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Dedicated to Academician of the Russian Academy of Sciences N.S. Zefirov
on occasion of his70th anniversary

Reactions of 1,2-Dihaloethanes with Chalcogenide Anions

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Abstract—Reactions of 1,2-dihaloethanes with chalcogenide anions generated from elemental chalcogens and dimethylchalcogens were performed in the hydrazine hydrate–KOH system. The use of anions Se_x^{2-} and Te_x^{2-} (x = 1–4) resulted in ethylene evolution and chalcogen regeneration (or in increased x value in an anion). Oligomers of Thiokol type formed only in the reaction of the 1,2-dichloroethane with a mixture of potassium disulfide and diselenide. The reductive cleavage of oligomers obtained in the hydrazine hydrate–KOH system followed by methylation led to the formation of 1,2-bis(methylthio)ethane, 1-methylseleno-2-methylthioethane, and 1,2-bis(methylseleno)ethane. The features of substitution with chalcogenide anions in vicinal dihalides are discussed. Mass spectra of compounds obtained were measured and analyzed.

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Polymers containing selenium and tellurium possess valuable electrophysical characteristics [1–3], and products of low molecular weight containing two or more chalcogen atoms are efficient ligands in complex formation [4, 5] and promising for preparation of new biologically active compounds [6]. We formerly developed preparation methods for polymethyleneselenides, -diselenides, -sulfidoselenides, -ditellurides, -selenidotellurides, -sulfidoselenidotellurides based on the reactions of chalcogens and their mixtures with dichloromethane in a system hydrazine hydrate–KOH [7, 8].

The reactions of 1,2-dihaloethane under similar conditions are far less thoroughly studied. 1,2-Dichloroethane readily reacted only with alkali metal polysulfides furnishing in virtually quantitative yield oligomeric polysulfides, Thiokols [9–11], widely used as sealants 9] and for preparation of 1,2-ethanedithiol and its derivatives [10]. A similar reaction of 1,2-dibromoethane with potassium polysulfide was also reported [11]. A reaction of 1,2-dichloroethane with a solution of sulfur and selenium in a system water–hydrazine hydrate–NaOH yielded poly(ethylenesulfidoselenides) [7]. The main unit in the macromolecules of these oligomers is assumed to be $–CH_2CH_2SSe–$ (or $–SeCH_2CH_2S–$). Selenium or tellurium Thiokol analogs based on dihaloethanes have not been reported, although both the chalcogen-containing oligomers and the products which can be obtained thereof (1,2-ethanediselenol or –ditellurol derivatives) may be of interest from theoretical and practical viewpoint.

We carried out a systematical investigation of a reaction between 1,2-dihaloethanes with elemental chalcogens in a system hydrazine hydrate–KOH. In the system were generated in situ potassium diselenides and from the chalogens ditellurides [12, 13].

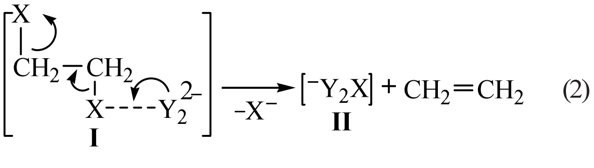
$$4Y + 4KOH + N_2H_4 \cdot H_2O \longrightarrow 2K_2Y_2 + N_2 + 5H_2O$$
$$Y = Se, Te.$$

It was found unexpectedly that reaction of 1,2-dihaloethanes with K_2Se_2 and K_2Te_2 resulted in ethylene evolution and in the recovery of elemental halcogenes in a free state. No oligomeric products were obtained. Neither products of dehydrohalogenation of 1,2-dihaloethanes (vinyl halides and acetylene) were detected.

$$K_2Y_2 + XCH_2CH_2X \xrightarrow[-\,2KX]{} 2Y + CH_2{=}CH_2 \qquad (1)$$
$$X = Cl, Br.$$

Reaction (1) is formally a redox process where the anions Y_2^{2-} are reductants, and 1,2-dihaloethane is oxidant. Hence instead of a nucleophilic substitution reaction (1) proceeds as 1,2-elimination of the halogen. At the same time polyselenides were obtained from 1,3-dihalopropane and Se in the system hydrazine hydrate–alkali and were used for preparation of 1,3-propanediselenol derivatives [14].

