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SYNTHESIS OF DERIVATIVES OF BENZOFURAZAN AND BENZOFUROXAN BASED ON 1,4-DIOXASPIRO[4,5]DECAN-8-ONE AND 4-HYDROXYCYCLOHEXANONE

V. A. Samsonov and L. B. Volodarsky

Starting from 1,4-dioxaspiro[4.5]decan-8-one and 4-hydroxycyclohexanone, we have synthesized derivatives of tetrahydrobenzofurazan and tetrahydrobenzofuroxan containing a hydroxy or dioxolane group in the 6 position of the ring. We have studied the behavior of the compounds obtained under acid hydrolysis conditions.

Keywords: benzofurazans, benzofuroxans, hydroxyimino ketones, dioximes.

Functional derivatives of benzofurazan and benzofuroxan have attracted the attention of researchers because some of these compounds exhibit biological activity [1], including pesticidal activity [2]. Direct introduction of substituents into the benzene ring of benzofurazan and benzofuroxan is hindered by the electron-acceptor nature of their heterocycles. We have shown that starting from 2,6-diisonitrosocyclohexanone, we can easily obtain tetrahydro derivatives of benzofurazan and benzofuroxan, and also 4,5-dihydro derivatives of benzodifurazan, benzodifuroxan, and benzofurazanofuroxan [3]. It seemed of interest to use such a route to synthesize tetrahydro derivatives of benzofurazan and benzofuroxan containing a keto-, hydroxy-, or other functional group on the six-membered ring. As the starting compound for the synthesis, we used 1,4-dioxaspiro[4,5]decan-8-one (**1**). During nitrosation of the latter, sodium salt of its 7,9-dihydroxyimino derivative (**2**) is easily formed. Reaction of compound **2** with hydroxylamine leads to trihydroxyimino derivative **3**, which when treated with sodium hypobromite or when boiled in aqueous ammonia is converted to the corresponding substituted tetrahydrobenzofurazan (**4**).

As a result of oxidation of compound **3** with nitric acid, the substituted dinitrotetrahydrobenzofuroxan (**5**) is formed. Upon oxidation of trioxime **3** by bromine in acetic acid in the presence of sodium acetate, we obtained the substituted hydroxyiminotetrahydrobenzofuroxan (**6**). We may hypothesize that the position of the N-oxide oxygen atom in compounds **5** and **6** is similar to what is observed upon oxidation of 1,2,3-trihydroxyiminocyclohexane (see [3]). The structure of compounds **4-6** is consistent with their spectral characteristics (Tables 1-3).

The dioxolane group in furoxan **5** proved to be quite stable to hydrolysis both in dilute and concentrated solutions of hydrochloric and perchloric acids; but when this compound is treated with acetic anhydride in the presence of sulfuric acid, acetoxyethoxy-substituted nitrobenzofuroxan (**7**) is easily formed. The ethylenedioxy-substituted hydroxyiminotetrahydrobenzofurazan **4** when treated with dilute hydrochloric acid is converted to dihydroxybenzofurazan **8**. Tetrahydrobenzofuroxan **6** decomposes under acid hydrolysis conditions, probably

Novosibirsk Institute of Organic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk 630090, Russia; e-mail: samson@nioch.nsc.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1135-1142, August, 2000. Original article submitted February 5, 2000.

