4-Hydroxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans and some their *O*-derivatives*

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Methods for the synthesis of 4-hydroxy- and 4-alkoxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans and difurazanyl ethers were developed. The methods involve displacement of the nitro group from 4-nitro-3-(α-nitroalkyl-*ONN*-azoxy)furazans under the action of aqueous solutions of alkalis, mono- and diatomic alcohols (in the presence of inorganic bases), and sodium carbonate in anhydrous acetonitrile.

Key words: furazans, (α-nitroalkyl-*ONN*-azoxy)furazans, 4-hydroxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans, 4-alkoxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans, 3,3´-bis(α-nitroalkyl-*ONN*-azoxy)difurazanyl ethers, nitrofurazans, hydroxyfurazans, nucleophilic substitution.

Earlier, the syntheses of 4-amino-3-(α-nitroalkyl-*ONN*-azoxy)furazans[1] and their high-energy derivatives (including new oxidants 3-(polynitromethyl-*ONN*-azoxy)-4-nitraminofurazans) have been reported.[2] As a next step in those investigations, here we studied nucleophilic substitution of the nitro group in a series of 4-nitro-3-(α-nitroalkyl-*ONN*-azoxy)furazans under the action of O-nucleophiles. The goal of the present work was to obtain 4-hydroxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans that could serve as intermediate products in the synthesis of high-energy compounds with potential attractive properties.

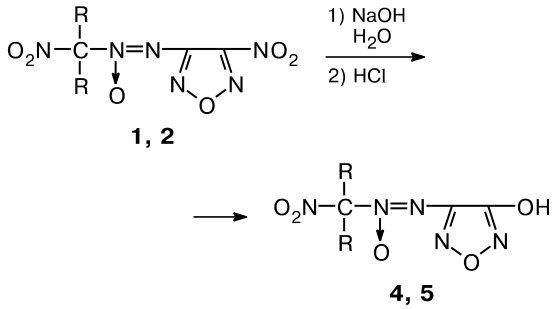
Results and Discussion

Nitrofurazans are known to undergo nucleophilic substitution in reactions with aqueous solutions of alkalis[3] to give hydroxyfurazans. We found that 4-nitro-3-(α-nitroalkyl-*ONN*-azoxy)furazans **1**—**3** react with alkalis in water and a water-miscible organic solvent (acetone or acetonitrile) even at 0—3 °C and that the nitro group directly bound to the furazan ring is replaced by a hydroxy group in 0.5 h. Treatment of the reaction mixture with HCl gives the desired products 4-hydroxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans **4**—**6** (Schemes 1 and 2).

With substrate **3**, the above transformation is complicated by hydrolysis of the 2,2-dimethyl-5-nitro-1,3-dioxan-5-yl substituent upon the treatment with HCl, yielding triol **6** (see Scheme 2).

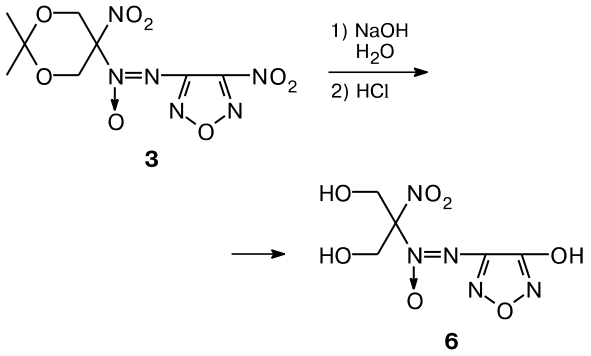
4-Hydroxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans **5** and **6** are yellow oils, while product **4** is a white crystalline solid with m.p. 85.0—87.0 °C. Hydroxyfurazans **4** and **5**

Scheme 1



R = Me (**1**, **4**); R + R = $(CH_2)_5$ (**2**, **5**)

Scheme 2



can form metal salts by exchanging the OH proton. For instance, treatment of compound **4** with EtONa in diethyl ether affords the sodium salt Na[**4**].

