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Synthesis and Reactivity of 5- and 6-Hydroxybenzo[*b*]furan-2-selenolates

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Abstract—Treatment of 2,4- and 2,5-diacetoxyacetophenone semicarbazones with selenium dioxide gave 4-(2,4- and 2,5-diacetoxyphenyl)-1,2,3-selenadiazoles which were readily deacylated by the action of hydrochloric acid. 4-(2,4- and 2,5-Dihydroxyphenyl)-1,2,3-selenadiazoles thus obtained underwent decomposition in the presence of potassium carbonate in acetonitrile with formation of 5- and 6-hydroxybenzo[*b*]furan-2-selenolates which were subjected to alkylation.

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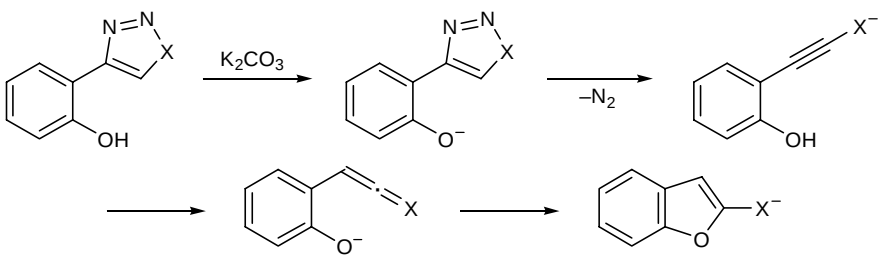
We recently described a new method for the synthesis of benzo[*b*]furan-2-thiolates and -selenolates via intramolecular cyclization of thioketenes and selenoketenes formed by decomposition of 4-(2-hydroxyphenyl)-1,2,3-thia- and -selenadiazoles in the presence of bases [1–4] (Scheme 1). In continuation of our studies on the developed procedure for the synthesis of fused heterocycles, the present article reports on the preparation of 4-(2,4- and 2,5-dihydroxyphenyl)-1,2,3-selenadiazoles and their transformation into 5- and 6-hydroxybenzo[*b*]furan-2-selenolates. 2,5- and 2,6-Disubstituted benzo[*b*]furans are promising as new building blocks for supramolecular chemistry. 5- and 6-Hydroxybenzo[*b*]furan-2-selenolates can be used for the synthesis of new dendrimers having peripheral hydroxy groups which may be subjected to further modifications [5, 6] or for the preparation of new crownophanes. We previously synthesized such a thio crown ether from 5-hydroxybenzo[*b*]furan-2-thiolate [7]. It should also be noted that some derivatives of benzo[*b*]furan-2-chalcogenolates exhibit biological activity [8]; for example, 5-hydroxybenzo[*b*]furan derivatives show antioxidant properties [9].

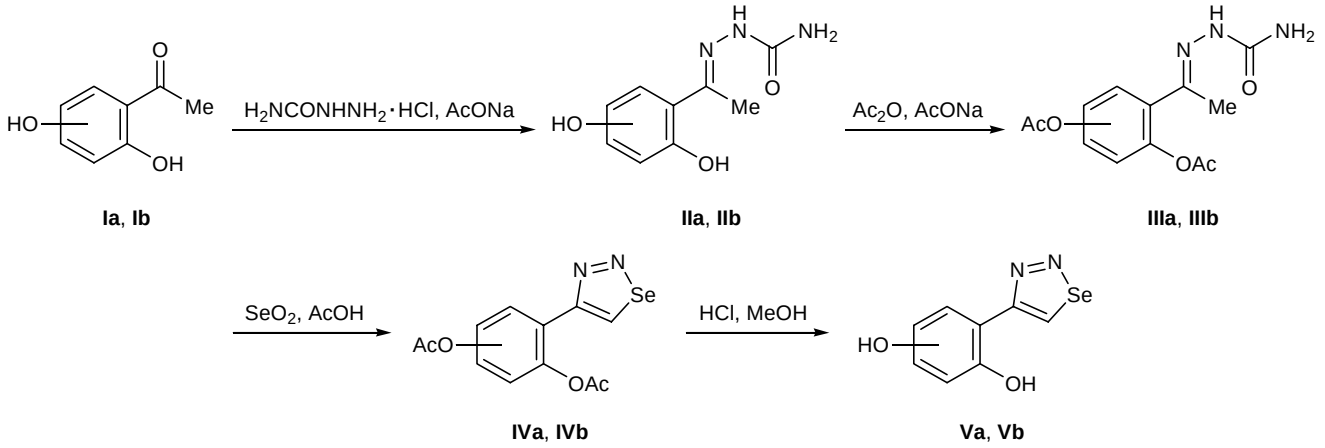
While attempting to obtain new derivatives of 5- and 6-hydroxybenzo[*b*]furan-2-selenolates having an additional functional group in position *5* or *6*, we initially converted 2,4- and 2,5-dihydroxyacetophenones **Ia** and **Ib** into the corresponding hitherto unknown semicarbazones **IIa** and **IIb**. However, we failed to obtain 1,2,3-selenadiazoles by a conventional procedure [10], i.e., by the action of selenium dioxide on semicarbazones **IIa** and **IIb**. Under these conditions, selenium dioxide acted as common oxidant [11]. We previously synthesized 4-(2-hydroxy-5-methoxyphenyl)- and 4-(2-hydroxy-5-benzyloxyphenyl)-1,2,3-selenadiazoles in an overall yield of ~50% by treatment of 2-hydroxy-5-methoxy- and 2-hydroxy-5-benzyloxyacetophenone semicarbazones with selenium

Scheme 1.



