Dedicated to Full Member of the Russian Academy of Sciences
G.A. Tolstikov on his 75th Anniversary

Reactions of β,β′-Dichlorodiethyl Ether with Elemental Chalcogens and Dimethyl Dichalcogenides in the System Hydrazine Hydrate–Base

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Abstract—β,β′-Dichlorodiethyl ether reacted with elemental selenium or tellurium, as well as with binary chalcogen mixtures (S/Se, S/Te, or Se/Te), activated in the system hydrazine hydrate–base to give oligomeric products containing oxygen and polychalcogenide fragments in the chain. Reductive cleavage of these oligomers gave rise to 3-oxapentane-1,5-dichalcogenols and their methyl derivatives. The latter were also synthesized from β,β′-dichlorodiethyl ether and the corresponding dimethyl dichalcogenides in the system hydrazine hydrate–KOH.

Like other dihalo ethers, β,β′-dichlorodiethyl ether (**I**) is an important reagent used in the synthesis of complex polyfunctional structures [1]. Ready replacement of the chlorine atoms therein by nucleophilic reagents such as chalcogenide ions opens the way to chalcogen-containing oligomers. Known analogs of such oligomers, prepared from other dihalogen derivatives, exhibit valuable electrical and physicochemical properties [2–4]. Low molecular weight compounds containing sulfur, selenium, or tellurium atoms in addition to oxygen are well known to act as donors in complex formation processes [5, 6]; these compounds could give rise to polydentate ligands that are linear hetero analogs of crown ethers [7].

The use of reductive systems based on hydrazine hydrate in the synthesis of organochalcogen compounds [8] ensures facile conversion of elemental chalcogens into chalcogenide or polychalcogenide ions which then effectively react with halogen-containing electrophiles in the same systems. The reaction of β,β′-dichlorodiethyl ether (**I**) with elemental sulfur in the systems hydrazine hydrate–alkali [9] and hydrazine hydrate–2-aminoethanol [10] resulted in the formation of a rare type of thiokols soluble in chloroform and
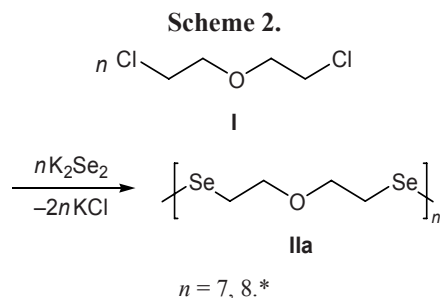
other important sulfur-containing products. The present article reports on the results of our study on the reactions of β,β′-dichlorodiethyl ether with selenium, tellurium, and dimethyl dichalcogenides, as well as with two different chalcogens or dichalcogenides simultaneously. Elemental selenium was activated in the system hydrazine hydrate–aqueous alkali, the molar ratio Se–KOH being 1:1 to ensure predominant generation of diselenide ions [11] according to Scheme 1.

Scheme 1.

$$4\,Se + 4\,KOH + N_2H_4 \cdot H_2O$$
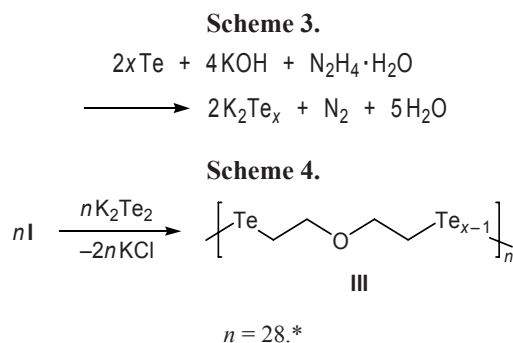$$\longrightarrow 2\,K_2Se_2 + N_2 + 5\,H_2O$$
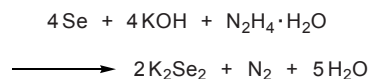
In the reaction of compound **I** with a solution prepared from elemental selenium and hydrazine hydrate–aqueous alkali we observed formation of black oligomer **IIa** (Scheme 2). Structurally related oligomer **IIb** was synthesized by reaction of β,β′-dichlorodiethyl ether with selenium in hydrazine hydrate–2-aminoethanol (the Se–$N_2H_4 \cdot H_2O$–$NH_2CH_2CH_2OH$ ratio was the same as in [11], 8:10:1).

Elemental tellurium can be activated using hydrazine hydrate–KOH without additional solvent [8]

Scheme 2.

$$n \; Cl{\sim\!\!\sim}O{\sim\!\!\sim}Cl$$

I

$$\xrightarrow[-2n\,KCl]{n\,K_2Se_2} \left[Se{\sim\!\!\sim}O{\sim\!\!\sim}Se \right]_n$$

IIa

$n = 7, 8.*$

(Scheme 3). The reaction of **I** with a solution of potassium ditelluride thus obtained gave 87% of oligomeric product **III** (Scheme 4)

Scheme 3.

$$2x\,Te \; + \; 4\,KOH \; + \; N_2H_4 \cdot H_2O$$
$$\longrightarrow \; 2\,K_2Te_x \; + \; N_2 \; + \; 5\,H_2O$$

Scheme 4.

$$n\mathbf{I} \; \xrightarrow[-2n\,KCl]{n\,K_2Te_2} \left[Te{\sim\!\!\sim}O{\sim\!\!\sim}Te_{x-1} \right]_n$$
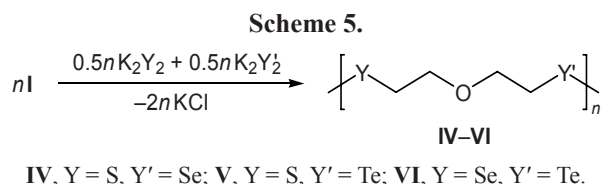
III

$n = 28.*$

The properties of oligomers **IIa**, **IIb**, and **III** are given in Experimental. In all cases, the amount of dichlorodiethyl ether **I** was larger than its stoichiometric amount according to Scheme 2 or 4 (Y:**I** = 2:1) in order to achieve complete decoloration of selenium and tellurium solutions. Nevertheless, the concentration of selenium and tellurium in the resulting oligomers **IIa** and **III**, respectively, considerably exceeded the theoretical value. Obviously, chloro ether **I** in the system hydrazine hydrate–KOH undergoes partial alkaline hydrolysis to give diethylene glycol or polyethylene glycols that are readily soluble in aqueous hydrazine. In keeping with the data of [8], alkaline hydrolysis of other halogen derivatives almost did not occur in analogous systems. Side hydrolysis processes reduce the overall basicity of the system, which favors increased number of chalcogen atoms (x) in polychalcogenide ions Y_x^{2-}. However, in the reaction of **I** with $K_2Te_{2.5}$ prepared according to Scheme 3 (KOH–Te ratio 2:2.5) only stoichiometric amount of the former was necessary to complete the process (decoloration of the polytelluride solution). The concentration of tellurium in the resulting oligomer **IIIa** was similar to the calculated value for ($TeCH_2CH_2OCH_2CH_2Te_{1.5}$) as

