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4-(2-Hydroxyaryl)-1,2,3-selenadiazoles as Precursors of Benzofuran-2-selenolates*

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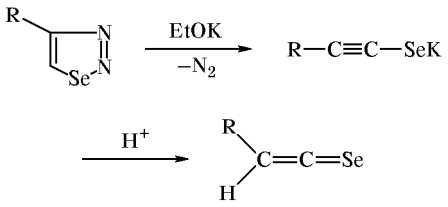
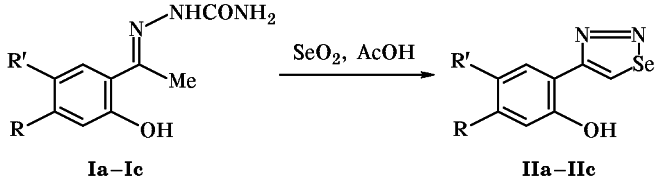
Abstract—The reaction of selenium dioxide with *o*-hydroxyacetophenone semicarbazones gives 4-(2-hydroxyaryl)-1,2,3-selenadiazoles which undergo ready decomposition by the action of potassium carbonate to form benzofuran-2-selenolates. The latter can be alkylated with methyl iodide and benzyl chloride and arylated with 2,4-dinitrochlorobenzene. Intermediate formation of 2-(*o*-hydroxyphenyl)ethyneselenolate during decomposition of 1,2,3-selenadiazoles was proved by the isolation of methyl *o*-methoxyphenylethynyl selenide when the substrate was treated with potassium carbonate in the presence of methyl iodide.

4-Substituted 1,2,3-selenadiazoles are known [1] to readily decompose by the action of strong bases, such as potassium ethoxide, butyllithium, etc., with liberation of nitrogen and formation of alkyneselenolates. The latter are widely used in organic synthesis for preparation of acetylenic selenides, in 1,3-anionic cycloadditions and other cyclization reactions, and for generation of highly reactive selenoketenes [2–7]:



We recently reported a new convenient procedure for synthesizing previously unknown 2-benzylselenobenzofuran via decomposition of readily accessible 4-(2-hydroxyphenyl)-1,2,3-selenadiazole [8, 9]. The present communication describes in detail the synthesis of 4-(2-hydroxyaryl)-1,2,3-selenadiazoles and their transformation into benzofuran-2-selenolates.

With a view to obtain new derivatives of acetylenic selenolates having one more reactive functionality, a hydroxy group, we synthesized 4-(2-hydroxyphenyl)-1,2,3-selenadiazole (**IIa**) and its analogs **IIb** and **IIc** containing a methyl group in the benzene ring. Compounds **IIa**–**IIc** were prepared by the known method [10], by the action of selenium dioxide in acetic acid on hydrazones derived from 2-hydroxyacetophenone (**Ia**), 2-hydroxy-4-methylacetophenone (**Ib**), and 2-hydroxy-5-methylacetophenone (**Ic**):



Ia–Ic **IIa–IIc**

I, **II**, R = R′ = H (**a**); R = Me, R′ = H (**b**); R = H, R′ = Me (**c**).

The structure of 4-(2-hydroxyaryl)-1,2,3-selenadiazoles **IIa**–**IIc** was confirmed by the IR, ^{1}H and ^{13}C NMR, and mass spectra. In the IR spectrum of **IIa** stretching vibrations of the O–H group appear as a broad band at 3336 cm^{-1}, in keeping with published data [11]. Both positions and multiplicities of signals in the ^{1}H and ^{13}C NMR spectra of selenadiazoles **IIa**–**IIc** are analogous to those observed in the spectra of 4-(2-hydroxyphenyl)-1,2,3-thiadiazole [12, 13]. As a result of replacement of the sulfur atom by a "heavy" selenium atom, the signal from proton in position 5 of the selenadiazole ring is located in a weaker field, δ 10.09 (**IIa**), 9.4 (**IIb**), and 9.52 ppm (**IIc**), as a singlet with satellites due to coupling with ^{77}Se (J = 40–42 Hz). The corresponding signal of 4-(2-hydroxyphenyl)-1,2,3-thiadiazole is observed at δ 8.82 ppm [13]. Likewise, the chemical shift of C^5 in

