, CHBr). ¹³C NMR spectrum, δ_{C} , ppm: 14.09 (CH₃), 22.58 (CH₂), 27.34 (CH₂), 28.55 (CH₂), 31.62 (CH₂), 33.92 (CH₂Se, ¹ J_{C-Se} = 69 Hz), 34.19 (CH₂Se, ¹ J_{C-Se} = 69 Hz), 37.66 (CH₂), 55.68 (CHBr), 55.84 (CHBr).

⁷⁷Se NMR spectrum, $δ_{Se}$, ppm: 202.0, 203.7. Found, %: C 41.23; H 7.15; Br 34.78; Se 16.87. C₁₆H₃₂Br₂Se. Calculated, %: C 41.49; H 6.96; Br 34.50; Se 17.05.

Dichloro(1-chlorohexan-2-yl)(2-chlorohexyl)-λ⁴**selane (13).** ¹H NMR spectrum, δ, ppm: 0.87–0.93 m (6H, CH₃), 1.30–1.54 m (6H, CH₂), 1.82–1.87 m (4H, CH₂), 2.11–2.18 m (2H, CH₂), 4.05–4.12 m (2H, CH₂Cl), 4.18–4.27 m (2H, CH₂Se), 4.51–4.58 m (1H, CHSe), 4.73–4.77 m (1H, CHCl). ¹³C NMR spectrum, δ_C, ppm: 14.18 (CH₃), 22.20, 22.74, 28.54, 29.30, 29.98, 37.50 (CH₂), 43.82, 44.02 (CH₂Cl), 57.21, 57.31 (CHCl), 65.55, 65.99 (SeCH₂), 76.39, 76.98 (SeCH).

Dichloro(1-chloroheptan-2-yl)(2-chloroheptyl)- λ^4 -selane (14). ¹H NMR spectrum, δ , ppm: 0.90–0.95 m (6H, CH₃), 1.30–1.46 m (6H, CH₂), 1.48–1.86 m (8H, CH₂), 2.17–2.22 m (2H, CH₂), 4.04–4.12 m (2H, CH₂Cl), 4.15–4.25 m (2H, CH₂Se), 4.46–4.51 m (1H, CHSe), 4.72–4.77 m (1H, CHCl). ¹³C NMR spectrum, δ_C , ppm: 14.19 (CH₃), 22.57, 22.67, 26.05, 26.82, 30.35, 31.16, 31.63, 37.59 (CH₂), 43.42, 43.60 (CH₂Cl), 56.68, 56.76 (CHCl), 65.51, 66.06 (CH₂Se), 76.50, 76.96 (CHSe).

Dichloro(1-chlorooctan-2-yl)(2-chlorooctyl)- λ^4 selane (15). ¹H NMR spectrum, δ , ppm: 0.90–0.96 m (6H, CH₃), 1.32–1.44 m (10H, CH₂), 1.54–1.70 m (6H, CH₂), 1.92–1.98 m (2H, CH₂), 2.21–2.30 m (2H, CH₂), 4.03–4.13 m (2H, CH₂Cl), 4.16–4.28 m (2H, CH₂Se), 4.48–4.54 m (1H, CHSe), 4.78–4.82 m (1H, CHCl). ¹³C NMR spectrum, δ_C , ppm: 14.27 (CH₃), 22.64, 22.66, 26.33, 27.14, 28.67, 29.20, 30.43, 31.56, 31.70, 37.65 (CH₂), 43.42, 43.60 (CH₂Cl), 56.68, 56.76 (CHCl), 65.51, 66.06 (SeCH₂), 76.50, 76.96 (CHSe).

Bis(2-chloro-2-phenylethyl)-λ⁴-selane (19). Yield 72%, colorless crystals, mp 91–93°C. ¹H NMR spectrum, δ, ppm: 3.88–3.97 m (2H, SeCH₂), 4.06–4.15 m (2H, SeCH₂), 5.38–5.47 m (2H, ClCH), 6.93–7.01 m (6H, Ph), 7.04–7.10 m (4H, Ph). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 57.18 (CHCl), 68.90, 69.00 (SeCH₂), 127.40, 129.23, 129.93, 136.81 (Ph). Found, %: C 45.02; H 3.93; Cl 32.79; Se 18.67. C₁₆H₁₆Cl₄Se. Calculated, %: C 44.79; H 3.76; Cl 33.05; Se 18.40.

The spectral studies were carried out using the facilities of the Baikal Joint Analytical Center, Siberian Branch, Russian Academy of Sciences.

REFERENCES

1. Riley, R.F., Flato, J., and Bengels, D., J. Org. Chem., 1962, vol. 27, p. 2651.

- Funk, H. and Papenroth, W., J. Prakt. Chem., 1959, vol. 8, p. 256.
- Migalina, Yu.V., Galla-Bobik, S.V., Ershova, I.I., and Staninets, V.I., *Zh. Obshch. Khim.*, 1982, vol. 52, p. 1563.
- Lendel, V.G., Pak, B.I., Migalina, Yu.V., Kuchi, P., Dzurilla, M., and Kristian, P., *Zh. Org. Khim.*, 1990, vol. 26, p. 1849.
- 5. Potapov, V.A., Musalov, M.V., Musalova, M.V., and Amosova, S.V., *Curr. Org. Chem.*, 2016, vol. 20, p. 136.
- Potapov, V.A., Volkova, K.A., Penzik, M.V., Albanov, A.I., and Amosova, S.V., *Russ. J. Gen. Chem.*, 2008, vol. 78, p. 1990.
- Potapov, V.A., Kurkutov, E.O., Albanov, A.I., and Amosova, S.V., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 1547.
- Amosova, S.V., Penzik, M.V., Albanov, A.I., and Potapov, V.A., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 1271.
- 9. Potapov, V.A., Kurkutov, E.O., and Amosova, S.V., *Russ. J. Gen. Chem.*, 2010, vol. 80, p. 1220.

- Potapov, V.A., Musalov, M.V., Amosova, S.V., Musalova, M.V., and Penzik, M.V., *Russ. J. Org. Chem.*, 2011, vol. 47, p. 950.
- Potapov, V.A., Musalov, M.V., Amosova, S.V., and Kurkutov, E.O., *Russ. J. Org. Chem.*, 2011, vol. 47, p. 1594.
- 12. Musalov, M.V., Potapov, V.A., and Amosova, S.V., *Russ. Chem. Bull., Int. Ed.*, 2011, vol. 60, p. 767.
- Kurkutov, E.O., Musalov, M.V., Potapov, V.A., Larina, L.I., and Amosova, S.V., *Russ. J. Org. Chem.*, 2016, vol. 52, p. 186.
- Musalov, M.V., Potapov, V.A., Kurkutov, E.O., Musalova, M.V., Khabibulina, A.G., and Amosova, S.V., *Arkivoc*, 2017, part (iii), p. 365.
- 15. Potapov, V.A, Khabibulina, A.G., Musalov, M.V., Albanov, A.I., and Amosova, S.V., *Russ. J. Org. Chem.*, 2017, vol. 53, p. 322.
- 16. Garratt, D.G., Ujjainwalla, M., and Schmid, G.H., J. Org. Chem., 1980, vol. 45, p. 1206.