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Synthesis of the Thiophene Series 1,3-Diselenanes

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Abstract — Direct reaction of propan-1,3-diselenol with thiophene-2-carbaldehydes in trimethylchlorosilane medium is studied. Synthetic procedure for preparation of the previously unknown 1,3-diselenanes of thiophene series is developed. Structure of the newly obtained compounds is established by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. Chromatomass spectrometric stidy of the products obtained is carried out. In some cases reaction may be directed to the synthetis of new types of polymers of original structure.
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Selenoacetals were practically unknown up to 1970. Similarly to their O- and S-analogs they do not react with a Grignard reagent and may be used for preparation of carbonyl compounds, allylic alcohols, epoxides, olefines, ketones, α-thio- and α-silylalkyllithium compounds, etc. [1]. Of special interest are cyclic selenoacetals, the 1,3-diselenanes containing hydrogen atom in C^2 position, which are selectively reduced with BuLi to α-selenoalkyllithium derivatives giving the products of the C–Se or C–H bond cleavage [2–4].

The known synthetic methods for preparing 1,3-diselenoacetals are complex and multystage due to the inavailability of propan-1,3-diselenol which is usually generated in situ from 1,3-dibromopropane as a salt or from diselenocyanates. The product obtained is commonly involved in the reaction with aldehydes in strong acidic media [5–7]. At the same time the reactions of propan-1,3-diselenol and its derivatives with carbonyl compounds are known to proceed under much milder conditions. They are carried out in presence of $ZnCl_2$ in CH_2Cl_2 [3, 8–10] or in CCl_4 solutions [1]. Diselenane yields reach 50–80%. Besides, several procedures for preparing 1,3-diselenanes are known: by reaction of substituted 1,2-selenolane with dimethyl diazomethanephosphonate in CH_2Cl_2 in the presence of BF_3 $(C_2H_5)_2O$ [11, 12], by the 1,3-bis(alkylseleno)allene UV irradiation [13], or by their reaction with diphenyldiazomethane [14]. 1,3-Diselenanes containing thiophene fragments in the molecule are unknown.

We have offered recently a new approach to the synthesis of formely unknown 1,3-dithiolanes and 1,3-dithianes of thiophene series [15,16]. The thiophene-2-carbaldehyde thioacetalization with alkanedithiols proceeds chemoselectively in the presence of 4–5-fold excess of trimethylchlorosilane (Me$_3$SiCl). On the other hand by the method of reductive cleavage of Se–Se bond in poly(trimethylenediselenide) we have prepared and isolated propan-1,3-diselenol [17] which has been involved in the reaction with thiophene-2-carbaldehyde proceeding with the formation of new heterocyclic system, 2-(1,3-diselenan-2-yl)thiophene [18].

Developing these studies we studied reaction of thiophene-2-carbaldehyde and its derivatives and analogs with propan-1,3-diselenol in Me$_3$SiCl medium with the purpose of obtaining 1,3-diselenanes containing thiophene fragments in the molecule. We found that Me$_3$SiCl behaves as catalyst in thiophene-carbaldehyde selenoacetalyzation, but this reaction proceeds not so effectively as the thioacetalization (1,3-dithianes are formed in practically quantitative yields). In Me$_3$SiCl medium (4–8-fold excess) the aldehydes **Ia–Ic** react with propan-1,3-diselenol at –5 to +5°C for 0.5–1 h to form 1,3-diselenanes **IIa–IIc** [Scheme (1)] in 12–57% yield (Table 1).
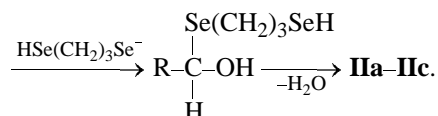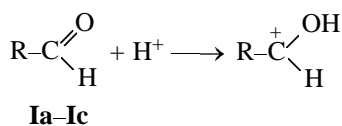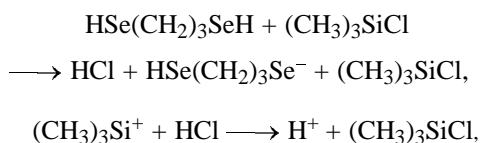
Scheme 1.

Table 1. Yields (%) of the products in the reaction of the thiophene series aldehydes **Ia–Ic** with $HSe(CH_2)_3SeH$

Run no.	1,3-Diselenanes **IIa–IIc**,[a] g (% from theory)	Polymers **VI'a–VIc**,[a] g (wt %)	1,2-diselenolane **IV**,[b] g
1	**IIa**, 0.32 (12.1)	**VI'a**, 0.67 (67.2)	0.32 (17.9)[c]
2[d]	**IIa**, 0.69 (34.0)	**VI''a**, 0.2 (26.0)	0.21 (15.4)[c]
3[d]	**IIb**, 1.68 (57.0)	**VIb**, 0.21 (7.6)	0.11 (6.0)
4[d]	**IIc**, 1.1 (44.7)	**VIc**, 0.2 (17.0)	0.09 (6.1)

[a] Yield on the aldehyde taken. [b] Yield on the propan-1,3-diselenol taken in the reaction. [c] In the experiments 1,2 the traces of 5-(2-thienylmethyl)thiophene-2-carbaldehyde **V** are present. [d] A solution of an aldehyde in Me_3SiCl was added to propane-1,3-diselenol.