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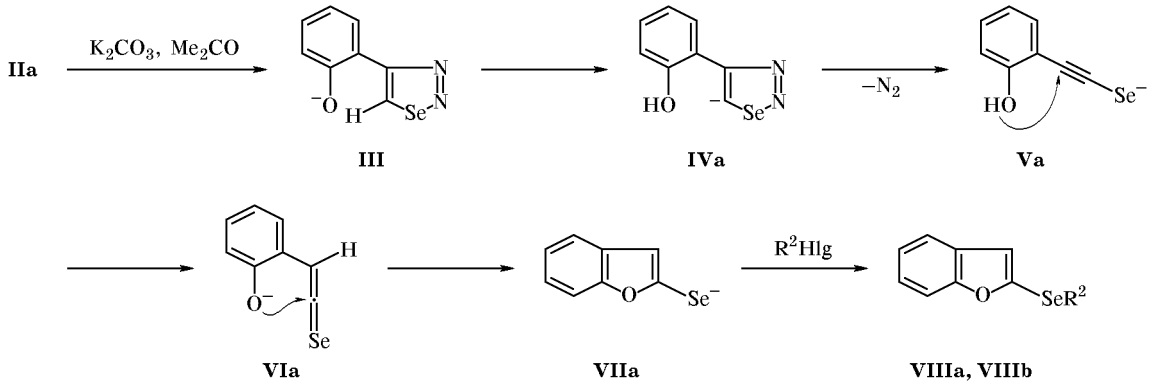
Scheme 1.



VIII, R^2 = Me, Hlg = I (**a**); R^2 = $PhCH_2$, Hlg = Cl (**b**).

selenadiazole **IIa** is δ_C 142.1 ppm ($J_{C,^{77}Se}$ = 133 Hz) against 131.4 ppm for C^5 of 4-(2-hydroxyphenyl)-1,2,3-thiadiazole [13].

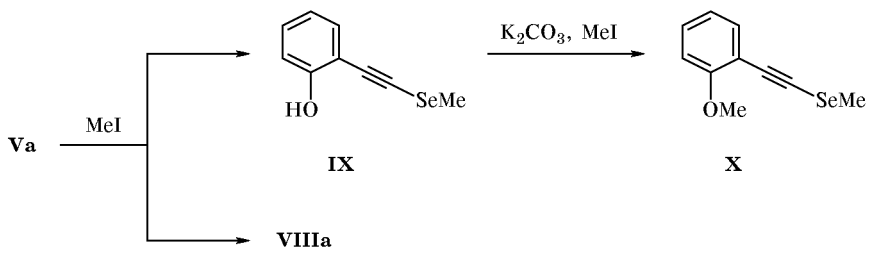
The mass spectra of compounds **IIa**–**IIc** contained the molecular ion peaks whose isotope compositions were consistent with the calculated ones. Further fragmentation of the molecular ions supports the assumed structure of selenadiazoles **IIa**–**IIc**. The main fragmentation pathway involves successive elimination of nitrogen molecule and selenium atom. A similar pattern is typical of photoinduced or thermal decomposition of these compounds [14].

While trying to alkylate 4-(2-hydroxyphenyl)-1,2,3-selenadiazole (**IIa**) at the hydroxy group, we have found that even such a weak base as potassium carbonate promotes decomposition of the substrate (Scheme 1). The product was not the corresponding alkyneselenolate but benzofuran-2-selenolate (**VIIa**) which is reponsible for intense color of the solution. The process is likely to include several stages: formation of phenoxide ion **III**, intramolecular proton migration with transfer of the negative charge to the heteroring, elimination of nitrogen molecule to give alkyneselenolate **Va**, intramolecular proton transfer with formation of selenoketene **VIa**, and intramolecular ring closure involving the hydroxy group and selenoketene fragment (Scheme 1).