X = S, Se.

Scheme 2.



Ia, **Ib** **IIa**, **IIb** **IIIa**, **IIIb**

IVa, **IVb** **Va**, **Vb**

I–**V**, 4-OH (**a**), 5-OH (**b**).

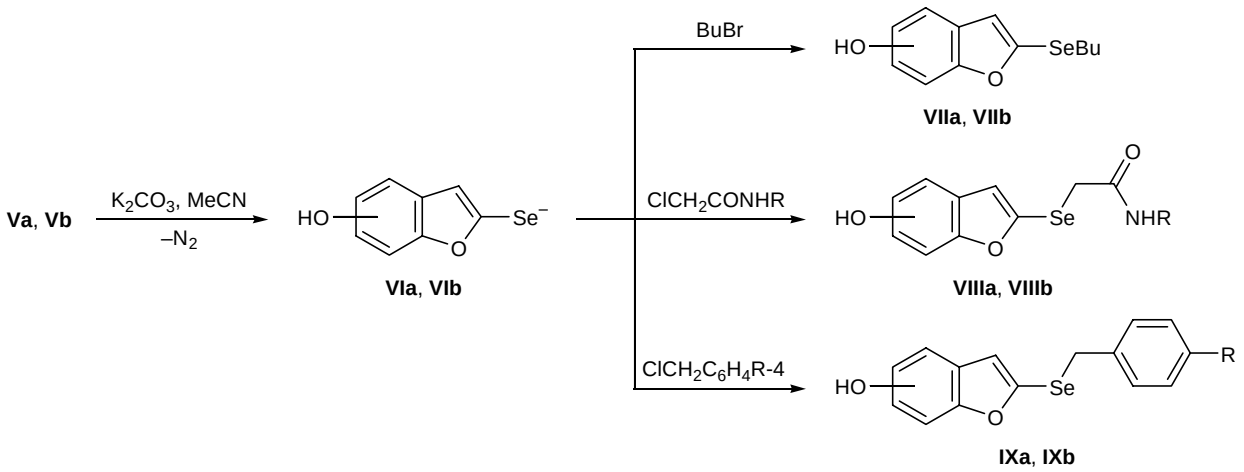
dioxide [12], but our attempts to remove methyl or benzyl protecting group resulted in decomposition of the selenadiazole ring. We also failed to obtain 2,4- and 2,5-diacetoxyacetophenone semicarbazones from 2,4- and 2,5-diacetoxyacetophenones; as a result, 2,4- and 2,5-dihydroxyacetophenone semicarbazones **IIa** and **IIb** were formed. We succeeded in obtaining the desired selenadiazoles according to Scheme 2. Treatment of semicarbazones **IIa** and **IIb** with acetic anhydride in the presence of sodium acetate gave the corresponding diacetoxy derivatives **IIIa** and **IIIb**, and reactions of the latter with selenium dioxide in acetic acid led to the formation of 4-(2,4- and 2,5-diacetoxyphenyl)-1,2,3-selenadiazoles **IVa** and **IVb**. Compounds **IVa** and **IVb** were subjected to hydrolysis with hydrochloric acid, and 4-(2,4- and 2,5-dihydroxyphenyl)-1,2,3-selenadiazoles **Va** and **Vb** were isolated in an overall yield of ~45%.

The structure of 4-(2,4- and 2,5-diacetoxyphenyl)-1,2,3-selenadiazoles **IVa** and **IVb** and 4-(2,4- and 2,5-dihydroxyphenyl)-1,2,3-selenadiazoles **Va** and **Vb** was confirmed by the ^{1}H and ^{13}C NMR and mass spectra. The positions and multiplicities of signals in the ^{1}H and ^{13}C NMR spectra of selenadiazoles **IVa**, **IVb**, **Va**, and **Vb** were similar to the corresponding parameters in the spectra of 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [13] and 4-(5-alkoxy-2-hydroxyphenyl)-1,2,3-selenadiazoles [12]. Signal from the 5-H proton in the selenadiazole ring appeared as a singlet at δ 9.44 (**IVa**), 10.04 (**IVb**), 9.83 (**Va**), and 10.27 ppm (**IVb**) with satellites due to coupling with selenium, ^2J(H–^{77}Se) = 39–43 Hz {cf. δ 10.09 ppm, ^2J(H–^{77}Se) = 42 Hz for 5-H in 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [13]}. The C^5 atom is characterized by a chemical shift of δ_C 140.75 (**IVa**), 145.06 (**IVb**), 139.34 (**Va**), or 147.71 ppm (**IVb**), ^1J(C–^{77}Se) = 135–145 Hz {cf. δ_C 142.1 ppm, ^1J(C–^{77}Se) = 133 Hz for 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [14]}.

