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Synthesis of Difurazanyl Ethers from 4,4′-Dinitroazoxyfurazan

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ABSTRACT: *Nonselective attacks at the carbon bonded to a nitro group and carbon bonded to the N(O) atom of the azoxy group were observed in the reactions of 4,4′-dinitroazoxyfurazan with bases and nucleophiles. A mechanism is presented to account for both of the pathways to products. A series of new difurazanyl ether derivatives was synthesized.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:48–56, 2000

INTRODUCTION

Nitrofurazans are well known for their high energy contents [1–10], and the methods of synthesis of these useful heterocycles have been reviewed by Boyer [11] and Sheremetev [12].

We have a long-standing interest in nucleophilic aromatic substitution (S_NAr) reactions of the 3-nitro-4 R-furazans and have probed their reactivity toward *S*- [13] and *O*-nucleophiles [8,14,15]. Furthermore, to study their reactivity, we have found that base-promoted transformation of the 3-nitro-4-R-furazans leads to derivatives of symmetrical difurazanyl ethers [7,15–20]. The transformation of the nitro group is made possible by the presence of another electron-withdrawing function, R, and by the use of solid anhydrous bases under dry conditions. This unusual reaction pathway to ether bond formation was identified, and a mechanism was proposed [19]. We have also investigated the role of water in the reaction of the bases with nitrofurazans. It turns out that the nitro group undergoes a regioselective displacement by a hydroxyl group under treatment of nitrofurazans with solid crystal hydrates of inorganic bases in dry CH_3CN, quickly affording the 3-hydroxy-4-R-furazans in high yields [21]. In contrast, the inclusion of water in the CH_3CN reaction medium decreased both the reaction rate and the yields of the hydroxyfurazans and gave a set of byproducts.

In earlier communications, we disclosed our initial results on the discovery of S_NAr reactions of 3-(R-*NNO*-azoxy)-4-R′-furazans. We found that these R-*NNO*-azoxy substituents might also function as leaving groups [7,22].

As part of our studies in this area, we became interested in replacement reactions of substituted furazans with different activated leaving groups. In this article, we describe the S_NAr reactions of 4,4′-dinitroazoxyfurazan **(1)** [23], which possesses three potential leaving groups, (namely two different nitro groups and the R-*NNO*-azoxy substituent).

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RESULTS AND DISCUSSION

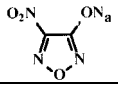
Reaction of 4,4′-Dinitroazoxyfurazan (**1**) *with Bases*

We have investigated the reactivity of **1** with bases (such as alkali metal salts), anticipating nitro group transformation products such as monoethers of type **2** and/or **9** (similarly to the reaction of 3,4-dinitrofurazan [19]), oligomeric ethers of type **10** (similarly to the reaction of 4,4′-dinitrobifurazan [17]), and macrocyclic ethers of type **11** (similarly to the reaction of 4,4′-dinitroazofurazan [18,20]), as illustrated in Scheme 1.

