Russian Journal of Organic Chemistry, Vol. 38, No. 10, 2002, pp. 1510–1518. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 10, 2002, pp. 1563–1571.

4-(2-Hydroxyaryl)-1,2,3-thiadiazoles as a Source of 2-Benzofuranthiolates*

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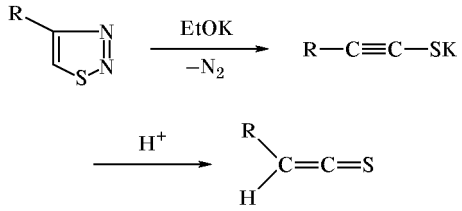
Received December 24, 2001

Abstract—Following the Hurd–Mori procedure, 4-(2-hydroxyaryl)-1,2,3-thiadiazoles were synthesized from *o*-hydroxyacetophenones. Treatment of the products with bases gives 2-benzofuranthiolates which can be involved in alkylation and arylation reactions.

1,2,3-Thiadiazoles having no substituent in position *5* readily decompose under the action of strong bases (e.g., potassium ethoxide or butyllithium). The reaction is accompanied by evolution of nitrogen, and the products are alkynethiolates [1, 2] (Scheme 1).

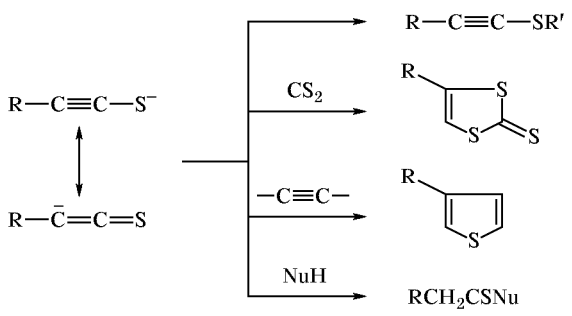
Scheme 1.



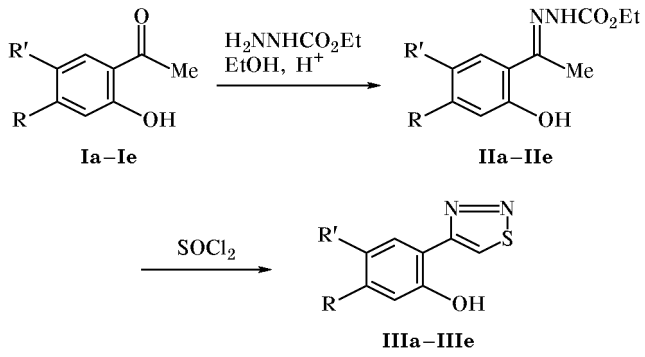
The resulting acetylenic thiolates are widely used in organic synthesis for the preparation of acetylenic sulfides and in cycloaddition reactions. Their protonation gives acetylenic thiols which are precursors of highly reactive thioketenes [3–9] (Scheme 2). On the other hand, 1,2,3-thiadiazoles attract interest as biologically active compounds [10–12]. The first commercial plant growth stimulator, "Bion," was recently synthesized on the basis of 1,2,3-benzothiadiazole-7-carboxylic acid derivatives [13]. Dehaen *et al.* [14] reported a new convenient procedure for preparation of 2-methylthiobenzofuran by decomposition of accessible 4-(2-hydroxyphenyl)-1,2,3-thiadiazole.

The present communication describes in detail the synthesis of 4-(2-hydroxyaryl)-1,2,3-thiadiazoles and their transformation into 2-benzofuranthiolates. While continuing our studies in the field of synthesis and reactivity of 5-unsubstituted 1,2,3-thiadiazoles having

Scheme 2.



Scheme 3.



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

* This study was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32740).

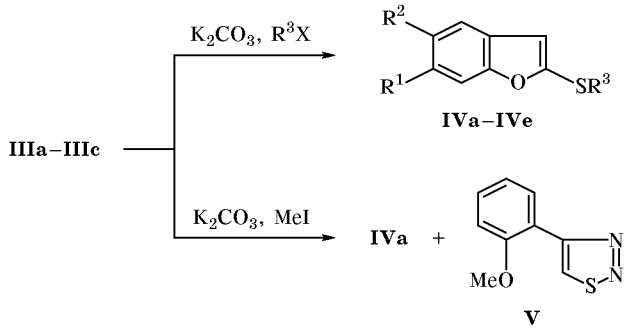
an active functional group (hydroxy), from *o*-hydroxyacetophenones **Ia**–**Ie** we obtained the corresponding ethoxycarbonylhydrazones **IIa**–**IIe** (Scheme 3). By the reaction of 2,5-dihydroxyacetophenone (**Ic**) with *p*-tolylsulfonylhydrazine we synthesized tosylhydrazone **IIc**. Treatment of hydrazones **IIa**–**IIe** with thionyl chloride (Hurd–Mori reaction [15]) gave new 4-(2-hydroxyaryl)-1,2,3-thiadiazoles **IIIa**–**IIIe** in an overall yield of 37–74%.

The structure of thiadiazoles **IIIa**–**IIIe** was confirmed by the IR, ^{1}H and ^{13}C NMR, and mass spectra. In the IR spectrum of thiadiazole **IIIa**, the O–H stretching vibration band is broadened and is located in the region 3200–3100 cm^{-1}, in keeping with published data [16]. The ^{1}H NMR spectra of **IIIa**–**IIIe** contain singlets from the 5-H and OH protons, which appear in a weaker field relative to the aromatic proton signals, e.g., for thiadiazole **IIIa**: δ 8.82 (5-H), 10.54 (OH), and 7.15–7.67 ppm (m, H_{arom}).

In the mass spectra of thiadiazoles **IIIa**–**IIIe** we observed the corresponding molecular ion peaks, whose isotopic composition conforms to the calculated data. Further fragmentation of the molecular ions supports their structure. The main decomposition pathway includes elimination of nitrogen molecule; the same process occurs under irradiation and at high temperature [10, 17].

We made an attempt to effect alkylation of 1,2,3-thiadiazoles **IIIa**–**IIIc** in the presence of a base (K_2CO_3). However, the reaction was accompanied by decomposition of the thiadiazole ring with evolution of nitrogen and formation of 2-benzofuranyl sulfides **IVa**–**IVe** (Scheme 4).