The cause of this unexpected path of the reaction between 1,2-dihaloethanes and diselenide and ditelluride anions may lie in the high reducing ability of the latter as compared to S_2^{2-} anions enabling them to attack the halogen atom to form a transition state (**I**).



(2)

A similar mechanism was suggested for the reaction of 2,3-dibromobutanes with sodium iodide affording 2-butene [15]. Highly reactive dichalcogen halides **II** arising in reaction (2) rapidly react with the other anions Y_2^{2-}.

$$\mathbf{II} + Y_2^{2-} \longrightarrow Y_4^{2-} + X^-$$

Further involvement of anions Y_4^{2-} in reaction (2) gives rise to still longer polychalcogenide chains and finally results in the formation of elemental chalcogens.

In reaction (1) (X = Cl) a potassium monoselenide (K_2Se) prepared in the system hydrazine hydrate–KOH with no solvent added was also used [16].

$$2Se + 4KOH + N_2H_4 \cdot H_2O \longrightarrow 2K_2Se + N_2 + 5H_2O$$

In further reaction of K_2Se with 1,2-dichloroethane as in reaction (1) ethylene was evolved, no oligomer products formed, but the elemental selenium did not separated: The system remained homogeneous even at the use of the triple excess of the 1,2-dichloroethane. The conservation of the homogeneity of the system may be due to transformation of the Se^{2-} anions into diselenide (Se_2^{2-}) and polyselenide anions (Se_x^{2-}) well soluble in the system hydrazine hydrate–KOH.

$$2K_2Se + ClCH_2CH_2Cl \longrightarrow CH_2{=}CH_2 + 2KCl + K_2Se_2$$

$$K_2Se + K_2Se_2 + ClCH_2CH_2Cl \longrightarrow CH_2{=}CH_2 + 2KCl + K_2Se_3 \text{ etc.} \qquad (3)$$

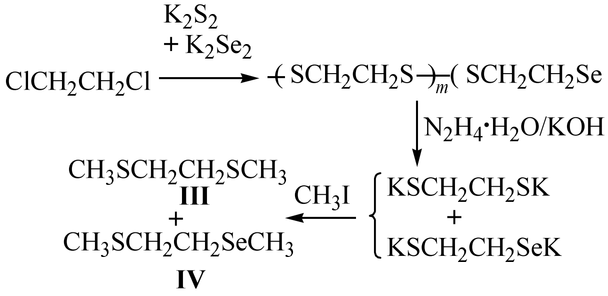
To prove the formation of anions Se_x^{2-} ($X \geq 2$) by reactions (3) the arising mixture of potassium polychalcogenide was treated with methyl iodide. The treatment afforded elemental selenium (66%), dimethyl diselenide (22%), and trace amounts of dimethyl selenide.

$$K_2Se_x + 2CH_3I \xrightarrow[-2KI]{} (CH_3)_2Se_x$$

$$(CH_3)_2Se_x \xrightarrow{(x > 2)} (CH_3)_2Se_2 + Se_{x-2}$$

The instability of dialkylpolyselenides is well known [17].