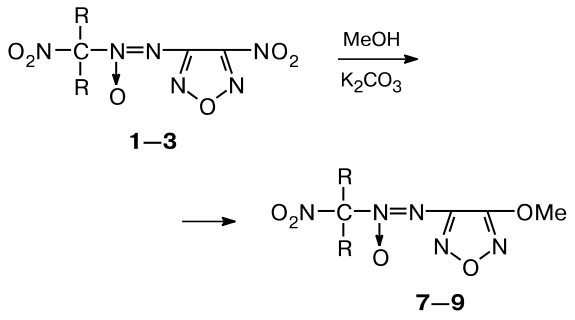
The reaction in methanol in the presence of inorganic bases proceeds even more violently than that in aqueous

* Dedicated to Academician of the Russian Academy of Sciences S. M. Aldoshin on the occasion of his 60th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 0514—0518, February, 2013.

solutions of alkalis. Although nitrofurazans **1**—**3** do not react even with boiling methanol when it is used alone, addition of K_2CO_3 or KOH promotes nucleophilic displacement of the nitro group from the furazan ring by a methoxy group. The reaction at 20 °C is completed in 0.5 h to give the corresponding 4-methoxy-3-(α-nitroalkyl-*ONN*-azoxy)furazans **7**—**9** (Scheme 3). Note that the use of K_2CO_3 ensures higher yields of the reaction products than does KOH (*e.g.*, 92 against 81% for compound **9**).

Scheme 3



R = Me (**1**, **7**); R + R = $(CH_2)_5$ (**2**, **8**); R + R = $CH_2OCMe_2OCH_2$ (**3**, **9**)

Reactions of 4-nitro-3-(α-nitroalkyl-*ONN*-azoxy)-furazans **1** and **3** with such a strong nucleophile as MeONa in methanol at 20 °C unexpectedly resulted in replacement of both the nitro groups, thus producing 4-methoxy-3-(α-methoxyalkyl-*ONN*-azoxy)furazans **10** and **11**, respectively (Scheme 4).

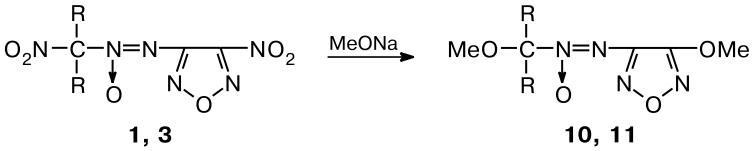
The structures of the methoxy and dimethoxy derivatives **7**—**11** were confirmed by ^1H, ^{13}C, and ^{14}N NMR spectra. Comprehensive assignment of the signals in the ^{13}C NMR spectra of these compounds was performed using 2D NMR experiments ({^1H—^{13}C} HMBC).

Methoxyfurazans **7**—**9** and **11** are white crystalline compounds. Interestingly, the replacement of the nitro group in the (α-nitroalkyl-*ONN*-azoxy) fragment by the methoxy group lowers the melting point (from 78.5—79.0 and 72.5—73.0 °C for **9** and **7**, respectively, to 48.0—49.5 °C for dimethoxy derivative **11**). Compound **10** is entirely liquid at room temperature.

Like other nitrofurazans,[4] 4-nitro-3-(α-nitroalkyl-*ONN*-azoxy)furazans react with glycols in the presence of bases to give glycol mono- and diethers. For instance, a reaction of an excess of compound **3** with ethylene glycol in acetonitrile in the presence of K_2CO_3 at 20 °C takes 96 h, affording diether **12** (Scheme 5). Monoether **13** is also formed as a by-product (7%), even when nitrofurazan **3** is employed in more than a twofold excess.