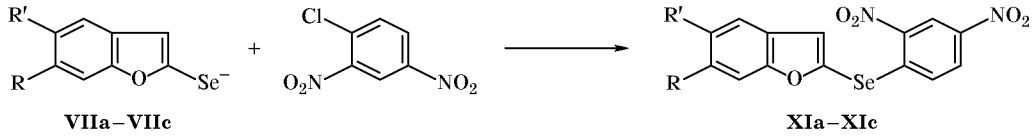
When the reaction was performed in the presence of benzyl chloride, we obtained 2-benzylselenobenzofuran (**VIIIb**) in good yield. The intermediate formation of *o*-hydroxyphenylethyneselenolate (**Va**) during decomposition of selenodiazole **IIa** was proved by carrying out the reaction in the presence of methyl iodide. As a result, we isolated 33% of *o*-methoxyphenylethynyl methyl selenide (**X**) and a small amount of 2-methylselenobenzofuran (**VIIIa**). When methyl iodide was added after preliminary decomposition of selenadiazole **IIa** with potassium carbonate for at least 30 min, the product was 2-methylselenobenzofuran (**VIIIa**) (yield 76%; Scheme 2).

The structure of alkylation products **VIIIa**, **VIIIb**, and **X** was confirmed by the ^1H and ^{13}C NMR and mass spectra. The NMR spectra of **VIIIa** and **VIIIb** resemble those obtained for 2-alkylthiobenzofurans [13]. In the mass spectra of **VIIIa** and **VIIIb** we observed the molecular ion peaks with the expected isotope compositions. The main fragmentation pattern includes cleavage of the weakest C_{sp^3}–Se bond, i.e., successive loss of the alkyl substituent, carbon(II) oxide molecule, and selenium atom. Elimination of

Scheme 2.



Scheme 3.



VIIa–VIIc **XIa–XIc**

the alkylseleno group occurs to a minor extent. The IR spectrum of *o*-methoxyphenylethynyl methyl selenide (**X**) contained an absorption band at 2150 cm^{-1}, belonging to stretching vibrations of the triple bond [15]. Selenide **X** showed in the ^1H NMR spectrum signals from aromatic protons and singlets from the OCH_3 and $SeCH_3$ groups at δ 3.87 and 2.38 ppm, respectively. The corresponding carbon signals in the ^{13}C NMR spectrum were observed at δ_C 55.7 (OCH_3) and 9.93 ppm ($SeCH_3$); also, signals from the acetylenic carbon atoms were present at δ_C 75.0 (C≡**C**Se) and 94.3 ppm (**C**≡CSe) [16]. Fragmentation of the molecular ion of **X** includes elimination of the methylseleno group with formation of *o*-methoxyphenylethynyl ion. The minor fragmentation pathway includes successive loss of one methyl group, carbon monoxide molecule, and the second methyl group.

The arylation of 4-(2-hydroxyaryl)-1,2,3-selenadiazoles **IIa**–**IIc** with 2,4-dinitrochlorobenzene in the presence of potassium carbonate shows the same general relations as does the alkylation. As a result, 2-(2,4-dinitrophenylseleno)benzofurans **XIa**–**XIc** were isolated in moderate yields (Scheme 3). The NMR spectral patterns of products **XIa**–**XIc** were analogous to those found for alkylseleno derivatives **VIIIa** and **VIIIb** and 2,4-dinitrotoluene [17]. Scheme 4 shows fragmentation pathways of the molecular ion of **XIa** as an example. Judging by the fragment ion peak intensities, the most probable is elimination of the 4-nitro-2-nitrosophenylseleno moiety. Analogous mass spectra were obtained for 2-(2,4-dinitrophenylseleno)benzofurans **XIb** and **XIc**.