Selenadiazoles **IVa**, **IVb**, **Va**, and **Vb** showed in the mass spectra the molecular ion peaks with *m*/*z* values corresponding to their molecular weights. Further fragmentation pattern was also consistent with the assumed structure. The main fragmentation pathway of the molecular ions derived from diacetoxy derivatives **IVa** and **IVb** included elimination of nitrogen molecule, followed by successive elimination of two neutral ketene molecules (which is typical of phenyl acetates [15]) and finally loss of selenium atom. The molecular ions of selenadiazoles **Va** and **Vb** decomposed via initial expulsion of nitrogen molecule, followed by elimination of selenium; this fragmentation pathway is the same as that observed in the light-induced or thermal decomposition of selenadiazoles [16].

Like 4-(2-hydroxyaryl)-1,2,3-selenadiazoles [13] and 4-(5-alkoxy-2-hydroxyphenyl)-1,2,3-selenadiazoles [12], 4-(2,4- and 2,5-dihydroxyphenyl)-1,2,3-selenadiazoles **Va** and **Vb** readily undergo decomposition with liberation of nitrogen molecule even by the action of such a weak base as potassium carbonate. The reaction is likely to include several steps: deprotonation of the phenolic hydroxy group, intramolecular charge transfer to the selenadiazole ring, decomposition of the heterocyclic anion with liberation of nitrogen to give the corresponding alkyneselenolate, intramolecular proton transfer with formation of selenoketene, and intramolecular ring closure with participation of the hydroxy group and selenoketene fragment (Schemes 1, 3); 5- and 6-hydroxybenzo[*b*]-

Scheme 3.



VII, 5-OH (**a**), 6-OH (**b**); **VIII**, 5-OH, R = H (**a**); 6-OH, R = 2,6-$Me_2C_6H_3$ (**b**); **IX**, 5-OH, R = H (**a**), *t*-Bu (**b**).

furan-2-selenolate ions **VIa** and **VIb** thus formed are intensely colored. Their formation was confirmed by alkylation with butyl bromide, chloroacetamides, and benzyl chlorides (Scheme 3). As a result, we obtained 30–89% of 5- and 6-hydroxy-2-butylselanylbenzo[*b*]furans **VIIa** and **VIIb**, 64–89% of 2-(5- and 6-hydroxybenzo[*b*]furan-2-ylselanyl)acetamides **VIIIa** and **VIIIb**, and 59–69% of 2-benzylselanyl-5-hydroxybenzo[*b*]furans **IXa** and **IXb**.

The structure of alkylation products **VII**–**IX** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The positions and multiplicities of signals in their ^{1}H and ^{13}C NMR spectra were similar to the corresponding parameters in the spectra of 2-alkylselanylbenzo[*b*]furans [13, 14]. The 3-H proton in the furan ring gave a singlet at δ 6.65–6.93 ppm (cf. δ 6.80 ppm for 3-H in 2-methylselanylbenzo[*b*]furan [14]). Likewise, the C^3 signal in the ^{13}C NMR spectra of **VII**–**IX** was located at δ_C 112.64–114.71 ppm against 110.8 ppm for 2-methylselanylbenzofuran [14].

The mass spectra of compounds **VII**–**IX** contained peaks from the molecular ions whose isotope composition was consistent with the calculated one. The main fragmentation pathway of the molecular ions of **VII**–**IX** involved cleavage of the weakest C_{sp^3}–Se bond with elimination of alkyl substituent and subsequent loss of selenium atom, in keeping with the decomposition of known 2-alkylselanylbenzo[*b*]furans [13, 14].

EXPERIMENTAL

The melting points were determined on a Boetius melting point apparatus. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance (300 and 75 MHz) and Bruker AMX-400 spectrometers (400 and 100 MHz, respectively), using residual proton and carbon signals of the deuterated solvents as reference. The mass spectra (electron impact, 70 eV) were obtained on a Kratos MS 890 instrument with direct sample admission into the ion source (ion source temperature 200°C); the *m*/*z* values are given below for ions containing ^{80}Se isotope. The progress of reactions was monitored by TLC on Silufol UV-254 plates; spots were visualized under UV light or by treatment with iodine vapor. The solvents used in this work were purified and dehydrated by standard procedures.

2,4-Dihydroxyacetophenone (**Ia**) was synthesized by acylation of resorcinol [17], and 2,5-dihydroxyacetophenone (**Ib**) was obtained by the Fries reaction of *p*-phenylene diacetate [18].