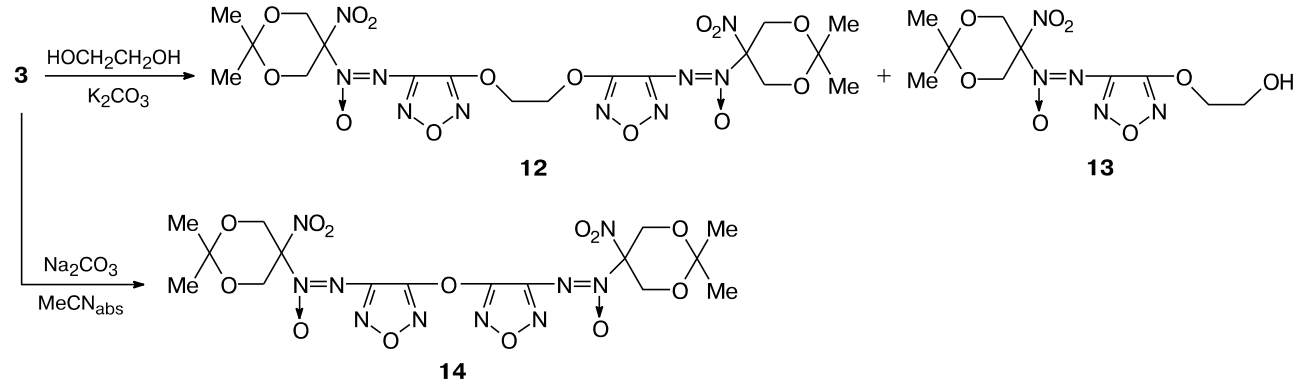
4-Nitro-3-(α-nitroalkyl-*ONN*-azoxy)furazans also react with weak bases in anhydrous media, which is typical of nitrofurazans.[5,6] Treatment of compound **3** with Na_2CO_3 in anhydrous acetonitrile (60—65 °C, 5 h) gives difurazanyl ether **14** in 63% yield (Scheme 5). This product is a white crystalline solid with m.p. 99.0—100.0 °C.

Scheme 4



R = Me (**1**, **10**); R + R = $CH_2OCMe_2OCH_2$ (**3**, **11**)

Scheme 5



In contrast to *NNO*-azoxyfurazans,[3,6] which eliminate the azoxy group in reactions with bases, the *ONN*-azoxy group in (α-nitroalkyl-*ONN*-azoxy)furazans does not act as a nucleofuge under similar conditions.

In our opinion, the results obtained suggest that the electronic effect of the α-nitroalkyl substituent at the *ONN*-azoxy group, as with N-nucleophilic substitution in this series,[1] has minor influence on the possibility of nucleophilic substitution of the nitro group directly bound to the furazan ring.

To sum up, we developed a method for the synthesis of 4-hydroxy- and 4-alkoxy-3-(α-nitroalkyl-*ONN*-azoxy)-furazans and difurazanyl ethers by nucleophilic displacement of the nitro group from 4-nitro-3-(α-nitroalkyl-*ONN*-azoxy)furazans under the action of aqueous solutions of alkalis, mono- and diatomic alcohols (in the presence of inorganic bases), and sodium carbonate in anhydrous acetonitrile. The *ONN*-azoxy group shows no nucleofugacity in reactions with nucleophilic reagents. In addition, we were the first to notice that the nitro group of the (α-nitroalkyl-*ONN*-azoxy) fragment act as a nucleofuge when (α-nitroalkyl-*ONN*-azoxy)furazans are treated with alkali metal alkoxides.

Experimental

The course of the reactions was monitored by TLC on Silufol UV-254 plates. IR spectra were recorded on a Bruker Alpha instrument. NMR spectra were recorded on Bruker AM-300 and Bruker AM-600 instruments. Chemical shifts are referenced to Me_4Si (^1H, ^{13}C) or $MeNO_2$ (^{14}N, the external standard, high-field chemical shifts are negative). High-resolution mass spectra were measured on a Bruker micrOTOF II instrument. Melting points were determined on a Kofler hot stage. The starting compounds 3-(1-methyl-1-nitroethyl-*ONN*-azoxy)-4-nitrofurazan (**1**),[1] 3-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-4-nitrofurazan (**3**),[1] and 4-nitro-3-(1-nitrocyclohex-1-yl-*ONN*-azoxy)furazan (**2**)[7] were prepared as described earlier.