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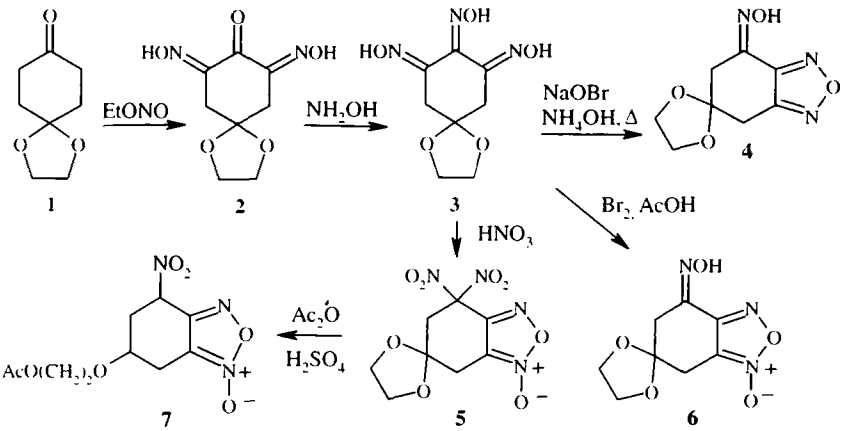
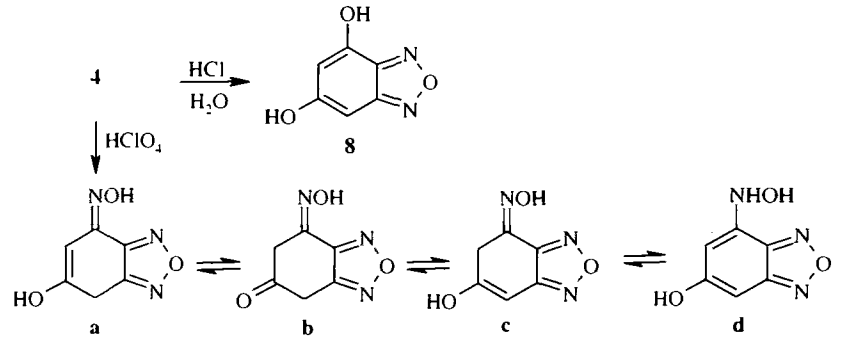


because of formation of the extremely unstable 4,6-dihydroxybenzofuroxan (see [1]). When tetrahydrobenzofurazan **4** reacted with perchloric acid, we obtained a product to which, based on spectral data and elemental analysis results, we assigned the structure of compound **9**. Possible tautomeric forms of the latter (**a-d**) are illustrated below. In the IR spectrum of product **9**, we observe absorption of the C=N bond (at 1650 cm^{-1}) and we do not see an absorption band for the C=O bond.



In the ^{1}H NMR spectra taken in acetone-d_6 and DMSO-d_6, there are three groups of signals which do not match the indicated spectra with regard to number and intensity. We assigned the signals in the 3.5-3.9 ppm region to protons of the CH_2 moiety; in the 5.8-6.5 ppm region, to the proton of the CH moiety; in the 8.3-12.4 ppm region, to protons of the OH, NHOH, NOH substituents. Based on analysis of the integrated intensity of the signals, we can hypothesize that compound **9** is found in solutions as a mixture of epimers. In DMSO-d_6, the epimers **a, c**, and **d** are present in the ratio of ~1:1:5, while in acetone-d_6 the epimers **a-d** are present in the ratio ~1:2:1:1.

To confirm this hypothesis, we recorded the ^{13}C NMR spectra of compound **9** in acetone-d_6 and in DMSO-d6. In the ^{13}C NMR spectrum in deuteroacetone, we observe four signals from carbon atoms of the CH_2 groups, four signals from the CH groups, a signal at 199.3 ppm for the C=O group, and 14 signals in the 140-160 ppm region from carbon atoms which are not bonded to hydrogen.

For a mixture of four tautomers, there should be 16 of the latter signals; but quite likely the chemical shifts of some atoms coincide. It is also possible that as a result of broadening of the signals, we could not reliably detect all of them. In the ^{13}C NMR spectrum in DMSO-d_6 there are two signals from carbon atoms of the CH_2 groups, four signals from the CH groups, and 11 signals from carbon atoms not bonded to hydrogen in the 135-165 ppm region. For a mixture of three compounds, there should be 12 of the latter signals; but probably, as in the preceding case, the signals of two carbon atoms coincide.