2,4-Dihydroxyacetophenone semicarbazone (IIa). A suspension of 7.7 g (50.7 mmol) of 2,4-dihydroxyacetophenone **Ia**, 6.8 g (61 mmol) of semicarbazide hydrochloride, and 10 g (122 mmol) of sodium acetate in a mixture of 50 ml of propan-2-ol and 50 ml of water was vigorously stirred for 2.5 h on heating at the boiling point. The mixture was cooled to 15–18°C and left overnight, and the precipitate was filtered off, washed with water (3×50 ml), and dried. Yield 9.8 g (93%). Orange crystals, mp 249–250°C (decomp.), R_f 0.47 (acetone–chloroform, 2:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.16 s (CH_3C=N), 6.11 s (NH_2), 6.21 d (3-H), 6.27 d.d (5-H), 7.30 d (6-H), 9.46 s (NH), 9.64 s (4-OH), 12.98 s (2-OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.27 (**C**H_3C=N), 103.43 (C^3), 106.74 (C^1), 112.65 (C^5), 129.16 (C^6), 149.98 (C=N), 155.73 (C=O), 159.56 (C^2), 160.05

(C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 210 (13) $[M + H]^+$, 209 (2) $[M]^+$, 193 (13) $[M - NH_2]^+$, 192 (4) $[M - NH_3]^+$, 167 $[M - CON]^+$, 166 (9) $[M - CONH]^+$, 152 (17) $[M - NCONH]^+$, 150 (16) $[M - NHCONH_2]^+$, 149 (11) $[M - CO(NH_2)_2]^+$, 136 (3) $[M - NNHCONH_2]^+$, 43 (100) $[NHCO]^+$. Found, %: C 51.45, 51.71; H 5.02, 5.17. $C_9H_{11}N_3O_3$. Calculated, %: C 51.67; H 5.30.

2,5-Dihydroxyacetophenone semicarbazone (IIb). A suspension of 13.3 g (87.5 mmol) of 2,5-hydroxyacetophenone (**Ib**), 11.7 g (104.9 mmol) of semicarbazide hydrochloride, and 17.3 g (86.6 mmol) of sodium acetate in a mixture of 250 ml of ethanol and 20 ml of water was vigorously stirred for 2.5 h on heating at the boiling point. The mixture was cooled to 15–18°C and left overnight, and the precipitate was filtered off, washed with water (5×100 ml) and methanol (100 ml), and dried. Yield 15.4 g (84%), yellow crystals, mp 249–235°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.16 s (CH_3C=N), 6.19 s (NH_2), 6.65 s (2H, 3-H, 4-H), 6.84 s (6-H), 8.81 s (5-OH), 9.60 s (NH), 11.88 s (2-OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.53 (**C**H_3C=N), 113.80 (C^1), 117.46 (C^6), 117.57 (C^3), 121.05 (C^4), 148.73 (C=N), 149.42 (C^2), 150.70 (C^5), 155.71 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 209 (32) $[M]^+$, 192 (100) $[M - NH_3]^+$, 166 (39) $[M - CONH]^+$, 149 (74) $[M - CO(NH_2)_2]^+$, 136 (39) $[M - NNHCONH_2]^+$, 43 (37) $[NHCO]^+$. Found, %: C 51.38, 51.52; H 5.18, 5.41. $C_9H_{11}N_3O_3$. Calculated, %: C 51.67; H 5.30.

2,4-Diacetoxyacetophenone semicarbazone (IIIa). A flask equipped with a magnetic stirrer and a reflux condenser and protected from atmospheric moisture was charged with 9.8 g (46.9 mmol) of semicarbazone **IIa**, 7.1 g (86.6 mmol) of sodium acetate, and 130 ml of acetic anhydride. The mixture was heated to 100°C under vigorous stirring (the mixture became homogeneous and turned yellowish) and was stirred for 0.5 h at 100°C. It was then cooled to 20–25°C and poured into 0.7 l of cold water. An oily material separated and crystallized in 30 min; the solid product was filtered off, washed with water (5×20 ml), and dried. Yield 9.3 g (68%), colorless crystals, mp 205–206°C, R_f 0.71 (acetone–chloroform, 2:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.11 s (CH_3C=N), 2.23 s and 2.27 s (CH_3CO), 6.31 s (NH_2), 7.02 d (3-H), 7.07 d.d (5-H), 7.59 d (6-H), 9.40 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 16.91 (**C**H_3C=N), 21.14 (**C**H_3CO), 117.44 (C^3), 119.85 (C^1), 130.41 and 130.85 (C^5, C^6), 142.73 (C^2), 148.38 (C=N), 150.80 (C^4), 155.36 (NC=O), 169.30 and 169.43 (CO). Mass spectrum, *m*/*z* (I_{rel}, %): 293 (7) $[M]^+$, 251 (65) $[M - CH_2CO]^+$, 234 (23) $[M - CH_2CO - NH_3]^+$, 209 (45) $[M - 2CH_2CO]^+$, 192 (100) $[M - 2CH_2CO - NH_3]^+$, 165 (70) $[M - 2CH_2CO - CONH_2]^+$, 149 (89) $[M - 2CH_2CO - NH_2CONH_2]^+$, 136 (65) $[M - 2CH_2CO - NNH_2CONH_2]^+$, 43 (6) $[CH_3CO]^+$. Found, %: C 53.14, 53.37; H 5.18, 5.29. $C_{13}H_{15}N_3O_3$. Calculated, %: C 53.24; H 5.16.