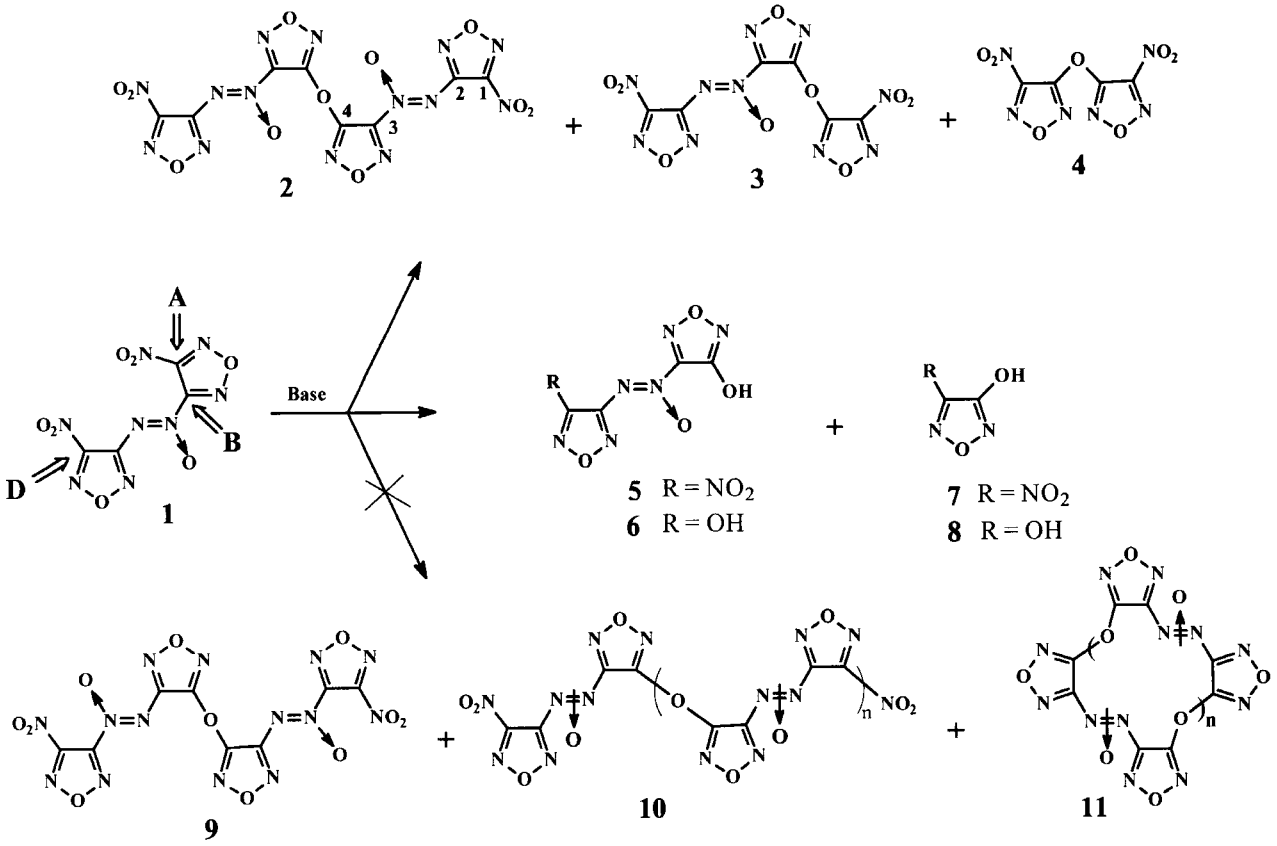
However, the reaction between **1** and the bases proceeds via nonselective attacks at the carbon bonded to the nitro group and the carbon bonded to the N(O) atom of the azoxy group to produce a mixture of three difurazanyl ethers, namely **2, 3,** and **4,** and four hydroxyfurazans, such as **5–8** (Scheme 1). Attempts to improve the yield of one kind or another of difurazanyl ethers by changing bases, concentration, and stoichiometry were all unsuccessful. The results of our study of reaction conditions are summarized in Table 1.

By use of column chromatography, the mixture

TABLE 1 Products for the Reaction of **1** with Bases in Acetonitrile at 81°C

		Products			
Entry	*Base*	*Isolated Yield (%)* (**2–4**)	*Ratio* (**2:3:4**)	*Isolated Yield (%)* (**5–8**)	*Ratio* (**5:6:7:8**)
1	Li_2CO_3[a]	64	42:47:11	31	12:7:68:13
2	Li_2CO_3[b]	62	41:48:11	35	11:6:70:13
3	Na_2CO_3[a]	43	31:53:16	51	10:9:56:25
4	Na_2CO_3[c]	42	30:53.5:16.5	53	10:8:58:24
5	$KHCO_3$[a]	68	41:45:14	26	13:4:67:16
6	KCN[a,d]	40	40:48:12	52	15:3:75:7
7	$NaNO_2$[a]	50	32:49:19	25	11:8:71:10
8		69	23:59:18	e	e

[a]The reactions were carried out using 1 equiv. of **1** (10 mmol) and 1 equiv. of base (10 mmol) in 25 mL of solvent.
[b]The reaction was carried out using 2 equiv. of base (20 mmol).
[c]The reaction was carried out using 250 mL of the solvent.
[d]The reaction mixture did not involve any cyano derivatives.
[e]The yields of hydroxyfurazans were not determined.



SCHEME 1

was completely separated, and the structures of the ethers and the hydroxyfurazans were determined based on ^{13}C and ^{14}N NMR, IR, and mass spectroscopy. Since **2** is symmetric, it displays four signals in its ^{13}C NMR spectrum at δ 157.3 (C1), 149.8 (C2), 152.9 (C3), and 156.5 (C4). Signals of the carbon atoms bonded to the nitro and azoxy groups were broadened by ^{13}C–^{14}N coupling. In the ^{14}N NMR spectrum, there are the usual narrow signals due to the N(O) atom of the azoxy group at δ −65.8 ppm ($\Delta\nu_{1/2}$ = 64 Hz) and the nitrogen atom of the nitro group at δ −36.9 ppm ($\Delta\nu_{1/2}$ = 19 Hz) indicating the nitro group position as distal, not proximate to the *N*-oxide of the azoxy group. The typical range for a nitrogen atom of the nitro group proximate to the *N*-oxide of the azoxy group of nitroazoxyfurazans is δ −43 to −45 ppm [7]. In addition, identification of the *N*-oxide position was made through selective ^{13}C-{^{14}N} double heteronuclear resonance and comparison with the established data [7,8,14,15,19,20].