4-Hydroxy-3-(1-methyl-1-nitroethyl-*ONN*-azoxy)furazan (4). A solution of compound **1** (0.110 g, 0.447 mmol) in acetone (0.8 mL) was added at 0—3 °C to a vigorously stirred solution of NaOH (0.090 g, 2.24 mmol) in water (1.0 mL). The resulting solution was stirred at 0—3 °C for 0.5 h, diluted with water (60.0 mL), and washed with CH_2Cl_2 (4×15 mL). Then 33% aqueous HCl (0.23 mL, 2.42 mmol) was added, and the product was extracted with Et_2O (7×10 mL). The combined extracts were dried with $MgSO_4$ and concentrated *in vacuo*. The residue was washed with hexane. The yield of compound **4** was 0.092 g (95%), white crystals, m.p. 85.0—87.0 °C (from CH_2Cl_2—hexane). MS (ESI), *m/z*: 240.0345 $[M + Na]^+$; calculated for $C_5H_7N_5O_5$: $[M + Na]^+$ 240.0339. IR (KBr), ν/cm^{-1}: 1607 (s, furazan); 1569 (vs, asymm., NO_2); 1505 (vs, N=N→O); 1377 (m, symm., NO_2); 1234 (s, N=N→O). ^1H NMR (acetone-d_6), δ: 2.36 (s, 6 H, Me); 11.53 (br.s, 1 H, OH). ^{13}C NMR (75 MHz, acetone-d_6), δ: 24.6 (Me); 114.5 (C—NO_2); 148.2 (C—N=N→O); 160.2 (C—OH). ^{14}N NMR (22 MHz, acetone-d_6), δ: −39.7 (N→O, $\Delta\nu_{0.5}$ = 64 Hz); 0.2 (NO_2, $\Delta\nu_{0.5}$ = 54 Hz).

4-Hydroxy-3-(1-methyl-1-nitroethyl-*ONN*-azoxy)furazan, sodium salt (Na[4]). Metallic sodium (0.012 g, 0.506 mmol) was dissolved in EtOH (0.25 mL). The solution was added at 5—10 °C to a stirred solution of compound **4** (0.100 g, 0.460 mmol) in Et_2O (4.0 mL). The resulting mixture was kept at 20 °C for 1 h. The precipitate that formed was filtered off and thoroughly washed with Et_2O. The yield of salt Na[**4**] was 0.058 g (53%), light yellow crystals. ^1H NMR (acetone-d_6), δ: 2.26 (s, 6 H, Me). Acidification of salt Na[**4**] released free hydroxyfurazan **4** identical in physicochemical characteristics with that obtained as described above.

4-Hydroxy-3-(1-nitrocyclohex-1-yl-*ONN*-azoxy)furazan (5). A solution of compound **2** (0.108 g, 0.378 mmol) in acetone (0.8 mL) was added at 0—3 °C to a stirred solution of NaOH (0.076 g, 1.89 mmol) in water (1.0 mL). The resulting solution was stirred at 0—3 °C for 0.5 h, diluted with water (60.0 mL), and washed with CH_2Cl_2 (4×15 mL). Then 33% aqueous HCl (0.20 mL, 2.11 mmol) was added, and the product was extracted with Et_2O (7×10 mL). The combined extracts were dried with $MgSO_4$ and concentrated *in vacuo*. The residue was washed with hexane. The yield of compound **5** was 0.085 g (88%), yellow oil. MS (ESI), *m/z*: 280.0654 $[M + Na]^+$; calculated for $C_8H_{11}N_5O_5$: $[M + Na]^+$ 280.0652. IR (KBr), ν/cm^{-1}: 1608 (vs, furazan); 1570 (vs, asymm., NO_2); 1506 (vs, N=N→O); 1332 (m, symm., NO_2); 1247 (m, N=N→O). ^1H NMR (acetone-d_6), δ: 1.62 (m, 2 H, $C\underline{H}_2(CH_2CH_2)_2$); 1.77 (m, 4 H, $CH_2(C\underline{H}_2CH_2)_2$); 2.76 (m, 4 H, $(CH_2)_2CNO_2$); 11.65 (br.s, 1 H, OH). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.8 ($CH_2(\underline{C}H_2CH_2)_2$), 22.8 ($\underline{C}H_2(CH_2CH_2)_2$), 32.5 ($(\underline{C}H_2)_2CNO_2$), 116.0 ($(CH_2)_2\underline{C}NO_2$), 147.3 (C—N=N→O); 159.1 (C—OH). ^{14}N NMR (22 MHz, acetone-d_6), δ: −43.2 (N→O, $\Delta\nu_{0.5}$ = 81 Hz); −1.72 (NO_2, $\Delta\nu_{0.5}$ = 78 Hz).