Scheme 4.



IV, $R^1 = R^2 = H$, $R^3 = Me$ (**a**); $R^1 = R^2 = H$, $R^3 = C_{16}H_{31}$ (**b**); $R^1 = R^2 = H$, $R^3 = PhCH_2$ (**c**); $R^1 = OH$, $R^2 = H$, $R^3 = C_{16}H_{31}$ (**d**); $R^1 = H$, $R^2 = OH$, $R^3 = C_{16}H_{31}$ (**e**).

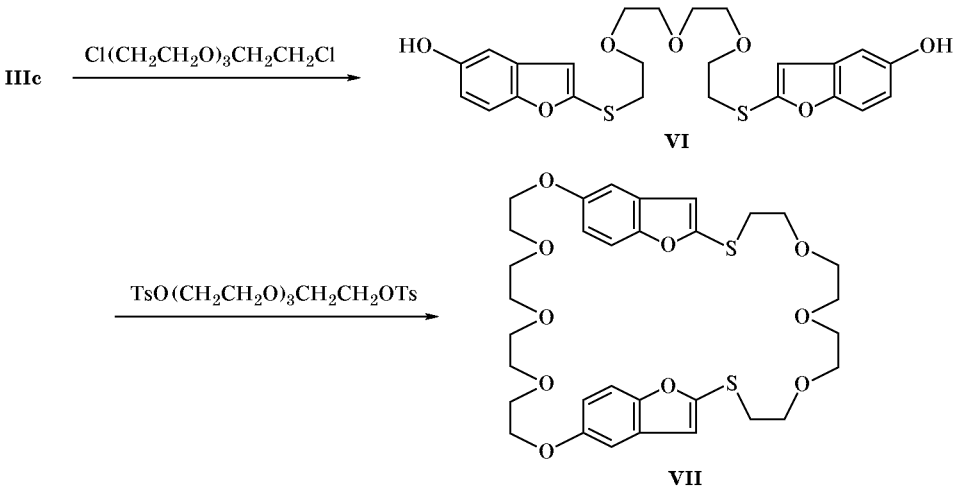
In all cases, the alkylating agent (benzyl bromide or 1-bromohexadecane) was simultaneously mixed with thiadiazole **IIIa**–**IIIc** and potassium carbonate. Under analogous conditions, the reaction of thiadiazole **IIIa** with a much stronger alkylating agent, methyl iodide, gave a considerable amount of methoxyphenylthiadiazole **V** (40%) together with 56% of benzofuranyl sulfide **IVa**. In order to obtain sulfide **IVa** in a good yield (90%), thiadiazole **IIIa** should be treated with a base before addition of methyl iodide. These data indicate intermediate formation of benzofuran-2-thiolates in the alkylation process.

The ^{1}H NMR spectra of 2-alkylthiobenzofurans **IVa**–**IVe** contain singlets at δ 6.65–6.76 ppm from the 3-H proton. The corresponding signal of difuryl diselenide appears as a singlet at δ 6.63 ppm [18]. In the ^{13}C NMR spectra of **IVa**–**IVe**, the chemical shifts of the furan ring carbons almost coincide with those typical of difuryl diselenide [18]. Benzofuryl sulfides give molecular ion peaks in the mass spectra; their isotope composition conforms to the assumed structures. The main fragmentation pathway of the molecular ions of **IVa**–**IVe** involves cleavage of the C_{sp^3}–S bond, i.e., elimination of the alkyl substituent, followed by expulsion of CO molecule.

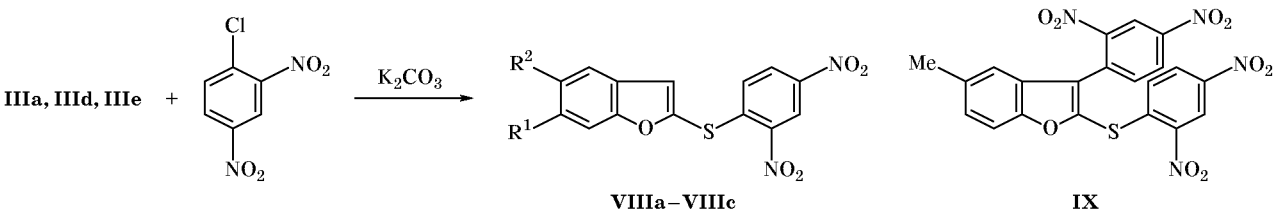
An interesting application of selective alkylation is illustrated by Scheme 5. 4-(2,5-Dihydroxyphenyl)-1,2,3-thiadiazole (**IIIc**) was treated with a base and with 0.5 equiv of 1,11-dichloro-3,6,9-trioxaundecane. As a result, 72% of 1,11-bis(5-hydroxy-2-benzofurylthio)-3,6,9-trioxaundecane (**VI**) was obtained. The latter was brought into reaction with tetraethylene glycol bis(*p*-toluenesulfonate), which led to formation of thia crown ether **VII** in 38% yield. Syntheses of such crown ethers usually require preliminary protection of the phenolic hydroxy group.

The arylation of 4-(2-hydroxyaryl)-1,2,3-thiadiazoles **IIIa**, **IIId**, and **IIIe** with 2,4-dinitrochlorobenzene in the presence of potassium carbonate followed a pattern similar to the alkylation. The isolated products were 2-(2,4-dinitrophenylthio)benzofurans **VIIIa**–**VIIIc** (Scheme 6). According to the TLC data, small amounts of by-products were also formed. By column chromatography we isolated 3-(2,4-dinitrophenyl)-2-(2,4-dinitrophenylthio)benzofuran (**IX**) from the product mixture obtained in the reaction of 4-(2-hydroxy-4-methylphenyl)-1,2,3-thiadiazole (**IIId**) with 2,4-dinitrochlorobenzene. The formation of such a by-product suggests radical anion nature of the colored thiadiazole decomposition products. When the reaction was carried out under argon, no intense coloration was observed, and the yield of by-products was considerably lower. This assumption is also supported by the known addition of two styrene molecules to 2-benzofuranthiol both at the sulfur atom and at position *3* of the benzofuran ring [19].