* The n value was estimated from the concentration of residual chlorine atoms at the ends of macromolecules.
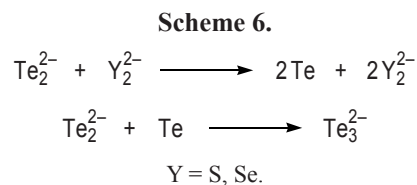
monomeric unit. This may be due to increase in the reactivity of polychalcogenides Y_x^{2-} with rise in x. When $x > 2$, almost no side hydrolysis of β,β′-dichlorodiethyl ether is observed.

Activation of selenium in the system hydrazine hydrate–2-aminoethanol also requires excess compound **I** to achieve complete decoloration of the selenium solution, but the concentration of selenium in oligomer **IIb** thus formed is even smaller than the theoretical value. A probable reason is the presence in the system of a large excess of hydrazine; being an effective reducing agent, it hampers increase of x.

In the reactions with two different chalcogens, each of them was activated separately according to Schemes 1 and 3, and the resulting chalcogen solutions were combined and brought into reaction with compound **I** (Scheme 5).

Scheme 5.

$$n\mathbf{I} \; \xrightarrow[-2n\,KCl]{0.5n\,K_2Y_2 + 0.5n\,K_2Y_2'} \left[Y{\sim\!\!\sim}O{\sim\!\!\sim}Y' \right]_n$$

IV–VI

IV, Y = S, Y′ = Se; **V**, Y = S, Y′ = Te; **VI**, Y = Se, Y′ = Te.

The products, oligomeric compounds **IV–VI** were enriched in the heavier chalcogen; correspondingly, the concentration of the lighter chalcogen therein was underestimated. In these reactions, apart from hydrolysis of **I**, an additional interaction between chalcogenide ions is possible due to their different abilities to undergo redox reactions [12]. Such a behavior of chalcogenides, especially of tellurides, in hydrazine hydrate-based systems was reported by us previously [13] (Scheme 6).

Scheme 6.

$$Te_2^{2-} \; + \; Y_2^{2-} \; \longrightarrow \; 2\,Te \; + \; 2\,Y_2^{2-}$$
$$Te_2^{2-} \; + \; Te \; \longrightarrow \; Te_3^{2-}$$

Y = S, Se.

Among compounds **II–VI**, only **IIb** is soluble in chloroform (and CDCl₃), so that we were able to record its ^{1}H NMR spectrum (see Experimental) which indicated fairly uniform distribution of selenium atoms over polyselenide fragments in the oligomer (Se_2). Taking into account the concentration of residual chlorine, we calculated the molecular weight of oligomer **IIb** and determined its average molecular formula:

$$Cl(CH_2)_2O(CH_2)_2Se[Se(CH_2)_2O(CH_2)_2Se]_9Se(CH_2)_2O(CH_2)_2Cl.$$
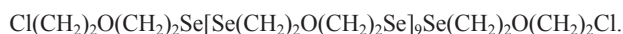
Despite relatively low average molecular weight, oligomers **IIa** and **IV** are soluble only partially, and the insoluble part is characterized by a larger average molecular weight (3200 a.m.u. for the insoluble fraction of **IIa**); obviously, oligomers with a lower molecular weight are soluble better, and the polyselenide fragments therein are shorter.

After separation of oligomers from the reaction mixture, the aqueous hydrazine layer was extracted with methylene chloride to isolate two types of heterocyclic compounds, 1,4-oxachalcogenanes **VIIa–VIIc** and 1-oxa-4,5-dichalcogenepanes **VIII** (Schemes 7 and 8). Among the latter, only derivatives **VIIIa–VIIIc** having similar chalcogen atoms and 1,4,5-oxathiaselenepane (**VIIId**) were identified by gas chromatography–mass spectrometry. The yield of compounds **VII** was as low as 5–10%; however, these heterocycles are important from the viewpoint of both theoretical and applied organic chemistry [14]. With selenium-containing derivative **VIIb** as an example we showed that they can be obtained in 45% yield using dilute solutions of chalcogens activated via conversion into chalcogenide ions (K_2Y). Compounds **VII** and **VIII** are likely to be formed concurrently with the formation of oligomers.
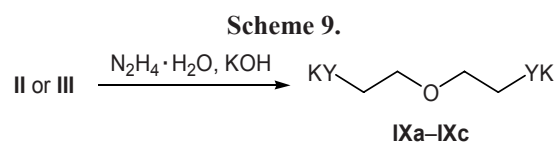
Scheme 7.

VIIa–VIIc

Y = S (**a**), Se (**b**), Te (**c**).

Scheme 8.
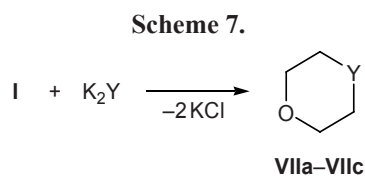
VIIIa–VIIIc
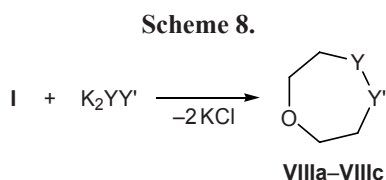
Y = Y′ = S (**a**), Se (**b**), Te (**c**); Y = S, Y′ = Se (**d**), Te (**e**).

The ^{1}H and ^{13}C NMR and mass spectra of 1,4-oxachalcogenanes **VIIa–VIIc** are given in Experimental. The mass spectra of the selenium- and tellurium-containing compounds are similar, while 1,4-oxathiane (**VIIa**) is characterized by somewhat different mass spectrum due to considerable contribution of fragmentation pathway involving elimination of CH_2O molecule.

Like other oligomeric dichalcogenides [8, 13] compounds **II–VI** in the system hydrazine hydrate–alkali

undergo reductive cleavage at the Y–Y bond to give the corresponding bis-chalcogenolates **IX**. Oligomers **II** and **III** having similar chalcogen atoms give rise to symmetric bis-chalcogenolates **IXa–IXc** (Scheme 9), while those containing different chalcogen atoms (**IV–VI**) are converted into both symmetric derivatives **IXa–IXc** and bis-chalcogenolates **IXd–IXf** with different chalcogen atoms (Scheme 10).