According to the Scheme (1) reaction pathway can be regarded as an intramolecular condensation of two selenyl groups with the aldehyde function. Me_3SiCl facilitates the aldehyde group protonation as it is shown in the Scheme (2).

Scheme 2.

$$HSe(CH_2)_3SeH + (CH_3)_3SiCl$$

$$\longrightarrow HCl + HSe(CH_2)_3Se^- + (CH_3)_3SiCl,$$

$$(CH_3)_3Si^+ + HCl \longrightarrow H^+ + (CH_3)_3SiCl,$$

Ia–Ic

Hydrogen chloride is generated in situ by the reaction of diselenol with Me_3SiCl.

Individuality and structure of the prepared 1,3-diselenanes **IIa–IIc** was established by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. ^{1}H NMR spectra contain the signals characteristic of all the proton groups. ^{1}H NMR spectrum of 1,3-diselenane fragment corresponds to the six-membered cycle in the *chair* conformation with equatorial orientation of the thienyl substituent. ^{13}C and ^{77}Se NMR data also confirm the structure of compounds obtained. The composition of 1,3-diselenanes **IIa–IIc** was confirmed by the elemental analysis.

In the 1,3-diselenanes **IIa–IIc** electron impact mass spectra the peaks of stable molecular ions are present (Table 2). Main fragment ions are connected with the cleavage of Se–C bond in $M^{+\cdot}$. The charge and the unpaired electron are localized on the heterocycle-containing fragment [Scheme (3)].

Scheme 3.
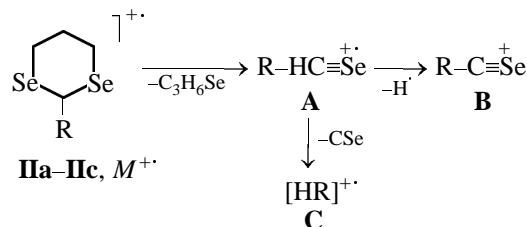
The largest peak in the spectrum relates to the radical ion **A** which loses a hydrogen atom to form the ion **B** or eliminates neutral CSe particle to give the odd-electronic ion **C** of thiophene or thieno[2,3-b]-thiophene.

It is known [19,20] that among the processes of elimination of the radicals $HS^\cdot$ and $HS_2^\cdot$ characteristic of 1,3-dithianes the second one proceeds most intensively. This direction of decay is observed in all the processes of decomposition of 2-aryl-1,3-dithianes and also in the spectrum of bis(1,3-dithiane) where the abstraction of $HS_2^\cdot$ from the molecular ion as well as from the ion $[M - C_3H_6S]^{+\cdot}$ [21,22] takes place. The authors [20] have offered the probable structure of the rearrangement ion $[M - HS_2]^+$ which eliminates $C_3H_4^\cdot$ radical with the formation of tropilium cation (the metastable ion is present). Analogous structure may be attributed probably also to 2-(1,3-diselenan-2-yl)-thiophene **IIa**. Its further decomposition leads to thiopyrrilium cation with m/z 97 [Scheme (4)].

Scheme 4.

IIa, m/z 298   **D**, m/z 137 m/z 298
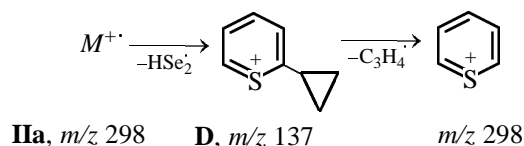
Among the other processes of 1,3-diselenanes **IIa–IIc** fragmentation, the abstraction of $C_3H_7^\cdot$ radical is expressed most clearly [Scheme (5)].
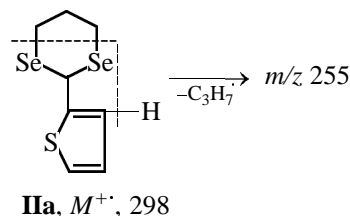
Scheme 5.

IIa, $M^{+\cdot}$, 298

Table 2. Mass spectra of 1,3-diselenanes (X = Se, **IIa–IIc**) and 1,3-dithianes (X = S, **IIIa–IIIc**), 70 eV, m/z^a (I, % of the total ionic curent)

Ion	**IIa**	**IIb**	**IIc**	**IIIa**	**IIIb**	**IIIc**
$M^{+\cdot}$	298 (15.9)	332 (15.6)	354 (15.0)	202 (17.2)	236 (17.4)	258 (20.7)
$[M - C_3H_6X]^{+\cdot}$ (**A**)	176 (36.9)	210 (39.9)	232 (43.7)	128 (34.3)	162 (38.6)	184 (36.6)
$[M - C_3H_7X]^{+}$ [b]	175 (36.9)	209 (39.9)	231 (43.7)	127 (34.3)	161 (38.6)	183 (36.6)
$[M - CH_2R]^{+}$ [c]	201 (1.3)	201 (2.3)	201 (2.7)	105 (3.5)	105 (7.1)	105 (4.1)
$[M - CH_3X]^{+}$	203 (0.2)	–	–	155 (0.7)	–	211 (0.9)
$[M - C_2H_5X]^{+}$	189 (0.2)	223 (–)	245 (0.2)	141 (1.0)	175 (0.5)	197 (0.9)
$[M - C_3H_7]^{+}$	255 (5.0)	289 (2.1)	311 (1.4)	159 (1.9)	193 (0.7)	215 (0.7)
$[M - HX]^{+\cdot}$	217 (0.6)	251 (3.4)	273 (0.9)	169 (0.5)	203 (1.4)	225 (1.1)
$[M - HX_2]^{+}$	137 (13.1)	171 (11.1)	193 (9.2)	137 (8.3)	171 (3.8)	193 (4.7)
$[M - HX_2 - C_3H_4]^{+}$	97 (7.8)	131 (4.9)	153 (12.6)	97 (3.2)	131 (1.5)	153 (7.1)
$R^{+\cdot}$	84 (2.1)	118 (2.2)	140 (2.6)	84 (4.0)	118 (3.3)	140 (9.6)
C_3H_6X	122 (3.5)	122 (2.8)	122 (2.5)	74 (5.1)	74 (7.8)	74 (3.1)
m/z 45	(4.1)	(4.8)	(2.6)	(12.3)	(10.8)	(5.9)
m/z 41	(4.9)	(6.6)	(3.7)	(3.5)	(4.0)	(2.9)
m/z 39	(4.5)	(4.4)	(2.8)	(4.4)	(3.2)	(1.8)