2,5-Diacetoxyacetophenone semicarbazone (IIIb). A flask equipped with a magnetic stirrer and a reflux condenser and protected from atmospheric moisture was charged with 15.4 g (73.7 mmol) of semicarbazone **IIb**, 11.2 g (137 mmol) of sodium acetate, and 150 ml of acetic anhydride. The mixture was heated to 100°C under vigorous stirring (the mixture became homogeneous and turned brownish) and was stirred for 0.5 h at 100°C. It was then cooled to 20–25°C and poured into 1 l of cold water. An oily material separated and crystallized in 1 h; the solid product was filtered off, washed with water (5×20 ml), and dried. Yield 12.8 g (59%), colorless crystals, mp 203–205°C, R_f 0.36 (chloroform). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (CH_3C=N), 2.24 s and 2.27 s (CH_3CO), 6.34 s (NH_2), 7.16 m (2H, 3-H, 4-H), 7.36 s (6-H), 9.45 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 16.78 (**C**H_3C=N), 21.15 (**C**H_3CO), 122.82 and 123.00 (C^4, C^6), 124.66 (C^1), 134.02 (C^3), 142.41 (C^2), 145.43 (C^5), 148.17 (C=N), 155.32 (NC=O), 169.59 and 169.76 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 293 (13) $[M]^+$, 251 (100) $[M - CH_2CO]^+$, 234 (20) $[M - CH_2CO - NH_3]^+$, 209 (51) $[M - 2CH_2CO]^+$, 192 (77) $[M - 2CH_2CO - NH_3]^+$, 165 (19) $[M - 2CH_2CO - CONH_2]^+$, 149 (51) $[M - 2CH_2CO - NH_2CONH_2]^+$, 136 (14) $[M - 2CH_2CO - NNH_2CONH_2]^+$, 43 (90) $[CH_3CO]^+$. Found, %: C 53.27, 53.39; H 5.09, 5.28. $C_{13}H_{15}N_3O_3$. Calculated, %: C 53.24; H 5.16.

4-(2,4-Diacetoxyphenyl)-1,2,3-selenadiazole (IVa). A flask equipped with a magnetic stirrer and a reflux condenser connected to a gas-washing bottle was charged with 5.6 g (19.1 mmol) of semicarbazone **IIIa**, 35 ml of glacial acetic acid, and 15 ml of acetic anhydride. The flask was protected from light, and 2.7 g (24.3 mmol) of powdered selenium dioxide was added under stirring. The mixture was heated to 75–80°C over a period of 1 h under vigorous stirring, and it turned red–brown. The mixture was cooled to 20–25°C and filtered from selenium, the filtrate was diluted with 300 ml of cold water, and the precipitate was filtered off, washed with cold water (5×20 ml), and dried. Yield 5.4 g (87%), brick-red crystals, mp 129–130°C. Recrystallization from ethyl acetate gave light yellow prisms which gradually turned red on exposure to light, mp 134–135°C (decomp.), R_f 0.78

(chloroform–acetone, 3:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.29 s and 2.34 s (CH_3CO), 6.95 s (3-H), 7.13 d (5-H), 8.07 d (6-H), 9.44 s (5'-H, $^2J_{H–Se}$ = 41.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.53 and 21.48 (CH_3), 117.65 (C^3), 120.23 (C^5), 123.19 (C^1), 132.06 (C^6), 140.75 ($C^{5'}$), 148.82 (C^4), 151.68 (C^2), 157.96 ($C^{4'}$), 169.02 and 169.23 (CO). Mass spectrum, *m*/*z* (I_{rel}, %): 326 (1) $[M]^+$, 298 (4) $[M – N_2]^+$, 256 (3) $[M – N_2 – CH_2CO]^+$, 214 (11) $[M – N_2 – 2CH_2CO]^+$, 134 (100) $[M – N_2 –2CH_3CO – Se]^+$. Found, %: C 44.27, 44.46; H 2.89, 3.17. $C_{12}H_{10}N_2O_4Se$. Calculated, %: C 44.33; H 3.10.

4-(2,5-Diacetoxyphenyl)-1,2,3-selenadiazole (IVb). The reaction was carried out as described above for compound **IVa**. Powdered selenium dioxide, 5.8 g (52.3 mmol), was added under stirring to a mixture of 12.8 g (43.7 mmol) of semicarbazone **IIIb**, 70 ml of glacial acetic acid, and 30 ml of acetic anhydride. The mixture was heated to 75–80°C over a period of 1 h under vigorous stirring (it turned red–brown), cooled to 20–25°C, and filtered from selenium. The filtrate was diluted with 0.5 l of cold water and extracted with methylene chloride (3×50 ml). The extracts were combined, washed with cold water (5×200 ml) to remove traces of acetic acid, dried, and evaporated on a rotary evaporator. Yield 11.5 g (81%), pale brown substance; the product was almost pure. Recrystallization from ethyl acetate or benzene gave colorless crystals with mp 133–134°C, R_f 0.27 (chloroform), 0.70 (chloroform–acetone, 10:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.27 s (CH_3CO), 7.35 d.d (4-H), 7.37 d (3-H), 7.88 d (6-H), 10.04 s (5'-H, $^2J_{H–Se}$ = 39 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.62 (CH_3), 124.16 (C^1), 125.12 (C^6), 125.80 (C^3), 126.81 (C^4), 145.06 ($C^{5'}$), 145.89 (C^5), 149.06 (C^2), 157.75 ($C^{4'}$), 170.04 and 170.08 (CO). Mass spectrum, *m*/*z* (I_{rel}, %): 326 (1) $[M]^+$, 298 (4) $[M – N_2]^+$, 256 (2) $[M – N_2 – CH_2CO]^+$, 214 (9) $[M – N_2 – 2CH_2CO]^+$, 134 (38) $[M – N_2 – 2CH_3CO – Se]^+$, 43 (100) $[CH_3CO]^+$. Found, %: C 44.35, 44.52; H 3.18, 3.40. $C_{12}H_{10}N_2O_4Se$. Calculated, %: C 44.33; H 3.10.