Scheme 9.

IXa–IXc

Y = S (**a**), Se (**b**), Te (**c**).

Scheme 10.

IXd–IXf
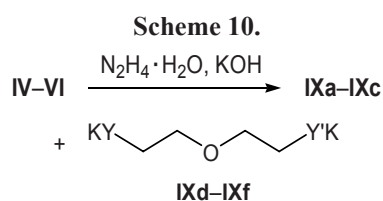
Y = S, Y′ = Se (**d**), Te (**e**); Y = Se, Y′ = Te (**f**).

Treatment of bis-selenolate **IXb** with an acid under mild conditions (0°C, argon) gave 8% of very unstable 3-oxapentane-1,5-diselenol (**X**) (Scheme 11). Its high reactivity follows from the formation of a large amount (45%) of the corresponding oxidation product, 1,4,5-oxadiselenepane (**VIIIb**) during the process. The structure of **X** was confirmed by the IR (ν_{SeH} 2295 cm^{-1}), ^{1}H and ^{13}C NMR (see Experimental), and GC–MS data (the mass spectrum contained peaks from fragment ions having a SeH moiety; no such peaks were present in the mass spectrum of **VIIIb**). Selenium analogs of thiols remain so far rare and difficultly accessible compounds [15]; therefore, the above reaction attracts practical interest despite poor yield of **X**.

Scheme 11.
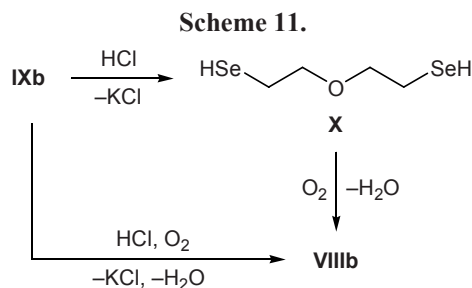
Our attempt to obtain 3-oxapentane-1,5-ditellurol (**Xa**) under analogous conditions resulted in the formation of a black material which contained 1,4,5-oxaditellurepane (**VIIIc**) (no more than 10%, according to

the ^{1}H NMR data) and other compounds. Insofar as reliable published data on spectral parameters of tellurols are lacking, it is difficult to assert with certainty that compound **Xa** is present or absent in the reaction mixture. Nevertheless, treatment of the product mixture with hydrazine hydrate–KOH and subsequent addition of methyl iodide to the homogeneous solution thus formed gave 75% of 5-oxa-2,8-ditelluranonane (**XIc**).

Bis-chalcogenolates **IX** formed as a result of reductive cleavage of oligomers **II**–**VI** (Schemes 9, 10) were subjected (without isolation) to alkylation with methyl iodide. We thus obtained symmetric (**XIa**–**XIc**) and unsymmetric (**XId**–**XIf**) methyl derivatives of the corresponding 1,5-dichalcogenols (Scheme 12).

Scheme 12.

Y^3 = S (**a**), Se (**b**), Te (**c**); Y^1 = S, Y^2 = Se (**d**), Te (**e**); Y^1 = Se, Y^2 = Te (**f**).
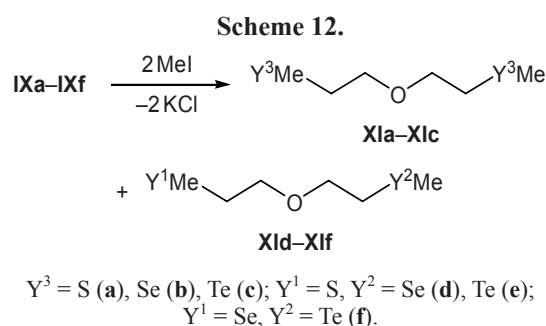
The yields of 5-oxa-2,8-dichalcogenanonanes **XIa**–**XIf** and by-products, their physical constants, and spectral parameters are given in Experimental. 1,4,5-Oxadichalcogenepanes **VIII** in the system hydrazine hydrate–KOH also undergo reductive cleavage with formation of dichalcogenolates **IX**. For example, 1,4,5-oxadiselenepane (**VIIIb**) obtained according to Scheme 11 was converted into 6-oxa-3,9-diselenaundecane (**XIg**) in 74% yield (Scheme 13).

Scheme 13.
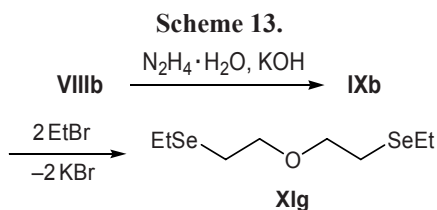
Compounds **XI** are stable multidentate ligands containing two chalcogen atoms in addition to oxygen atom. Taking into account their possible application in complex formation processes [7], we have developed another synthetic approach to these compounds on the basis of reductive cleavage of dimethyl dichalcogenides, followed by alkylation of methanechalcogenolates with β,β′-dichlorodiethyl ether (**I**), as shown in Scheme 14. In the reaction with a mixture of di-

Scheme 14.

Y = S, Se, Te.
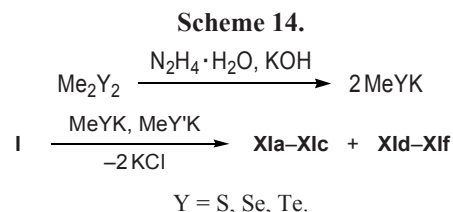
methyl disulfide and dimethyl diselenide, the alkylation at 40–45°C in 1 h gave a considerable amount of intermediate products **XIIa** and **XIIb** (Scheme 15).

Scheme 15.
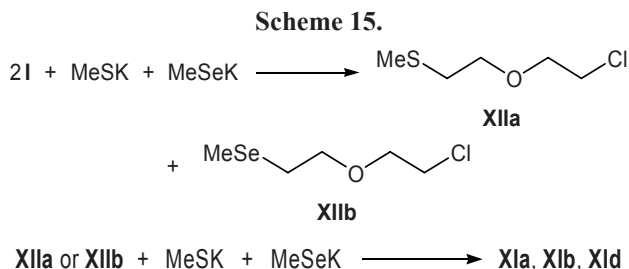
Raising the temperature led to complete conversion of **XII** into **XI**. However, even under these conditions, traces of MeTeCH$_2$CH$_2$OCH$_2$CH$_2$Cl (**XIIc**) were formed from a mixture of Me$_2$S$_2$ with Me$_2$Te$_2$ or of Me$_2$Se$_2$ with Me$_2$Te$_2$. Compounds **XIIa**–**XIIc** were identified by GC–MS. Among cyclic by-products, only 1,4-oxatellurane (**VIIc**) was detected. The formation of the latter indicates that dimethyl ditelluride is unstable and that its reductive cleavage may be accompanied by decomposition with liberation of elemental tellurium, which is typical of many organic ditellurides [16]. The subsequent activation of tellurium via conversion into K$_2$Te enables the reaction with compound **I** according to Scheme 7.