4-Hydroxy-3-(2-hydroxy-1-hydroxymethyl-1-nitroethyl-*ONN*-azoxy)furazan (6). A solution of compound **3** (0.100 g, 0.314 mmol) in acetone (0.8 mL) was added at 0—3 °C to a stirred solution of NaOH (0.063 g, 1.57 mmol) in water (1.0 mL). The resulting solution was stirred at 0—3 °C for 0.5 h, diluted with water (60.0 mL), and washed with Et_2O (4×15 mL). Then 33% aqueous HCl (0.37 mL, 3.93 mmol) was added, and the product was extracted with Et_2O (7×10 mL). The combined extracts were dried with $MgSO_4$ and concentrated *in vacuo*. The residue was washed with hexane. The yield of compound **6** was 0.063 g (81%), yellow oil. Found (%): C, 24.35; H, 2.95; N, 28.42. $C_5H_7N_5O_7$ (M = 249.14). Calculated (%): C, 24.10; H, 2.81; N, 28.11. IR (KBr), ν/cm^{-1}: 1699 (vs, furazan); 1576 (vs, asymm., NO_2); 1510 (vs, N=N→O); 1362 (s, symm., NO_2); 1239 (s, N=N→O). ^1H NMR (acetone-d_6), δ: 4.64 (s, 4 H, CH_2); 5.26 (br.s, 2 H, $CH_2O\underline{H}$); 11.58 (br.s, 1 H, OH). ^1H NMR (DMSO-d_6), δ: 4.82 (s, 4 H, CH_2); 6.10 (br.s, 2 H, $CH_2O\underline{H}$); 12.20 (br.s, 1 H, OH). ^{13}C NMR (75 MHz, acetone-d_6), δ: 60.5 (CH_2), 114.5 (C—NO_2), 147.4 (C—N=N→O), 160.0 (C—OH). ^{14}N NMR (22 MHz, acetone-d_6), δ: −49.1 (N→O, $\Delta\nu_{0.5}$ = 92 Hz); −9.1 (NO_2, $\Delta\nu_{0.5}$ = 88 Hz).

4-Methoxy-3-(1-methyl-1-nitroethyl-*ONN*-azoxy)furazan (7). Potassium carbonate (0.074 g, 0.536 mmol) was added at 20 °C to a stirred solution of compound **1** (0.110 g, 0.447 mmol) in MeOH (6.0 mL). The resulting suspension was stirred at 20 °C for 0.5 h and filtered. The mother liquor was concentrated *in vacuo*. The product was purified by preparative TLC (chromatographed three times) on silica gel with ethyl acetate—hexane (1 : 5) as an eluent. The yield of compound **7** was

0.098 g (95%), white crystals, m.p. 72.5—73.0 °C (from hexane). MS (ESI), *m/z*: 254.0488 $[M + Na]^+$; calculated for $C_6H_9N_5O_5$: $[M + Na]^+$ 254.0496. IR (KBr), ν/cm^{-1}: 1589 (vs, furazan); 1585 (vs, asymm., NO_2); 1517 (s, N=N→O); 1417 (s, symm., NO_2); 1264 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 2.36 (s, 6 H, C—Me); 4.19 (s, 3 H, O—Me). ^{13}C NMR (75 MHz, acetone-d_6), δ: 24.6 (C—Me), 59.9 (O—Me), 114.6 (C—NO_2), 147.5 (C—N=N→O), 162.4 (C—OMe). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −40.0 (N→O, $\Delta\nu_{0.5}$ = 58 Hz); −0.8 (NO_2, $\Delta\nu_{0.5}$ = 51 Hz).