TABLE 1 Characteristics of Synthesized Compounds

Compound*	Empirical formula	Found, % / Calculated, %			mp, °C	UV spectrum, λ_{max} (log ε)	IR spectrum, cm^{-1}	Yield, %
		C	H	N				
2	$C_6H_{10}N_2O_5$	44.8 / 44.9	4.7 / 4.7	13.1 / 13.0	225 (decomp.)	270 (3.89)	1710 (C=O)	86
3	$C_8H_{11}N_3O_5$	41.9 / 41.9	4.8 / 4.8	18.3 / 18.3	182-183 (decomp.)	255 (3.84)		73
4	$C_8H_9N_3O_4$	45.5 / 45.5	4.3 / 4.3	19.9 / 19.9	186-188	259 (3.82)	1650 (C=N)	50
5	$C_8H_8N_4O_8$	33.4 / 33.3	2.8 / 2.8	19.5 / 19.4	138-140	288 (3.45)	1660 (C=N)	64
6	$C_8H_9N_3O_5$	42.3 / 42.3	4.0 / 4.0	18.5 / 18.5	223-225	225 (4.18), 288 (3.77)	1630 (C=N)	58
7	$C_{10}H_9N_3O_7$	42.5 / 42.4	3.2 / 3.2	14.8 / 14.8	121-122	285 (3.08), 440 (3.63)	1740 (C=O), 1360, 1550 (NO_2)	85
8	$C_6H_4N_2O_3$	47.4 / 47.4	2.6 / 2.7	18.4 / 18.4	149-151	280 (3.60), 333 (3.75)	1650 (C=N)	48
9	$C_6H_5N_3O_3$	43.1 / 43.1	3.0 / 3.0	25.0 / 25.1	145-148	247 (4.16), 303 (3.64)	1650 (C=N)	52
10a	$C_6H_7N_3O_2$	47.0 / 47.0	4.6 / 4.6	27.4 / 27.4	146-148	258 (3.75)		
10b	$C_6H_7N_3O_2$	47.1 / 47.0	4.6 / 4.6	27.4 / 27.4	186-188	258 (3.75)		50
12	$C_6H_8N_2O_4$	41.9 / 41.9	4.7 / 4.7	16.2 / 16.3	200 (decomp.)	270 (4.02)	1710 (C=O)	75
14	$C_{13}H_{12}N_2O_5$	56.5 / 56.5	4.4 / 4.4	10.2 / 10.1	222 (decomp.)	235 (3.86), 272 (3.70)	1730 (C=O)	64

* Compounds **2, 5, 6, 9, 10, 12, 14** were recrystallized from alcohol; **4, 7, 8** were recrystallized from 1:1 ethylacetate–hexane mixture; **3** was recrystallized from water.

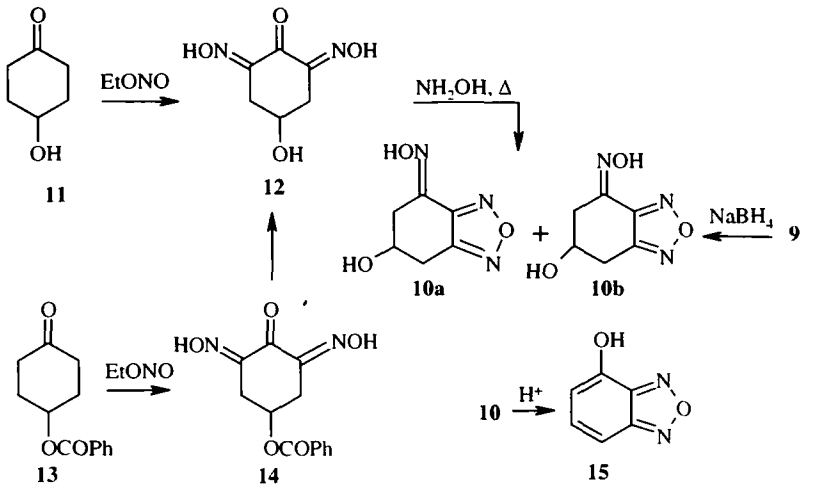
When compound **9** is treated with sodium borohydride, 6-hydroxy-4-hydroxyimino-4,5,6,7-tetrahydrobenzofurazan (**10**) is formed, which we also synthesized starting from 4-hydroxycyclohexanone (**11**). Nitrosation of the latter leads to 4-hydroxy-2,6-dihydroxyiminocyclohexanone (**12**), which when treated with excess free hydroxylamine is converted to tetrahydrobenzofurazan **10**. Compound **12** is also obtained by nitrosation of 4-benzoyloxycyclohexanone (**13**) followed by base hydrolysis of the 4-benzoyloxy-2,6-dihydroxyiminocyclohexanone (**14**) formed. Compound **10** is a mixture of isomers **10a** and **10b**, which differ in the configurations of the oxime groups. The ratio of the chromatographically separated isomers is ~4:1. Based on ^{13}C NMR spectra and [4], we assigned the structure **10a** with an *E* configuration of the oxime group to the isomer with the higher content in the mixture, and we assigned structure **10b** to the second isomer.

