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To the memory of A. A. Petrov

Synthesis and Reactivity of 5-Alkoxybenzo[b]furan-2-selenolates

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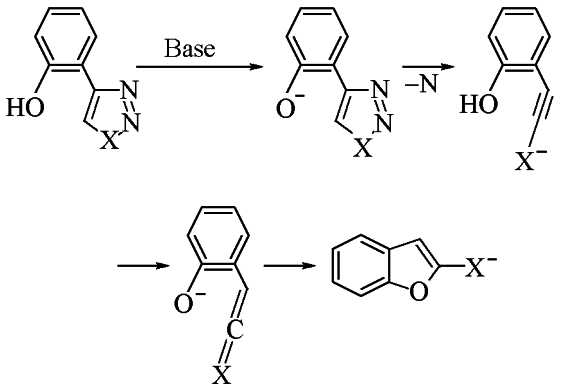
Abstract—By reaction of selenium(IV) oxide with 5-alkoxy-2-hydroxyacetophenone semicarbazones 4-(5-alkoxy-2-hydroxyphenyl)-1,2,3-selenadiazoles were prepared. The latter readily decomposed when treated with potassium carbonate yielding 5-alkoxybenzo[*b*]furan-2-selenolates. The selenolates obtained underwent alkylation effected by monochloroacetamide and were arylated by 2,4-dinitrochlorobenzene. The oxidation of selenolates with iodine furnished bis(5-alkoxybenzo[b]furan-2-yl) diselenides.

All known methods of benzo[b]furans preparation are mostly based on the intramolecular cyclization of monosubstituted or ortho-disubstituted benzenes [1]. We recently found a new synthetic method for 2-benzo[b]furanthiolates and -selenolates proceeding from transformations of 4-(2-hydroxyphenyl)-1,2,3-thia- or -selenadiazoles, and also ortho-disubstituted benzenes [2–5]. We proved that this method of benzo[*b*]furans synthesis occurred through intramolecular addition of the ortho-hydroxy group to the products arising at decomposition of 1,2,3-thia and -selenadiazoles effected by bases, namely, to thioketenes and selenoketenes [5] (Scheme 1).

Scheme 1.



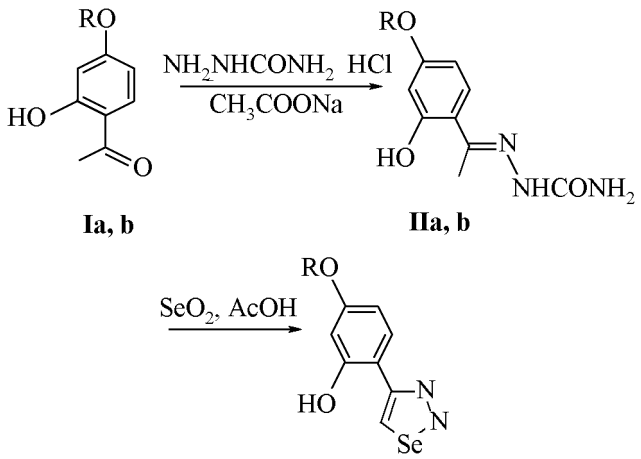
X = S, Se.

In extension of these studies we report here on the synthesis of 4-(5-alkoxy-2-hydroxyphenyl)-1,2,3-selenadiazoles and their conversion into 5-alkoxybenzo[b]furan-2-selenolates.

It should be noted that some derivative of 2-benzo[*b*]furanchalcogenolates possess a biological activity [6], and derivatives of 5-hydroxybenzo[b]furans are antioxidants [7].

In attempt to prepare new derivatives of 2-benzo[b]furanselenolates with a second functional group in position *5* of the benzene ring of the benzofuran we first synthesized by a common procedure [8] from 2-hydroxy-5-methoxy- and 2-hydroxy-5-benzyloxyacetophenones **Ia, b** the corresponding previously unknown semicarbazones **IIa, b** (Scheme 2). Then treating semicarbazones **IIa, b** with selenium(IV) oxide in acetic acid we obtained 4-(2-hydroxy-5-methoxy- and -benzyloxy)-1,2,3-selenadiazoles (**IIIa, b**) in an overall yield ~50%.

Scheme 2.



Ia, b **IIa, b** **IIIa, b**

I–**III**, R = Me (**a**), $PhCH_2$ (**b**).

The structure of 4-(2-hydroxy-5-methoxy- and -benzyloxy)-1,2,3-selenadiazoles (**IIIa, b**) was confirmed by ^1H, ^{13}C NMR, and mass spectra.In the ^1H

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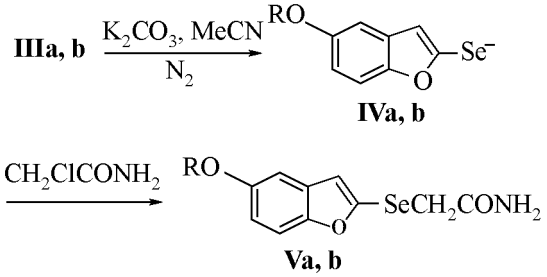
and ^{13}C NMR spectra of selenadiazole **IIIa, b** the signals from protons and carbon nuclei both by chemical shifts and multiplicity were similar to analogous signals in the ^{1}H and ^{13}C NMR spectra of 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [9]. Proton signals from H^5 in the selenadiazole ring appeared as singlets in the region 10.12 ppm for **IIIa** and 10.11 ppm for **IIIb** with satellites from spin-spin coupling H–C–^{77}Se, ^{2}J 40–42 Hz. In the spectrum of 4-(2-hydroxyphenyl)-1,2,3-selenadiazole the signal of this proton appeared at 10.09 ppm accompanied by satellites from spin-spin coupling H–C–^{77}Se, ^{2}J 42 Hz [9]. Analogous pattern is observed with the ^{13}C NMR spectra: The chemical shift of C^5 in the selenadiazole ring amounts to 142.9 ppm in compounds **IIIa, b**, and to 142.1 ppm with satellites C–^{77}Se, *J* 133 Hz in 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [9]. The peaks of molecular ions in the mass spectra of selenadiazoles **IIIa, b** have an isotope composition corresponding to that calculated from the assumed structure. The fragmentation pattern also confirms the structure of selenadiazoles **IIIa, b**. The principal path of molecular ion decomposition consists in ejection first of a nitrogen molecule and then of the selenium atom in agreement with selenadiazoles decomposition under light and on heating [10].