Scheme 5.



Scheme 6.

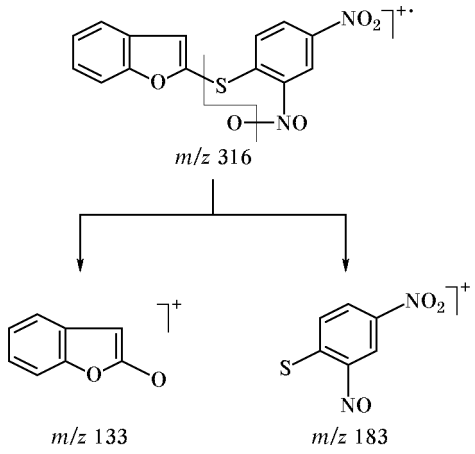


VIII, $R^1 = R^2 = H$ (**a**); $R^1 = Me$, $R^2 = H$ (**b**); $R^1 = H$, $R^2 = Me$ (**c**).

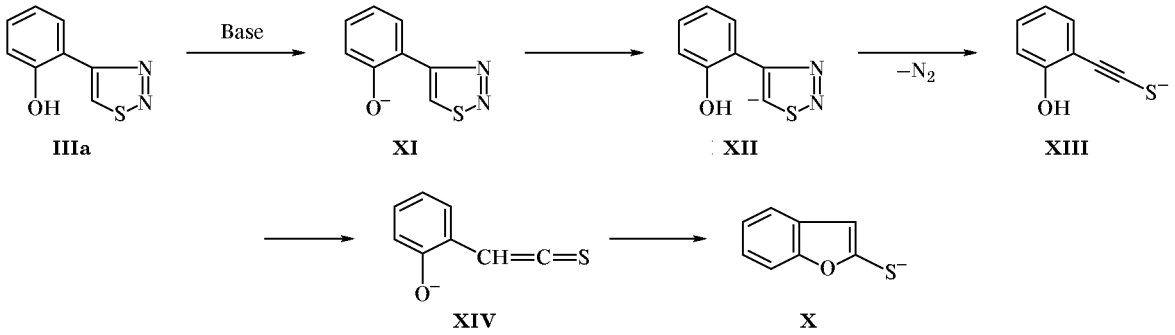
The structure of arylation products **VIIIa**–**VIIIc** and **IX** was confirmed by the ^1H and ^{13}C NMR and mass spectra. The ^1H and ^{13}C NMR spectral patterns (both signal positions and their multiplicities) of the benzofuran and 2,4-dinitrophenyl fragments in 2-(2,4-dinitrophenylthio)benzofurans **VIIIa**–**VIIIc** and **IX** resemble those observed for 2-alkylthiobenzofurans **IVa**–**IVe** and 2,4-dinitrotoluene [20], respectively. The mass spectra of **VIIIa**, **VIIIb**, and **IX** contain peaks from the molecular ions whose isotope composition conforms to the assumed structures. The main fragmentation pathways of compounds **VIII** and **IX** under electron impact are illustrated by Scheme 7 for the molecular ion of 2-(2,4-dinitrophenylthio)-benzofuran (**VIIIa**) as an example. In keeping with the fragment ion peak intensities, the most probable pathway involves formation of 4-nitro-2-nitroso-phenylseleno and benzofuran-2-yloxy ions.

^1H NMR study of the mechanism of decomposition of 4-(2-hydroxyphenyl)-1,2,3-thiadiazole (**IIIa**) (using Bu_4NOH as a base) showed that the reaction of **IIIa** with a base gives 2-benzofuranthiolate ion (**X**). The process includes several steps (Scheme 8): formation of phenoxide ion **XI**, intramolecular proton transfer from the heteroring to give anion **XII**, elimination of nitrogen from **XII** with formation of alkynethiolate **XIII** (as is usually observed for 1,2,3-thiadiazoles having no substituent in the 5-position [1, 2]), intramolecular proton transfer leading to thioketene **XIV**, and ring closure with participation of the hydroxy group. Intermediates **X**, **XI**, and **XIII** were detected by ^1H NMR spectroscopy.

Scheme 7.



Scheme 8.



EXPERIMENTAL

The melting points were determined on a Boetius device. The IR spectra were recorded on an IKS-29 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on Bruker Avance (300 MHz for ^{1}H and 75 MHz for ^{13}C) and Bruker AMX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) instruments using solvent signals as reference. The mass spectra (70 eV) were run on a Kratos MS 890 high-resolution mass spectrometer with direct sample admission into the ion source heated to 200°C. 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.

2,4-Dihydroxyacetophenone ethoxycarbonylhydrazone (IIb). To a solution of 10 g (32.9 mmol) of 2,4-dihydroxyacetophenone **Ib** in a mixture of 75 ml ethanol and 75 ml of water we added 6.84 g (32.9 mmol) of ethyl hydrazinecarboxylate. The mixture was heated for 22 h under reflux and was left to stand overnight in a refrigerator. The precipitate was filtered off, washed with diethyl ether (2 × 50 ml), and dried under reduced pressure. Yield 9.50 g (61%), mp 209°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.27 t ($CH_2C\mathbf{H}_3$), 2.24 s ($C\mathbf{H}_3C{=}N$), 4.19 q ($C\mathbf{H}_2CH_3$), 6.24 d (6-H), 6.30 d.d (5-H), 9.22 s (3-H), 9.75 s (4-OH), 10.50 s (2-OH), 13.05 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.3, 14.5, 61.0, 103.1, 106.6, 111.7, 129.3, 154.1, 159.8, 160.1. Mass spectrum, *m*/*z* (I_{rel}, %): 238 (100.0) M^+, 237 (26), 221 (44), 192 (33), 165 (23), 150 (20), 149 (25), 136 (59), 135 (39), 107 (21).