TABLE 2. ^1H NMR Spectra and Mass Spectra of Synthesized Compounds

Compound	Chemical shifts, δ, ppm, in $(CD_3)_2SO_2$, spin–spin coupling constant (*J*), Hz	*m/z* (*I*, %)*
2	2.92 (4H, s, 6- and 10-CH_2); 3.87 (4H, s, 2 OCH_2); 12.57 (2H, s, 2 NOH)	214 (5) M$^+$, 197 (100), 112 (25), 68 (25)
3	2.77 (4H, s, 6- and 10-CH_2); 3.87 (4H, s, 2 OCH_2); 11.46 (2H, s, 2 NOH); 12.77 (1H, s, NOH)	229 (10) M$^+$; 212 (100), 194 (40), 124 (20), 112 (25), 86 (30), 68 (30)
4	3.05 (2H, s, 5-CH_2); 3.18 (2H, s, 7-CH_2); 4.00 (4H, c, 2 OCH_2); 12.34 (1H, s, NOH)	211 (90) M$^+$, 194 (100), 155 (20), 151 (15), 127 (40), 112 (30), 93 (20), 86 (30), 83 (20)
5	3.10 (2H, s, 7-CH_2); 3.50 (2H, s, 5-CH_2); 4.03 (4H, s, 2 OCH_2)	282 (5) M$^+$; 242 (100), 212 (40), 182 (50), 166 (20), 135 (90), 128 (30), 113 (20), 73 (40)
6	2.93 (2H, s, 5-CH_2); 3.15 (2H, s, 7-CH_2); 3.97 (4H, s, 2 OCH_2); 12.30 (1H, s, NOH)	227 (40) M$^+$; 210 (25), 197 (95), 167 (100), 112 (20), 95 (80), 86 (70), 68 (30)
7	2.00 (3H, s, CH_3); 4.37 (4H, s, 2 OCH_2); 7.30 (1H, d, 7-H, J = 2); 8.18 (1H, d, 5-H, J = 2)	283 (10) M$^+$; 87 (100), 43 (60)
8	6.37 (2H, d, 5- and 7-H); 10.7 (2H, br. s, 2 OH)	152 (100) M$^+$; 96 (20), 69 (30)
9	3.54 and 3.88 (two s, CH_2); 5.83, 6.26, 6.27 and 6.34 (s, d, J_{AB} = 2, s, d, J_{AB} = 2 respectively, CH); 8.91, 9.56, 10.60, 10.80, 11.48 and 12.41 (two s, two br. s, and two s respectively, OH, NOH)	167 (100) M$^+$; 139 (20); 109 (15), 82 (20), 68 (30), 52 (30)
9*[2]	3.56, 3.74, 3.85 и 3.94 (four s, CH_2); 5.87, 6.30, 6.33 и 6.52 (four s, CH); 8.30, 8.66, 9.00, 10.00 and 11.60 (two s, two br. s, and two s respectively, NH, OH)	
10a	2.48-2.58 (2H, m, 5-CH_2); 2.99-3.20 (2H, m, 7-CH_2); 4.37 (1H, m, 6-H); 5.17 (1H, s, OH); 12.06 (1H, s, NOH)	169 (100) M$^+$; 152 (25), 141 (30)
10b	2.70-2.80 (2H, m, 5-CH_2); 3.03-3.05 (2H, m, 7-CH_2); 4.40 (1H, m, 6-H); 5.18 (1H, s, OH); 12.17 (1H, NOH)	124 (40), 94 (20), 86 (20), 66 (25)
12	2.63-3.10 (4H, m, 3- and 5-CH_2); 4.13-4.40 (1H, m, 4-H); 4.19 (1H, s, OH); 12.41 (1H, s, NOH)	172 (100) M$^+$; 155 (30), 109 (20), 93 (20), 70 (30), 66 (25)
14	2.75-3.30 (4H, m, 3- and 5-CH_2); 5.18-5.57 (1H, m, 4-H); 7.33-7.83 (5H, m, H_{Ph}); 12.79 (2H, s, 2 NOH)	