4-(5-Alkoxy-2-hydroxyphenyl)-1,2,3-selenadiazoles (IIIa, b) like the 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [9] readily decompose with nitrogen evolution even when treated with such a weak base as potassium carbonate. This reaction is presumably a multistage process: formation of a phenolate, intramolecular charge transfer to the selenadiazole ring, decomposition of the heterocycle anion with nitrogen liberation and alkyneselenolate generation, intramolecular proton transfer providing selenoketene followed by intramolecular cyclization involving the hydroxy group and the selenoketene fragment to furnish brightly colored solution of 5-alkoxybenzo[*b*]-furan-2-selenolate anions (**IVa, b**) (Schemes 1, 3).

Scheme 3.



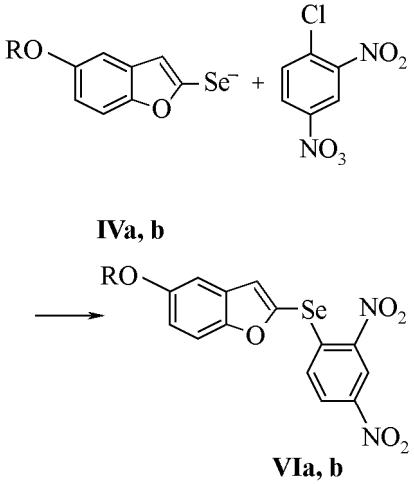
IV, V, R = Me (**a**), $PhCH_2$ (**b**).

The formation of 2-benzo[*b*]furan anions **IVa, b** is proved by their alkylation with chloroacetamide: In 30–50% yield were obtained 2-(5-alkoxybenzo[*b*]-furan-2-ylselenyl)acetamides (**Va, b**) (Scheme 3).

The structure of the alkylation products **Va, b** obtained was confirmed by ^{1}H, ^{13}C NMR, and mass spectra. In the ^{1}H and ^{13}C NMR spectra of acetamides **Va, b** the proton and carbon signals both by chemical shifts and multiplicity are similar to the respective spectra of 2-alkylselenobenzo[*b*]furans [9] and chloroacetamide [11]. The peaks of molecular ions in the mass spectra of compounds **Va, b** have an isotope composition corresponding to that calculated from the structure assigned thereto. Further fragmentation of molecular ions also is consistent with the structure of 2-(5-alkoxybenzo[*b*]furan-2-ylselenyl)acetamides (**Va, b**). The main fragmentation path in benzofurans **Va, b** is directed to the less strong bond $C_{sp}{}^{3}$–Se, i.e first occurs ejection of the acetamide substituent $[M-58]^{+}$, and then of the selenium atom.

5-Alkoxybenzo[*b*]furan-2-selenolate anions **IVa, b** reacted similarly with 2,4-dinitrochlorobenzene. As a result in 39–53% yield were isolated 2-(2,4-dinitrophenylselenyl)-5-alkoxybenzo[*b*]furans (**VIa, b**) (Scheme 4).

Scheme 4.



VI, R = Me (**a**), CH_2Ph (**b**).

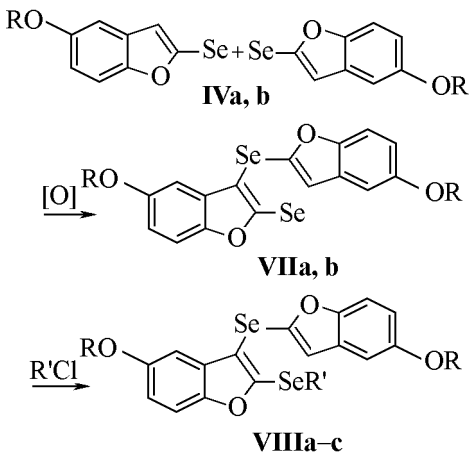
The structure of the arylation products **VIa, b** obtained was confirmed by ^{1}H, ^{13}C NMR, and mass spectra. In the ^{1}H and ^{13}C NMR spectra of 2-(2,4-dinitrophenylselenyl)-5-alkoxybenzo[b]furans (**VIa, b**) the proton and carbon signals both by chemical shifts and multiplicity are similar to the respective spectra of benzofuran fragment and 2,4-dinitrophenyl substituent in 2-(2,4-dinitrophenylselenyl)benzo[*b*]furans

[9]. Chemical shifts and multiplicity of signals from protons and carbon atoms of alkoxy substituents in the spectra of compounds **VIa, b** are consistent with the published data [12]. In the mass spectra of 2-(2,4-dinitrophenylselenyl)-5-alkoxybenzo[*b*]furans (**VIa, b**) were observed molecular ion peaks with isotope composition corresponding to the assumed structure. Further fragmentation of molecular ions is similar in pattern to that observed on 2-(2,4-dinitrophenylselenyl)benzo[*b*]furan [9]: A 2-nitroso-4-nitrophenylselenium ion is ejected. The composition of the most abundant fragment ions in the mass spectra of benzofurans **VIa, b** depends on the structure of respective alkoxy substituent: for 2-(2,4-dinitrophenylselenyl)-5-methoxybenzo[*b*]furan (**VIa**) it is a cation of 5-methoxy-2,3-dehydrobenzo[*b*]furan-2-one, and for 2-(2,4-dinitrophenylselenyl)-5-benzyloxybenzo[b]furan (**VIb**) it is benzyl cation.