2,5-Dihydroxyacetophenone *p*-tolylsulfonylhydrazone (IIc). To a solution of 2 g (13.1 mmol) of 2,5-dihydroxyacetophenone (**Ic**) in 50 ml of toluene we added 2.45 g (13.1 mmol) of *p*-tolylsulfonylhydrazine. The mixture was heated for 2 h under reflux with simultaneous removal of water (as azeotrope with toluene) using a Dean–Stark trap and was left to stand overnight in a refrigerator. The precipitate was filtered off and dried under reduced pressure. Yield 3.81 g (90%); mp 192°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.22 s (CH_3), 2.37 s ($C\mathbf{H}_3C{=}N$), 6.66 d (6-H), 6.71 d.d (4-H), 6.84 d (3-H), 7.44 d and 7.78 d (H_{arom} in Ts), 8.9 s (NH), 10.93 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.6 ($\mathbf{C}H_3C{=}N$), 21.0 (CH_3), 114.0, 117.4, 118.6, 119.6, 127.4, 129.8, 135.4, 143.9, 149.3, 150.2, 158.1. Mass spectrum, *m*/*z* (I_{rel}, %): 320 (83) M^+, 165 (90), 148 (47), 136 (100.0), 120 (23), 107 (47), 91 (80), 79 (44), 65 (65), 53 (27), 51 (22), 39 (38).

2-Hydroxy-4-methylacetophenone ethoxycarbonylhydrazone (IId). A solution of 5.4 g (36 mmol) of 2-hydroxy-4-methylacetophenone (**Id**), 3.74 g (36 mmol) of ethyl hydrazinecarboxylate, and 3 drops of acetic acid in 15 ml of ethanol was heated for 30 min under reflux, cooled to 15–18°C, and left overnight. The precipitate was filtered off and dried under reduced pressure. Yield 7.3 g (86%); mp 159–161°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24 t ($CH_2C\mathbf{H}_3$), 2.25 s ($CH_3C{=}N$), 2.28 s (CH_3), 4.21 q ($C\mathbf{H}_2CH_3$), 6.78 s (3-H), 6.69 d (5-H), 7.49 d (6-H), 10.68 s (2-OH), 12.87 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.8, 13.9, 20.3, 60.6, 116.9, 118.9, 127.3, 140.1, 153.5, 157.6, 165.0, 167.5. Mass spectrum, *m*/*z* (I_{rel}, %): 236 (78.6) M^+, 219 (35.6), 190 (85.8), 163 (31.6), 147 (82.3), 134 (100), 118 (43.9), 105 (39.5), 91 (59.2).

2-Hydroxy-5-methylacetophenone ethoxycarbonylhydrazone (IIe). A solution of 9.3 g (62 mmol) of 2-hydroxy-5-methylacetophenone (**Ie**), 6.4 g (62 mmol) of ethyl hydrazinecarboxylate, and 3 drops of acetic acid in 30 ml of ethanol was heated for 30 min under reflux, cooled, and left overnight. The precipitate was filtered off and dried under reduced pressure. Yield 12 g (82%); mp 137–139°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.25 t ($CH_2C\mathbf{H}_3$), 2.22 s ($CH_3C{=}N$), 2.26 s (CH_3),

4.17 q ($C\mathbf{H}_2CH_3$), 6.73 d (3-H), 7.03 d (4-H), 7.31 s (5-H), 10.6 s (2-OH), 12.63 s (NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.3, 14.4, 20.2, 61.1, 116.8, 119.2, 126.8, 128, 131.2, 154.1, 156, 165.7. Mass spectrum, *m*/*z* (I_{rel}, %): 236 (17.1) M^+, 219 (9.9), 190 (47.4), 163 (7.6), 147 (100), 134 (58.7), 118 (36.6), 105 (31), 91 (31.7).

4-(2-Hydroxyphenyl)-1,2,3-thiadiazole (IIIa) [14]. A flask equipped with a reflux condenser and a gas-outlet tube (which was connected to a system for absorption of gaseous hydrogen chloride) was charged with 11.8 g (50 mmol) of ethoxycarbonylhydrazone **IIa**. It was cooled to 0–5°C, and 80 ml of thionyl chloride cooled to 0–5°C was added. The cooling bath was removed, and vigorous reaction gradually started with evolution of HCl. When intense gas evolution ceased, the mixture was heated for 1 h at 60°C. It was then cooled to 20–25°C, and excess thionyl chloride was distilled off under reduced pressure. Cold water, 50 ml, was added to the residue, and the precipitate was filtered off and dried to obtain 8.5 g (88%) of the crude product. Recrystallization from water gave 6.2 g (64%) of compound **IIIa** as colorless needles with mp 106°C. IR spectrum (KBr), ν, cm^{-1}: 3200–3100, 3000, 1593, 1470, 1258. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.00 t.d (5-H), 7.15 d.d (3-H), 7.36 t.d (4-H), 7.67 d.d (6-H), 8.82 s (5-H, thiadiazole), 10.54 s (OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 114.5 (C^1), 118.3 (C^3), 120.1 (C^5), 127.4 (C^4), 130.0 (C^6), 131.4 (C^5, thiadiazole), 156.0 (C^2), 162.3 (C^4, thiadiazole). Mass spectrum, *m*/*z* (I_{rel}, %): 178 (14.5) M^+, 150 (22.4) $[M-N_2]^+$, 122 (37.3), 121 (100), 83 (18), 90 (55), 77 (32). Found, %: C 54.21, 53.98; H 3.41, 3.13. $C_8H_6N_2OS$. Calculated, %: C 53.93, H 3.37.

4-(2,4-Dihydroxyphenyl)-1,2,3-thiadiazole (IIIb) was synthesized in a similar way from 8 g (33.61 mmol) of compound **IIb** and 70 ml of thionyl chloride. The only difference was that the mixture was heated for 3 h. The product was purified by column chromatography on silica gel L 40/100 μm using methylene chloride–ethyl acetate (10:3) as eluent. Yield 4.00 g (61%), mp 209°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.43 d (6-H), 6.55 d (5-H), 8.08 d (3-H), 9.22 s (5-H, thiadiazole), 9.7 s (4-OH), 10.32 s (2-OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 102.9, 107.4, 130.2, 131.9 (C^5, thiadiazole), 156.0, 158.8 (C^4, thiadiazole), 159.2. Found, %: C 49.43; H 3.18; N 14.19. $C_8H_6N_2O_2S$. Calculated, %: C 49.48; H 3.11; N 14.42.