The reaction of 1,2-dichloroethane with an equimolar mixture of dichalcogenide ions (S_2^{2-} and Se_2^{2-}) was studied in more detail (cf. [7]). In this case each anion was generated separately from the elemental chalcogens in an alkaline water solution of hydrazine hydrate [12, 18] and they were mixed just before addition of the 1,2-dichloroethane. The resulting oligomeric product was of nonuniform composition with inclusions of elemental sulfur and selenium. The product was insoluble in organic solvents, but completely dissolved in the system hydrazine hydrate–KOH due to reductive cleavage of the bridges S–S, Se–Se, and S–Se affording thiolates and selenolates of low molecular weight [11, 14]. The subsequent alkylation of the latter with methyl iodide gave rise to the corresponding methylthio and methylseleno derivatives. The main two products of the reductive cleavage were 1,2-bis(methylthio)ethane (**III**) and 1-methylseleno-2-methylthioethane (**IV**). No 1,2-bis(methylseleno)ethane (**V**) was found among the reaction products. This indicates that in the oligomer in question the $–CH_2CH_2–$ fragments of the molecule are bound either by disulfide or by selenidosulfide bridges, and therefore the structure of the oligomer and the scheme of its cleavage may be described as follows.



(4)

The relative quantity of *m* and *n* units may be approximately evaluated by the ratio of yields of compounds **III** and **IV** equal to 2.5:1 (see EXPERIMENTAL). The lack of bridges with two selenium atoms in the macromolecule originates from the possibility of the pathway through the transition state **I** and liberation of the elemental selenium. The selenyl chloride (**II**) (X =

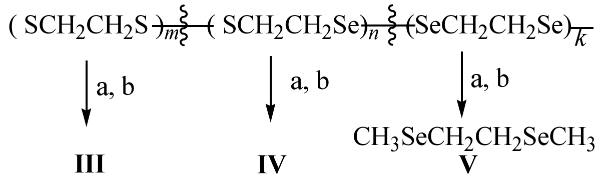
Cl) formed in this case by reaction (2) could also react with polysulfide anions. Presumably this reaction results in the formation of the elemental sulfur.

$$-\mathrm{Se_2Cl} + \mathrm{S_2^{2-}} \xrightarrow[-\mathrm{Cl^-}]{} (\mathrm{Se_2S_2})^{2-}$$

The completion of reaction (4) revealed by the total decoloration of the polychalcogenide solution required twice as much 1,2-dichloroethane as corresponded to the stoichiometric amount according to the reaction equation. This fact may be caused by the repeated activation of elemental selenium (or sulfur) with hydrazine [19] for the hydrazine hydrate is used in excess.

$$4\mathrm{Se} + 5\mathrm{N_2H_4{\cdot}H_2O} \longrightarrow 2(\mathrm{N_2H_5})_2\mathrm{Se_2} + \mathrm{N_2} + 5\mathrm{H_2O}$$

At the higher ratio Se:S in reaction (4) (2:1 and 4:1) the yield of the oligomers formed increased, and the selenium content also grew, but apparently only owing to the larger amount of the elemental selenium. The reductive cleavage of these oligomers resulted in the same compounds **III** and **IV** whose overall yield attained 35 and 18% respectively, and their ratio insignificantly changed in favor of compound **IV**. However in these reaction products 1,2-bis(methylseleno)ethane (**V**) was detected, 0.5% at the ratio Se:S = 2:1, and around 1% at the ratio 4:1 (according to GLC and GC-MS data). The structure of oligomers obtained at these ratios and the character of products arising at their reductive cleavage followed by methylation may be described as follows.



a–$\mathrm{N_2H_4{\cdot}H_2O/KOH}$; b – $\mathrm{CH_3I}$.