Thus we have developed synthetic approaches to oligomeric, linear, and cyclic compounds having conformationally labile C–O bonds and heavy chalcogen atoms using accessible reagents. The proposed procedures are convenient from the preparative viewpoint.

EXPERIMENTAL

tor temperature 250°C; carrier gas helium, flow rate 0.7 ml/min; oven temperature programming from 60 to 260°C at a rate of 15 deg/min; detector temperature 250°C; quadrupole mass analyzer; electron impact ionization, 70 eV; ion source temperature 200°C; a.m.u. range 34–650). Liquid products were analyzed by GLC on LKhM 80-MD-2 (2000×3-mm column, stationary phase 5% of DC-550 on Chromaton N-AW-HMDS; linear oven temperature programming at a rate of 12 deg/min; carrier gas helium) and Tsvet-500 chromatographs (2000×5-mm steel column, stationary phase 5% of XE-60 on Chromaton N-AW-HMDS; linear oven temperature programming from 30 to 230°C at a rate of 12 deg/min; carrier gas helium).

Oligomer IIa. A mixture of 2.8 g (0.05 mol) of potassium hydroxide, 2.5 g (0.05 mol) of hydrazine hydrate, 15 ml of water, and 3.95 g (0.05 mol) of powdered selenium was heated for 2 h at 80–85°C and cooled to room temperature, and 4.18 g (0.029 mol) of β,β′-dichlorodiethyl ether (**I**) was added (Se–**I** molar ratio 1.7:1). The mixture was stirred for 2 h at 65–70°C, and the precipitate of **IIa** was separated, washed with water, and dried. Yield 4.33 g (75%, calculated on the initial selenium), mp 86–140°C (decomp.), M 1750. IR spectrum, ν, cm^{-1}: 2925, 2851, 2782 w, 1467, 1413, 1352, 1272, 1180, 1102 v.s, 1031, 983, 932 w, 746, 668. Found, %: Cl 4.10; Se 74.93. Calculated, %: Se 68.70 (per monomeric unit). Treatment of oligomer **IIa** with chloroform gave a dark brown extract and a black insoluble residue (found, %: Se 93.73; Cl 2.25). The ^{1}H NMR spectrum of the chloroform solution contained the following signals, δ, ppm: 2.76 m (CH$_2$Se), 3.11 m (CH$_2$Se$_2$), 3.27 m (CH$_2$Se$_3$) (intensity ratio 1:25:10). After separation of oligomer **IIa**, the aqueous hydrazine layer was treated with 50 ml of methylene chloride containing 1 g of toluene. The extract contained 1,4-oxaselenane (**VIIb**, 5 wt % with respect to the amount of toluene) and 1,4,5-oxadiselenepane (**VIIIb**, 9%).

Compound **VIIb**. ^{1}H NMR spectrum, δ, ppm: 2.65 m (2H, CH$_2$Se), 4.00 m (2H, CH$_2$O). ^{13}C NMR spectrum, δ$_C$, ppm: 17.07 (CH$_2$Se, $^1J_{C,Se}$ = 56 Hz), 69.39 (CH$_2$O). ^{77}Se NMR spectrum: δ$_{Se}$ 150.75 ppm. Mass spectrum, m/z (hereinafter, for ^{80}Se) (I/I_{tot}, %): 152 (16.1) $[M]^{+\cdot}$, 124 (3.2) $[M – C_2H_4]^{+\cdot}$, 108, 107 (33.3) $[C_2H_4Se]^{+\cdot}$, $[C_2H_3Se]^+$, 94 (34.1) $[CH_2Se]^{+\cdot}$, 80 (7.1) $[Se]^+$, 43 (31) $[C_3H_7]^+$, 41 (33) $[C_3H_5]^+$.

Compound **VIIIb**. ^{1}H NMR spectrum, δ, ppm: 3.14 t (2H, CH$_2$Se), 3.78 t (2H, CH$_2$O). ^{13}C NMR spectrum, δ$_C$, ppm: 29.29 (CH$_2$Se, $^1J_{C,Se}$ = 74.5 Hz), 70.75

(CH$_2$O). Mass spectrum, m/z (I/I_{tot}, %): 232 (17.3) $[M]^{+\cdot}$, 204 (2.5) $[M – C_2H_4]^{+\cdot}$, 160 (29) $[SeSe]^{+\cdot}$, 43 (23) $[C_3H_7]^+$, 41 (1) $[C_3H_5]^+$.

The reaction of 3.65 g (0.025 mol) of compound **I** with a solution of K$_2$Se prepared from 3.28 g (0.058 mol) of KOH, 9 g of (0.18 mol) of hydrazine hydrate, 90 ml of water, and 2 g (0.025 mol) of powdered selenium (Se–KOH molar ratio 1:2.3) under analogous conditions gave a mixture containing (according to the GLC data) 1,4-oxaselenane (**VIIb**, 45%, calculated on the initial compound **I**) and 1,4,5-oxadiselenepane (**VIIIb**, 10%).

Oligomer IIb. A flask was charged with 7.5 g (0.15 mol) of hydrazine hydrate, 0.95 g (0.015 mol) of 2-aminoethanol, and 4 g (0.05 mol) of powdered selenium. The mixture was heated for 2 h at 70–75°C and cooled to 50°C, 5.4 g (0.038 mol) of compound **I** was added (Se–**I** molar ratio 1.3:1), and the mixture was stirred for 3.5 h at 60–70°C. Yield 4.2 g (72%, calculated on the initial selenium), mp 86–140°C (decomp.), M 2200. IR spectrum, ν, cm^{-1}: 2926, 2851, 2779, 2725 w, 1470, 1440, 1414, 1395, 1351, 1272, 1180, 1102 v.s, 1031, 982, 931, 745, 667, 550 v.w. ^{1}H NMR spectrum, δ, ppm: 2.75 m (2H, CH$_2$Se), 3.11 m (2H, CH$_2$Se$_2$), 3.28 m (2H, CH$_2$Se$_3$), 3.35 m (2H, CH$_2$Se$_4$) (intensity ratio 1:40:8:1), 3.76 m (2H, CH$_2$O), 3.83 m (2H, CH$_2$Cl). Found, %: Cl 3.21; Se 65.31. Calculated, %: Se 68.70. The aqueous hydrazine phase was extracted with chloroform, and the extract contained 10% of 1,4-oxaselenane (**VIIb**) and 2% of 1,4,5-oxadiselenepane (**VIIIb**). Removal of the solvent from the extract gave almost pure compound **VIIb**.