4-(2,5-Dihydroxyphenyl)-1,2,3-thiadiazole (IIIc). Thionyl chloride, 10 ml, was added at –78°C to 1.1 g (3.44 mmol) of *p*-tolylsulfonylhydrazone **IIc**. When vigorous evolution of HCl ceased, the cooling bath was removed, and the mixture was stirred for 2 h. Excess thionyl chloride was distilled off under reduced pressure, and the product was purified by column chromatography on silica gel L 40/100 μm using methylene chloride–ethyl acetate (10:3) as eluent. Yield 0.46 g (69%); mp 216°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.74 d (6-H), 6.89 d.d (4-H), 7.73 d (3-H), 9.02 s (5-OH), 9.43 s (5-H, thiadiazole), 9.77 s (2-OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 114.9, 117.26, 117.33, 134.7 (C^5, thiadiazole), 147.4, 150.0, 158.4 (C^4, thiadiazole). Mass spectrum, *m*/*z* (I_{rel}, %): 194 (94) M^+, 166 (35), 137 (100.0), 110 (37), 105 (28), 94 (27), 82 (20), 66 (31), 65 (31), 55 (21), 53 (28), 45 (26), 39 (44). Found, %: C 49.52; H 3.15; N 14.32. $C_8H_6N_2O_2$. Calculated, %: C 49.48; H 3.11; N 14.42.

4-(2-Hydroxy-4-methylphenyl)-1,2,3-thiadiazole (IIId) was synthesized as described above for compound **IIIa** from 4.9 g (20.8 mmol) of hydrazone **IId** and 20 ml of thionyl chloride. Yield 3.5 g (87%); mp 115–117°C (from water). R_f 0.5 (eluent $CHCl_3$). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (CH_3), 6.8 d (5-H), 6.96 s (3-H), 7.52 d (6-H), 8.72 s (5-H, thiadiazole), 10.44 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.4 (CH_3), 111.9 (C^1), 118.6 (C^3), 121.2 (C^5), 127.2 (C^6), 129.1 (C^5, thiadiazole), 142.0 (C^4), 156 (C^2), 162.4 (C^4, thiadiazole). Mass spectrum, *m*/*z* (I_{rel}, %): 192 (52.2) M^+, 164 (95.1) $[M-N_2]^+$, 135 (100), 131 (58), 103 (44.4), 91 (69.7), 77 (39.1). Found, %: C 59.27, 59.48; H 4.41, 4.18. $C_9H_8N_2OS$. Calculated, %: C 59.34, H 4.17.

4-(2-Hydroxy-5-methylphenyl)-1,2,3-thiadiazole (IIIe) was synthesized as described above for thiadiazole **IIIa** from 11.8 g (50 mmol) of compound **IIe** and 80 ml of thionyl chloride. Yield 8.5 g (88%); mp 88–90°C (from water). R_f 0.43 (eluent $CHCl_3$). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (CH_3), 6.82 d (3-H), 6.96 s (6-H), 7.35 d (4-H), 8.51 s (5-H, thiadiazole), 10.69 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.3 (CH_3), 112.2 (C^1), 117.4 (C^3), 124.6 (C^6), 129.9 (C^4), 128.4 (C^5, thiadiazole), 132.6 (C^5), 159.2 (C^2), 159.3 (C^4, thiadiazole). Mass spectrum, *m*/*z* (I_{rel}, %): 192 (31.3) M^+, 164 (50.5) $[M-N_2]^+$, 135 (100), 131 (25), 103 (23), 91 (43.1), 77 (14.8). Found, %: C 59.19, 59.44; H 4.04, 4.35. $C_9H_8N_2OS$. Calculated, %: C 59.34, H 4.17.

2-Methylthiobenzofuran (IVa) and 4-(2-methoxyphenyl)-1,2,3-thiadiazole (V). *a*. A suspension of 1 g (5.62 mmol) of thiadiazole **IIIa**, 0.93 g (6.74 mmol) of potassium carbonate, and 1.2 g (8.43 mmol) of methyl iodide in 40 ml of dry acetone

was heated for 10 h under reflux with vigorous stirring. The mixture was filtered, the filtrate was evaporated under reduced pressure, and the residue was subjected to chromatography in a 3 × 30-cm column charged with silica gel L 40/100 μm using methylene chloride–cyclohexane (1 : 2) as eluent. Removal of the solvent from the first fraction gave 0.52 g (56%) of benzofuran **IVa** as a light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.52 s (SCH_3), 6.66 s (3-H), 7.18 t.d (5-H), 7.22 t.d (6-H), 7.41 d (7-H), 7.46 d (4-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.0 (CH_3S), 107.8 (C^3), 110.7 (C^7), 120.1 (C^4), 122.8 (C^5), 123.9 (C^6), 128.5 (C^9), 152.2 (C^2), 156.0 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 164 (92) M^+, 149 (100) $[M-CH_3]^+$, 121 (50), 77 (32), 69 (10), 63 (18), 51 (17). Found: M^+ 164.0298. C_9H_8OS. Calculated: *M* 164.0296.

From the second fraction, 0.47 g (40%) of thiadiazole **V** was isolated. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.96 s (OCH_3), 7.06 d.d (3-H), 7.14 t.d (5-H), 7.41 t.d (4-H), 8.50 d.d (6-H), 9.06 s (5-H, thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.5 (CH_3), 111.2, 119.6, 121.1, 130.0, 130.3, 133.3 (C^5, thiadiazole), 156.3, 158.4 (C^4, thiadiazole). Mass spectrum, *m*/*z* (I_{rel}, %): 192 (30) M^+, 164 (81) $[M-N_2]^+$, 149 (100) $[M-N_2-CH_3]^+$, 131 (50), 121 (100.0), 119 (43), 91 (40), 77 (71), 51 (41), 49 (28), 45 (29), 39 (27).

b. A suspension of thiadiazole **IIIa** and K_2CO_3 in dry acetone was refluxed for 1 h. Methyl iodide was then added. The only product was benzofuran **IVa**. Yield 90%.