The formation of bisselenide fragments in these oligomers apparently occurred by coupling with a diselenide anion of the already existing macromolecules with the terminal chlorine atoms [contrary to reaction (2)].

$$\sim\!\sim\mathrm{SeCH_2CH_2Cl} + \mathrm{Se_2^{2-}} + \mathrm{ClCH_2CH_2S}\sim\!\sim \xrightarrow[-2\mathrm{Cl^-}]{} \sim\!\sim\mathrm{SeCH_2CH_2Se_2CH_2CH_2S}\sim$$

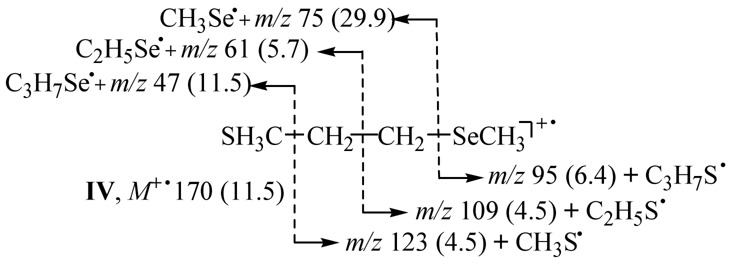
The yield of bisselenide **V** indicates that the probability of such fragments formation is very low.

The structure of compounds **III** and **IV** is confirmed by ^{1}H NMR method (see EXPERIMENTAL), and that of all three compounds **III–V** was proved by GC-MS procedure. Compounds **III–V** at electron impact furnish sufficiently stable molecular ions that appear in the mass spectra as peak clusters characteristic of the presence in the molecule of two sulfur atoms in compound **III**, one in compound **IV**, and of two selenium atoms in compound **V**. Mass spectrum of compound **IV** was measured for the first time, those of compounds **III** and **V** were already published [20–22] and registered in the standard electronic library NIST. This fact helped in confirming structures **III** and **V**.

The characteristic ions and the probable paths of their formation for compound **IV** are given on the scheme. The intensity is reported as percent to the total ionic current. The main fragmentation processes as in the case of compounds **III** and **V** are initiated both by the radical center and by the charged species, and they consist in a simple rupture of the C–C bonds. The first pathway provides the corresponding radicals, the second even ions. The peaks of S-containing ions are as a rule stronger than the Se-containing. The most abundant ion is $[\mathrm{C_3H_7S}]^+$ of *m/z* 75 (29.9). Besides in the spectrum appear peaks of rearranged ions $[\mathrm{CHSe}]^+$ of *m/z* 93 (6.0), (^{80}Se), $[\mathrm{CHS}]^+$ of *m/z* 45 (3.6), and $[\mathrm{C_3H_5}]^+$ of *m/z* 41 (16.4).

Analysis of the fragmentation of the molecular ion of compound **IV** revealed that the probability of rupture is significantly higher for C–Se bond than for C–S bond. Ions of *m/z* 75 and 123 (^{80}Se isotope), respectively, are diagnostic for detecting the fragments $\mathrm{CH_3YCH_2CH_2}$–:

Scheme.



For Y = S the ion with *m/z* 75 is present in the spectrum, for Y = Se that of *m/z* 123. The presence of these ion peaks we used for identification of minor products heavier than compounds **III** and **V** which were formed at the cleavage of the oligomers.

Compound **VI**: $CH_3SCH_2CH_2SCH_2CH_2SeCH_3$ (yield 0.3%) $M^{+\cdot}$ 230, diagnostic ions of *m/z* 75 and 123 are present.

Compound **VII**: $CH_3SeCH_2CH_2SCH_2CH_2SeCH_3$ (yield 0.3%) $M^{+\cdot}$ 278, strong peak of ion with *m/z* 123, ion of *m/z* 75 is lacking.

Compound **VIII**: $CH_3SCH_2CH_2SeCH_2CH_2SeCH_3$ (yield 1%) $M^{+\cdot}$ 278, ions of *m/z* 75 and 123 are present.

Compound **IX**: $CH_3SeCH_2CH_2SeCH_2CH_2SeCH_3$ (yield 1%) $M^{+\cdot}$ is lacking, strong peak of ion with *m/z* 123, 95 (CH_3Se), ion of *m/z* 75 is lacking.