[a] ^{80}Se and ^{35}Cl isotopes. [b] Total intensity with the ion $[M - C_3H_6X]^{+}$. [c] Total intensity with the ion $[M - CH_3X]^{+}$.

Formation of the rearrangement ion $[M - CH_3Se]^{+}$ (**D**) proceeds only at the fragmentation of 2-(1,3-diselenan-2-yl)thiophene **IIa** [Scheme (6)].

Scheme 6.
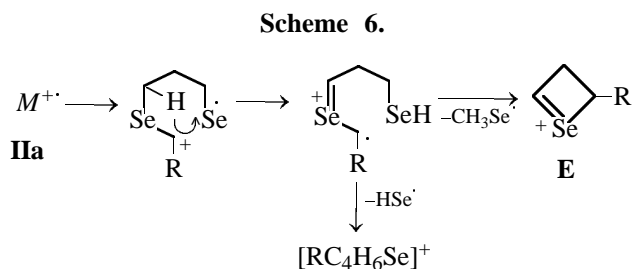
We investigated for comparison the mass spectra of the synthesized previously related 1,3-dithianes **IIIa–IIIc** [16]. As it could be expected, the fragmentation of 2-(1,3-dithian-2-yl)thiophene **IIIa**, its chlorine-substituted derivative **IIIb**, and 2-(1,3-dithian-2-yl)thieno[2,3-b]thiophene **IIIc** practically coinsides with that of 2-aryl-1,3-dithiane molecular ions [21]. Besides, the mass spectra of all compounds **II** and **III** contain the ion peaks connected with fragmentation of the rearrangement ion $[HR]^{+\cdot}$ (Table 2). Thus, the character of fragmentation of 1,3-diselenanes **IIa–IIc** under study and their sulfur analogs is defined by the same rules as the decay of 2-aryl-1,3-dithianes. The nature of heterocycle does not affect the pathway of fragmentation of the molecular ion.

According to GLC data, the reaction mixtures in all the experiments besides 1,3-diselenanes **IIa–IIc** contain also a substance with the outcome temperature 95°C. In the process of isolation of the reaction product (see exp. 2 in the Table 1 and Experimental) a fraction was obtained which according to chromato-mass spectrometric studies contains 1,2-diselenolane **IV** and 5-(2-thienylmethyl)thiophene-2-carbaldehyde **V** in 4.9 : 1 ratio. In the Table 1 the product yields are listed. Formation of compound **IV** in the reaction is evidently caused by the oxidation of diselenol which is extremely unstable even at reduced temperature.

The compound **IV** mass spectrum contains stable molecular ion which is presented by peak claster in the mass range 195–204 D. The molecular ion fragmentation proceeds analogously to the fragmentation of the 1,2-diselenolane prepared by the reductive cleavage of poly(trimethylenediselenides) [23]. Position and multiplicity of signals in ^1H and ^{13}C NMR spectra are also identical with those in the published previously 1,2-diselenolane spectra [23].

As it was mentioned previously, the aldehyde **V** was traced in this fraction by chromatomass spectroscopy. In the Scheme (7) the main directions of its molecular ion fragmentation are presented.

The $M^{+\cdot}$ peak intensity is 75% of the largest peak. Main fragment ions are connected with the cleavage of C–C bonds of methylene group. Elimination of thienyl radical leads to the ion peak with m/z 125 which is of the highest intensity. Stability of this ion arises evidently from the thiophene ring extension to thiapyrane that is characteristic of the aromatic cyclic structures [19, 24]. The driving force of the

Scheme 7.

m/z 125 (100) V, $M^{+\cdot}$, 208 (75) m/z 111 (47)

m/z 180 (7) + CO m/z 179 (6) + HCO·

m/z 83 (10) + CO
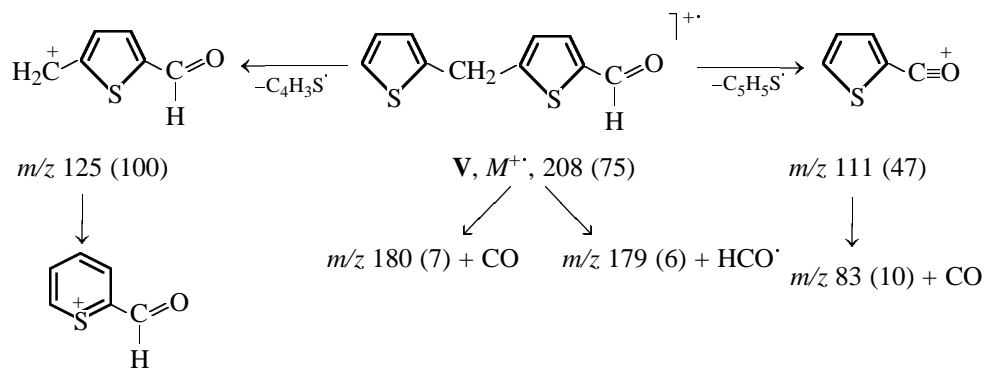
second direction of decay is the formation of acyl ion with m/z 111. Elimination of CO and HCO· radical from $M^{+\cdot}$ leads to appearance of low intensity peaks related to the ions with m/z 180(7) and 179(6).