2-Hexadecylthiobenzofuran (IVb). A suspension of 0.5 g (2.81 mmol) of thiadiazole **IIIa**, 0.47 g (3.37 mmol) of K_2CO_3, and 1.03 g (3.37 mmol) of 1-bromohexadecane in 40 ml of dry acetone was heated for 10 h under reflux with vigorous stirring. The mixture was cooled and filtered, and the filtrate was evaporated under reduced pressure. The residue was subjected to chromatography on a 3 × 30-cm column charged with silica gel L 40/100 μm (eluent methylene chloride). Yield 0.97 g (92%), colorless crystals, mp 30°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (CH_3), 1.25 m [12(CH_2)], 1.40 t.d ($SCH_2CH_2C\mathbf{H}_2$), 1.66 t.d ($SCH_2C\mathbf{H}_2$), 2.93 t (SCH_2), 6.76 d (3-H, ^3J = 0.9 Hz), 7.20 t.d (5-H), 7.25 t.d (6-H), 7.43 m (7-H), 7.49 m (4-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.3, 22.7, 28.5, 29.1, 29.4, 29.5, 29.6, 29.7, 31.9, 34.7 (CH_2S), 110.6, 110.9, 120.3, 122.8, 124.2, 128.7, 150.9 (C^2), 156.2. Mass spectrum, *m*/*z* (I_{rel}, %): 374 (100.0) M^+, 151 (13), 150 (97), 149 (19) $[M-C_{16}H_{33}]^+$, 121 (15), 71 (11), 69 (11), 57 (31), 55 (27), 43 (65), 41 (44). Found, %: C 76.77; H 10.10. $C_{24}H_{38}OS$. Calculated, %: C 76.95; H 10.22.

2-Benzylthiobenzofuran (IVc). A suspension of 1 g (5.62 mmol) of thiadiazole **IIIa**, 0.93 g (6.74 mmol) of K_2CO_3, and 0.85 g (6.74 mmol) of benzyl chloride in 40 ml of dry acetone was heated for 10 h under reflux with vigorous stirring. The mixture was cooled and filtered, and the filtrate was evaporated under reduced pressure. The residue was subjected to chromatography on a 3 × 30-cm column charged with silica gel L 40/100 μm using methylene chloride–cyclohexane (1 : 2) as eluent. Yield 1.28 g (91%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.14 s (SCH_2), 6.65 s (3-H), 7.17–7.45 m (H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 39.3 (CH_2S), 110.9, 111.8 (C^3), 120.5, 122.8, 124.8, 127.3, 128.5, 128.8, 137.1, 149.6 (C^2), 156.3. Mass spectrum, *m*/*z* (I_{rel}, %): 240 (58) M^+, 149 (11) $[M-CH_2Ph]^+$, 121 (19), 91 (100), 77 (16), 69 (25), 39 (12). Found: M^+ 240.0609. $C_{15}H_{12}OS$. Calculated: *M* 240.0609.

2-Hexadecylthio-6-hydroxybenzofuran (IVd). A suspension of 0.5 g (2.58 mmol) of thiadiazole **IIIb**, 0.429 g (3.09 mmol) of K_2CO_3, and 0.79 g (2.58 mmol) of 1-bromohexadecane in 30 ml of dry acetone was vigorously stirred for 10 h at 18°C. The mixture was filtered, the filtrate was evaporated under reduced pressure, and the residue was subjected to chromatography on a 3 × 30-cm column charged with silica gel L 40/100 μm (eluent methylene chloride). Yield 0.48 g (46%); colorless crystals, mp 65°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (CH_3), 1.25 m [12(CH_2)], 1.39 t.d ($SCH_2CH_2C\mathbf{H}_2$), 1.63 t.d ($SCH_2C\mathbf{H}_2$), 2.87 t (SCH_2), 4.95 m, 6.73 d (3-H), 6.76 d.d (5-H), 6.95 d (7-H), 7.32 d (4-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.3, 22.7, 28.4, 29.1, 29.4, 29.5, 29.6, 29.7, 31.9, 35.2 (CH_2S), 98.1, 111.7 (C^3), 111.9, 120.7, 122.2, 149.2, 153.7, 157.2. Mass spectrum, *m*/*z* (I_{rel}, %): 390 (100) M^+, 167 (12), 166 (83), 165 (21), 137 (12), 69 (11), 57 (24), 55 (23), 43 (44), 41 (30). Found, %: C 73.64; H 9.81. $C_{24}H_{38}O_2S$. Calculated, %: C 73.80; H 9.71.

2-Hexadecylthio-5-hydroxybenzofuran (IVe). 1-Bromohexadecane, 0.25 g (0.82 mmol), was added at 18°C to a suspension of 0.16 g (0.82 mmol) of thiadiazole **IIIc** and 0.1 g (0.90 mmol) of potassium *tert*-butoxide in 10 ml of dry acetone. The mixture was stirred at 18°C and filtered, the filtrate was evaporated under reduced pressure, and the residue was subjected to chromatography on a 3 × 20-cm column charged with silica gel L 40/100 μ (eluent methylene chloride). Yield 0.31 g (97%); colorless

crystals, mp 72°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (CH_3), 1.25 m [12(CH_2)], 1.4 t.d ($SCH_2CH_2CH_2$), 1.65 t.d (SCH_2CH_2), 2.92 t (SCH_2), 4.69 m, 6.65 d (3-H), 6.76 d.d (6-H), 6.89 d (4-H), 7.27 d (7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.3, 22.7, 28.5, 29.1, 29.3, 29.5, 29.6, 29.7, 31.9, 34.7 (CH_2S), 105.2, 110.1 (C^3), 111.3, 112.7, 129.5, 151.3, 151.4, 151.9 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 390 (51) M^+, 167 (13), 160 (100.0), 137 (15), 71 (12), 57 (31), 55 (28), 43 (62), 41 (46). Found, %: C 73.64; H 9.81. $C_{24}H_{38}O_2S$. Calculated, %: C 73.80; H 9.71.