By means of TLC we established that alkylation and arylation of compounds **III** was accompanied by insignificant side processes. From the reaction products obtained from 4-(5-benzyloxy-2-hydroxyphenyl)-1,2,3-selenadiazole (**IIIb**) and chloroacetamide in the presence of a base was isolated by column chromatography a side product, 2-[5-benzyloxy-3-(5-benzyloxybenzo[b]furan-2-ylselenyl)benzo[*b*]furan-2-ylselenyl]acetamide (**VIIIa**). And in reaction products obtained from 4-(2-hydroxy-5-methoxy and -benzyloxyphenyl)-1,2,3-selenadiazoles (**IIIa, b**) with a base and 2,4-dinitrochlorobenzene the separation by column chromatography provided as side products 2-(2,4-dinitrophenylselenyl)-5-methoxy-3-(5-methoxybenzo[*b*]furan-2-ylselenyl)benzo[b]furan (**VIIIb**) and 2-(2,4-dinitrophenylselenyl)-5-benzyloxy-3-(5-benzyloxybenzo[b]furan-2-ylselenyl)benzo[*b*]-furan (**VIIIc**) (Scheme 5). Presumably the formation of these side products testifies to the anion-radical nature of the brightly colored decomposition products of selenadiazoles. In reactions carried out under argon no bright coloration of the reaction mixture was observed, and the yield of side products of arylation was considerably reduced. This assumption is supported by the published facts of dimerization occurring with enthiyl and selenyl radicals resulting in 1,4-dithiynes and selenines [13, 14].

The structure of the side products of alkylation and arylation was confirmed by ^{1}H, ^{13}C NMR, and mass spectra. In the ^{1}H NMR spectrum of acetamide **VIIIa** in contrast to the spectrum of acetamide **Vb** are observed two signals corresponding to CH_2PH protons of benzyl substituent, resonances of CH_2CONH_2 protons of a single acetamide substituent, and one singlet from an H^3 proton in the benzofuran ring.

Scheme 5.



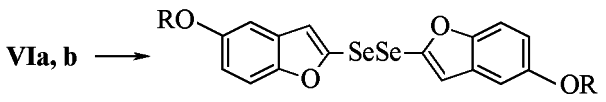
VII, R = Me (**a**), CH_2Ph (**b**); **VIII**, R = CH_2Ph, R' = CH_2CONH_2 (**a**); R = Me, R' = 2,4-$(NO_2)_2C_6H_3$ (**b**); R = CH_2Ph, R' = 2,4-$(NO_2)_2C_6H_3$ (**c**).

In the ^{13}C NMR spectrum of acetamide **VIIIa** appear analogous changes as compared with the respective spectrum of acetamide **Vb**. The ^{1}H and ^{13}C NMR spectra of arylation products are changed in the same respect as compared with the respective spectra of the main arylation products **VIa, b**. In the mass spectrum of the side alkylation product **VIIIa** was detected a weak peak of the molecular ion with the isotope composition corresponding to the calculation in keeping with the assumed structure. The fragmentation of the molecular ion also supports the structure of acetamide **VIIIa**. Taking into consideration the intensity of fragment peaks the most probable process consists in ejection of the acetamide substituent. Further in succession occur ejection of selenium atom and formation of ions of di(benzyloxybenzofuran-2-yl) and 5-benzyloxybenzofuran. The second decomposition path consists in hydrogen migration resulting in the corresponding benzofuran-2-selenol and 1,4-diselenine, similar to thermal decomposition of diphenyl disulfide [13] and fragmentation in the mass spectrum of bis(2-benzo[*b*]furanyl) diselenides [15]. The fragmentation of molecular ions of other side products **VIIIb, c** follows a similar pattern save the specific features regarding the presence of a 2,4-dinitrophenyl substituent [9].

Oxidation of 5-alkoxybenzo[*b*]furan-2-selenolate anions (**IVa, b**) with iodine afforded in good yield bis(5-methoxybenzo[*b*]furan-2-yl) diselenide (**IXa**)

and bis(5-benzyloxybenzo[*b*]furan-2-yl) diselenide (**IXa**) (Scheme 6).

Scheme 6.



IXa, b

R = **Me** (**a**), CH_2Ph (**b**).

The structure of bis(5-alkoxybenzo[b]furan-2-yl) diselenides (**IXa, b**) was confirmed by ^1H, ^{13}C NMR, and mass spectra that are consistent with the corresponding spectral data for such diselenides [15].