Compound **V** is formed evidently in the reaction of the starting aldehyde **Ia** with its reduction products. Under the reaction conditions it is involved in the process of polymerization together with the starting aldehyde **Ia**.

Besides the above-mentioned products the polymers **VI'a**–**VIc** containing the atoms of sulfur, selenium, oxygen, and chlorine (Table 3) are obtained. Their formation is caused most probably by the diselenol oxidation with aldehyde **Ia**–**Ic**. Selenols are readily oxidized compounds. We have shown previously that selenophenol on heating to 120°C reacts with dialkyldisulfides to give the corresponding alkanethiols and diphenyldiselenide. This formally redox reaction proceeds according to the free radical mechanism due to the stage of the chalcogenyl radicals transfer [25]. Selenophenol analogously reduces polysulfide polymers to alkanedithiols and gives diphenyldiselenide [26].

Among the aldehydes under study the strongest oxidant for propan-1,3-diselenol is the unsubstituted compound **Ia**. The order of loading this reagent in the reaction mixture is important for its reaction according to the Scheme (1). At the addition of diselenol to the aldehyde **Ia** trimethylchlorosilane solution the 2-(1,3-diselenan-2-yl)thiophene is formed only in 12% yield while the polymer **VI'a** contains large amount of selenium (66.11%). At the same time at the addition of the aldehyde **Ia** trimethylchlorosilane solution to propan-1,3-diselenol the 1,3-diselenane **IIa** yield increases to 34%, and the selenium content in the obtained polymer **VI"a** decreases to 5.70% while the sulfur content increases from 6.17% to 30.75%. This result arises from the fact that in the first case

diselenol is oxidized mainly by the aldehyde excess. In exp. 2 (Table 1) the aldehyde **Ia** Me$_3$SiCl solution is added to diselenol. In this case diselenol excess does not favor its fast oxidation with the aldehyde **Ia**. That is why reaction accelerates, and the polymer **VI"a** amount decreases. According to the Scheme (2) diselenol excess leads to subsequent HCl generation in the amount sufficient for the formation of 1,3-diselenane. Because of low concentration of the aldehyde protonated forms the competing reactions of the aldehyde reduction most probably to the alcohol **F** and diselenol oxidation to 1,2-diselenolane **IV** or to diselenides are observed.

$$I + HSe(CH_2)_3SeH \longrightarrow R–CH_2OH$$
$$F$$

 [or $HSe(CH_2)_3SeSe(CH_2)_3SeH$]

IV
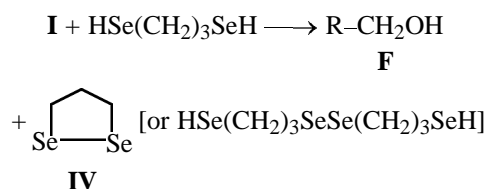
Under the reaction conditions compound **V** containing two thiophene rings bound with the methylene bridge is also formed. It may appear as the product of the starting aldehyde **Ia** alkylation with the alcohol **F**. Despite the higher reacivity of compound **F** as the substrate of ring alkylation, participation of two alcohol molecules in the reaction is little possible because of its low concentration.
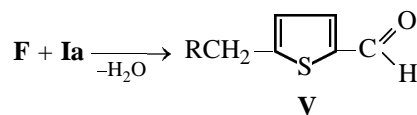
Further reactions of aldehydes **I** and **V**, alcohol **F** and diselenol lead to the formation of polymeric compounds only. Composition of the polymers **VI'a**–**VIc** obtained is determined by the number of links formed from the thienyl and diselenol fragments. Chain interception may take place due to the addition of hydrogen chloride, and basing on the content of

Table 3. Characteristics of polymers **VIa**–**VI'c** and **VI''a** formed in the reactions of aldehydes **Ia**–**Ic** with propan-1,3-diselenol