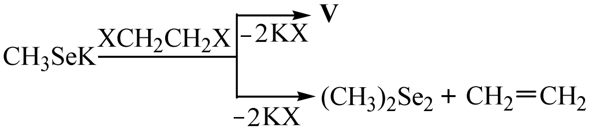
The formation of compounds **VI–IX** indicates the presence in the solution of the initial potassium dichalcogenides of monochalcogenide anions (S^{2-} and Se^{2-}) which afford monochalcogenide units in the oligomer chain.

The presence of elemental selenium in the oligomers was confirmed by the formation of dimethyl selenide and dimethyl diselenide in the course of reductive cleavage of the oligomers followed by methylation; the preparation of these compounds from the elemental selenium had been described in [12].

Compound **III** we previously synthesized from dimethyl disulfide and dichloroethane in a sytem hydrazine hydrate–alkali metal hydroxide in an 82–85% yield [23].

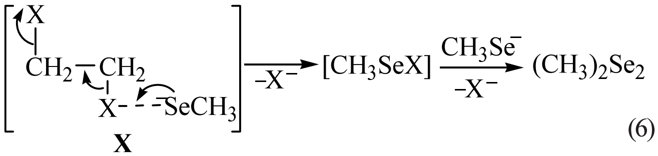
We attempted to prepare compound **V** by a similar procedure.

$$2(CH_3)_2Se_2 + N_2H_4{\cdot}H_2O + 4KOH$$
$$\longrightarrow 4CH_3SeK + N_2 + 5H_2O$$



$$CH_3SeK \xrightarrow{XCH_2CH_2X} \begin{cases} \xrightarrow{-2KX} \mathbf{V} \\ \xrightarrow[-2KX]{} (CH_3)_2Se_2 + CH_2{=}CH_2 \end{cases} \qquad (5)$$

Dimethyl diselenide in the system hydrazine hydrate–KOH was completely reduced and afforded a homogeneous solution [24]; however the treatment of the solution obtained with the double excess of 1,2-dibromo- or 1,2-dichloroethane with respect to the stoichiometric amounts according to reaction (5) gave rise to ethylene, compound **V** (20%), and half of the dimethyl diselenide (53%) was recovered. Apparently here reaction occurred analogous to reaction (2) through a transition state **X**.



X

(6)

The generation of a small quantity of compound **V** is probably due to a successive attack on the carbon atoms of the substrate of two CH_3Se^- anions, since the already formed $CH_3Se–CH_2$ bond is stable under the conditions of reaction (5), for compound **V** (same as compound **IV**) does not change in the system hydrazine hydrate–KOH. Apparently the similar situation was observed when compound **V** was synthesized from selenium, methyllithium, and 1,2-dichloroethane in ethyl ether solution (yield of compound **V** 53%) [22].

$$2(CH_3Se)_2 + 5N_2H_4{\cdot}H_2O \longrightarrow 4N_2H_5SeCH_3 + N_2 + 5H_2O$$

The dimethyl diselenide arising by reaction (6) is constantly activated with excess hydrazine hydrate used as solvent affording anions CH_3Se^- [25].

In the reaction of an equimolar mixture of Na_2S_2 and Na_2Te_2 (separately generated [13, 16]) with 1,2-dichloroethane no oligomer products were obtained. Alongside ethylene we obtained a black powder of a mixture of elemental sulfur and tellurium. This was confirmed by the reaction of the powder with the system hydrazine hydrate–KOH giving rise to a deeply colored solution. The subsequent methylation of the solution yielded a mixture of Me_2S and Me_2Te. In this mixture even compound **III** was lacking according to GLC and GC-MS.

$$(CH_3)_2Te_2 \xrightarrow{N_2H_4{\cdot}H_2O/KOH} 2CH_3TeK$$
$$\xrightarrow[-2KCl]{ClCH_2CH_2Cl} CH_2{=}CH_2 + (CH_3)_2Te_2$$

The attempt to prepare bis(methyltelluro)ethane from dimethyl ditelluride and 1,2-dichloroethane in the system hydrazine hydrate–KOH [see reaction (5)] resulted in ethylene formation and complete recovery of dimethyl ditelluride. The presence of a small amount of dimethyl telluride was due to the partial decomposition of the dimethyl ditelluride [17].