1,11-Bis(5-hydroxybenzofuran-2-ylthio)-3,6,9-trioxaundecane (VI). A mixture of 1 g (5.16 mmol) of thiadiazole **IIIc**, 0.71 g (5.16 mmol) of K_2CO_3, and 0.16 g (0.5 equiv, 2.58 mmol) of 1,11-dichloro-3,6,9-trioxaundecane in 40 ml of dry acetone was heated for 12 h under reflux. The mixture was filtered, the filtrate was evaporated under reduced pressure, and the residue was subjected to column chromatography (3 × 20-cm column) on silica gel L 40/100 μm using methylene chloride–ethyl acetate (10 : 3) as eluent. Yield 0.90 g (72%); colorless crystals, mp 125°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.11 t (SCH_2), 3.62 t, 4.45–4.50 m, 6.75 d.d (6-H), 6.86 d (3-H), 6.87 d (4-H), 7.31 d (7-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 33.3 (CH_2S), 69.1, 69.6, 69.7 (CH_2O), 104.8, 109.3 (C^3), 111.0, 113.0, 129.0, 149.8, 150.2 (C^2), 153.4. Mass spectrum, *m*/*z* (I_{rel}, %): 490 (68) M^+, 192 (14), 167 (12), 166 (36), 165 (100.0), 137 (22), 87 (10), 73 (15), 45 (24). Found, %: C 58.54; H 5.40. M^+ 490.1120. $C_{24}H_{38}O_2S$. Calculated, %: C 58.76; H 5.34. *M* 490.1120.

2,7,10,13,24,27,30,33,36,44-Decaoxa-4,16-dithiapentacyclo[35.3.1.1^{3,40}.1^{17,20}.1^{19,23}]tetratetraconta-1(40),3(42),17,19,21,23(43),37(41),38-octaene (VII). A mixture of 0.70 g (24.5 mmol) of sodium hydride (as 80% suspension in mineral oil) and 200 ml of tetrahydrofuran was stirred for 30 min, and a solution of 0.6 g (1.22 mmol) of compound **VI** in 200 ml of tetrahydrofuran was added dropwise. The mixture was heated to 65°C, and a solution of 0.74 g (1.47 mmol) of tetraethylene glycol bis(*p*-toluenesulfonate) in 200 ml of THF was added dropwise over a period of 12 h. The mixture was stirred for 72 h at 65°C and cooled to room temperature, several drops of water were added, and the mixture was evaporated under reduced pressure. The residue was treated with a mixture of 200 ml of toluene and 100 ml of water, and the organic phase was separated and washed in succession with 50 ml of 0.5 N aqueous sodium hydroxide, 80 ml of 2 N hydrochloric acid, and 2 × 100 ml of water. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (3 × 20-cm column) on silica gel L 40/100 μm using methylene chloride–ethyl acetate (10 : 3) as eluent. Yield 0.3 g (38%); colorless crystals, mp 64°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.09 t (SCH_2), 3.58 t, 3.65–3.75 m, 3.84 t, 4.06 t, 6.65 s (3-H), 6.83 d.d (6-H), 6.87 d (4-H), 7.23 d (7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 33.9 (CH_2S), 68.4, 69.8, 70.0, 70.5, 70.7, 70.79, 70.84 (CH_2O), 104.1, 11.1 (C^3), 111.3, 113.8, 129.0, 150.6 (C^2), 151.4, 155.2. Mass spectrum, *m*/*z* (I_{rel}, %): 648 (100.0) M^+, 192 (10), 191 (21), 165 (28), 148 (11), 89 (10), 45 (50), 43 (19). Found, %: C 59.31; H 6.25. $C_{32}H_{40}O_{10}S_2$. Calculated, %: C 59.24; H 6.21.

2-(2,4-Dinitrophenylthio)benzofuran (VIIIa). A suspension of 0.5 g (2.8 mmol) of thiadiazole **IIIa** and 0.46 g (3.4 mmol) of K_2CO_3 in 10 ml of dry acetonitrile was heated for 30 min under reflux with intense stirring. The reaction was accompanied by vigorous evolution of nitrogen, and the mixture turned light yellow. A solution of 0.57 g (2.8 mmol) of 2,4-dinitrochlorobenzene in 5 ml of acetonitrile was added dropwise, and the mixture became dark blue. It was refluxed for 4 h and filtered, and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography (3 × 20-cm column) on silica gel L 40/100 μm using chloroform–heptane (1 : 1) as eluent. Yield 0.82 g (93%); mp 145–148°C (from $CHCl_3$–heptane). R_f 0.75 (eluent $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.14 d (4-H), 7.36 t.d (5-H), 7.38 s (3-H), 7.46 t.d (6-H), 7.55 d (7-H), 7.7 d (6-H, dinitrophenyl), 8.22 d.d (5-H, dinitrophenyl), 9.13 d (3-H, dinitrophenyl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 111.9, 119.4, 121.4, 121.8, 123.9, 126.9, 127.4, 127.7, 129.5, 142.8, 144.2, 144.9, 145.2, 157.4. Mass spectrum, *m*/*z* (I_{rel}, %): 316 (19) M^+, 183 (66) [*M* – 2-oxobenzofuran]$^+$, 133 (100) [*M* – 2-NO-4-$NO_2C_6H_3S$]$^+$, 105 (27), 77 (25). Found, %: C 52.81, 52.75; H 2.71, 2.84. $C_{14}H_8N_2O_5S$. Calculated, %: C 53.16, H 2.53.

2-(2,4-Dinitrophenylthio)-6-methylbenzofuran (VIIIb) was synthesized in a similar way from 0.5 g (2.6 mmol) of thiadiazole **IIId**, 0.45 g (3.3 mmol) of K_2CO_3, and 0.52 g (2.6 mmol) of 2,4-dinitrochlorobenzene. The product was isolated by chromatography on a 3 × 20-cm column charged with silica gel L 40/100 μm (eluent chloroform–hexane, 1 : 1). Yield 0.51 g (59%); mp 156–161°C (from $CHCl_3$–hexane); R_f 0.66 (eluent $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.52 s (CH_3), 7.13 d (4-H), 7.18 d (5-H), 7.32 s (3-H), 7.34 s (7-H), 7.55 d (6-H, dinitrophenyl), 8.19 d.d (5-H, dinitrophenyl), 9.11 d (3-H, dinitro-

phenyl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.3 (CH_3), 112.3, 119.8, 121.7, 121.8, 125.6, 125.9, 127.7, 129.9, 138.0, 142.2, 144.6, 145.6, 145.6, 158.3. Mass spectrum, *m/z* (I_{rel}, %): 330 (14) M^+, 183 (21) [*M* – 2-oxobenzofuran]$^+$, 147 (100) [*M* – 2-NO-4-$NO_2C_6H_3S$]$^+$, 91 (14), 49 (8). Found, %: C 54.31, 54.59; H 3.31, 3.24. $C_{15}H_{10}N_2O_5S$. Calculated, %: C 54.54, H 3.03.