Comp. no.	Appearance	mp, °C	Found, %					IR spectrum, cm^{-1}
			C	H	Cl	S	Se	
VI'a	Brown powder	93–106	21.86	2.99	1.33	6.17	66.11	2957, 2910, 2885, 2882, 2820 [$\nu(CH_2)$], 1650, 1550 w [$\nu(C=C)$], 1473, 1456, 1418, 1397, 1335 [$\delta(CH, CH_2)$], 1281, 1209, 1100, 1063, 919, 820, 723, 698 [$\delta(CH, thiophen)$], 669, 573 (CCl), 526, 415 [$\nu(CSe)$]
VI''a	Black powder	does not melt up to ~270	53.77	3.36	1.11	30.75	5.70	3087 [$\nu(CH, thiophen)$], 2961, 2916, 2871 [$\nu(CH_2)$], 1660 [$\nu(C=O)$], 1505 [$\nu(C=C)$], 1488, 1455, 1425, 1415, 1373, 1342 [$\delta(CH, CH_2)$], 1284, 1233, 1213, 1133, 1079, 845, 818, 722, 685 [$\delta(CH, thiophen)$], 640, 611 (CCl), 539, 468 [$\nu(CSe)$]
VIb	Dark grey heterogeneous powder with black admixtures	Melting begins at 294	32.59	3.08	1.45	10.00	50.6	2957, 2920 [$\nu(CH_2)$], 1662 v.w [$\nu(C=O)$], 1653, 1634, 1550 v.w [$\nu(C=C)$], 1444, 1434, 1419, 1398, 1335 [$\delta(CH, CH_2)$], 1282, 1209, 1100, 1059, 989, 929, 880, 851, 818, 791, 723, 694 [$\delta(CH)$], 666, 570 (CCl), 526, 478, 430 [$\nu(CSe)$]
VIc	Yellowish brown powder	does not melt up to 300	42.18	2.97	2.02	23.20	28.6	3082 [$\nu(CH, thiophen)$], 2918, 2836 [$\nu(CH_2)$], 1659 [$\nu(C=O)$], 1534, 1504 [$\nu(C=C)$], 1434, 1415, 1378, 1347 [$\delta.(CH, CH_2)$], 1280, 1240, 1209, 1131, 1091, 1050, 973, 883, 844, 818 [$\delta(CH)$], 3082 [$\nu(CH, thiophen)$], 2918, 2836 [$\nu(CH_2)$], 1659, 747, 714 [$\delta(CH)$], 651, 639 (CCl), 514, 481, 465 [$\nu(CSe)$]

chlorine, sulfur, and selenium we estimated the polymer molecular mass, and also the numbers of thienyl (m) and diselenol (n) fragments in the polymer chain. The polymer **VIa** ($M \sim 2700$) is enriched with selenol fragments ($m = 5$, $n = 11$) while in the polymer **VI''a** ($M \sim 3200$, $m = 30$, $n = 1$) the greater part of links is formed in the course of aldehyde decomposition. The polymer **VIb** ($M \sim 2400$, $m = 7$, $n = 8$) is close in composition to the polymer **VI'a** (Table 3) manifesting substitution of chlorine atom in its chain by hydrogen probably in the course of the polymer formation. The polymer **VIa** molecular mass is about 1800. Its sulfur (23.20%) and selenium (28.60%) contents (Table 3) permits to assume the presence of twice more links ($m = 6$) formed from the thieno-[2,3-*b*]thienyl residues than the links ($n = 3$) derived from diselenol fragments. Participation of 1,3-diselenane molecules in the formation of the polymeric product seems improbable because of the established stability of these compounds toward the acid medium.

With the purpose of investigation the polymers **VI'a**–**VIc** structure we carried out reductive cleavage of the polymer **VI'a** with hydrazine hydrate–base system and the subsequent alkylation of the particles obtained with methyl iodide. As we expected, GLC and spectroscopic data showed that the reductive cleavage products are thiophene and bis(methylseleno)propane $CH_3Se(CH_2)_3SeCH_3$ **VII**. The results obtained show that the polymer formation in this reaction proceeds without the thiophene ring cleavage. At the same time the presence of Se–Se bond in the polymers indicates participation of the oligomeric chains formed from propan-1,3-diselenol in the formation of the polymeric product.

Thus, we offered sufficiently convenient preparative procedure for obtaining the unknown previously 1,3-diselenanes of thiophene series based on the direct reaction of propan-1,3-diselenol with the corresponding aldehydes in $(CH_3)_3SiCl$ medium. The selectivity

of diselenane formation is determined by the possibility of proceeding the competing reaction of aldehyde reduction leading finally to the formation of polymeric product. The structure of newly obtained compounds was established by NMR and chromatomass spectrometry, and their composition by the elemental analysis. In some cases the reaction may be directed to the formation of the new type polymers of original structure, exhibiting high thermal stability.

EXPERIMENTAL

The IR spectra of the polymeric compounds were registered on a Bruker JFS-25 spectrometer in KBr pellets. The ^{1}H and ^{13}C NMR spectra of compounds in CDCl$_3$ were taken on a Bruker DPX-400 spectrometer (operating frequency 400.1 and 100.6 MHz respectively) against internal HMDS. For obtaining ^{77}Se NMR spectra external Me$_2$Se=O was used, operating frequency 76.30 MHz. Analysis of reaction mixtures and obtained compounds was carried out on a LHM-8MD-2 chromatograph with linear programming of the column temperature. The 2000×3 mm column was filled with 5% XE-60 silicon on Chromaton N-AW-HMDS, carrier gas helium. Mass spectra were obtained on a Shimadzu GCMS-QP5050A gas chromatomass spectrometer, electron impact ionization (60 eV), 60 m capillary column, SE-54 immobile phase, injector temperature 250°C, the temperature grow rate 10 deg min^{-1} in the range 70–260°C.