Oligomer III. A flask was charged with 2.8 g (0.05 mol) of potassium hydroxide, 20 g (0.4 mol) of hydrazine hydrate, and 6.38 g (0.05 mol) of powdered tellurium. The mixture was heated for 2 h at 85–90°C and cooled to 50°C, and 4.88 g (0.033 mol) of compound **I** was added (Te–**I** molar ratio 1.5:1). Yield 7.1 g (87%), mp 68–123°C (decomp.), M 9300. IR spectrum, ν, cm^{-1}: 2968, 2922, 2848, 1471, 1457, 1397, 1346, 1259, 1172, 1070 s, 1049, 1025, 957, 717, 625. Found, %: Cl 0.75; Te 80.20. Calculated, %: Te 78.05. The aqueous hydrazine phase was extracted with diethyl ether. The ether extract contained 6% of 1,4-oxatellurane (**VIIc**) and 3% of 1,4,5-oxaditellurepane (**VIIIc**).

Compound **VIIc**. ^{1}H NMR spectrum, δ, ppm: 2.76 t (2H, CH$_2$Te), 4.12 t (2H, CH$_2$O). ^{13}C NMR spectrum, δ$_C$, ppm: –6.42 (CH$_2$Te, $^1J_{C,Te}$ = 134 Hz), 70.95 (CH$_2$O).

^{125}Te NMR spectrum: δ_{Te} 177.52 ppm. Mass spectrum, m/z (hereinafter for ^{130}Te) (I/I_{tot}, %): 202 (19.2) $[M]^{+\cdot}$, 174 (10.8) $[M - C_2H_4]^{+\cdot}$, 158, 157 (14.6) $[C_2H_4Te]^{+\cdot}$, $[C_2H_3Te]^+$, 144 (13.7) $[CH_2Te]^{+\cdot}$, 130 (22.5) $[Te]^+$, 43 (14.6) $[C_3H_7]^+$, 41 (2) $[C_3H_5]^+$.

Compound **VIIIc**. Mass spectrum, m/z (I/I_{tot}, %): 332 (23.6) $[M]^{+\cdot}$, 304 (5.8) $[M - C_2H_4]^{+\cdot}$, 260 (39.3) $[TeTe]^{+\cdot}$, 43 (10) $[C_3H_7]^+$, 41 (3) $[C_3H_5]^+$.

The reaction of 1.8 g (0.0125 mol) of compound **I** with a solution prepared from 3.95 g (0.03 mol) of tellurium, 1.4 g (0.025 mol) of potassium hydroxide (Te–KOH molar ratio 2.5:2.0), and 10 g (0.2 mol) of hydrazine hydrate under the conditions described above for the synthesis of oligomer **III** (Te–**I** molar ratio 2:1) gave 3.2 g (65%, calculated on the initial tellurium) of oligomer **IIIa**, mp 70–130°C (decomp.), M 2450. IR spectrum, ν, cm^{-1}: 2930, 2851, 1463, 1450, 1425, 1406, 1390, 1346, 1296, 1279, 1258, 1175, 1140, 1091, 1071, 1027, 958, 711, 444. Found, %: Cl 2.81; Te 82.00. Calculated, %: Te 82.00.

Oligomers IV–VI (*general procedure*). A solution of potassium disulfide was prepared from 1.4 g (0.025 mol) of KOH, 1.25 g (0.025 mol) of hydrazine hydrate, 7.5 ml of water, and 0.8 g (0.025 mol) of powdered sulfur. A solution of potassium diselenide was prepared using the same amounts of KOH, hydrazine hydrate, and water and 2 g (0.025 mol) of powdered selenium. The solutions were combined, the mixture was heated to 50°C, and 3.9 g (0.027 mol) of compound **I** was added [(S+Se)–**I** molar ratio 2:1]. We isolated 2.4 g (51%, calculated on the initial selenium) of oligomer **IV**, mp 118–130°C (decomp.), M 1790. IR spectrum, ν, cm^{-1}: 3483 w, 2919, 2854 s, 2783, 2727 w, 1470, 1450, 1415, 1398, 1353, 1275 s, 1182, 1104 v.s, 1033, 984, 745, 667, 486. Found, %: Cl 3.97; S 16.02; Se 59.21. Calculated, %: C 17.49; Se 43.16. The aqueous hydrazine layer was extracted with methylene chloride. The extract contained 7% of 1,4-oxathiane (**VIIa**), 6% of 1,4-oxaselenane (**VIIb**), 3% of 1,4,5-oxadiselenepane (**VIIIb**), and 2% of 1,4,5-oxathiaselenepane (**VIIId**). ^{1}H NMR spectrum of **VIIa**, δ, ppm: 2.58 t (2H, CH$_2$S), 3.75 t (2H, CH$_2$O). ^{13}C NMR spectrum, δ_C, ppm: 27.00 (CH$_2$S), 68.62 (CH$_2$O). Mass spectrum of **VIIId**, m/z (I/I_{tot}, %): 184 (11.8) $[M]^{+\cdot}$, 140 (11.1) $[M - C_2H_4O]^{+\cdot}$, 112 (14.3) $[SSe]^{+\cdot}$, 61 (4.5) $[C_2H_5S]^+$, 43 (20) $[C_3H_7]^+$, 41 (1) $[C_3H_5]^+$.

A solution of potassium disulfide was prepared from 2.8 g (0.05 mol) of potassium hydroxide, 20 g (0.4 mol) of hydrazine hydrate, and 1.6 g (0.05 mol) of

powdered sulfur; a solution of potassium ditelluride was prepared using the same amounts of potassium hydroxide and hydrazine hydrate and 6.4 g (0.05 mol) of powdered tellurium. The solutions were combined, the mixture was heated to 50°C, and 8.37 g (0.059 mol) of compound **I** was added [(S+Te)–**I** molar ratio 1.7:1]. We isolated 4.5 g (39%, calculated on the initial tellurium) of oligomer **V**, mp 105–120°C (decomp.), M 6900. IR spectrum, ν, cm^{-1}: 2961, 2923, 2850, 1498 v.w, 1475, 1462, 1425, 1406 v.w, 1377, 1347, 1271, 1177, 1141, 1091 v.s, 1073, 1027, 955, 888, 716, 436 w, 418. Found, %: Cl 1.02; S 1.25; Te 80.54. Calculated, %: C 13.79; Te 55.17. The aqueous hydrazine phase was extracted with methylene chloride. The extract contained 7% of oxathiane **VIIa**, 4% of oxatellurane **VIIc**, and traces of 1,4,5-oxathiatellurepane (**VIIIe**).