As we reported earlier, mass spectral investigation provides additional support for the assignment of azoxyfurazan structures [8]. For **2,** the EI-MS diagnostic fragments at *m/z* 468 (M^+), 310 ($M - ONNFNO_2)^+$, 158 $(ONNFNO_2)^+$, and 152 $(FOF)^+$ were consistent with the distal to *N*-oxide position of the nitro group (when F is the furazan ring).

Compounds **3** [8], **4** [19], **5** [21], **7** [15,19,21,23a], and **8** [8,15,24] were identical in all respects (^{13}C and ^{14}N NMR, IR, MS, and m.p.) with those published in the literature.

With regard to the yields (Table 1) of the reaction products illustrated in Scheme 1, the following observation can be made. In general, the reaction produced a mixture of seven compounds, which obviously arose by the attacks at the carbon bonded to the nitro group proximate to the *N*-oxide of the azoxy group (attack A) as well as at the carbon bonded to the N(O) atom of the azoxy group (attack B). In no case could we isolate any of the oligomeric ethers of type **10** or macrocyclic ethers of type **11**. Only the formation of the ether **2** proceeded in the expected manner by attack A. The unexpected asymmetrical ether **3** always predominated, and the product ratios were little affected by the reaction conditions. In a single case, that leading to the dihydroxy derivative **6,** the attack at the carbon bonded to the nitro group distal to the *N*-oxide of the azoxy group (attack D) was observed. In this system, there is no evidence of any ether, for example type **9,** forming from the attack on the dinitro compound **1** at the center D.

Mechanism

Our previous report on the mechanism of difurazanyl ether formation from nitrofurazans in the presence of the solid anhydrous inorganic bases (heterophase conditions) has postulated an initial intramolecular nitro–nitrite rearrangement [19]. Subsequent reaction of the nitrite ester with a molecule of base-stimulated starting nitrofurazan produces the difurazanyl ether with the elimination of N_2O_3. The synthesis of **2** followed the trend typically observed (Scheme 2).

On the other hand, the formation of **3** and **4** correspond to the formal attacks of an anion of 3-hydroxy-4-nitrofurazan at C-NO_2 and C-N(O)N bonds with concomitant S_NAr displacement. The anion, as well as anions of the other hydroxyfurazans, are present in the reaction mixture (See Scheme 1, Table 1). However, earlier we found that the 3-hydroxy-4-nitrofurazan anion is not a nucleophile [8,19,25]. Furthermore, no compounds were formed in a conceivable reaction with more nucleophilic hydroxyfurazan anions such as, for example, the anion of 3,4-dihydroxyfurazan.