* Ion peaks with relative intensity higher than 10% are given.

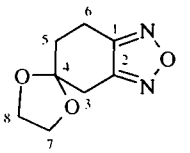
*[2] The ^1H NMR spectrum was recorded in $(CD_3)_2CO$.



Compound **10** is smoothly converted to 4-hydroxybenzofurazan (**15**) when treated with 20% H_2SO_4.

Thus we have synthesized tetrahydro derivatives of benzofurazan and benzofuroxan containing hydroxy and dioxolan groups at the 6 position of the ring. We have studied some reactions of the compounds obtained.

TABLE 3. ^{13}C NMR Spectra of Benzofurazan and Benzofuroxan Derivatives



Compounds **4-6, 8, 10a,b**

Compound	Chemical shifts, δ, ppm, solvent $(CD_3)_2SO$						
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7,8)}$
4	148.2	152.7	30.2	106.9	33.7	141.8	64.8
5	145.9	111.5	29.7	104.7	38.5	111.9	65.3
6	155.7	108.3	32.3	106.6	33.9	140.4	65.0
8	143.3	151.0	82.6	161.7	105.8	146.9	
10a	148.4	152.5	28.0	62.9	31.3	143.2	
10b	138.7	152.5	28.6	63.7	36.2	143.6	

Compound **9**

Solvent	Chemical shifts, δ, ppm		
	CH_2	CH	carbon atoms not bonded to hydrogen
$(CD_3)_2SO$	25.2; 30.2	80.9; 84.8; 91.8; 100.2	139.8; 140.6; 140.7; 145.1; 146.0; 150.7; 150.8; 152.6; 159.2; 162.2; 163.2
$(CD_3)_2CO$	26.2; 30.6; 35.8; 39.4	83.3; 84.8; 93.6; 102.6	140.6; 141.3; 141.4; 141.6; 142.1; 151.3; 151.5; 151.9; 154.0; 154.8; 161.0;162.1; 162.4; 163.0; 199.3

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr pellets (concentration 0.25%); the UV spectra were recorded on a Specord UV-vis in ethanol. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker WP-200 SY spectrometer. The mass spectra were taken on a Finnigan MAT MS-8200 by direct injection of the sample into the ion source and ionizing potential 70 eV. The ionization chamber temperature was 120-200°C. Tables 1-3 give the characteristics of the synthesized compounds.

Compounds **2, 11**, and **13** were synthesized by the procedures in [5, 6, and 7] respectively.

7,9-Dihydroxyimino-1,4-dioxaspiro[4,5]decan-8-one (2). Acetic acid was added in 3.1 ml portions every 8 h at room temperature to a mixture of compound **1** (10 g, 64 mmol), $NaNO_2$ (18 g, 262 mmol), ethanol (40 ml), and water (26 ml). Then the reaction flask was tightly sealed. The total volume of acetic acid was 15.5 ml. After the last portion of acetic acid was added, the reaction mass obtained was held for 8 h, the residue was filtered off and washed with 50% alcohol (20 ml) and then dried. Monosodium salt of compound **2** was obtained. A 5% HCl solution was added dropwise to a solution of the indicated salt (0.2 g) in water (5 ml) until pH 4. The residue was filtered off, washed with water, and dried. Obtained 0.15 g of compound **2**.