A solution of potassium diselenide was prepared from 2.8 g (0.05 mol) of potassium hydroxide, 20 g (0.4 mol) of hydrazine hydrate, and 4 g (0.05 mol) of powdered selenium; a solution of potassium ditelluride was prepared using the same amounts of potassium hydroxide and hydrazine hydrate and 6.4 g (0.05 mol) of powdered tellurium. The solutions were combined, the mixture was heated to 50°C, and 10.8 g (0.076 mol) of compound **I** was added [(Se+Te)–**I** molar ratio 1.4:1]. We isolated 7 g (50%, calculated on the initial tellurium) of oligomer **VI**, mp 100–115°C (decomp.). IR spectrum, ν, cm^{-1}: 2958 w, 2920, 2850, 1464, 1403, 1348, 1261, 1160, 1094 v.s, 1075, 1026, 978, 668 w, 502. Found, %: Se 14.96; Te 67.30. Calculated, %: Se 28.32; Te 45.88. The aqueous hydrazine phase was extracted with methylene chloride. The extract contained 7% of 1,4-oxaselenane (**VIIb**) and 4% of 1,4-oxatellurane (**VIIc**).

3-Oxapentane-1,5-diselenol (X). Oligomer **IIa**, 5 g (0.022 mol), was dissolved in a mixture of 15 g (0.3 mol) of hydrazine hydrate and 5 g (0.089 mol) of potassium hydroxide on heating for 2.5 h at 75–80°C. The mixture was cooled to 25°C and poured into a mixture of ice with 40 ml of concentrated hydrochloric acid under stirring in a stream of argon. An oily material separated and was extracted into methylene chloride. The extract was purged with argon and dried over MgSO$_4$. The solvent was distilled off, and the residue (2.66 g, a mixture of compounds **X** and **VIIIb**) was subjected to vacuum distillation. A fraction with bp 105°C (2 mm) was almost pure diselenol **X**. Yield 0.41 g (8%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: −0.46 t (1H, SeH, $^1J_{Se,H}$ = 46.7 Hz), 2.74 m (2H, CH$_2$Se), 3.66 t (2H, OCH$_2$). ^{13}C NMR

spectrum, δ_C, ppm: 16.76 (CH$_2$Se, $J_{C,Se}$ = 51.2 Hz), 72.35 (CH$_2$O). Mass spectrum, m/z (I/I_{tot}, %): 109 and 108 (23) [C$_2$H$_4$SeH]$^+$, 95 and 93 (18) [CH$_2$SeN]$^+$, [CHSe]$^+$, 81 and 80 (24) [HSe]$^+$, [Se]$^+$. Found, %: C 20.78; H 4.18; Se 67.42. C$_4$H$_{10}$OSe$_2$. Calculated, %: C 20.69; H 4.31; Se 68.09.

1,4,5-Oxadiselenepane (VIIIb) was the main component of a fraction with bp 125–130°C (2 mm). Yield 2.24 g (45%), yellow oily substance. No absorption band at 2295 cm^{-1} (νSe–H) was present in the IR spectrum. Found, %: C 21.61; H 3.69; Se 67.68. C$_4$H$_8$OSe$_2$. Calculated, %: C 20.87; H 3.48; Se 68.68.

Reductive cleavage of oligomer III. Compound **III**, 5.6 g (0.017 mol), was dissolved at 80–85°C in a mixture of 4.9 g (0.087 mol) of potassium hydroxide and 15 g (0.3 mol) of hydrazine hydrate. The mixture was poured into a mixture of 110 g of ice and 92 ml of concentrated hydrochloric acid in a stream of argon. Abundant precipitation of elemental tellurium and gas evolution were observed. The mixture was extracted with methylene chloride, the extract was filtered from tellurium and dried over MgSO$_4$, and the solvent was distilled off under reduced pressure. The residue, 2.4 g, was a dark red liquid. According to the GC–MS data, it contained 1,4-oxatellurane (**VIIc**) and unidentified products. IR spectrum, ν, cm^{-1}: 3451, 3041, 2972, 2927, 2851, 2770, 2715 v.w, 2299 v.w, 2125 v.w, 2027 w, 1621, 1468, 1450, 1404, 1380, 1346, 1263, 1195, 1173, 1141, 1093, 1073, 1027, 991 w, 955, 907, 889, 735, 701, 627, 537, 499, 477. ^{1}H NMR spectrum, δ, ppm: 2.80 m, 3.32 m, 3.72 m (intensity ratio 2:3:5). According to the ^{1}H NMR data, the residue contained 10% of 1,4-oxatellurane (**VIIc**).

A 0.93-g portion of the residue was dissolved in a mixture of 1 g (0.018 mol) of potassium hydroxide and 3.75 g (0.075 mol) of hydrazine hydrate on heating to 80–85°C, and a required amount of methyl iodide was added dropwise to the resulting solution. The mixture was extracted with methylene chloride, the solvent was distilled off, and the residue was evacuated to obtain 0.75 g of a product which was identified as 5-oxa-2,8-ditelluranonane (**XIc**) on the basis of the GC–MS and ^{1}H NMR data (see below).

5-Oxa-2,8-dichalcogenanonanes XIa–XIf (*general procedure***).** *a*. Oligomer **II–VI** was dissolved in the system hydrazine hydrate–potassium hydroxide, as described above for compound **IIa**, and a required amount of methyl iodide was added dropwise to the resulting solution at room temperature. The organic phase was separated, analyzed by GC–MS, and subjected to vacuum distillation. From oligomer **IIa** we

isolated 52% of 5-oxa-2,8-diselenanonane (**XIb**), bp 98–100°C (2 mm). ^{1}H NMR spectrum, δ, ppm: 2.02 s (3H, CH$_3$Se, $^2J_{H,Se}$ = 10.3 Hz), 2.70 t (2H, CH$_2$Se), 3.69 t (2H, CH$_2$O). ^{13}C NMR spectrum, δ_C, ppm: 4.51 (CH$_3$Se, $^2J_{C,Se}$ = 62 Hz), 24.19 (CH$_2$Se, $^2J_{C,Se}$ = 63 Hz), 70.80 (OCH$_2$). Mass spectrum, m/z (I/I_{tot}, %): 262 (8.9) [M]$^+$, 247 (8.2) [M – CH$_3$]$^+$, 203 (2.5), 175 (3.6), 123 (19.4), 108 (8.3), 95 (16.5), 41 (1.9). Found, %: C 27.77; H 5.38; Se 60.99. C$_6$H$_{14}$OSe$_2$. Calculated, %: C 27.70; H 5.39; Se 60.76.