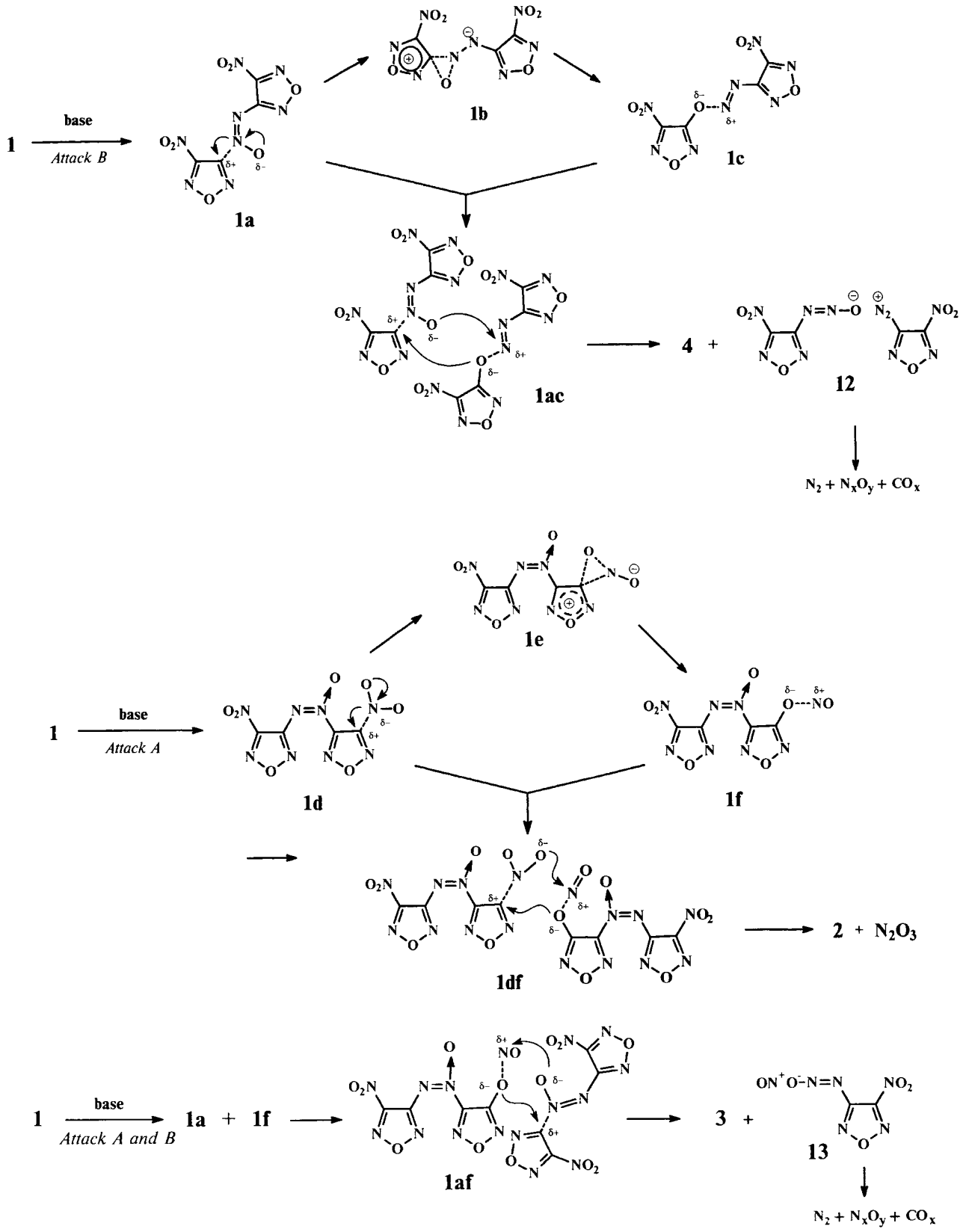
To understand the pathways to ethers **3** and **4** in the reaction, the mechanistic speculation shown in Scheme 2 may be considered. Thus, the initial step in the reaction is the interaction of the nitro compound with the surface of the solid base (where precisely the transformation occurs with dipole **1a**), followed by electron transfer within the F-N-O moiety with the formation of a bipolar molecule that produces the oxazirine intermediate **1b**. The diazo ether **1c** is formed by the cleavage of the latter compound. A reaction of the diazo ether **1c** with another molecule of base-stimulated starting material **1a,** via complex **1ac,** generates the difurazanyl ether **4** and eliminates diazonium diazotate **12** that decomposes, presumably to give uncharacterized small molecules such as N_2, N_xO_y, and CO_x.

On the other hand, nitro–nitrite rearrangement of **1,** as we have described earlier [19], may produce the nitrite ester **1f.** On reaction of the ester **1f** with starting material that had undergone base-stimulation on the azoxy moiety, **1a,** the formation of the initial complex **1af** occurred. The unsymmetrical ether **3** yielded, by an electron-transfer process involving the loss of nitronium diazotate, a completely destroyed compound **13.**

Reactions of **1** *with Nucleophiles*

Although our primary interest has been the exploration of synthetic aspects of base-promoted transformation of nitrofurazans, we intended to conduct an additional study to clarify the reactivity of **1.**

Earlier in the course of our investigations of hydroxyfurazan reactivity directed toward synthesis of furazanyl ethers [8,15,19,24–27], we observed that


base
Attack B
1
1a
1b
1c
1ac
4 +
12
$N_2 + N_xO_y + CO_x$
base
Attack A
1d
1e
1f
1df
2 + N_2O_3
base
Attack A and B
1a + 1f
1af
3 +
13
$N_2 + N_xO_y + CO_x$

SCHEME 2

the nature of the substitutient in the hydroxyfurazan plays a critical role in controlling the efficiency of ether formation.

At the outset of our study, a series of hydroxyfurazan salts, namely **7, 14,** and **15,** were reacted with **1.** Reaction of the sodium salt of 3-hydroxy-4-nitrofurazan **7** resulted in displacement of both nitro and azoxy groups to give a mixture of ethers **2–4** (Table 1, entry 8). Although, according to our concept, **7** (similarly to other salts from Table 1) is only a promoter for transformation of **1** to ethers **2–4,** an increase of the ether **3** proportion in the obtained mixture, with a slightly higher combined yield of the ethers.