2-(2,4-Dinitrophenylthio)-5-methylbenzofuran (VIIIc) was synthesized in a similar way from 0.5 g (2.6 mmol) of thiadiazole **IIIe**, 0.45 g (3.3 mmol) of K_2CO_3, and 0.52 g (2.6 mmol) of 2,4-dinitrochlorobenzene. The product was isolated by chromatography on a 3 × 20-cm column charged with silica gel L 40/100 μm (eluent chloroform–hexane, 1 : 1). From the first fraction we isolated 0.4 g (46%) of benzofuran **VIIIc**; mp 168–170°C (from $CHCl_3$–hexane); R_f 0.73 (eluent $CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.49 s (CH_3), 7.12 d (7-H), 7.26 d (6-H), 7.3 s (3-H), 7.46 s (4-H), 7.42 d (6-H, dinitrophenyl), 8.19 d.d (5-H, dinitrophenyl), 9.11 d (3-H, dinitrophenyl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.2 (CH_3), 111.4, 119.2, 121.3, 121.4, 127.3, 127.8, 128.3, 129.5, 133.6, 142.6, 144.2, 145.1, 145.2, 155.8. Mass spectrum, *m/z* (I_{rel}, %): 330 (21) M^+, 183 (28) [*M* – 2-oxobenzofuran]$^+$, 147 (100) [*M* – 2-NO-4-$NO_2C_6H_3S$], 119 (15), 91 (20). Found, %: C 54.24, 54.56; H 3.27, 3.34. $C_{15}H_{10}N_2O_5S$. Calculated, %: C 54.54, H 3.03.

From the second fraction we isolated 0.14 g (11%) of 3-(2,4-dinitrophenyl)-2-(2,4-dinitrophenylthio)-5-methylbenzofuran (**IX**); mp 186–191°C (from $CHCl_3$–cyclohexane); R_f 0.43 (eluent $CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (CH_3), 7.22 s (4-H), 7.33 d (6-H), 7.4 s (5-H), 7.65 d (6-H, C_6H_3S), 8.08 d (6-H, 3-C_6H_3), 8.43 d.d (5-H, C_6H_3S), 8.67 d.d (5-H, 3-C_6H_3), 8.93 d (3-H, C_6H_3S), 8.94 d (3-H, 3-C_6H_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.9 (CH_3), 111.9, 119.5, 120.5, 121.4, 126.7, 127.2, 128.0, 128.3, 129.0, 129.5, 130.5, 134.0, 134.8, 140.6, 141.9, 143.9, 135.3, 147.9. 148.5, 154.5. Mass spectrum, *m/z* (I_{rel}, %): 486 (46) M^+, 313 (100) [*M* – 2-NO-4-$NO_2C_6H_3S$]$^+$, 269 (14), 237 (35), 223 (34), 206 (43), 195 (59), 183 (98) [2-NO-4-$NO_2C_6H_3S$]$^+$, 178 (59), 166 (78), 139 (30), 115 (14), 85 (17), 75 (21), 63 (29). Found, %: C 50.53, 54.68; H 2.71, 2.82. $C_{21}H_{12}N_4O_9S$. Calculated, %: C 50.81, H 2.42.

^1H NMR study of the decomposition of 4-(2-hydroxyphenyl)-1,2,3-thiadiazole (IIIa). An NMR ampule was charged with a solution of 4-(2-hydroxyphenyl)-1,2,3-thiadiazole (**IIIa**) in CD_3CN, an equimolar amount of tetrabutylammonium hydroxide was added, and ^1H NMR spectra of the resulting mixture were recorded at 18°C on a Bruker AMX-400 spectrometer (400 MHz). After 5 min, the formation of phenoxide ion **XI** was detected: the hydroxy proton signal at δ 9.69 ppm disappeared, and the 5-H signal (thiadiazole ring) shifted downfield from δ 9.2 to 9.76 ppm. The signals from the phenyl protons, 3-H, 4-H, 5-H, and 6-H displaced upfield by Δδ 0.42, 0.34, 0.64, and 0.17 ppm, respectively. A weak evolution of nitrogen was observed, and after 21 h the spectrum contained signals from a 1 : 1 mixture of phenoxide **XI** and *o*-hydroxyphenylethynethiolate (**XIII**). The proton in position *5* of the thiadiazole ring is partially replaced by deuterium, which confirms the formation of anion **XII**. The reaction was complete in 93 h, and the ^1H NMR spectrum of the final solution contained only signals from 2-benzofuranthiolate (**X**), δ, ppm: 5.98 s (3-H), 6.81 t and 6.90 t (5-H, 6-H), 7.06 d (4-H, 7-H). When the reaction was carried out in DMSO-d_6, after 15 min the ^1H NMR spectrum contained signals belonging to phenoxide ion **XI** (35%), *o*-hydroxyphenylethynethiolate (**XIII**) (48%), and 2-benzofuranthiolate (**X**) (17%). In the ^{13}C NMR spectrum, signals from *o*-hydroxyphenylethynethiolate (**XIII**) appeared at δ_C 71.8 (d, **C**≡CS) and 101.2 ppm (C≡**C**S). After 3 h, the signals belonging to phenoxide **XI** disappeared, and those corresponding to a 1 : 1 mixture of *o*-hydroxyphenylethynethiolate (**XIII**) and 2-benzofuranthiolate (**X**) were observed. ^{13}C NMR spectrum of 2-benzofuranthiolate (**X**) (DMSO-d_6), δ_C, ppm: 99.1 d (C^3, $^1J_{CH}$ = 173 Hz), 173.9 d (C^2, $^2J_{CH}$ = 9 Hz). The reaction was complete in 7 days, and the final ^1H NMR spectrum contained only signals of 2-benzofuranthiolate (**X**).

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