From oligomer **IIb** we obtained 79% of compound **XIb**. Oligomer **III** gave rise to 65% of 5-oxa-2,8-ditelluranonane (**XIc**), bp 137–140°C (2 mm) and 20% of 1,4-oxatellurane (**VIIc**), bp 58–62°C (2 mm).

Compound **XIc**. ^{1}H NMR spectrum, δ, ppm: 1.90 s (3H, CH$_3$Te, $^2J_{H,Te}$ = 20.3 Hz), 2.76 t (2H, CH$_2$Te), 3.72 t (2H, OCH$_2$). ^{13}C NMR spectrum, δ_C, ppm: –22.19 (CH$_3$Te, $^1J_{C,Te}$ = 158 Hz), 2.44 (CH$_2$Te, $^1J_{C,Te}$ = 159.3 Hz), 72.04 (OCH$_2$). ^{125}Te NMR spectrum: δ_{Te} 184.33 ppm. Mass spectrum, m/z (I/I_{tot}, %): 362 (4.5) [M]$^+$, 347 (16.5), 275 (11.9), 173 (5.3), 145 (27.3), 130 (9.2), 43 (4.1), 41 (1.0). Found, %: C 20.91; H 4.06; Te 70.68. C$_6$H$_{14}$OTe$_2$. Calculated, %: C 20.16; H 3.92; Te 71.44.

From oligomer **IV** we obtained 4% of 5-oxa-2,8-dithianonane (**XIa**), bp 92–96°C (2 mm), 8% of 5-oxa-2,8-diselenanonane (**XIb**), 5% of 5-oxa-2-thia-8-selenanonane (**XId**), bp 96°C (2 mm), 2% of 1,4-oxathiane (**VIIa**), and 1% of 1,4-oxaselenane (**VIIb**).

Compound **XIa**. ^{1}H NMR spectrum, δ, ppm: 2.14 s (3H, CH$_3$S), 2.67 t (2H, CH$_2$S), 3.62 t (2H, CH$_2$O). ^{13}C NMR spectrum, δ, ppm: 15.88 (CH$_3$S), 33.37 (CH$_2$S), 70.11 (OCH$_2$). Mass spectrum, m/z (I/I_{tot}, %): 166 w [M]$^+$, 75 (24.7), 74 (27.7), 61 (6.4), 47 (11.5), 41 (14.0). Found, %: C 43.00; H 8.20; S 38.00. C$_6$H$_{14}$OS$_2$. Calculated, %: C 43.40; H 8.40; S 38.55.

Compound **XId**. ^{1}H NMR spectrum, δ, ppm: 2.02 s (3H, CH$_3$Se, $^2J_{H,Se}$ = 10.5 Hz), 2.14 s (3H, CH$_3$S), 2.68 t (2H, CH$_2$Se), 3.64 t (2H, OCH$_2$CS), 3.69 t (2H, OCH$_2$CSe). ^{13}C NMR spectrum, δ_C, ppm: 4.54 (CH$_3$Se, $^2J_{C,Se}$ = 61 Hz). Mass spectrum, m/z (I/I_{tot}, %): 214 (4.3) [M]$^+$, 139 (4.3), 123 (7.4), 95 (9.7), 75 (3.4), 61 (5.8), 47 (6.9), 41 (22.6). Found, %: C 34.81; H 6.60; S 14.73; Se 36.13. C$_6$H$_{14}$OSSe. Calculated, %: C 33.81; H 6.57; S 15.03; Se 37.08.

From oligomer **V** we obtained 65% of 5-oxa-2,8-ditelluranonane (**XIc**), 4% of 5-oxa-2-thia-8-telluranonane (**XIe**), bp 102–108°C (1.5 mm), and 14% of 1,4-oxatellurane (**VIIc**). No 5-oxa-2,8-dithianonane (**XIa**) was detected among the products.

Compound **XIe**. ^{1}H NMR spectrum, δ, ppm: 1.19 s (3H, CH$_3$Te, $^2J_{H,Te}$ = 21 Hz), 2.14 s (3H, CH$_3$S), 2.67 t (2H, CH$_2$Te), 2.78 t (2H, CH$_2$S), 3.62 t (2H, CH$_2$O), 3.75 t (2H, CH$_2$O). ^{13}C NMR spectrum, δ$_C$, ppm: –22.21 (CH$_3$Te, $^1J_{C,Te}$ = 155 Hz), 16.17 (CH$_3$S), 33.71 (CH$_2$S), 70.21 (OCH$_2$CTe, $^1J_{C,Te}$ = 160 Hz), 72.13 (OCH$_2$CS). Mass spectrum, m/z (I/I_{tot}, %): 264 (9.1) $[M]^{+\cdot}$, 249 (6.2), 145 (13.4), 119 (4.1), 75 (20.9), 61 (7.7), 47 (10.7), 41 (13.5). Found, %: C 27.85; H 5.33; S 11.61; Te 48.06. C$_6$H$_{14}$OSTe. Calculated, %: C 27.52; H 5.35; S 12.23; Te 48.78.

From oligomer **VI** we obtained 6% of 5-oxa-2,8-diselenanonane (**XIb**), 9% of 5-oxa-2,8-ditelluranonane (**XIc**), 31% of 5-oxa-2-selena-8-telluranonane (**XIf**), 8% of 1,4-oxaselenane (**VIIb**), and 10% of 1,4-oxatellurane (**VIIc**).