4-Methoxy-3-(1-nitrocyclohex-1-yl-*ONN*-azoxy)furazan (8). Potassium carbonate (0.058 g, 0.420 mmol) was added at 20 °C to a stirred solution of compound **2** (0.100 g, 0.350 mmol) in MeOH (6.0 mL). The resulting suspension was stirred at 20 °C for 0.5 h and filtered. The mother liquor was concentrated *in vacuo*. The product was purified by preparative TLC (chromatographed four times) on silica gel with ethyl acetate—hexane (1 : 7) as an eluent. The yield of compound **8** was 0.081 g (85%), white crystals, m.p. 57.5—58.0 °C (from H_2O—Pr^iOH). MS (ESI), *m/z*: 294.0807 $[M + Na]^+$; calculated for $C_9H_{13}N_5O_5$: $[M + Na]^+$ 294.0809. IR (KBr), ν/cm^{-1}: 1588 (vs, furazan); 1567 (vs, asymm., NO_2); 1499 (s, N=N→O); 1425 (s, symm., NO_2); 1261 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.66 (m, 2 H, $CH_2(CH_2CH_2)_2$); 1.80 (m, 4 H, $CH_2(CH_2CH_2)_2$); 2.78 (m, 4 H, $(CH_2)_2CNO_2$); 4.20 (s, 3 H, Me). ^{13}C NMR (75 MHz, acetone-d_6), δ: 23.0 ($CH_2(CH_2CH_2)_2$), 23.9 ($CH_2(CH_2CH_2)_2$), 33.7 ($(CH_2)_2CNO_2$), 60.2 (Me), 117.2 ($(CH_2)_2CNO_2$), 147.8 (C—N=N→O), 162.5 (C—OMe). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −42.1 (N→O, $\Delta\nu_{0.5}$ = 64 Hz); −2.0 (NO_2, $\Delta\nu_{0.5}$ = 71 Hz).

3-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-4-methoxyfurazan (9). ***A.*** Potassium carbonate (0.052 g, 0.377 mmol) was added at 20 °C to a stirred solution of compound **3** (0.100 g, 0.314 mmol) in MeOH (6.0 mL). The resulting suspension was stirred at 20 °C for 0.5 h and filtered. The mother liquor was concentrated *in vacuo*. The product was purified by preparative TLC (chromatographed five times) on silica gel with ethyl acetate—hexane (1 : 5) as an eluent. The yield of compound **9** was 0.087 g (92%), white crystals, m.p. 78.5—79.0 °C (from hexane). MS (ESI), *m/z*: 326.0715 $[M + Na]^+$; calculated for $C_9H_{13}N_5O_7$: $[M + Na]^+$ 326.0707. IR (KBr), ν/cm^{-1}: 1593 (vs, furazan); 1576 (vs, asymm., NO_2); 1501 (s, N=N→O); 1377 (s, asymm., NO_2); 1257 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.49, 1.54 (both s, 3 H, C—Me); 4.20 (s, 3 H, O—Me); 4.94 (s, 4 H, CH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.4, 24.5 (both C—Me), 60.0 (O—Me), 62.6 (CH_2), 100.9 (CMe_2), 107.4 (C—NO_2), 147.3 (C—N=N→O), 162.5 (C—OMe). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −51.5 (N→O, $\Delta\nu_{0.5}$ = 64 Hz); −11.5 (NO_2, $\Delta\nu_{0.5}$ = 81 Hz).

B. Potassium hydroxide (0.023 g, 0.408 mmol) was added at 20 °C to a solution of compound **3** (0.100 g, 0.314 mmol) in MeOH (6.0 mL). The resulting solution was stirred at 20 °C for 0.5 h and concentrated *in vacuo*. The product was purified by preparative TLC (chromatographed five times) on silica gel with ethyl acetate—hexane (1 : 5) as an eluent. The yield of compound **9** was 0.077 g (81%). This sample is identical in physicochemical characteristics with that obtained according to procedure ***A***.