When a more violent nucleophile such as the sodium salt of 3-hydroxy-4-cyanofurazan **14** was allowed to react with **1** in acetonitrile at reflux, a mixture of the known ethers (29%), namely **2** (9%), **3** (17%), and **4** (3%), and new ethers (36%), such as **16** (21%) and **17** (15%), were formed (Scheme 3). These ethers were then separated and purified by silica gel chromatography.

To some extent, the more potent nucleophile, the sodium salt of 3-hydroxy-4-methylfurazan **15,** gave only three products (Scheme 4) under similar conditions, two of which were identified as new ethers **18** and **19** in yields of 26% and 21%, respectively. The third and minor product, formed in a yield of 12%, was identified as the ether **3.**

By this means, the reactions were always accompanied by one or more competing reactions and produced mixtures involving compounds, which were obtained both from base-promoted (such as hydroxyfurazan salts) transformation of **1** and with the participation of hydroxyfurazan nucleophiles. The formation of these ethers proceeds by the attack at the carbon bonded to the nitro group proximate to the N-oxide of the azoxy group (attack A) as well as the carbon bonded to the N(O) atom of the azoxy group (attack B).

This observation led us to examine the reaction of hydroxyfurazan salts with an azoxyfurazan involving no terminal leaving groups. When 4,4′-dicyanoazoxyfurazan **20** was utilized as the substrate, the sodium salt of 3-hydroxy-4-cyanofurazan **14** replaced the cyanofurazanylazoxy moiety to give symmetrical ether **21** in 40% yield (Scheme 5). The same ether **21** was formed in 5% yield on treatment of **20** with $NaNO_2$ in refluxing acetonitrile. However, all of our attempts to generate ether **21** from the reaction of **20** with Na_2CO_3 failed because of hydrolysis.

When the sodium salt of 3-hydroxy-4-nitro-furazan **7** was added to a solution of **20** in acetonitrile at reflux, no trace of **16** was ever observed, even though many fractions from this reaction mixture were screened by mass spectrometry.

These experiments have demonstrated that the formation of difurazanyl ether derivatives may occur by the usual nucleophilic displacement in the case of the more powerful nucleophiles.

As an extension of the aforementioned reactions, we allowed **1** to react with ammonia under anhydrous conditions. On being stirred with an excess of ammonia in $CHCl_3$ solution (homogeneous conditions) at 20°C, **1** reacted completely in less than 1 hour, and the reaction proceeded also via nonselective attack at each of the carbons (Attack A and B) to produce a mixture of five products (Scheme 6). Compound **22** (59%) was the predominant product. Amine **23** and azide **24** were isolated after column chromatography, in yields of 17 and 3%, respectively. Two water-soluble products **7** and **25** were also formed in yields of 11 and 7%, respectively. No unreacted compound **1** was recovered.

When the experiment was repeated employing only 10 equiv. of NH_3 under otherwise identical conditions, **22, 23, 24, 25,** and **7** were obtained in yields of 39, 14, 5, 13, and 9%, respectively. Starting compound **1** was also recovered in 18% yield.

The most interesting result of the reaction with ammonia is the isolation of azide **24** and triazene **25**. The compound formation was accomplished by trapping of the intermediate diazotate generated from the leaving nitrofurazanazoxy moiety with ammonia and the amine **23,** respectively.

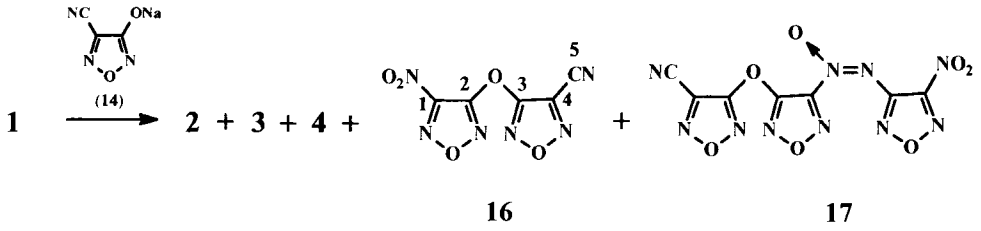
CONCLUSIONS

We reported here the reactivity of 4,4′-dinitroazoxyfurazan **1** with respect to bases and some nucleophiles. The reactions produced a mixture of compounds, which were formed by the attack at the carbon bonded to the nitro group proximate to the *N*-oxide of the azoxy group (attack A) as well as the carbon bonded to the N(O) atom of the azoxy group (attack B). The unexpected finding is that the reactions of **1** usually do not result in substitution by the attack at the carbon bonded to the nitro group distal to the *N*-oxide of the azoxy group (attack D). In one case, the products generated from the leaving nitrofurazanazoxy moiety were identified.