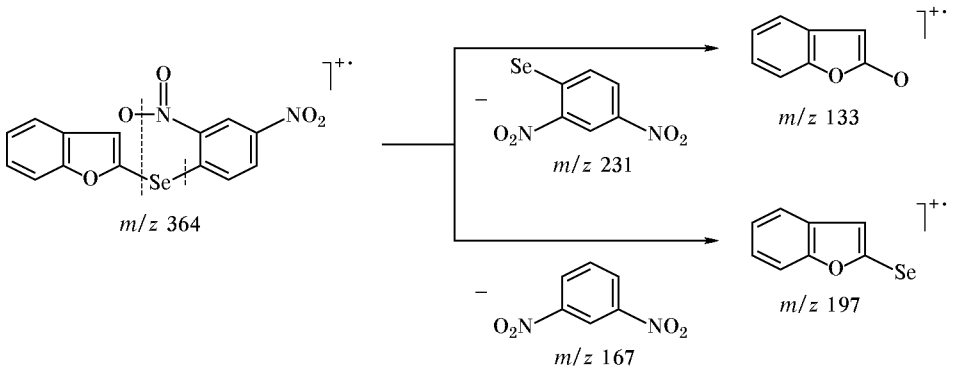
We tried to study the mechanism of decomposition of 4-(2-hydroxyphenyl)-1,2,3-selenadiazole (**IIa**) in the presence of Bu_4NOH as a base by ^1H NMR spectroscopy. Even after 5 min, only signals corresponding to benzofuran-2-selenolate (**VIIa**) were observed in the spectrum.

EXPERIMENTAL

The melting points were determined on a Boetius device. The IR spectra were recorded on an IKS-29 spectrometer. The ^1H and ^{13}C NMR spectra were obtained on Bruker Avance (300 and 75 MHz, respectively) and Bruker AMX-400 (400 and 100 MHz) instruments using solvent signals as reference. The mass spectra were run on a Kratos MS-890 high-resolution mass spectrometer with direct admission of samples into the ion source; energy of ionizing electrons 70 eV; ion source temperature 200°C. The *m*/*z* values are given for the major ^{80}Se isotope. The progress of reactions was monitored by TLC on Silufol UV-254 plates; spots were visualized by UV light and iodine vapor. All solvents were dried and purified by standard procedures.

4-(2-Hydroxyphenyl)-1,2,3-selenadiazole (IIa). A mixture of 7.7 g (40 mmol) of 2-hydroxyacetophenone semicarbazone (**Ia**), 15 ml of glacial acetic acid, and 4.6 g (42 mmol) of powdered selenium dioxide was stirred for 4–5 h at 60–70°C with protection from light until gaseous products no longer evolved. The mixture was cooled to 20–25°C and filtered from the precipitated selenium, 50 ml of water

Scheme 4.



was added to the filtrate, and the precipitate was filtered off and dried. Yield of the crude product 6.5 g (72%). Recrystallization from aqueous ethanol gave 5 g (55%) of selenadiazole **IIa** as light brown plates with mp 103–105°C; R_f 0.4 (benzene). IR spectrum (5% solution in MeCN), ν, cm^{-1}: 3525, 3336, 2995, 2940, 1710, 1590, 1312, 1268, 1245, 1060, 919, 805, 760, 703, 490. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.98 q (5-H), 7.06 d (3-H), 7.27 q (4-H), 8.24 d (6-H), 10.1 s (5-H, selenadiazole, $^2J_{H,Se}$ = 42 Hz), 10.35 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 116.4 (C^3), 118.8 (C^1) 119.5 (C^5), 129.6 (C^6), 130.1 (C^4), 142.1 d (C^5, selenadiazole, $^1J_{C,H}$ = 196, $^1J_{C,Se}$ = 133 Hz), 154.7 (C^2), 155.2 (C^4, selenadiazole). Mass spectrum, *m*/*z*, (I_{rel}, %): 226 (1.5) M^+, 198 (11.4) $[M-N_2]^+$, 197 (11.3) $[M-N_2-H]^+$, 118 (100), $[2\text{-}HOC_6H_4C{\equiv}CH]^+$. Found, %: C 42.21, 42.33; H 2.91, 3.03. $C_8H_6N_2OSe$. Calculated, %: C 42.69; H 2.69.