4-Methoxy-3-(1-methoxy-1-methylethyl-*ONN*-azoxy)furazan (10). Metallic sodium (0.047 g, 2.04 mmol) was dissolved in MeOH (2.0 mL), whereupon a solution of compound **1** (0.100 g, 0.407 mmol) in MeOH (1.0 mL) was added at 20 °C with stirring. The resulting mixture was kept at 20 °C for 0.5 h. The solvent was removed *in vacuo*. The product was purified by preparative TLC (chromatographed three times) on silica gel with ethyl acetate—hexane (1 : 3) as an eluent. The yield of compound **10** was 0.088 g (80%), yellow oil. MS (ESI), *m/z*: 239.1841 $[M + Na]^+$; calculated for $C_7H_{12}N_4O_4$: $[M + Na]^+$ 239.1845. IR (KBr), ν/cm^{-1}: 1588 (vs, furazan); 1517 (s, N=N→O); 1262 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 2.18 (s, 6 H, C—Me); 2.84 (s, 3 H, C(NON)O—Me); 4.19 (s, 3 H, O—Me). ^{13}C NMR (75 MHz, acetone-d_6), δ: 24.8 (C—Me), 49.9 (C(NON)O—Me), 60.0 (O—Me), 109.7 (C(NON)O—Me), 148.0 (C—N=N→O), 162.2 (C—OMe). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −29.4 (N→O, $\Delta\nu_{0.5}$ = 165 Hz).

4-Methoxy-3-(5-methoxy-2,2-dimethyl-1,3-dioxan-5-yl-*ONN*-azoxy)furazan (11). Metallic sodium (0.036 g, 1.57 mmol) was dissolved in MeOH (2.0 mL), whereupon a solution of compound **3** (0.100 g, 0.314 mmol) in MeOH (1.0 mL) was added at 20 °C with stirring. The resulting mixture was kept at 20 °C for 0.5 h. The solvent was removed *in vacuo*. The product was purified by preparative TLC (chromatographed three times) on silica gel with ethyl acetate—hexane (1 : 3) as an eluent. The yield of compound **11** was 0.086 g (87%), white crystals, m.p. 48.0—49.5 °C (from hexane). MS (ESI), *m/z*: 311.0953 $[M + Na]^+$; calculated for $C_{10}H_{16}N_4O_6$: $[M + Na]^+$ 311.0962. IR (KBr), ν/cm^{-1}: 1592 (vs, furazan); 1501 (vs, N=N→O); 1254 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.38, 1.46 (both s, 3 H, C—Me); 3.49 (s, 3 H, C(NON)O—Me), 4.15 (s, 3 H, O—Me); 4.18, 4.62 (both d, 4 H, CH_2, J = 13.20 Hz). ^{13}C NMR (75 MHz, acetone-d_6), δ: 22.3, 24.1 (both C—Me), 52.7 (C(NON)O—Me), 59.7 (O—Me), 62.9 (CH_2), 99.7 (CMe_2), 103.2 (C(NON)O—Me), 148.2 (C—N=N→O), 161.9 (C—OMe). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −27.8 (N→O, $\Delta\nu_{0.5}$ = 180 Hz).