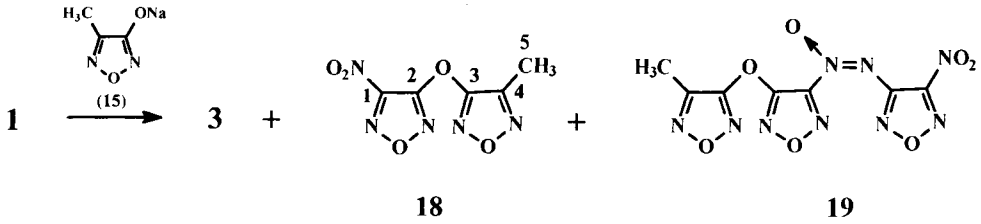
EXPERIMENTAL

CAUTION! Nitrofurazans are high explosives and may be sensitive to shock or heating and must be handled with appropriate precautions.

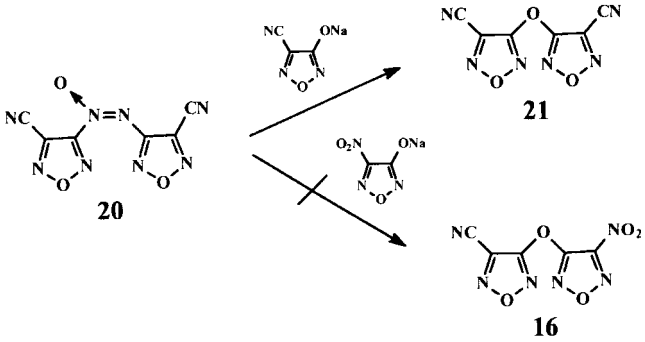
Melting points were determined on a Kofler hot-stage microscope and are uncorrected. IR spectra



SCHEME 3



SCHEME 4



SCHEME 5

were recorded using a Perkin-Elmer 577 spectrometer as thin films on KBr disks. Mass spectra were obtained on a Varian MAT-311A instrument. ^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 75.47, and 21.68 MHz, respectively. The ^{1}H and ^{13}C chemical-shift values are expressed in δ values relative to the chemical shift of the solvent-*d*. The ^{14}N chemical shift values were measured relative to external nitromethane. Analytical thin-layer chromatography (TLC) was conducted on precoated silica gel plates (Silufol F_{254}). The plates were visualized under UV irradiation, and the slides were then sprayed with DPA reagent (5% diphenylamine in hexane).

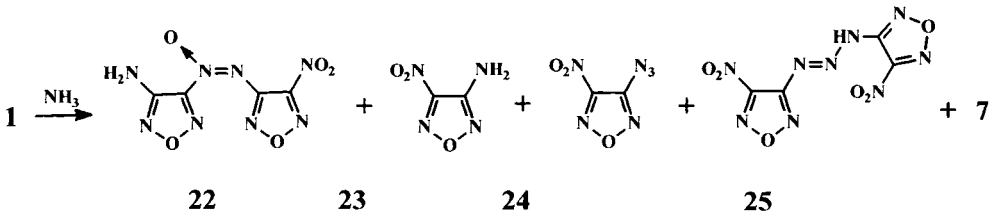
Reaction of 4,4′-Dinitroazoxyfurazan (**1**) *with Base*

To a solution of **1** (2.72 g, 10 mmol) in CH_3CN (25 mL) was added base (10 mmol) under a dry atmosphere at 50°C. The resulting suspension was stirred for 0.5 to 2.5 hours under reflux. The progress of the reaction was monitored by TLC. The reaction mixture was cooled. After addition of CH_2Cl_2 (3 × 50 mL), the resulting mixture was washed (H_2O), dried ($MgSO_4$), filtered, and evaporated. The residue was a mixture of **2, 3,** and **4.** The products were separated by silica gel flash chromatography using benzene/hexane (2:1) as eluent. The yields are shown in Table 1.

The first fraction, 3,3-dinitrodifurazanyl ether (**4**) was obtained as colorless crystals, m.p. 63–64°C, (m.p. 63–64°C [19]). The second fraction was obtained as a colorless liquid of 4-nitro-4′-(4′-nitrofurazanyl-*NNO*-azoxy)-difurazanyl ether (**3**) that crystallized on standing, m.p. 40–41°C, (in [8], m.p. 41–42°C). The third fraction was obtained as colorless crystals of bis-3,3′-(4-nitrofurazanyl-*NNO*-azoxy)-difurazanyl ether (**2**), m.p. 109–110°C. MS *m/z* 468 (M^+), 452 ($M^+ - O$), 422 ($M^+ - NO_2$), 339, 322, 310 ($M^+ - ONNFNO_2$), 292, 262, 226, 210, 162, 158 $(ONNFNO_2)^{+\cdot}$, 152 $(FOF)^{+\cdot}$, 122, 111. IR: ν = 1580 cm^{-1}, 1520, 1350, 1225, 1180, 1015, 940, 840. $C_8N_{14}O_{11}$ (468.18): calcd: C, 20.52; N, 41.88. Found: C, 20.65; N, 40.98.