2-(1,3-Diselenan-2-yl)thiophene (IIa). *a.* To a solution of 0.996 g of thiophen-2-carbaldehyde (**Ia**) in 10.2 ml of silane 1.8 g of freshly prepared propan-1,3-diselenol was added dropwise at –3 to –5°C. The mixture obtained was stirred for 1 h at 0°C under argon and then heated to room temperature. The reaction progress was monitored by GLC. The grey powder obtained (1g) was filtered off and several times washed with chloroform. The obtained solutions were joined and evaporated at reduced pressure to give brown crystalline residue of the crude 2-(1,3-diselenan-2-yl)thiophene (**IIa**) (0.49 g, 18.6%). The product was extracted with hexane and the extract was cooled to give light cream crystals of the pure compound **IIa**. Yield 0.32 g (12.1%), mp 89°C. IR spectrum (KBr), ν, cm^{-1}: 3071 [ν(CH), thiophene], 2922, 2887 [ν(CH$_2$)], 1419, 1242, 1213, 1032 [δ(CH) in CH$_2$], 971 [δ(CH), thiophene], 843 [ν(C–Se)]. ^{1}H NMR spectrum, δ, ppm: 2.07 d.t.t [1H, H$_a^{5'}$, J(H$_a^{5'}$–H$_e^{5'}$) 14.25, ^3J(H$_a^{5'}$–H$_a^{4'(6')}$) 11.45, ^3J(H$_a^{5'}$–H$_e^{4'(6')}$) 2.40 Hz], 2.22 d.t.t [1H, H$_e^{5'}$, ^3J(H$_e^{5'}$–H$_a^{4'(6')}$) 5.9, ^3J(H$_e^{5'}$-H$_e^{4'(6')}$) 2.8 Hz], 2.95 d.d.d [2H, H$_e^{4'(6')}$, ^2J(H$_e^{4'(6')}$–H$_a^{4'(6')}$)

13.4 Hz], 3.11 d.d.d (2H, H$_a^{4'(6')}$), 5.69 s (1H, H$_a^{2'}$), thiophene ring: 6.91 d.d [1H, H^4; ^3J(H^4–H^3) 3.3, ^3J(H^4–H^5) 5.0 Hz], 7.11 d (1H, H^3), 7.22 d (1H, H^5). ^{13}C NMR spectrum, δ$_C$, ppm: 20.92 (C$^{2'}$), 25.05 (C$^{5'}$), 25.26 (C$^{4'(6')}$), thiophene ring: 125.03 (C^5), 125.84 (C^3), 126.75 (C^4), 144.66 (C^2). ^{77}Se NMR spectrum, δ$_{Se}$ 410.52 ppm. Found, %: C 32.72; H 3.73; S 11.18; Se 52.94. [M]$^{+\cdot}$ 298 (^{80}Se). C$_8$H$_{10}$SSe$_2$. Calculated, %: C 32.43; H 3.38; S 10.81; Se 53.38. M 296.

The powderlike residue obtained after the diselenane **IIa** separation (exp. 1, Table 1) was many times washed with ether on a Schott filter and dried to give 0.67 g of polymer **VI'a** insoluble in acetone, ether, chloroform, benzene, and DMSO (Tables 1 and 3).

The liquid part of reaction mixture (exp. 1., Table 1) obtained after the filtering grey powder off, was evaporated in a water-jet pump vacuum to give 0.38 g of the residue as a light yellow oil. Acording to chromatomass spectral data it contained 1,2-diselenolane **IV** and 5-(2-thienylmethyl)-thiophene-2-carbaldehyde **V** in 4.9:1 ratio. According to GLC 1,2-diselenolane **IV** content in this mixture was 0.32 g (yield 17.9% on the of involved 1,3-propanediselenol), and the aldehyde **V** content was 0.06 g (yield 6.6% on involved thiophene-2-carbaldehyde **Ia**). Spectral data for 1,2-diselenolane **IV**: ^{1}H NMR spectrum, δ, ppm: 2.83 quintet (2H, C–CH$_2$–C), 3.30 t (4H, CH$_2$Se); ^{13}C NMR spectrum, δ$_C$, ppm: 39.99 (C–CH$_2$–C), 31.51 t (CH$_2$Se) (cf. [23]).

b. A mixture of 0.773 g of compound **Ia** and 3.5 ml of Me$_3$SiCl was cooled to 0–5°C and added dropwise at 0°C to 1.39 g of freshly prepared propan-1,3-diselenol. After 20 min of keeping under argon at 3–5°C a precipitate was formed. Reaction mixture was held at the same temperature for 1 h with periodical shaking and then heated to room temperature. The precipitate formed was filtered off and the reaction mixture was treated as described above to give 0.98 g (48%) of the crude reaction product. After additional purification similar to that of the experiment *a* 0.69 g (34%) of pure 2-(1,3-diselenan-2-yl)thiophene **IIa** was isolated.

The polymer **VI''a** of compounds **IV** and **V** was isolated and identified analogously to the procedure of exp. 1.