4-(2-Hydroxy-4-methylphenyl)-1,2,3-selenadiazole (IIb) was synthesized as described above for compound **IIa** from 6.7 g (33 mmol) of semicarbazone **Ib**, 15 ml of AcOH, and 3.9 g (35 mmol) of selenium dioxide. Yield 5.5 g (70%). Light brown plates, mp 108–109°C (from aqueous ethanol), R_f 0.54 ($CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (CH_3), 6.8 d (5-H), 6.95 s (3-H), 7.53 d (6-H), 9.4 s (5-H, selenadiazole, $^2J_{H,Se}$ = 40 Hz), 10.01 s (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.31 (CH_3), 113.55 (C^1), 118.4 (C^3), 121.3 (C^5), 127.32 (C^6), 136.7 (C^5, selenadiazole, $^1J_{C,H}$ = 190, $^1J_{C,Se}$ = 135 Hz), 141.54 (C^4), 155.46 (C^2), 162.33 (C^4, selenadiazole). Mass spectrum, *m*/*z* (I_{rel}, %): 240 (1.7) M^+, 212 (8.7) $[M-N_2]^+$, 132 (100) $[2\text{-HO-4-}CH_3\text{-}C_6H_3C{\equiv}CH]^+$. Found, %: C 44.75, 44.91; H 3.43, 3.57. $C_9H_8N_2OSe$. Calculated, %: C 45.0; H 3.33.

4-(2-Hydroxy-5-methylphenyl)-1,2,3-selenadiazole (IIc) was synthesized as described above for compound **IIa** from 6.7 g (33 mmol) of semicarbazone **Ic**, 15 ml of AcOH, and 3.9 g (35 mmol) of selenium dioxide. Yield 5.5 g (70%). Light brown plates, mp 96–98°C (from aqueous ethanol), R_f 0.36 (benzene). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (CH_3), 7.03 d (5-H), 7.15 d (4-H), 7.45 s (6-H), 9.52 s (5-H, selenadiazole, $^2J_{H,Se}$ = 40 Hz), 9.89 s (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.54 (CH_3), 115.76 (C^1), 117.89 (C^3), 127.7 (C^5), 129.3 (C^6), 131.77 (C^5, selenadiazole, $^1J_{C,H}$ = 190, $^1J_{C,Se}$ = 135 Hz), 137.44 (C^4), 153.37 (C^2), 162.26 (C^4, selenadiazole). Mass spectrum, *m*/*z*, (I_{rel}, %): 240 (8.9) M^+, 212 (54.6) $[M-N_2]^+$, 132 (100) $[2\text{-HO-4-}CH_3\text{-}C_6H_3C{\equiv}CH]^+$. Found, %: C 45.03, 44.88; H 3.51, 3.57. $C_9H_8N_2OSe$. Calculated, %: C 45.0; H 3.33.