7,8,9-Trihydroxyimino-1,4-dioxaspiro[4,5]decane (3). $NH_2OH \cdot HCl$ (7.4 g, 106 mmol) and NaOH (2.12 g, 53 mmol) were added to a solution of sodium salt (13 g, 53 mmol) of compound **2** in methanol (50 ml). The reaction mass was stirred at room temperature for 3 h and held at the same temperature for 2 days. NaCl residue was filtered out and the filtrate was evaporated down. The residue was suspended in water and 9.12 g of compound **3** was filtered out.

6-Ethylenedioxy-4-hydroxyimino-4,5,6,7-tetrahydrobenzofurazan (4). A mixture of trioxime **3** (2 g, 8.74 mmol) and 25% aqueous solution of ammonia (25 ml) was boiled for 20 min and then cooled and extracted with ethyl acetate (3×50 ml). The combined extract was washed with a saturated NaCl solution, dried over $MgSO_4$, and evaporated down. The residue was chromatographed on a column with silica gel (eluent ethyl acetate–hexane, 1:1), and 0.92 g of compound **4** was isolated.

4,4-Dinitro-6-ethylenedioxy-4,5,6,7-tetrahydrobenzofuroxan (5). Nitric acid (specific gravity 1.50) (10 ml) was added dropwise to a suspension of trioxime **3** (6 g, 26.2 mmol) in chloroform (400 ml) with stirring at room temperature. The solution obtained was stirred at room temperature for 1.5 h, then washed with water, dried over $MgSO_4$, and evaporated. Compound **5** (4.92 g) was isolated by chromatographic separation of the residue on silica gel (eluent chloroform).

6-Ethylenedioxy-4-hydroxyimino-4,5,6,7-tetrahydrobenzofuroxan (6). Trioxime **3** (3.45 g, 15 mmol) was added to a solution of sodium acetate (4.2 g, 30.9 mmol) in acetic acid (75 ml). The reaction mixture was stirred until trioxime was completely dissolved. A solution of bromine (2.40 g, 15 mmol) in acetic acid (20 ml) was added dropwise to the cooled solution over a 20 min period. The reaction mass was stirred at room temperature for 1 h and then evaporated down. The residue was suspended in water and 1.98 g of compound **6** was filtered out.

4-Nitro-6-(2-acetoxyethoxy)benzofuroxan (7). Conc. H_2SO_4 (2 ml) was added dropwise to a solution of furoxan **5** (2.0 g, 69.5 mmol) in acetic anhydride (25 ml). The mixture was stirred at room temperature for 3 h and poured onto 250 g of crushed ice. The residue was filtered out, washed with water, and dried. Obtained 1.66 g of compound **7**.

4,6-Dihydroxybenzofurazan (8). A mixture of 1% HCl solution (100 ml) and oxime **4** (1.0 g, 4.74 mmol) was boiled for 30 min, cooled, and extracted with ether (3×50 ml). The combined extract was washed with a saturated NaCl solution, dried over $MgSO_4$, and evaporated. The residue was suspended in chloroform and then the residue was filtered out. Obtained 0.34 g of compound **8**.

4-Hydroxyimino-6-oxo-4,5,6,7-tetrahydrobenzofurazan (9). Oxime **4** (2.0 g, 9.5 mmol) was added to perchloric acid (20 ml) and the mixture was stirred at room temperature for 5 minutes until oxime was completely dissolved. The reaction mass was then poured into water (400 ml), the product was extracted with ethyl acetate (4×100 ml). The combined extract was washed with a saturated NaCl solution, dried over $MgSO_4$, and evaporated. The residue was suspended in hexane and then the precipitate was filtered out. Obtained 0.82 g of compound **9**.