Reductive cleavage of the polymer VI'a. To a solution of 0.42 g of KOH in 1.9 g of hydrazine hydrate 0.3 g of the polymer **VI'a** was added and resulting mixture was heated at 66–77°C with vigorous stirring for 2 h. The reaction mixture becomes dark grey. For better dissolution of the polymer **VI'a** 0.1 g of KOH

and 1 g of hydrazine hydrate were added and resulting mixture was additionally heated at 77–80°C for 1.5 h. Then the mixture was cooled to room temperature and 2.23 g of methyl iodide was added. Reaction proceeded with heat evolution and discoloration of the mixture. After the additional stirring for 20 min at 30–35°C and cooling to room temperature the reaction mixture was diluted with water, extracted with methylene chloride and filtered to remove unreacted polymer (0.06 g). The extract was washed with water and dried over $MgSO_4$. The solution obtained contained thiophene and bis(methylseleno)propane **VII** in 1:2 ratio (GLC). After the extract concentrating, 0.71 g of the reddish brown liquid containing compound **VII** was obtained. ^{1}H NMR spectrum, δ, ppm: 1.99 quintet (2H, C–CH_2–C), 2.01 s (3H, $SeCH_3$), 2.62 t [2H, $SeCH_2$, $^3J(CH_2CH_2Se)$ 7.22 Hz]. $[M]^{+\cdot}$ 232 (^{80}Se) (cf. [27]). Weight of the unreacted polymer after drying was 0.05 g.

2-(1,3-Diselenan-2-yl)-5-chlorothiophene (IIb).

A mixture of 1.30 g of compound **Ib** and 4.5 of Me_3SiCl was cooled to 0°C and added dropwise at 0 to –3°C to 1.8 g of freshly prepared propan-1,3-diselenol. After keeping the reaction mixture under argon for 0.5 h it was heated to room temperature, and the brown solid precipitated from the reaction mixture was filtered off and treated as described above. Compound **IIb**, 1.68 g (57%) was obtained as clear light yellow crystals, mp 74–75%. ^{1}H NMR spectrum, δ, ppm: 2.04 d.t.t [1H, $H_a^{5'}$, $^2J(H_a^{5'}-H_e^{5'})$ 14.9, $^3J(H_a^{5'}-H_a^{4'(6')})$ 10.3, $^3J(H_a^{5'}-H_e^{4'(6')})$ 2.8 Hz], 2.2 d.t.t [1H, $H_e^{5'}$, $^3J(H_e^{5'}-H_a^{4'(6')})$ 6.7, $^3J(H_a^{5'}-H_e^{4'(6')})$ 3.0 Hz], 2.96 d.d.d [2H, $H_e^{4'(6')}$, $^2J(H_e^{4'(6')}-H_a^{4'(6')})$ 13.4 Hz], 3.04 d.d.d (2H, $H_a^{4'(6')}$), 5.46 d [1H, $H_a^{2'}$, $^4J(H_a^{2'}-H^3)$ 0.83 Hz], thiophene ring: 6.73 d [1H, H^4, $^3J(H^4-H^3)$ 4.0 Hz], 6.88 d.d (1H, H^3). ^{13}C NMR spectrum, δ_C, ppm: 20.32 [($C^{2'}$), $^1J(C^{2'}-Se)$ 77.44 Hz]. 24.75 [$C^{4'(6')}$, $^1J(C-Se)$ 53.29 Hz], 25.08 ($C^{5'}$), thiophene ring: 125.59 (C^3), 125.95 (C^4), 129.41 (C^5), 144.04 (C^2). ^{77}Se NMR spectrum, δ_{Se} 409.30 ppm. Found, %: C 29.69; H 2.44; S 10.38; Se 47.64; Cl 10.41. $C_8H_9ClSSe_2$. Calculated.%: C 29.05; H 2.72; S 9.68; Se 47.81; Cl 10.74. $[M]^{+\cdot}$ 332 (^{80}Se on ^{35}Cl). M 330.5.

The polymer **VIb** (Tables 1 and 3) was isolated analogously to the samples **VI'a** and **VI''a**.

2-(1,3-Diselenan-2-yl)thieno[2,3-b]thiophene (IIc).

Cooled mixture of 1.18 g of the aldehyde **Ic** and 4.5 ml of Me_3SiCl was added dropwise at 0 to –5°C to 1.41 g of the freshly prepared propan-1,3-diselenol. Reaction proceeded vigorously with the heat evolution,

and self heating the reaction mixture to 3°C. After keeping of the reaction mixture under argon for 0.5 h it was heated to room temperature. Dark precipitate formed was filtered off and treated as described above. Compound **IIc** was obtained as light yellow crystals, yield 1.1 g (44.7%), mp 88–89°C. ^{1}H NMR spectrum, δ, ppm: 2.09 d.d.t [1H, $H_a^{5'}$, $^2J(H_a^{5'}-H_e^{5'})$ 14.8, $^3J(H_a^{5'}-H_a^{4'(6')})$ 10.54, $^3J(H_a^{5'}-H_e^{4'(6')})$ 2.75 Hz], 2.21 d.t.t [1H, $H_e^{5'}$, $^3J(H_e^{5'}-H_a^{4'(6')})$ 6.51, $^3J(H_e^{5'}-H_e^{4'(6')})$ 3.06 Hz], 2.97 d.d.d [2H, $H_e^{4'(6')}$, $^2J(H_e^{4'(6')})$ 13.45 Hz], 3.08 d.d.d (2H, $H_a^{4'(6')}$), 5.63 d [1H, $H_a^{2'}$, $^4J(H_a^{2'}-H^3)$ 0.98, $^2J(H_a^{2'}-Se)$ 8.8 Hz], thieno[2,3-b]thiophene system: 7.12 d [1H, H^4, $^3J(H^5-H^4)$ 5.14 Hz], 7.27 d (1H, H^5), 7.29 d (1H, H^3). ^{13}C NMR spectrum, δ_C, ppm: 21.55 (C^2), 25.04 ($C^{4'(6')}$), 25.16 ($C^{5'}$), thieno[2,3-b]thiophene system: 119.07 (C^3), 120.02 (C^4), 120.87 (C^7), 127.61 (C^5), 130.14 (C^8), 145.84 (C^2). ^{77}Se NMR spectrum, δ_{Se}, ppm: 410.82. Found, %: C 33.90; H 2.70; S 18.00; Se 44.58. $C_{10}H_{10}S_2Se_2$. Calculated, %: C 34.09; H 2.44; S 18.18; Se 44.88. $[M]^{+\cdot}$ 354 (^{80}Se). Calculated: M 352.