2-Methylselenobenzofuran (VIIIa). A suspension of 0.4 g (1.8 mmol) of selenadiazole **IIa**, 5 ml of anhydrous acetone, and 0.3 g (2.2 mmol) of K_2CO_3 was refluxed for 2 h under vigorous stirring, and 0.43 g (3 mmol) of methyl iodide was added to the colored mixture. The mixture was refluxed for 1 h and filtered, and the filtrate was evaporated under reduced pressure. The residue was subjected to chromatography on a 3 × 20-cm column charged with silica gel L 40/100 μm (eluent heptane–CCl_4, 1:1). Removal of the solvent from the appropriate fraction gave 0.29 g (76%) of compound **VIIIa** as a light yellow oil, R_f 0.7 (heptane–CCl_4, 1:1). IR spectrum, ν, cm^{-1}: 3058, 2910, 2820, 1595, 1430, 1296, 1248, 1167, 1035, 1000, 913, 873, 736, 608. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 s ($SeCH_3$), 6.80 s (3-H), 7.16 t.d (5-H), 7.24 t.d (6-H), 7.48 d (7-H), 7.57 d (4-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 8.0 (CH_3Se), 110.8 (C^3), 111.5 (C^7), 120.0 (C^4), 122.8 (C^5), 123.9 (C^6), 128.8 (C^9), 145.0 (C^2), 157.0 (C^8). Mass spectrum, *m*/*z*, (I_{rel}, %): 212 (100) M^+, 197 (83.8) $[M-CH_3]^+$, 169 (33.2) $[M-CH_3-CO]^+$, 132 (10.2) $[M-Se]^+$, 131 (15.3) $[M-HSe]^+$, 89 (44.6) $[C_7H_6]^+$. Found, %: C 46.89, 47.12; H 3.93, 3.62. C_9H_8OSe. Calculated, %: C 47.17; H 3.77.

2-Benzylselenobenzofuran (VIIIb). A suspension of 0.5 g (2.2 mmol) of selenadiazole **IIa**, 5 ml of anhydrous acetone, 0.31 g (2.4 mmol) of benzyl chloride, and 0.6 g (4.3 mmol) of K_2CO_3 was refluxed for 5 h with protection from light until initial compound **IIa** disappeared (TLC). The precipitate was filtered off, and the light brown solution was evaporated under reduced pressure. The tarry residue was subjected to chromatography on a 3 × 20-cm column charged with silica gel L 40/100 μm, using benzene as eluent. Removal of the solvent from the appropriate fraction gave 0.41 g (65%) of compound **VIIIb** as a light yellow oil, R_f 0.8 (benzene). IR spectrum, ν, cm^{-1}: 3060, 3030, 2920, 2850, 1916, 1495, 1440, 1302, 1253, 1160, 1040, 921, 750, 698, 600. ^1H NMR spectrum (CCl_4), δ, ppm: 7.61–6.4 m (H_{arom}), 6.52 s (3-H), 3.96 s (CH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 288 (38.7) M^+, 197 (19.8) $[M-CH_2Ph]^+$, 169 (16.8) $[M-CH_2Ph-CO]^+$, 91 (100) $[C_7H_7]^+$. Found, %: C 54.12, 53.81; H 3.34, 3.62. $C_{15}H_{12}OSe$. Calculated, %: C 53.92; H 3.54.

***o*-Methoxyphenylethynyl methyl selenide (X).** A suspension of 0.4 g (1.8 mmol) of selenadiazole **IIa**, 5 ml of anhydrous acetone, 0.426 g (3 mmol) of methyl iodide, and 0.3 g (2.2 mmol) of K_2CO_3 was