EXPERIMENTAL

Melting points were measured on Boetius heating block. ^1H and ^{13}C NMR spectra were registered on spectrometers Bruker Avance (300 and 75 MHz respectively) and Bruker AMX400 (400 and 100 MHz respectively, as internal references served the residual protons (^1H) and carbon nuclei (^{13}C) of deuterated solvents. Mass spectra were recorded on Kratos MS 890 instrument with direct admission of the sample into the ion source, ionizing electrons energy 70 eV, temperature of ionizing chamber 200°C. The mass of molecular ions in the mass spectra is given for the principal isotope ^{80}Se. The reaction progress was monitored by TLC on Silufol UV-254 plates, development under UV irradiation or in iodine vapor. All solvents used in the study were purified and dried by standard procedures. 2,5-Dihydroxyacetophenone was prepared by Fries reaction from hydroquinone diacetate [16]. 2-Hydroxy-5-methoxyacetophenone [17] and 2-hydroxy-5-benzyloxyacetophenone [18] were prepared from 2,5-dihydroxyacetophenone.

2-Hydroxy-5-methoxyacetophenone semicarbazone (IIa). A dispersion of 4.9 g (29 mmol) of 2-hydroxy-5-methoxyacetophenone (**Ia**), 3.45 g (31 mmol) of semicarbazide hydrochloride, and 5.2 g (64 mmol) of sodium acetate in 40 ml of 2-propanol and 55 ml of water was boiled at vigorous stirring for 2 h, then cooled to 15–18°C and left overnight. The separated precipitate was filtered off, washed with water, and dried. Yield of semicarbazone **IIa** 4.8 g (73%), mp 221–223°C (ethanol). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.22 s ($CH_3C=N$), 3.72 s (CH_3O), 6.21 s (NH_2), 6.76 d (H^5), 6.83 d.d (H^6), 7.00 s (H^3), 9.63 s (OH), 12.05 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.7 ($CH_3C=N$), 55.8 (CH_3O), 112.9 (C^3), 116.2 (C^5), 117.7 (C^6), 121.3 (C^2), 148.6 (C=N), 151.8 (C^4), 151.9 (C=O), 155.7 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 223 (64) M^+, 206 (100) $[M–NH_3]^+$, 191 (10) $[M–NH_3– CH_3]^+$, 180 (31) $[M–CONH]^+$, 163 (78) $[M– CO(NH_2)_2]^+$, 162 (86) $[M–CONH_2NH_3]^+$, 148 (86) $[M–NHNHCONH_3]^+$, 107 (41) [*p*-quinone]$^+$, 79 (43) [*p*-quinone – CO]$^+$. Found, %: C 53.65, 53.77; H 5.12, 4.98. $C_{10}H_{13}N_3O_3$. Calculated, %: C 53.81; H 5.83.

5-Benzyloxy-2-hydroxyacetophenone semicarbazone (IIb). A dispersion of 1.2 g (5 mmol) of 5-benzyloxy-2-hydroxyacetophenone (**Ib**), 0.6 g (5.5 mmol) of semicarbazide hydrochloride, and 0.9 g (11 mmol) of sodium acetate in 10 ml of 2-propanol and 5 ml of water was boiled at vigorous stirring for 8 h, then cooled to 15–18°C and left overnight. The separated precipitate was filtered off, washed with water, and dried. Yield of semicarbazone **IIb** 1.25 g (83%), mp 223–226°C (ethanol). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.20 s ($CH_3C=N$), 5.05 s (CH_2O), 6.22 s (NH_2), 6.76 d (H^5), 6.91 d.d (H^6), 7.10 d (H^3), 7.38 m (Ph), 9.63 s (OH), 12.07 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.7 ($CH_3C=N$), 70.3 (CH_2O), 114.2 (C^3), 117.2 (C^5), 117.6 (C^6), 121.3 (C^2), 128 and 128.7 (*o*-, *m*-, *p*-CPh), 137.8 (C^1 Ph) 148.5 (C=N), 150 (C=O), 152.1 (C^4), 155.7 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 299 (20) M^+, 282 (11) $[M–NH_3]^+$, 256 (3) $[M–CONH]^+$, 238 (2) $[M–CONH_2NH_3]^+$, 208 (48) $[M–Bn]^+$, 191 (22) $[M–Bn–NH_3]^+$, 165 (22) $[M–Bn–CONH]^+$, 147 (51) $[M–Bn–CONH_2NH_3]^+$, 91 (100) $[Bn]^+$. Found, %: C 64.43, 64.36; H 5.81, 5.78. $C_{16}H_{17}N_3O_3$. Calculated, %: C 64.21; H 5.69.

4-(2-hydroxy-5-methoxy)-1,2,3-selenadiazole (IIIa). In a flask protected from light and equipped with a magnetic stirrer and a reflux condenser connected to a bubbler trap was mixed 2.23 g (10 mmol) of 2-hydroxy-5-methoxyacetophenone semicarbazone (**IIa**), 10 ml of glacial acetic acid and then at stirring was added 1.16 g (10.5 mmol) of fine powder of selenium(IV) oxide. The reaction mixture at vigorous stirring was heated to 60°C and then stirred at 60–65°C for 4–5 h till the end of gas evolution. After cooling to 20–25°C the reaction mixture was filtered to separate from precipitated selenium. The filtrate was diluted with 20 ml of water, the separated precipitate was filtered off and dried. The yield of selenadiazole **IIIa** 1.8 g (71%). Light-brown plates, mp 102–103°C (methanol – water), R_f 0.27 (eluent benzene). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.76 s (CH_3), 6.90 d.d (H^4), 6.99 d (H^3), 7.82 d (H^6), 9.93 s (OH), 10.12 s (H^5 Ht, with satellites

HSe, ^2J 42 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 55.8 (CH_3), 99.5 (C^1), 114.6 (C^6), 119.3 (C^3, C^4), 142.9 (C^5 Ht), 149 (C^5), 152.6 (C^2), 158.8 (C^4 Ht). Mass spectrum, *m/z* (I_{rel}, %): 256 (8) M^+, 228 (17) $[M-N_2]^+$, 213 (6) $[M-N_2-CH_3]^+$, 148 (100) $[M-N_2-Se]^+$, 133 (45) $[M-N_2-CH_3-Se]^+$, 91 (8) $[Bn]^+$, 77 (32) $[Ph]^+$. Found, %: C 42.43, 42.31; H 2.90, 3.05. $C_9H_8N_2O_2Se$. Calculated, %: C 42.19; H 3.12.