Hence the reaction of 1,2-dihaloethanes with chalcogenide anions takes two probable routes: nucleophilic substitution and dehalogenation involving ethylene evolution and oxidative coupling of the chalcogenide anions. With selenium and especially with tellurium the second route is prevailing.

EXPERIMENTAL

IR spectra of products were measured on spectrophotometers Specord-75IR (from thin films) and Bruker IFS-25 (from pellets with KBr). ^{1}H NMR spectra were registered on spectrometer Bruker DPX-400 (400.1 MHz) from solution in $CDCl_3$, internal reference HMDS.

Mass spectra were obtained on an instrument SHIMADZU CMS-QP5050A, column SPB™-5, 60 m long, internal diameter 0.25 mm, stationary phase film 0.25 μm thick; injector temperature 250°C, carrier gas helium, flow rate 0.7 ml min^{-1}, oven temperature program from 60°C, ramp 15°C min^{-1} to 260°C, detector temperature 250°C. Quadrupol mass-analyzer, electron impact ionization, electrons energy 70 eV, ion source temperature 200°C, detected mass range 34–650 D.

The liquid products obtained were analyzed on a chromatograph LKhM 80-MD-2, column 2000×3 mm, liquid phase XE-60 (5%), ramp ramp 12°C min^{-1}, carrier gas helium.

Gas analysis was carried out on a chromatograph Tsvet-100 eqiupped with a flame ionization detector, column 3000 × 3 mm, oven temperature 80°C, solid phase modified alumina.

Reaction of 1,2-dichloroethane with selenium in a system hydrazine hydrate–KOH. To a solution of 7 g (0.125 mol) of KOH in 25 g (0.5 mol) of hydrazine hydrate at 60–80°C was added by portions within 1 h 3.95 g (0.05 mol) of selenium powder. The reaction mixture was maintained for 2 h at 80–85°C [16], cooled to 45°C, and at this temperature to the obtained solution of K_2Se was added dropwise 2.47 g (0.025 mol) of 1,2-dichloroethane. The reaction occurred with heat evolution and gas liberation. The gaseous products were passed through traps cooled to –40°C and then bubbled through a solution of bromine (4 g) in carbon tetrachloride (30 ml). On adding the calculated quantity of 1,2-dichloroethane the reaction mixture remained homogeneous and deeply colored indicating the presence Se_x^{2-} anions. Therefore two portions of dichloroethane, 0.025 mol each, were added dropwise in succession to the reactor. The complete decoloration of the solution of 4 g of Br_2 in CCl_4 was attained after adding dropwise into the reaction mixture of 3.1 g (0.031 mol) of 1,2-dichloroethane, and therewith ethylene was obtained in an 80% yield. The absorption of the gas products by the bromine solution afforded the only compound, 1,2-dibromoethane (GLC and GC-MS data). No products of vinyl chloride or acetylene bromination were found in the CCl_4 solution. The GC analysis of the gas flushed with argon flow confirmed the presence of ethylene. The negative test with Ilosvay reagent indicated the absence of acetylene in the gas obtained. On completion of 1,2-dichloroethane addition the mixture was heated to 70–75°C for 7 h, cooled to 20–25°C, and within 0.5 h into the reaction mixture 14.2 g (0.1 mol) of methyl iodide was introduced. The reaction proceeded with heat evolution, separation of elemental selenium (1.8 g), and formation of a viscous black tarry product (2 g). The latter two substances were separated from the water layer and extracted with ethyl ether. On removing the solvent from the extract we isolated virtually pure dimethyl diselenide (GLC, comparison with reference), yield 1.2 g (22% calculated on selenium used in the reaction). Additional 0.8 g of elemental selenium was isolated from the tarry product, overall yield of Se 2.6 g (66%).