The polymer **VIa** (Tables 1 and 3) was isolated similarly to the above-mentioned polymers.

REFERENCES

1. Clarembeau, M., Cravador, A., Dumont, W., Hevesi, L., Krief, A., Lucchetti, J., and Ende, D. Van, *Tetrahedron,* 1985, vol. 41, no. 21, p. 4793.

2. Krief, A. and Defrere, L., *Tetrahedron Lett.,* 1996, vol. 37, no. 44, p. 8011.

3. Krief, A. and Defrere, L., *Tetrahedron Lett.,* 1996, vol. 37, no. 15, p. 2667.

4. Krief, A. and Defrere, L., *Tetrahedron Lett.,* 1996, vol. 37, no. 44, p. 8015.

5. Geens, A. and Anteunis, M., *Bull. Soc. Chim. Belg.,* 1971, vol. 80, p. 639.

6. Geens, A., Swaelens, G., and Anteunis, M., *J. Chem. Soc., D,* 1969, no. 9, p. 439.

7. Pinto, B.M., Johnston, B.D., and Nagelkerke, R., *Heterocycles,* 1989, vol. 28, no. 1, p. 389.

8. Jensen, K.A. and Yenriksen, L., *Chem. Scand. Acta Chim.,* 1970, no. 9, p. 3213.

9. Baudoux, G., Norberg, B., Wouters, J., Defrere, L., Krief, A., and Eurard, G., *Acta Cryst., C,* 1998, vol. 54, no. 9, p. 1505.

10. Krief, A., Elie, B., and Willy, D., *Tetrahedron Lett.,* 1993, vol. 34, no. 52, p. 8517.

11. Mikolajczyk, M., Mikina, M., Graczyk, P.P., Wieczo-

rek, M.W., and Bujackz, G., *Tetrahedron Lett.,* 1991, vol. 32, no. 33, p. 4189.

12. Mikolajczyk, M., Mikina, M., Graczyk, P.P., and Balczewski, P., *Synthesis,* 1996, no. 11, p. 1232.

13. Shimizu, T., Miyasaka, D., and Kamigata, N., *J. Org. Chem.,* 2001, vol. 66, no. 5, p. 1787.

14. Shimizu, T., Miyasaka, D., and Kamigata, N., *J. Org. Chem.,* 2001, vol. 66, no. 21, p. 7202.

15. Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., Albanov, A.I., and Deryagina, E.N., *Zh. Org. Khim.,* 2003, vol. 39, no. 10, p. 1598.

16. Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., Albanov, A.I., and Deryagina, E.N., *Zh. Org. Khim.,* 2006, vol. 42, no. 2, p. 272.

17. Levanova, E.P., Sukhomazova, E.N., Papernaya, L.K., Albanov, A.I., and Deryagina, E.N., *Zh. Obshch. Khim.,* 2004, vol. 74, no. 10, p. 1755.

18. Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., Albanov, A.I., and Deryagina, E.N., *Zh. Org. Khim.,* 2004, vol. 40, no. 3, p. 468.

19. Vulfson, N.S., Zaikin, V.G., and Mikaya, A.I., *Mass-spektrometriya organicheskikh soedinenii* (Mass Spectrometry of Organic Compounds), Moscow: Khimiya, 1986; Zaikin, V.G., Varlamov, A.V., Mikaya, A.I.,

and Prostakov, N.S., *Osnovy mass-spektrometrii organicheskikh soedinenii* (Basic Mass Spectrometry of Organic Compounds), Moscow: MAIK "Nauka-Interperiodika," 2001.

20. Bowie, J.N. and White, P.Y., *OMS,* 1972, vol. 6, p. 317.

21. Bowie, J.H. and White, P.Y., *OMS,* 1969, vol. 2, p. 611.

22. Bowie, J.H., White, P.Y., and Blumenthal, T., *OMS,* 1987, vol. 22, p. 541.

23. Russavskaya, N.V., Levanova, E.P., Sukhomazova, E.N., Grabel'nykh, V.A., Klyba, L.V., Zhanchipova, E.R., Albanov, A.I., and Korchevin, N.A., *Zh. Obshch. Khim.,* 2006, vol. 76, no. 2, p. 243.

24. Lebedev, A.T., *Mass-spektrometriya v organicheskoi khimii* (Mass Spectrometry in Organic Chemistry), Moscow: BINOM, 2003.

25. Deryagina, E.N., Papernaya, L.K., Shilkina, T.A., and Vvedenskii, V.Yu., *Zh. Obshch. Khim.,* 1998, vol. 68, no. 3, p. 471.

26. Shilkina, T.A., Papernaya, L.K., and Deryagina, E.N., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 2, p. 283.

27. Gylliver, D.J., Hope, E.G., Levason, W., Myrray, S.G., Potter, D.M., and Marshall, G.L., *J. Chem. Soc., Perkin Trans. 2,* 1984, no. 3, p. 429.