4-(5-benzyloxy-2-hydroxy)-1,2,3-selenadiazole (IIIb). Under conditions similar to described under the previous experiment was mixed 1.2 g (4 mmol) of 5-benzyloxy-2-hydroxyacetophenone semicarbazone (**IIb**), 10 ml of glacial acetic acid and then at stirring was added 0.5 g (4.5 mmol) of fine powder of selenium(IV) oxide. The reaction mixture at vigorous stirring was heated to 60 and then stirred at 60–65°C for 3 h till the end of gas evolution. After cooling to 20–25°C the reaction mixture was filtered to separate from precipitated selenium. The filtrate was diluted with 20 ml of water, the separated precipitate was filtered off and dried. The yield of selenadiazole **IIIb** 0.8 g (62%). Light-brown plates, mp 105–107°C (2-propanol–water), R_f 0.46 (eluent chloroform). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.1 s (CH_2), 6.98 m (H^3, H^4), 7.41 m (Ph), 7.91 d (H^6), 9.98 s (OH), 10.11 s (H^5 Ht, with satellites HSe, ^2J 40 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 70.1 (CH_2), 115.9 (C^1), 117.2 (C^6), 117.6 (C^4), 119.3 (C^3), 127.9, 128.1 and 128.7 (*o*-, *m*-, *p*-CPh), 137.7 (C^1 Ph), 142.9 (C^5 Ht), 149.2 (C^5), 151.6 (C^2), 158.8 (C^4 Ht). Mass spectrum, *m/z* (I_{rel}, %): 332 (0.5) M^+, 304 (5) $[M-N_2]^+$, 224 (5) $[M-N_2-Se]^+$, 91 (100) $[Bn]^+$. Found, %: C 53.98, 54.12; H 3.97, 3.86. $C_{15}H_{12}N_2O_2Se$. Calculated, %: C 54.22; H 3.61.

2-(5-Methoxybenzo[*b*]furan-2-ylselenyl)acetamide (Va). A dispersion of 0.4 g (1.6 mmol) of selenadiazole **IIIa**, 10 ml of dry acetonitrile, 0.15 g (1.6 mmol) of chloroacetamide, and 0.26 g (1.9 mmol) of K_2CO_3 was boiled for 7 h in a setup protected from light till disappearance of the initial selenadiazole **IIIa** (TLC monitoring). The precipitate was filtered off, and the light-brown solution was evaporated at reduced pressure. The resinous residue was subjected to chromatography on a column 3 × 20 cm packed with silica gel of L 40/100 grade, eluent dichloromethane–ethyl acetate, 1 : 1. The fraction with the reaction product was collected, the solvent was removed to afford 0.25 g (56%) of acetamide **Va**, light-brown crystals, R_f 0.48 (eluent dichloromethane–ethyl acetate, 1 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.57 s (CH_2, with satellites HSe, ^2J 14.6 Hz), 3.83 s (CH_3), 5.68 s and 6.16 s (NH_2), 6.89 d.d (H^6), 6.91 s (H^3), 6.97 d (H^4), 7.35 d (H^7). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 29.7 (CH_2), 55.9 (CH_3), 102.8 (C^4), 111.5 (C^7), 113.8 (C^6), 114.8 (C^3), 128.9 (C^9), 142.6 (C^8), 152.4 (C^5), 156.1 (C^2), 171.4 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 285 (91) M^+, 227 (100) $[M-CH_2CONH_2]^+$, 212 (11) $[M-CH_2CONH_2-CH_3]^+$, 163 (37) $[M-CH_2CNH_2-Se]^+$, 147 (4) $[M-CH_2CONH_2-Se]^+$, 122 (12) $[M-CH_2CONH_2-CH_3-Se]^+$. Found, %: C 46.14, 46.27; H 4.03, 4.15. $C_{11}H_{11}NO_3Se$. Calculated, %: C 46.32; H 3.86.