4-(2,4-Dihydroxyphenyl)-1,2,3-selenadiazole (Va). A flask equipped with a magnetic stirrer and a reflux condenser and protected from light was charged with 1.5 g (4.6 mmol) of 1,2,3-selenadiazole **IVa**, 40 ml of methanol, and 2 ml of concentrated hydrochloric acid. The mixture was heated for 6 h at 45–50°C under vigorous stirring (until it turned light yellow and homogeneous), cooled to 15–18°C, left overnight, and filtered from selenium. The solvent was removed from the filtrate on a rotary evaporator, 50 ml of methylene chloride was added to the residue, and the mixture was filtered. The precipitate was washed on a filter with methylene chloride (3×10 ml) and dried. Yield 1.0 g (90%), pale yellow prisms, mp 115°C (decomp.), R_f 0.46 (chloroform–acetone, 3:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.18 s (2OH), 6.39 d.d (5-H), 6.56 d (3-H), 8.04 d (6-H), 9.83 s (5'-H, $^2J_{H–Se}$ = 43 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 103.42 (C^1), 107.67 (C^3), 110.89 (C^5), 131.35 (C^6), 139.34 ($C^{5'}$, $^1J_{C–Se}$ = 135 Hz), 156.35 (C^2), 159.06 (C^4), 159.48 ($C^{4'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 242 (16) $[M]^+$, 214 (16) $[M – N_2]^+$, 134 (84) $[M – N_2 – Se]^+$, 42 (100) $[CH_2CO]^+$. Found, %: C 39.78, 40.01; H 2.23, 2.44. $C_8H_6N_2O_2Se$. Calculated, %: C 39.86; H 2.51.

4-(2,5-Dihydroxyphenyl)-1,2,3-selenadiazole (Vb) was synthesized in a similar way from 12.5 g (7.7 mmol) of 1,2,3-selenadiazole **IVb** in 50 ml of methanol containing 2 ml of concentrated hydrochloric acid. Yield 1.7 g (92%), light yellow prisms, mp 170–171°C (decomp.), R_f 0.4 (chloroform–acetone, 5:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.68 d.d (4-H), 6.85 d (3-H), 7.676 d (6-H), 9.20 s and 9.61 s (OH), 10.27 s (5'-H, $^2J_{H–Se}$ = 40 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 115.72 (C^6), 116.17 (C^1), 118.6 (C^4), 120.49 (C^3), 147.71 ($C^{5'}$, $^1J_{C–Se}$ = 145 Hz), 150.35 (C^5), 154.09 (C^2), 159.08 ($C^{4'}$). Mass spectrum, *m*/*z* (I_{rel}, %): 242 (10) $[M]^+$, 214 (21) $[M – N_2]^+$, 134 (100) $[M – N_2 – Se]^+$, 105 (21) $[M – N_2 – Se – HCO]^+$. Found, %: C 39.97, 40.12; H 2.45, 2.67. $C_8H_6N_2O_2Se$. Calculated, %: C 39.86; H 2.51.

2-Butylselanylbenzo[*b*]furan-5-ol (VIIa). A flask equipped with a magnetic stirrer and a reflux condenser connected to a gas-washing bottle was protected from light, filled with argon, and charged with 0.5 g (2.075 mmol) of selenadiazole **Vb**, 0.35 g (2.5 mmol) of freshly calcined potassium carbonate, 0.284 g (2.075 mmol) of butyl bromide, and 40 ml of freshly distilled acetonitrile. The mixture was vigorously stirred for 24 h at ~20°C, and it changed from light yellow to brown. The solvent was removed on a rotary evaporator, and the dark brown tarry residue was treated with boiling hexane (3×15 ml). The extract was cooled, and the precipitate was filtered off and dried. Yield 0.20 g (36%), colorless needles, mp 59°C, R_f 0.6 (chloroform–acetone, 1:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.9 t (CH_3), 1.42 t.d (CH_2CH_2-CH_2), 1.7 q (CH_3CH_2), 2.95 t (SH_2Se), 5.13 s (OH), 6.73 s (3-H), 6.75 d.d (6-H), 6.91 d (4-H), 7.29 d (7-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.48 (CH_3), 22.67 (CH_3CH_2), 28.45 ($CH_2CH_2CH_2$), 32.57 (CH_2Se), 105.16 (C^7), 111.25 (C^4), 112.64 (C^3), 113.69 (C^6), 129.63 (C^{3a}), 145.36 (C^5), 151.38 (C^2), 152.34 (C^{7a}). Mass spectrum, *m*/*z* (I_{rel}, %): 270 (51) $[M]^+$, 214