1,2-Bis[3-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)furazan-4-yloxy]ethane (12). Potassium carbonate (0.045 g, 1.05 mmol) was added at 20 °C to a stirred solution of compound **3** (0.100 g, 0.314 mmol) and $HOCH_2CH_2OH$ (0.011 g, 0.173 mmol) in dry MeCN (0.4 mL). The resulting suspension was stirred at 20 °C for 96 h and filtered. The mother liquor was concentrated *in vacuo*. The residue was separated into two fractions by preparative TLC (chromatographed four times) on silica gel with ethyl acetate—hexane (1 : 2) as an eluent. First fraction (R_f 0.85): compound **12** (0.059 mg, 62%), yellow oil. MS (ESI), *m/z*: 605.1541 $[M + H]^+$; calculated for $C_{18}H_{24}N_{10}O_{14}$: $[M + H]^+$ 605.1546. IR (KBr), ν/cm^{-1}: 1594 (vs, furazan); 1576 (vs, asymm., NO_2); 1509 (s, N=N→O); 1380 (s, symm., NO_2); 1249 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.48, 1.51 (both s, 6 H, Me); 4.91 (s, 8 H, $(CH_2)_2CNO_2$); 4.94 (s, 4 H, CH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.6, 24.3 (both Me), 62.6 ($(CH_2)_2CNO_2$), 71.3 (CH_2), 100.9 (CMe_2), 107.4 (C—NO_2), 147.4 (C—N=N→O), 161.6 (C—OCH_2). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −50.5 (2 N→O, $\Delta\nu_{0.5}$ = 73 Hz); −11.6 (2 NO_2, $\Delta\nu_{0.5}$ = 86 Hz). Second fraction (R_f 0.35): compound **13** (0.007 mg, 7%).

3-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-4-(2-hydroxyethoxy)furazan (13). MS (ESI), *m/z*: 334.0983 $[M + H]^+$; calculated for $C_{10}H_{15}N_5O_8$: $[M + H]^+$ 334.0993. IR (KBr), ν/cm^{-1}: 3435 (m, OH); 1593 (vs, furazan); 1581 (vs, asymm., NO_2); 1509 (s, N=N→O); 1381 (s, symm., NO_2); 1253 (s, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.46, 1.52 (both s, 3 H, Me); 3.93 (m, 2 H, CH_2OH); 4.19 (br.s, 1 H, OH); 4.52 (t, 2 H, CH_2CH_2OH, J = 4.50 Hz); 4.92 (q, 4 H, $(OCH_2)_2CNO_2$, J = 12.00 Hz). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.6, 24.7 (both Me), 60.2 (CH_2OH), 62.8 ($(CH_2)_2CNO_2$), 75.7 (CH_2CH_2OH), 101.0 (CMe_2), 107.7 ($C—NO_2$), 147.6 (C—N=N→O), 162.2 ($C—OCH_2$). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −51.7 (N→O, $\Delta\nu_{0.5}$ = 90 Hz); −11.3 (NO_2, $\Delta\nu_{0.5}$ = 76 Hz).

Bis[3-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-furazan-4-yl] ether (14). Sodium carbonate (0.037 g, 0.345 mmol) was added at 20 °C to a stirred solution of compound **3** (0.100 g, 0.314 mmol) in dry MeCN (6.0 mL). The resulting solution was kept at 65 °C for 5 h and concentrated *in vacuo*. The product was purified by preparative TLC (chromatographed four times) on silica gel with ethyl acetate—hexane (1 : 4) as an eluent. The yield of compound **14** was 0.055 g (63%), white crystals, m.p. 99.0—100.0 °C (from hexane). MS (ESI), *m/z*: 583.1111 $[M + Na]^+$; calculated for $C_{16}H_{20}N_{10}O_{13}$: $[M + Na]^+$ 583.1104. IR (KBr), ν/cm^{-1}: 1590 (s, furazan); 1577 (vs, asymm., NO_2); 1484 (s, N=N→O); 1379 (m, symm., NO_2); 1258 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.49, 1.52 (both s, 6 H, Me); 4.93 (s, 8 H, CH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.8, 24.2 (both Me), 62.6 (CH_2), 101.1 (CMe_2), 107.9 ($C—NO_2$), 147.8 (C—N=N→O), 158.4 (C—O). The signals in the spectrum were assigned using HMBC experiments. ^{14}N NMR (22 MHz, acetone-d_6), δ: −48.2 (2 N→O, $\Delta\nu_{0.5}$ = 134 Hz); −12.5 (2 NO_2, $\Delta\nu_{0.5}$ = 108 Hz).

We are grateful to M. I. Struchkova, A. S. Shashkov, E. D. Lubuzh, N. G. Kolotyrkina, V. I. Kadentsev, and A. O. Chizhov for performing spectroscopic measurements.

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Received November 19, 2012;
in revised form February 6, 2013