Reaction of 1,2-dichloroethane with selenium (tellurium) in a system hydrazine hydrate–water–KOH. To a solution of 2.8 g (0.05 mol) of KOH in 15 ml of water containing 2.5 g (0.05 mol) of hydrazine hydrate was added at 60–80°C 3.95 g (0.05 mol) of selenium powder. The mixture was maintained for 2 h at 80–85°C [12], cooled to 45°C, then to the solution of K_2Se_2 thus obtained was introduced 9.9 g (0.1 mol) of 1,2-dichloroethane. The reaction occurred with heat evolution and ethylene liberation (1,2-dibromoethane formation in the solution of Br_2 in CCl_4) and with separation of elemental selenium which was filtered off, washed in succession with water and acetone, and dried. Yield 3.6 g (91%).

In a similar reaction of 4.95 g (0.05 mol) of 1,2-dichloroethane with potassium ditelluride prepared from 6.38 g (0.05 mol) of tellurium powder, 5.6 g (0.1 mol) of KOH, and 25 g (0.5 mol) of hydrazine hydrate was proved ethylene formation (as above) and was isolated 6.0 g (94%) of metallic tellurium.

Reactions of 1,2-dibromoethane with solutions of selenium and tellurium were carried out in the same fashion.

Reaction of 1,2-dichloroethane with an equimolar mixture of potassium disulfide and diselenide. A solution of potassium disulfide was prepared from 5.6 g (0.1 mol) of KOH, 5 g (0.1 mol) of hydrazine hydrate, 30 ml of water, and 3.2 g (0.1 mol) of sulfur powder at 65–70°C. Under similar conditions in another flask potassium diselenide solution was prepared from 7.9 g (0.1 mol) of selenium powder. Into the combiner solution 29 g (0.4 mol) of 1,2-dichloroethane was added. The formed oligomer was separated, washed with water, with acetone, and dried. The oligomer was ground into powder and extracted with boiling benzene to isolate 0.6 g (19%) of elemental sulfur. The residue (10.1 g) was a powder of dark claret color, mp 85–150°C (decomp.). IR spectrum, ν, cm^{-1}: 2915, 1406, 1233, 1187, 1163, 1089, 1026, 784, 762, 718, 675, 602, 496, 475. Found, %: C 6.30; H 1.35; Cl 2.43; S 25.30; Se 77.18. In a similar way at the ratio S:Se = 1 : 2 (1.6 g of sulfur and 7.8 g of selenium) we obtained 7.6 g of oligomer with notable inclusions of elemental selenium, t.decomp. 80–185°C. Found, %: S 14.06; Se 86.83. At the ratio S:Se = 1 : 4 (0.8 g of sulfur and 7.8 g of selenium) we obtained 8.0 g of nonuniform product with the selenium content 88.14%, t.decomp. 65–190°C.

Bis(methylthio)ethane (III) and 1-methylseleno-2-methylthioethane (IV). To a solution of 8 g (0.14 mol) of KOH in 35 g (0.7 mol) of hydrazine hydrate was added by portions at 50°C 3.8 g of oligomer prepared by reaction (4). The reaction mixture was stirred for 2 h at 70–75°C, cooled, and at 20–25°C into the homogeneous solution 15.4 g (0.108 mol) of methyl iodide was added. The mixture was stirred for 0.5 h at 40–42°C and then cooled. The reaction products were extracted into CH_2Cl_2, the extract was dried with $MgSO_4$. The solvent was distilled off, the residue was kept for 0.5 h at the pressure of 5 mm Hg, and thus a mixture of compounds was obtained: 1.06 g (59% with respect to S content in the oligomer) of bis(methylthio)ethane (**III**) [^{1}H NMR spectrum, δ, ppm: 2.13 s (CH_3S), 2.75 s (CH_2S)], and 1.41 g (23% with respect to Se content in the oligomer) of 1-methylseleno-2-methylthioethane (**IV**) [^{1}H NMR spectrum, δ, ppm: 1.25 s (CH_3Se), 2.03 s (CH_3S), 2.78 m (CH_2S, CH_2Se)].