The aqueous phase was strongly acidified with H_2SO_4 and extracted with Et_2O (4 × 20 mL). The combined extracts were dried ($MgSO_4$) and filtered. The solvent was removed by rotary evaporation, and the residue was separated by silica gel column chromatography using $CH_2Cl_2 \rightarrow CH_3OH$ as eluent.

The first fraction, 3-hydroxy-4-nitrofurazan (**7**) was obtained as a yellow oil (m.p. 20–21°C [15,19,23a]). On the basis of spectroscopy and TLC,



SCHEME 6

the substance corresponded in all respects to the compound described earlier [15]. The second fraction, 3-hydroxy-4-(4-nitrofurazanyl-*NNO*-azoxy) furazan (**5**), m.p. 107–108°C, (m.p. 107–108°C [21]). The third fraction was obtained as colorless crystals of 3,4-dihydroxyfurazan (**8**), m.p. 189–190°C (m.p. 189–190°C [15,24]). The fourth fraction was obtained as colorless crystals of 4,4′-dihydroxyazoxyfurazan (**6**), m.p. 171–172°C. MS *m/z:* 214 (M^+), 198 ($M^+ - O$). IR ν = 3590 $cm^{-1,}$ 3110, 1610, 1490, 1450, 1340, 1265, 1190, 1040, 940, 880. $C_4H_2N_6O_5$ (214.10): Calcd: C, 22.44; H, 0.94; N, 39.25. Found: C, 21.99; H, 0.99; N, 38.80. Compound **6** is strongly acidic and gives stable mono- and disalts, for example: monopotassium salt, m.p. 210°C (dec.); dipotassium salt, m.p. 180°C (dec.); monoammonium salt, m.p. 208–210°C (dec); diammonium salt, m.p. 213–215°C; dihydrazinium salt, m.p. 113–115°C (dec).

Reaction of 4,4′-Dinitroazoxyfurazan (**1**) *with the N_a-Sodium Salt of 3-Hydroxy-4-cyanofurazan* (**14**)

To a suspension of **14** (0.53 g, 4 mmol) in CH_3CN (10 mL) was added a solution of **1** (1.08 g, 4 mmol) in CH_3CN (15 mL) under a dry atmosphere at 25°C. The resulting suspension was stirred for 0.5 to 1 hours (TLC monitoring) under reflux. The reaction mixture was cooled. After addition of CH_2Cl_2 (150 mL), the resulting mixture was washed (H_2O), dried ($MgSO_4$), filtered, and evaporated. The residue was a mixture of the ethers. The products, **2** (the fifth fraction), **3** (the third fraction), **4** (the second fraction), **16** (the first fraction), and **17** (the fourth fraction) were separated by silica gel flash chromatography using benzene/CCl_4 (1:2) as eluent.

3-Cyano-3′-nitrodifurazanyl ether (**16**) was obtained as colorless crystals, m.p. 49–50°C. MS *m/z:* 224 (M^+), 178 ($M^+ - NO_2$). IR: ν = 1595 $cm^{-1,}$ 1570, 1500, 1490, 1400, 1350, 1230, 1195, 1035. ^{13}C NMR ([D_6]acetone): δ = 106.4 (C5), 128.9 (C4), 153.8 (C1), 156.1 (C2), 162.2 (C3). ^{14}N NMR ([D_6]acetone) δ = −38.6 ($\Delta\nu_{1/2}$ = 10.2 Hz, NO_2). $C_5N_6O_5$ (224.09): Calcd: C, 26.80; N, 37.50. Found: C, 26.47; N, 37.56.

3-Cyano-3′-(4-nitrofurazanyl-*NNO*-azoxy)-difurazanyl ether (**17**) was obtained as a colorless oil. MS *m/z:* 336 (M^+), 320 ($M^+ - O$), 290 ($M^+ - NO_2$), 244, 214, 178 $(NCFOF)^+$. IR: ν = 1590 $cm^{-1,}$ 1520, 1350, 1240, 1210, 1170, 1030, 930. ^{14}N NMR ([D_6]acetone) δ = −37.3 ($\Delta\nu_{1/2}$ = 12.5 Hz, NO_2), −68.2 ($\Delta\nu_{1/2}$ = 55 Hz, N → O). $C_7N_{10}O_7$ (336.14): Calcd: C, 25.01; N, 41.67. Found: C, 25.17; N, 41.46.