Compound **XIf**. ^{1}H NMR spectrum, δ, ppm: 1.90 s (3H, CH$_3$Te, $^2J_{H,Te}$ = 21 Hz), 2.01 s (3H, CH$_3$Se, $^2J_{H,Se}$ = 10 Hz), 2.66 t (2H, CH$_2$Se), 2.76 t (2H, CH$_2$Te, $^2J_{H,Te}$ = 26 Hz), 3.68 t (2H, OCH$_2$CSe, $^3J_{HH}$ = 7.2 Hz), 3.74 t (2H, OCH$_2$CTe, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: –22.01 (CH$_3$Te), 2.69 (CH$_2$Te, $^1J_{C,Te}$ = 117 Hz), 4.64 (CH$_3$Se, $^1J_{C,Se}$ = 63 Hz), 24.33 (CH$_2$Se, $^1J_{C,Se}$ = 62 Hz), 70.54 (OCH$_2$CSe), 72.57 (OCH$_2$CTe). Mass spectrum, m/z (I/I_{tot}, %): 312 (5.4) $[M]^{+\cdot}$, 297 (13.1), 225 (9.6), 145 (14.1), 123 (9.3), 107 (6.2), 95 (12.4), 43 (2.7), 41 (19.2). Found, %: C 23.01; H 4.58; Se+Te 66.86. C$_6$H$_{14}$OSeTe. Calculated, %: C 23.33; H 4.51; Se+Te 66.94.

b. Dimethyl dichalcogenide (Me$_2$S$_2$, Me$_2$Se$_2$, or Me$_2$Te$_2$) was dissolved in the system hydrazine hydrate–KOH on heating to 80–85°C, and a required amount of compound **I** was slowly added to the resulting solution or to a mixture of solutions containing equimolar amounts of two dimethyl dichalcogenides, maintained at 50°C. The mixture was stirred for 2.5 h at 60–65°C, and the organic layer was separated, analyzed by GC–MS, and subjected to vacuum distillation. The reaction with dimethyl disulfide gave 66% of 5-oxa-2,8-dithianonane (**XIa**), the reaction with dimethyl diselenide gave 68% of 5-oxa-2,8-diselenanonane (**XIb**), and dimethyl ditelluride gave rise to 60% of 5-oxa-2,8-ditelluranonane (**XIc**) and 5% of 1,4-oxatellurane (**VIIc**).

Under analogous conditions, from a mixture of dimethyl disulfide and dimethyl diselenide we obtained 52% of 5-oxa-2,8-dithianonane (**XIa**), 34% (calculated on the initial dimethyl diselenide) of 5-oxa-2,8-diselenanonane (**XIb**), and 62% of 5-oxa-2-thia-8-selenanonane (**XId**).

From a mixture of dimethyl disulfide and dimethyl ditelluride we obtained 55% of 5-oxa-2,8-dithianonane (**XIa**), 25% of 5-oxa-2,8-ditelluranonane (**XIc**), 58% of 5-oxa-2-thia-8-telluranonane (**XIf**), 8% of 1,4-oxatellurane (**VIIc**), and traces of 1-chloro-3-oxa-6-telluraheptane (**XIIc**). Mass spectrum of **XIIc**, m/z (^{35}Cl): 252 $[M]^{+\cdot}$, 224 $[M – C_2H_4]^+$, 173 [CH$_3$TeCH$_2$CH$_2$]$^+$, 159 [CH$_3$TeCH$_2$]$^+$, 145 [CH$_3$Te]$^+$, 130 [Te]$^+$, 107 $[M – CH_3Te]^+$, 93 $[M – CH_3TeCH_2]^+$, 63 [CH$_2$CH$_2$Cl]$^+$, 45 [C$_2$H$_4$OH]$^+$.

From a mixture of dimethyl diselenide and dimethyl ditelluride we obtained 79% of 5-oxa-2,8-diselenanonane (**XIb**), 13% of 5-oxa-2,8-ditelluranonane (**XIc**), 72% of 5-oxa-2-selena-8-telluranonane (**XIf**), 6% of 1,4-oxatellurane (**VIIc**), and traces of 1-chloro-3-oxa-6-telluraheptane (**XIIc**).

The reaction with a mixture of dimethyl disulfide and dimethyl diselenide under milder conditions (see text) gave 18% of **XIa**, 27% of **XIb**, 42% of **XId**, 15% of 1-chloro-3-oxa-6-thiaheptane (**XIIa**), and 14% of 1-chloro-3-oxa-6-selenaheptane (**XIIb**). Mass spectrum of **XIIa**, m/z (^{35}Cl): 154 $[M]^{+\cdot}$, 118 $[M – HCl]^+$, 93 $[M – CH_3SCH_2]^+$, 75 [CH$_3$SCH$_2$CH$_2$]$^+$, 63 [CH$_2$CH$_2$Cl]$^+$, 61 [CH$_3$SCH$_2$]$^+$, 49 [CH$_2$Cl]$^+$, 47 [CH$_3$S]$^+$, 45 [CHS]$^+$, [CH$_2$CH$_2$OH]$^+$, 43 [C$_2$H$_3$O]$^+$, 41 [C$_2$HO]$^+$. Mass spectrum of **XIIb**, m/z (^{35}Cl): 202 $[M]^{+\cdot}$, 123 [CH$_3$SeCH$_2$CH$_2$]$^+$, 109 [CH$_3$SeCH$_2$]$^+$, 95 [CH$_3$Se]$^+$, 93 [CHSe]$^+$, 63 [CH$_2$CH$_2$Cl]$^+$, 45 [CH$_2$CH$_2$OH]$^+$, 43 [C$_2$H$_3$O]$^+$, 41 [C$_2$HO]$^+$.

6-Oxa-3,9-diselenaundecane (XIg). A mixture of 0.19 g (0.0008 mol) of 1,4,5-oxadiselenepane (**VIIIb**), 0.28 g (0.005 mol) of potassium hydroxide, and 1.8 g (0.036 mol) of hydrazine hydrate was stirred for 2.5 h at 76–80°C. The mixture was cooled to room temperature, 0.73 g (0.006 mol) of ethyl bromide was slowly added, and the mixture was stirred for 0.5 h at 35–40°C, cooled to room temperature, and extracted with methylene chloride. The extract was dried over MgSO$_4$, and the solvent was removed. The residue, 0.17 g, was identified as 6-oxa-3,9-diselenaundecane (**XIg**) on the basis of the GLC, ^{1}H and ^{13}C NMR, GC–MS, and analytical data. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH$_3$), 2.55 q (2H, CH$_2$Se), 2.72 t (2H, CH$_2$Se), 3.68 t (2H, OCH$_2$). ^{13}C NMR spectrum, δ$_C$, ppm: 15.79 (CH$_3$), 17.57 (CH$_2$Se), 22.19 (SeCH$_2$), 71.13 (OCH$_2$). Mass spectrum, m/z (I/I_{tot}, %): 290 (1.7) $[M]^{+\cdot}$, 261 (10.7) $[M – C_2H_5]^+$, 189 (10.9), 151 (3.3), 137 (10.3), 109 (22.9), 93 (8.1), 55 (11.5), 45 (4.5), 41 (3.7). Found, %: C 33.62; H 6.18; Se 55.01. C$_8$H$_{18}$OSe$_2$. Calculated, %: C 33.33; H 6.25; Se 54.86.

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