2-(5-Benzyloxybenzo[*b*]furan-2-ylselenyl)acetamide (Vb). A dispersion of 0.4 g (1.2 mmol) of selenadiazole **IIIb**, 20 ml of dry acetonitrile, 0.11 g (1.2 mmol) of chloroacetamide, and 0.2 g (1.4 mmol) of K_2CO_3 was boiled for 5 h in a setup protected from light till disappearance of the initial selenadiazole **IIIb** (TLC monitoring). The gray-brown reaction mixture was evaporated at reduced pressure. The resinous residue was subjected to chromatography on a column 3×20 cm packed with silica gel of L 40/100 grade, eluent chloroform–ethyl acetate, 1 : 1. The fraction with the reaction product was collected, the solvent was removed to afford 0.14 g (32%) of acetamide **Vb**, light-brown plates, mp 146–149°C, R_f 0.25 (eluent chloroform–ethyl acetate, 1 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.63 s (CH_2CO, with satellites HSe, ^2J 15 Hz), 5.11 s (CH_2Ph), 6.95 d.d (H^6), 7.01 s (H^3), 7.11 s and 7.54 s (NH_2), 7.18 d (H^4), 7.4 m (Ph), 7.46 d (H^7). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 30.8 (CH_2Se), 70.3 (CH_2Ph), 104.5 (C^4), 111.6 (C^7), 113.5 (C^6), 113.9 (C^3), 128 (C°), 128.1 (C*m*), 128.7 (C*p*), 129.3 (C^9), 137.5 (C^1 Ph), 145 (C^8), 151.9 (C^5), 155 (C^2), 170.5 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 361 (17) M^+, 303 (1) $[M-CH_2CONH_2]^+$, 223 (6) $[M-CH_2CONH_2-Se]^+$, 91 (100) $[Bn]^+$. Found, %: C 56.42, 56.29; H 4.44, 4.51. $C_{17}H_{15}NO_3Se$. Calculated, %: C 56.66, H 4.16. By chromatography of the resinous residue of the reaction mixture was separated also the second reaction product, 2-[5-benzyloxy-3-(5-benzyloxybenzo[*b*]furan-2-ylselenyl)benzo[*b*]furan-2-ylselenyl]acetamide (**VIIIa**).Yield of acetamide **VIIIa** 0.05 g (12%). Light-brown plates, mp 105–115°C, R_f 0.4 (eluent chloroform–ethyl acetate, 1 : 1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.79 s (CH_2CO, with satellites HSe, ^2J 15 Hz), 5.00 s and 5.07 (CH_2Ph), 6.96 m (H^6 + $H^{6'}$), 7.07 s (H^3 + $H^{3'}$), 7.06 m (Ph), 7.16 s and 7.61 s (NH_2), 7.15 d (H^4 + $H^{4'}$), 7.39 m (Ph + H^7 + $H^{7'}$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 30.5 (CH_2Se); 70.2, 75.6 (CH_2Ph); 103.6, 104.7 (C^4 + $C^{4'}$); 111.9, 112.3 (C^7 + $C^{7'}$); 113.6, 114.5, 114.7,

115.1 (C^3 + C^6 + $C^{3'}$ + $C^{6'}$); 127.5, 127.9, 128.1, 128.7, 129.0 (°, *m*, *p*-CPh); 130.6 (C^9 + $C^{9'}$); 137.3, 137.5 (C^1 + $C^{1'}$Ph); 143.3 (C^8 + $C^{8'}$); 151.5, 151.8 (C^5 + $C^{5'}$); 155.1, 155.5 (C^2 + $C^{2'}$); 170.3 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 663 (0.3) M^+, 604 (1) $[M–CH_2CONH_3]^+$, 525 (1) $[M–CH_2CONH_2–Se]^+$, 524 (1) $[M–CH_2CONH_3–Se]^+$, 446 (2) [di(5-BnO-benzofuran-2-yl)]$^+$, 304 (1.4) [5-BnO-benzofuran-2-SeH], 223 (1.3) [5-BnO-benzofuran]$^+$, 91 (100) $[Bn]^+$. Found, %: C 57.99, 57.83; H 4.03, 3.87. $C_{32}H_{25}NO_5Se_2$. Calculated, %: C 58.12; H 3.81.

2-(2,4-Dinitrophenylselenyl)-5-methoxybenzo[*b*]-furan ((VIa). A dispersion of 0.5 g (2 mmol) of selenadiazole **IIIa**, 10 ml of dry acetonitrile, 0.32 g (2.3 mmol) of K_2CO_3 was boiled at vigorous stirring for 10 min. Vigorous nitrogen evolution was observed, and the reaction mixture turned dark-blue. Then to the reaction mixture was added dropwise a solution of 0.4 g (2 mmol) of 1-chloro-2,4-dinitrobenzene in 5 ml of acetonitrile. The color of the reaction mixture changed to light-yellow. The reaction mixture was boiled for 5 h, then filtered, and the filtrate was evaporated at reduced pressure. The residue was subjected to chromatography on a column 3 × 20 cm packed with silica gel of L 40/100 grade, eluent chloroform–heptane, 1 : 2. From the first fraction on removing the solvent was obtained 0.3 g (39%) of benzofuran **VIa**, light-yellow crystals, mp 119–122°C ($CHCl_3$–heptane). R_f 0.5 (eluent $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.88 s (CH_3O), 7.04 d.d (H^6), 7.11 d (H^4), 7.29 d (H^7), 7.31 d (H^3), 7.46 d (H^6 arom), 8.16 d. d (H^5 arom), 9.16 d (H^3 arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 56.3 (CH_3O), 103.6 (C^7), 112.7 (C^3), 116.2 (C^3 arom), 121.2 (C^4), 121.7 (C^5), 127.7 (C^1 arom), 128.8 (C^6), 132.2 (C^9), 142.0 (C^5 arom), 143.5 (C^6 arom), 145.4 (C^2), 146.5 (C^4 arom), 153.7 (C^2 arom), 156.9 (C^8). Mass spectrum, *m/z* (I_{rel}, %): 394 (10) M^+, 231 (6) [*M* – 2-oxo-5-methoxybenzofuran]$^+$, 163 (100) [*M* – 2-NO-4-$NO_2C_6H_3Se]^+$, 135 (11) [*M* – 2-NO-4-$NO_2C_6H_3Se$ – CO]$^+$, 119 (4) [*M* – 2-NO-4-$NO_2C_6H_3Se$ – $CO_2]^+$. Found, %: C 45.97, 46.12; H 2.73, 2.87. $C_{15}H_{10}N_2O_6Se$. Calculated, %: C 45.83; H 2.56.