(21) $[M - C_4H_8]^+$, 185 (21) $[M - C_4H_8 - CHO]^+$, 134 (100) 214 (21) $[M - C_4H_8 - Se]^+$, 105 (48) $[M - C_4H_8 - Se - CHO]^+$, 57 (50) $[C_4H_8]^+$. Found, %: C 53.42, 53.71; H 5.41, 5.53. $C_{12}H_{14}O_2Se$. Calculated, %: C 53.55; H 5.24.

2-Butylselanylbenzo[*b*]furan-6-ol (VIIb). The reaction was carried out as described above for compound **VIIa** using 0.5 g (2.075 mmol) of selenadiazole **Va**, 0.35 g (2.5 mmol) of freshly calcined potassium carbonate, 0.284 g (2.075 mmol) of butyl bromide, and 40 ml of freshly distilled acetonitrile. The mixture was vigorously stirred for 24 h at ~20°C (it changed from light yellow to red and then to dark cherry). The solvent was removed on a rotary evaporator, and the dark brown tarry residue was subjected to column chromatography (3×10 cm) on silica gel L 100/160 using chloroform as eluent. Yield 0.17 g (30%), pale yellow oily substance which gradually crystallized to colorless solid, mp 63–64°C, R_f 0.3 (chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (CH_3), 1.43 t.d ($CH_2CH_2CH_2$), 1.7 q (CH_3CH_2), 2.91 t (CH_2Se), 5.31 s (OH), 6.8 d (5-H), 6.81 s (3-H), 6.97 s (7-H), 7.33 d (4-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.26 (CH_3), 22.42 (CH_3CH_2), 28.56 ($CH_2CH_2CH_2$), 32.34 (CH_2Se), 97.89 (C^7), 111.72 (C^5), 114.05 (C^3), 120.32 (C^4), 122.27 (C^{3a}), 142.4 (C^{7a}), 153.29 (C^6), 157.84 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 270 (48) $[M]^+$, 214 (51) $[M - C_4H_8]^+$, 185 (23) $[M - C_4H_8 - CHO]^+$, 134 (100) 214 (21) $[M - C_4H_8 - Se]^+$, 105 (39) $[M - C_4H_8 - Se - CHO]^+$, 57 (30) $[C_4H_8]^+$. Found, %: C 53.61, 53.83; H 5.12, 5.41. $C_{12}H_{14}O_2Se$. Calculated, %: C 53.55; H 5.24.

2-(5-Hydroxybenzo[*b*]furan-2-ylselanyl)acetamide (VIIIa). A flask equipped with a magnetic stirrer and a reflux condenser connected to a gas-washing bottle was protected from light and charged with 0.40 g (1.66 mmol) of selenadiazole **Vb**, 0.62 g (4.5 mmol) of freshly calcined potassium carbonate, 0.155 g (1.66 mmol) of chloroacetamide, and 30 ml of freshly distilled tetrahydrofuran. The mixture was heated for 3 h under reflux with vigorous stirring (the mixture turned light brown), cooled to 15–18°C, and filtered from inorganic salts, the filtrate was evaporated on a rotary evaporator, and the residue (0.44 g), was recrystallized from 20 ml of water with addition of a small amount of charcoal. Yield 0.40 g (89%), fine colorless needles, mp 160–161°C, R_f 0.42 (ethyl acetate). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.61 s (CH_2), 6.69 d.d (6-H), 6.87 d (4-H), 6.93 s (3-H), 7.32 d (7-H), 9.21 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 30.51 (CH_2), 104.82 (C^7), 111.05 (C^4), 113.14 (C^3, C^6), 129.24 (C^{3a}), 144.11 (C^5), 150.91 (C^2), 153.48 (C^{7a}), 170.27 (CO). Mass spectrum, *m*/*z* (I_{rel}, %): 271 (59) $[M]^+$, 213 (100) $[M - CH_2CONH_2]^+$, 185 (9) $[M - CH_2CONH_2 - CHO]^+$, 149 (51) $[M - CH_2CO - Se]^+$. Found, %: C 44.35, 44.51; H 3.53, 3.62. $C_{10}H_9NO_3Se$. Calculated, %: C 44.47; H 3.36.