refluxed for 5 h with protection from light until initial compound **IIa** disappeared. An additional portion of methyl iodide, 0.21 g (1.5 mmol), was added, and the mixture was stirred for 15 min. The resulting suspension was filtered, and the light brown filtrate was evaporated under reduced pressure. The tarry residue was subjected to chromatography on a 3×20-cm column charged with silica gel L 40/100 μm, using benzene as eluent. A fraction containing product **X** was evaporated under reduced pressure. Yield 130 mg (33%), light yellow oily substance; R_f 0.71 (benzene), 0.2 (heptane–CCl_4, 1:1). IR spectrum, ν, cm^{-1}: 3060, 3000, 2926, 2830, 2150, 1589, 1562, 1485, 1440, 1250, 1180, 1160, 1110, 1043, 1020, 913, 743. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s ($SeCH_3$), 3.87 s (OCH_3), 6.80 d (3-H), 6.88 t.d (5-H), 7.29 t.d (4-H), 7.40 d (6-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 9.93 (CH_3Se), 55.7 (OCH_3), 75.0 (C≡**C**Se), 94.3 (**C**≡CSe), 110.5 (C^6), 120.3 (C^3), 123.1 (C^4), 129.5 (C^5), 133.3 (C^2), 157.0 (C^1), 110.8 (C^3), 111.5 (C^7), 120.0 (C^4), 122.8 (C^5), 123.9 (C^6), 128.8 (C^9), 145.0 (C^2), 157.0 (C^8). Mass spectrum, *m*/*z*, (I_{rel}, %): 226 (63.6) M^+, 211 (6.3) $[M-CH_3]^+$, 183 (6.3) $[M-CH_3-CO]^+$, 168 (14) $[M-2CH_3-CO]^+$, 131 (100) $[M-CH_3Se]^+$, 91 (24.7) $[C_7H_7]^+$. Found, %: C 52.89, 53.02; H 4.63, 3.71. $C_{10}H_{10}OSe$. Calculated, %: C 53.1; H 4.42.

2-(2,4-Dinitrophenylseleno)benzofuran (XIa). A suspension of 0.226 g (1 mmol) of selenadiazole **IIa**, 10 ml of anhydrous acetonitrile, and 0.16 g (1.2 mmol) of K_2CO_3 was refluxed for 10–30 min under vigorous stirring, and 0.202 g (1 mmol) of 2,4-dinitrochlorobenzene in 5 ml of acetonitrile was added to the dark cherry reaction mixture. The mixture turned yellow–green. It was refluxed for 5 h, cooled to 20°C, poured into 25 ml of water, neutralized with 6% hydrochloric acid, and extracted with chloroform (2×10 ml). The extract was dried over calcined calcium chloride and evaporated under reduced pressure. The residue was subjected to chromatography on a 3×20-cm column charged with silica gel L 40/100 μm (eluent heptane–$CHCl_3$, 1:1). Yield 0.15 g (41%), yellow crystals with mp 166–167°C (from 2-propanol), R_f 0.55 (heptane–$CHCl_3$, 1:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.87 s (3-H), 7.15 t.d (5-H), 7.32 t.d (6-H), 7.43 d (7-H), 7.52 d (4-H), 7.72 d (6-H, dinitrophenyl), 8.17 d.d (5-H, dinitrophenyl), 9.17 d (3-H, dinitrophenyl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 111.3 (C^3), 112.2 (C^7), 116.3 (C^3, C_6H_3), 120.9 (C^4), 122.3 (C^5), 124.2 (C^1, C_6H_3), 124.7 (C^6), 128.3 (C^9), 132.2 (C^5, C_6H_3), 141.6 (C^6, C_6H_3), 145.2 (C^2), 147.5 (C^4, C_6H_3), 157.1 (C^2, C_6H_3), 158.0 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 364 (19) M^+, 231 (36) $[M-2\text{-O-}C_8H_5O]^+$, 197 (10) $[M-2,4\text{-}(NO_2)_2C_6H_3Se]^+$, 133 (100) $[M-2\text{-NO-4-}NO_2C_6H_3Se]^+$, 89 (14) $[C_7H_6]^+$. Found, %: C 46.37, 46.18; H 2.45, 2.62. $C_{14}H_8N_2O_5Se$. Calculated, %: C 46.15; H 2.20.