From the second fraction was isolated 0.12 g (20%) of 2-(2,4-dinitrophenylselenyl)-5-methoxy-3-(5-methoxybenzo[*b*]furan-2-ylselenyl)benzo[*b*]furan (**VIIIb**), yellow crystals, mp 192–194°C ($CHCl_3$–heptane). R_f 0.33 (eluent $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.78 s (CH_3O'), 3.87 s (CH_3O), 6.76 m (H^4+ $H^{4'}$+ $H^{7'}$), 6.83 d (H^7), 7.07 m (H^6 + H^{61}), 7.18 d ($H^{3'}$), 7.46 d (H^6 arom), 7.73 d.d (H^5 arom), 8.96 d (H^3 arom). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.8, 55.9 (CH_3O + CH_3O'); 102.7, 102.9 (C^7 + $C^{7'}$); 111,4; 112.7; 114.0; 116.0; 116.9; 118.9; 121.0; 127.0; 128.3; 130.3; 131.0; 141.4; 142.3; 144.8; 145.7; 147.4; 151.7; 152.5; 156.1, 157.1 (C^8 + $C^{8'}$). Mass spectrum, *m/z* (I_{rel}, %): 620 (16) M^+, 452 (1) [*M*–H–2,4-$(NO_2)_2C_6H_3]^+$, 373 (100) [*M* – 2,4-$(NO_2)_2C_6H_3Se]^+$, 309 (57) [*M*–2-NO-4-$NO_2C_6H_3Se$–Se]$^+$, 227 (7) [2-Se-5-$CH_3OC_8H_4O]^+$, 163 (11) [2-oxo-5-methoxybenzofuran]$^+$. Found, %: C 46.84, 46.59; H 2.91, 2.73. $C_{24}H_{16}N_2O_8Se_2$. Calculated, %: C 46.63; H 2.61.

2-(2,4-Dinitrophenylselenyl)-5-benzyloxybenzo-[*b*]furan (VIb). A dispersion of 0.4 g (1.2 mmol) of selenadiazole **IIIb**, 10 ml of dry acetonitrile, 0.2 g (1.4 mmol) of K_2CO_3 was boiled at vigorous stirring for 10 min. Vigorous nitrogen evolution was observed, and the reaction mixture turned dark-blue. Then to the reaction mixture was added dropwise a solution of 0.24 g (1.2 mmol) of 1-chloro-2,4-dinitrobenzene in 5 ml of acetonitrile. The color of the reaction mixture changed to light-yellow. The reaction mixture was boiled for 4 h, then filtered, and the filtrate was evaporated at reduced pressure. The residue was subjected to chromatography on a column 3 × 20 cm packed with silica gel of L 40/100 grade, eluent chloroform–hexane, 1 : 2. From the first fraction on removing the solvent was obtained 0.3 g (53%) of benzofuran **VIb**, yellow crystals, mp 154–156°C ($CHCl_3$ – heptane). R_f 0.7 (eluent benzene). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.17 s (CH_2O), 7.1 d. d (H^6), 7.15 d (H^4), 7.28 d (H^7), 7.38 m [Ph(Bn) + H^3], 7.61 d (H^6 Ar), 8.38 d. d (H^5 Ar), 8.95 d (H^3 Ar). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 72.2 (CH_2O); 105.3 (C^7); 112.7 (C^3); 116.4 (C^3 Ar); 121.3 (C^4); 121.8 (C^5); 128.0, 128.8 [C^1 Ar + *o*, *m*, *p*-CPh(Bn) + C^6]; 131.8 (C^9); 137.4 [C^1Ph(Bn)]; 141.9 (C^5 Ar); 142.0 (C^6 Ar); 144.9 (C^2); 146.3 (C^4 Ar); 153.0 (C^2 Ar); 155.4 (C^8). Mass spectrum, *m/z* (I_{rel}, %): 470 (6) M^+, 231 (2) [*M* – 2-oxo-5-benzyloxybenzofuran]$^+$, 239 (2) [*M* – 2-NO-4-$NO_2C_6H_3Se]^+$, 119 (4) [*M* – 2-NO-4-$NO_2C_6H_3Se$ – $CO_2]^+$, 91 (100) $[PhCH_2]^+$, 65 (6) $[C_5H_5]^+$. Found, %: C 53.54, 53.63; H 2.92, 2.74. $C_{21}H_{14}N_2O_6Se$. Calculated, %: C 53.75; H 3.01. From the second fraction we isolated 0.1 g (23%) of 2-(2,4-dinitrophenylselenyl)-5-benzyloxy-3-(5-benzyloxybenzo[*b*]furan-2-ylselenyl)benzo[b]furan (**VIIIc**), yellow crystals, mp 162–165°C. ($CHCl_3$ – heptane). R_f 0.72 (eluent $CHCl_3$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.03 s, 5.1 s (CH_2O + CH_2O'); 6.75 s