4-Hydroxy-2,6-dihydroxyiminocyclohexanone (12). A. Gaseous ethyl nitrite was supplied to a solution of ketone **11** (10 g, 88 mmol) in ethanol (40 ml) containing dry HCl (1.5 g), while maintaining the temperature in the reaction mass within the range 5-8°C. Ethyl nitrite was obtained by dropwise addition of a solution of conc. H_2SO_4 (8.7 ml) in ethanol (9 ml) and water (68 ml) to a solution of $NaNO_2$ (21 g) in ethanol (9 ml) and water (76 ml). After delivery of the ethyl nitrite was complete, the reaction mass was held for 8 h at 5°C, and then for 8 h at room temperature. The precipitate was filtered out and dried. Obtained 2.12 g (14%) of compound **12**.

B. Dioxime **14** (2.76 g, 10 mmol) was added to a solution of NaOH (1.2 g, 30 mmol) in water (150 ml). The mixture was stirred at room temperature until complete dissolving and held at the same temperature for 12 h. The reaction mass was cautiously acidified with a 10% HCl solution to pH 5 and benzoic acid was extracted with ether (3×50 ml). The aqueous solution was evaporated to dryness. Methanol (100 ml) was added to the residue, NaCl precipitate was filtered out, the filtrate was evaporated, and 1.29 g of compound **12** was obtained which was identical to a sample obtained from ketone **11** (mp, IR and UV spectra).

4-Benzoyloxy-2,6-dihydroxyiminocyclohexanone (14). Conc. HCl (57 ml, 660 mmol) was added to a solution of ketone **13** (32.7 g, 150 mmol) in isopropanol (750 ml). A solution of $NaNO_2$ (32 g, 460 mmol) in water (100 ml) was added dropwise with stirring to the reaction mass cooled at 0°C over a 1 h period keeping the temperature at 0-2°C. Then the mixture was stirred at 0°C for 2 h and allowed to stand in a cooler for 3 days. The reside was filtered out, washed with water, and dried. Obtained 26.3 g of dioxime **14**.

6-Hydroxy-4-hydroxyimino-4,5,6,7-tetrahydrobenzofurazan (10). A. $NaBH_4$ (0.02 g) was added to a solution of oxime **9** (0.1 g, 0.6 mmol) in ethanol (10 ml). The mixture obtained was stirred for 2 h at room temperature, after which water (20 ml) was added and it was acidified with a 5% HCl solution to pH 4 and extracted with ethyl acetate (3×20 ml). The combined extract was washed with a saturated NaCl solution, dried over $MgSO_4$, and evaporated. The residue was suspended in hexane, and 0.05 g of compound **10** was filtered out.

B. Compound **12** (0.72 g, 41.8 mmol) was added to a solution of NaOH (0.4 g, 10 mmol) in water (20 ml) and the mixture was stirred until compound **12** was completely dissolved. $NH_2OH \cdot HCl$ (0.7 g, 10 mmol) was added to the solution obtained; the mixture was boiled for 30 min and then cooled and extracted with ethyl acetate (4×15 ml). The combined extract was dried over $MgSO_4$ and evaporated. Chromatography of the residue on silica gel (eluent ethyl acetate–hexane, 3:1) resulted in separation of 0.42 g of compound **10**, identical to a sample obtained from ketone **9** (mp, IR, and UV spectra). Compound **10** (obtained both from ketone **9** and from compound **12**) was a mixture of isomers **10a** and **10b**, which were separated by chromatography on silica gel (eluent ethyl acetate–hexane, 1:1).

4-Hydroxybenzofurazan (15). Tetrahydrobenzofurazan **10** (1 g, 5.9 mmol) was added to a 20% H_2SO_4 solution (20 ml). The mixture obtained was heated up to 60°C and stirred for 10 min until compound **10** completely dissolved; then it was cooled and extracted with ether (4×20 ml). The combined extract was washed with water, dried over $MgSO_4$, and evaporated. The residue was triturated with hexane. Obtained 0.41 g (50%) phenol **15**; mp 146-148°C (ether–hexane, 1:1). Lit. mp 148-150°C [8].

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