Reaction of 1,2-dichloroethane with an equimolar mixture of potassium disulfide and ditelluride. A solution of potassium disulfide solution was prepared from 2.8 g (0.05 mol) of KOH, 2.5 g (0.05 mol) of hydrazine hydrate, 15 ml of water, and 1.6 g (0.05 mol) of sulfur powder as described above. The solution of K_2Te_2 was prepared from 6.38 g (0.05 mol) of tellurium powder, 5.6 g (0.1 mol) of KOH, and 25 g (0.05 mol) of hydrazine hydrate. The solutions were combined, and at 25–30°C 14.5 g (0.2 mol) of 1,2-dichloroethane was added dropwise. Ethylene liberation was confirmed by 1,2-dibromoethane formation in the bromine solution in CCl_4. The separated black precipitate (7.4 g) consisted of a uniform mixture of tellurium and sulfur. Yield 92%. The obtained mixture of sulfur and tellurium was ground into powder, and 4 g of this powder was introduced into a solution of 11.2 g (0.2 mol) of KOH in 20 g (0.4 mol) of hydrazine hydrate. On complete dissolution of the powder the solvent was heated for 2 h at 85–90°C, cooled to 20–25°C, and at this temperature 15.4 g (0.108 mol) of methyl iodide was added dropwise. The formed organic layer was separated, washed with water, and dried with $MgSO_4$. We obtained 3.65 g of a mixture, consisting of 0.75 g (42%) of dimethyl sulfide and 2.90 g (74%) of dimethyl telluride, which were identified by GLC by comparison with authentic samples.

Bis(methylseleno)ethane (V). At 30°C 2.3 g (0.012 mol) of dimethyl diselenide was added to a solution of 3.4 g (0.06 mol) of KOH in 15 g (0.3 mol) of hydrazine hydrate. The mixture was stirred for 1.5 h at 75–80°C. On cooling to 20°C 4.58 g (0.24 mol) of 1,2-dibromoethane was added at stirring. The reaction with heat evolution and ethylene liberation (see above) did not result in changing the dark claret color of the solution. The mixture was diluted with water (50 ml) and extracted with ether. The extract was dried with $MgSO_4$. On distilling off ether we obtained a residue (2.42 g) that according to GLC and GC-MS contained 18% of 1,2-bis-(methylseleno)ethane (**V**) (yield 20% with respect to the taken dimethyl diselenide) and 76% of dimethyl diselenide (recovered in a 53%). ^{1}H NMR spectrum of compound **V**, δ, ppm: 2.05 s (CH_3Se), 2.83 s (CH_2Se). Mass spectrum (*m/z* value is given for ^{80}Se): 218 [M^+], 123 [$M - SeCH_3$]$^+$, 95 [$SeCH_3$]$^+$. The spectral characteristics are consistent with the published data [22].

Reaction of dimethyl ditelluride with 1,2-dichloroethane. To a solution of 5.04 g (0.09 mol) of KOH in 22.5 g (0.45 mol) of hydrazine hydrate was added at 35–40°C 4.9 g (0.017 mol) of dimethyl ditelluride. The reaction mixture was stirred for 2 h at 80–85°C, cooled, and at 25–30°C into the homogeneous solution was added 3.36 g (0.034 mol) of 1,2-dichloroethane. The reaction was performed and workup was carried out as described above for the dimethyl diselenide. The solution was extracted with CH_2Cl_2. According to the data of GLC, GC-MS, and ^{1}H NMR the extract contained 30% of dimethyl telluride and 70% of dimethyl ditelluride.

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