(H^3); 6.87 d (H^4); 7.45 m [H^7 + Ph(Bn) + H^6 Ar]; 7.77 d.d (H^5Ar); 8.99 d (H^3 Ar). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 71.2 (CH_2O + CH_2O'); 104.4, 104.8 (C^7 + $C^{7'}$); 111.9, 113.1 ($C^{3'}$ + $C^{2'}$); 115.1 (C^3 Ar); 116.4, 117.9 (C^4); 119.3, 121.4 (C^5); 127.4, 128.0, 128.4, 128.6, 128.7,129.0 [C^1 Ar + *o*, *m*, *p*-CPh(Bn) + C^6 + $C^{6'}$]; 130.6, 131.4 (C^9 + $C^{9'}$); 137.0, 137.3 [C^1Ph(Bn) + $C^{1'}$Ph(Bn)]; 141.9 (C^5 Ar); 142.6 (C^6 Ar); 145.2, 146.1 (C^2 + C^3); 152.2 (C^4 Ar); 153.0 (C^2 Ar); 155.7, 156.6 (C^8 + $C^{8'}$). Mass spectrum, *m/z* (I_{rel}, %): 605 (0.2) [*M* – 2,4-$(NO_2)_2C_6H_3$]$^+$, 604 (0.2) [*M* – 2,4-$(NO_2)_2C_6H_4$)]$^+$, 525 (0.2) [*M* – 2,4-$(NO_2)_2C_6H_3Se$]$^+$, 446 (0.4) [*M* – 2,4-$(NO_2)_2C_6H_4Se$ – Se]$^+$, 303 (0.6) [5-$PhCH_2$–OC_8H_4O-2-Se]$^+$, 91 (100) [$PhCH_2$]$^+$, 77(3) [Ph], 65 (6) [C_5H_5]$^+$. Found, %: C 56.25, 56.38; H 3.42, 3.29. $C_{36}H_{24}N_2O_8Se_2$. Calculated, %: C 56.13; H 3.14.

Bis(5-methoxybenzo[*b*]furan-2-yl) diselenide (IXa). In a flask protected from light equipped with a magnetic stirrer and reflux condenser connected to a flask with absorbing solution was mixed 0.53 g (2 mmol) of 4-(2-hydroxy-5-methoxy)-1,2,3-selenadiazole (**IIIa**), 15 ml of dry acetonitrile, and 0.33 g (3.3 mmol) of sodium carbonate. The reaction mixture was boiled at vigorous stirring for 3 h till the end of nitrogen evolution and disappearance of the initial selenadiazole **IIIa** (according to TLC, R_f 0.27, eluent benzene). On cooling to 20°C to the reaction mixture was added dropwise at vigorous stirring a solution of 0.25 g (1 mmol) of iodine in 10 ml of ethanol. The color of the reaction mixture changed from cherry-red to dark yellow. The mixture was stirred for 3 h and then poured into 25 ml of 6% hydrochloric acid. The reaction product was extracted into 25 ml of chloroform, the extract was dried with calcined calcium chloride, the solvent was removed on a rotary evaporator. The resinous residue was subjected to chromatography on a column 3×20 cm packed with silica gel of L 40/100 grade, eluent chloroform–heptane, 1 : 1. Yield of diselenide **IXa** 0.38 g (81%). Yellow crystals, mp 123–125°C (ethyl acetate–hexane), R_f 0.45 (eluent–heptane $CHCl_3$, 1 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (CH_3O), 6.96 s (H^3), 6.97 d (H^6), 6.99 s (H^4), 7.41 d (H^7). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.9 (CH_3O), 102.8 (C^7), 111.9 (C^3), 115.0 (C^4), 117.6 (C^6), 128.8 (C^9), 143.6 (C^5), 153.0 (C^8), 156.1 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 454 (3.1) M^+, 452 (9) [*M* – 2H]$^+$, 372 (3) [*M* – Se – 2H]$^+$, 294 (97) [*M* – 2Se]$^+$, 227 (100) [5-methoxy-2-benzofuranselenolate]$^+$, 148 (24) [5-methoxybenzofuran]$^+$. Found, %: C 48.04, 47.79; H 2.91, 3.15. $C_{18}H_{14}O_4Se_2$. Calculated, %: C 47.82; H 3.12.

Bis(5-benzyloxybenzo[*b*]furan-2-yl) diselenide (IXb). In a setup described under preparation procedure for compound **IXb** was mixed 0.33 g (1 mmol) of 4-(5-benzyloxy-2-hydroxy)-1,2,3-selenadiazole (**IIIb**), 10 ml of dry acetonitrile, and 0.17 g (1.2 mmol) of sodium carbonate. The reaction mixture was boiled at vigorous stirring for 3 h till the end of nitrogen evolution and disappearance of the initial selenadiazole **IIIb** (according to TLC, R_f 0.46, eluent chloroform). On cooling to 20°C to the reaction mixture was added dropwise at vigorous stirring a solution of 0.13 g (0.5 mmol) of iodine in 5 ml of ethanol. The color of the reaction mixture changed from cherry-red to dark yellow. The mixture was stirred for 3 h and then poured into 25 ml of 6% hydrochloric acid. The extraction of the reaction product, drying and removal of the solvent were carried out as above in preparation procedure for compound **IXa**. The resinous residue was subjected to chromatography on a column 3×20 cm packed with silica gel of L 40/100 grade, eluent benzene. Yield of diselenide **IXb** 0.18 g (54%). Yellow crystals, mp 103–105°C, R_f 0.84 (eluent chloroform). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.12 s (CH_2O), 6.97 s (H^3), 7.08 d.d (H^6), 7.38 m (H^4 + H^7 + Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 71.2 (CH_2O); 104.8 (C^7); 112.4 (C^3); 116.1 (C^4); 117.9 (C^6); 127.9, 128.4, 129.0 (C^9 + *o*, *o*, *p*-CPh); 137.38, 137.41 (C^1Ph); 144.1 (C^5); 153.5 (C^8); 155.6 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 606 (0.3) M^+, 604 (0.5) [*M* – 2H]$^+$, 526 (1) [*M* – Se]$^+$, 446 (7) [*M* – 2Se]+, 303 (2) [5-benzyloxy-2-benzofuranselenolate]$^+$, 91 (100) [$PhCH_2$]$^+$, 65 (9) [C_5H_5]$^+$. Found, %: C 59.96, 59.81; H 3.93, 3.74. $C_{30}H_{22}O_4Se_2$. Calculated, %: C 59.63; H 3.67.

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