2-(2,4-Dinitrophenylseleno)-6-methylbenzofuran (XIb) was synthesized as described above for compound **XIa** from 0.239 g (1 mmol) of selenadiazole **IIb**, 0.16 g (1.2 mmol) of K_2CO_3, and 0.202 g (1 mmol) of 2,4-dinitrochlorobenzene. By column chromatography we isolated 0.21 g (56%) of product **XIb** as yellow crystals with mp 162–165°C (from 2-propanol), R_f 0.7 ($CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (CH_3) 6.76 s (3-H), 7.18 d (5-H), 7.33 s (7-H), 7.35 d (4-H), 7.56 d (6-H, C_6H_3), 8.15 d.d (5-H, C_6H_3), 9.16 d (3-H, C_6H_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.8 (CH_3), 111.4 (C^3), 111.9 (C^7), 120.7 (C^5, C_6H_3), 121 (C^4), 121.4 (C^5), 125.3 (C^1, C_6H_3), 125.4 (C^6), 127.3 (C^9), 131.8 (C^5, C_6H_3), 137.2 (C^6, C_6H_3), 140.3 (C^2), 143.2 (C^4, C_6H_3), 147 (C^2, C_6H_3), 158.6 (C^8). Mass spectrum, *m*/*z*, (I_{rel}, %): 378 (10) M^+, 231 (7) $[M-2\text{-O-6-}CH_3\text{-}C_8H_4O]^+$, 211 (2) $[M-2,4\text{-}(NO_2)_2C_6H_3Se]^+$, 147 (100) $[M-2\text{-NO-4-}NO_2C_6H_3Se]^+$. Found, %: C 47.39, 47.61; H 2.23, 2.45. $C_{15}H_{10}N_2O_5Se$. Calculated, %: C 47.62; H 2.64.

2-(2,4-Dinitrophenylseleno)-5-methylbenzofuran (XIc) was synthesized as described above for compound **XIa** from 0.5 g (2.08 mmol) of selenadiazole **IIc**, 0.344 g (2.49 mmol) of K_2CO_3, and 0.42 g (2.08 mmol) of 2,4-dinitrochlorobenzene. Yield 0.5 g (63%), yellow crystals, mp 157–159°C (from 2-propanol), R_f 0.57 ($CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.49 s (CH_3), 6.72 s (3-H), 7.35 d (6-H), 7.3 s (4-H), 7.45 d (7-H), 7.62 d (6-H, C_6H_3), 8.15 d.d (5-H, C_6H_3), 9.16 d (3-H, C_6H_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.7 (CH_3), 111.7 (C^3), 120.9 (C^7), 121.6 (C^3, C_6H_3), 121.7 (C^4), 127.7 (C^5), 128.3 (C^1, C_6H_3), 128.4 (C^6), 132.2 (C^9), 133.82 (C^5, C_6H_3), 141.5 (C^6, C_6H_3), 143.5 (C^2), 145.4 (C^4, C_6H_3), 146.5 (C^2, C_6H_3), 158.6 (C^8). Mass spectrum, *m*/*z*, (I_{rel}, %): 378 (15) M^+, 231 (15) $[M-2\text{-O-5-}CH_3C_8H_4O]^+$, 211 (4) $[M-2,4\text{-}(NO_2)_2C_6H_3Se]^+$, 147 (100) $[M-2\text{-NO-4-}NO_2C_6H_3Se]^+$, 91 (10) $[C_7H_7]^+$. Found, %: C 47.34, 47.53; H 2.47, 2.61. $C_{15}H_{10}N_2O_5Se$. Calculated, %: C 47.62; H 2.64.

^1H NMR study of the decomposition of 4-(2-hydroxyphenyl)-1,2,3-selenadiazole (IIa). A solution of compound **IIa** in DMSO-d_6 was placed in an NMR ampule, an equimolar amount of tetrabutylammonium hydroxide was added, and ^1H NMR spectra were recorded on a Bruker AMX-400 instrument (400 MHz).

After 5 min, signal from the hydroxy proton of the initial compound disappeared, and those corresponding to benzofuran-2-selenolate (**VIIa**) appeared. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.02 s (3-H), 7.07 d (4-H and 7-H), 6.77 t and 6.87 t (5-H and 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 105.7 (C^3), 107.9 (C^7), 115.2 (C^5), 118.4 (C^4), 121 (C^6), 132.8 (C^9), 155.9 (C^8), 164.4 (C^2).

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