***N*-(2,6-Dimethylphenyl)-2-(6-hydroxybenzo[*b*]furan-2-ylselanyl)acetamide (VIIIb).** The reaction was carried out as described above for **VIIIa**. A mixture of 0.5 g (2.075 mmol) of selenadiazole **Va**, 0.37 g (2.7 mmol) of freshly calcined potassium carbonate, 0.41 g (2.075 mmol) of 2-chloro-*N*-(2,6-dimethylphenyl)acetamide, and 50 ml of freshly distilled acetone was vigorously stirred for 48 h at ~20°C, 0.15 g (2.7 mmol) of ammonium chloride was added, the mixture was stirred for 2 h and filtered from inorganic salts, and the solvent was removed from the filtrate on a rotary evaporator. The residue, 0.7 g, was recrystallized from 30 ml of aqueous methanol with addition of a small amount of charcoal. Yield 0.50 g (64%), fine colorless needles, mp 200–201°C, R_f 0.31 (chloroform–acetone, 10:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.15 s (CH_3), 3.71 s (CH_2CO), 6.74 d (5-H), 6.87 s (3-H), 6.94 d (7-H), 7.02 m (H_{arom}), 7.29 d (4-H), 9.36 br.s (OH, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 17.18 (CH_3); 30.39 (CH_2CO); 96.43 (C^7); 112.32 (C^5); 114.71 (C^3); 120.33 (C^{3a}, C^4); 126.27, 127.47, 134.65, 135.11 (C_{arom}); 140.33 (C^{7a}); 155.93 (C^6); 157.93 (C^2); 166.81 (CO). Mass spectrum, *m*/*z* (I_{rel}, %): 375 (52) $[M]^+$, 213 (44) $[M - CH_2CONHC_6H_3(CH_3)_2]^+$, 134 (25) $[M - CHCONHC_6H_3(CH_3)_2 - Se]^+$, 121 (100) $[NH_2C_6H_3(CH_3)_2]^+$, 120 (100) $[NHC_6H_3(CH_3)_2]^+$. Found, %: C 57.42, 57.49; H 4.78, 4.87. $C_{18}H_{17}NO_3Se$. Calculated, %: C 57.77; H 4.58.

2-Benzylselanylbenzo[*b*]furan-5-ol (IXa). Under analogous conditions, a mixture of 0.40 g (1.66 mmol) of selenadiazole **Vb**, 0.62 g (4.5 mmol) of freshly calcined potassium carbonate, 0.21 g (1.66 mmol) of benzyl chloride, and 30 ml of freshly distilled tetrahydrofuran was heated for 3 h under reflux with vigorous stirring, cooled to 15–18°C, and evaporated on a rotary evaporator. The dark brown tarry residue was treated with boiling hexane (3×15 ml). The extract was cooled, and the precipitate was filtered off and dried. Yield 0.30 g (59%), colorless plates, mp 94–95°C, R_f 0.40 (methylene chloride). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.18 s (CH_2), 4.88 s (OH), 6.65 s (3-H), 6.75 d (6-H), 6.89 s (4-H), 7.22 m (H_{arom}), 7.33 d (7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 32.17 (CH_2); 105.20 (C^7); 111.19 (C^4); 112.91 (C^3);

114.25 (C^6); 127.01, 128.39, 128.65, 129.32, 137.95 (C_{arom}); 129.33 (C^{3a}); 144.77 (C^5); 151.29 (C^{7a}); 152.35 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 304 (46) $[M]^+$, 213 (18) $[M - CH_2Ph]^+$, 91 (100) $[CH_2Ph]^+$. Found, %: C 59.72, 59.41; H 4.08, 4.19. $C_{15}H_{12}O_2Se$. Calculated, %: C 59.43; H 3.99.

2-(4-*tert*-Butylbenzylselanyl)benzo[*b*]furan-5-ol (IXb). Under analogous conditions, a mixture of 0.34 g (1.41 mmol) of selenadiazole **Vb**, 0.49 g (3.55 mmol) of freshly calcined potassium carbonate, 0.257 g (1.66 mmol) of *p*-*tert*-butylbenzyl chloride, and 20 ml of freshly distilled tetrahydrofuran was heated for 2 h under reflux with vigorous stirring, cooled to 15–18°C, and evaporated on a rotary evaporator. The brown residue was treated with boiling hexane (3×15 ml). The extract was cooled, and the precipitate was filtered off and dried. Yield 0.35 g (69%), colorless crystals, mp 121–122°C, R_f 0.32 (methylene chloride). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 s (CH_3), 4.18 s (CH_2), 4.87 s (OH), 6.67 s (3-H), 6.79 d.d (6-H), 6.91 d (4-H), 7.16 d (*o*-H), 7.32 d (*m*-H), 7.35 d (7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 31.14 (CH_3), 31.97 (CH_2), 34.34 (**C**CH_3), 105.16 (C^7), 111.14 (C^4), 112.79 (C^3), 113.97 (C^6), 125.37 (C^m), 128.38 (C^o), 129.37 (C^{3a}), 134.68 (C^i), 145.14 (C^5), 150.06 (C^p), 151.26 (C^{7a}), 152.30 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 360 (23) $[M]^+$, 213 (37) $[M - CH_2C_6H_4C(CH_3)_3]^+$, 147 (100) $[CH_2C_6H_4C(CH_3)_3]^+$, 132 (68) $[CH_2C_6H_4C(CH_3)_3 - CH_3]^+$, 117 (61) $[CH_2C_6H_4C(CH_3)_3 - 2CH_3]^+$. Found, %: C 63.77, 63.43; H 5.39, 5.62. $C_{19}H_{20}O_2Se$. Calculated, %: C 63.52; H 5.61.

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