Reaction of 4,4′-Dinitroazoxyfurazan (**1**) *with the Sodium Salt of 3-Hydroxy-4-methylfurazan* (**15**)

To a suspension of **15** (0.53 g, 4 mmol) in CH_3CN (10 mL), a solution of **1** (1.08 g, 4 mmol) in CH_3CN (10 mL) was added under a dry atmosphere at 55°C. The resulting suspension was stirred for 0.5 to 1 hours under reflux. The reaction mixture was cooled. After addition of CH_2Cl_2 (150 mL), the resulting mixture was washed (H_2O), dried ($MgSO_4$), filtered, and evaporated. The residue was a mixture of the ethers. The products, **3** (the third fraction), **18** (the first fraction), and **19** (the second fraction) were separated by silica gel flash chromatography using benzene/CCl_4 (1:2) as eluent.

3-Methyl-3′-nitrodifurazanyl ether (**18**) was obtained as colorless thin needles, m.p. 40–41°C. MS *m/z:* 213 (M^+), 167 ($M^+ - NO_2$), 137 ($M^+ - NO_2 - NO$). IR: ν = 2990–2930 $cm^{-1,}$ 1630, 1603, 1525, 1465, 1375, 1245, 1200, 1050. ^{13}C NMR ([D_6]acetone): δ = 7.5 (C5), 146.6 (C4), 153.9 (C1), 157.1 (C2), 162.1 (C3). ^{14}N NMR ([D_6]acetone) δ = −37.8 ($\Delta\nu_{1/2}$ = 20 Hz, NO_2). $C_5H_3N_5O_5$ (213.11): Calcd: C, 28.18; H, 1.42; N, 32.86. Found: C, 28.52; H, 1.36; N, 33.05.

3-Methyl-3′-(4-nitrofurazanyl-NNO-azoxy)-difurazanyl ether (**19**) was obtained as a colorless oil. MS *m/z:* 325 (M^+), 309 ($M^+ - O$), 295 ($M^+ - NO$), 264 ($HM^+ - NO_2$), 233 ($HM^+ - O - NO - NO_2$), 210, 197, 167 $(MeFOF)^+$, 158 $(ON_2FNO_2)^+$, 142. IR: ν = 1590 $cm^{-1,}$ 2930, 1590, 1520, 1460, 1350, 1240, 1210, 1160, 1045, 935. ^{14}N NMR ([D_6]acetone) δ = −37.5 ($\Delta\nu_{1/2}$ = 11.0 Hz, NO_2), −67.3 ($\Delta\nu_{1/2}$ = 62 Hz, N → O). $C_7H_3N_9O_7$ (325.16): Calcd: C, 25.86; H, 0.93; N, 38.77. Found: C, 26.07; H, 1.00; N, 38.55.

Reaction of 4,4′-Dicyanoazoxyfurazan (**20**) *with the Sodium Salt of 3-Hydroxy-4-cyanofurazan* (**14**)

To a suspension of **14** (1.33 g, 10 mmol) in CH_3CN (20 mL) was added a solution of **20** (2.32 g, 10 mmol) in CH_3CN (20 mL) under a dry atmosphere at 25°C. The resulting suspension was stirred for 2.5 to 3.5 hours under reflux. After cooling and addition of CH_2Cl_2 (150 mL), the resulting mixture was washed (H_2O), dried ($MgSO_4$), filtered, and evaporated. Crystallization of the crude product from CCl_4 gave ether **21** as a colorless, crystalline solid. The yield was 40%, m.p. 68–69°C (m.p. 68–69°C [17]).

Reaction of 4,4′-Dicyanoazoxyfurazan (**20**) *with* $NaNO_2$

To a solution of **20** (2.32 g, 10 mmol) in CH_3CN (25 mL) was added sodium nitrite (1.4 g, 20 mmol) under a dry atmosphere. The resulting suspension was stirred for 3.5 to 4 hours under reflux. The reaction mixture was cooled and diluted with CH_2Cl_2 (150 mL). The resulting mixture was washed (H_2O), dried ($MgSO_4$), filtered and evaporated. Crystallization of the crude product from CCl_4 gave ether **21** as a colorless, crystalline solid. Yield was 5%, m.p. 68–69°C (m.p. 68–69°C [17]).

Reaction of 4,4′-Dinitroazoxyfurazan (**1**) *with Ammonia*

To a concentrated solution of ammonia in $CHCl_3$ (500 mL) was added a solution of **1** (2.72 g, 10 mmol) in CH_2Cl_2 (20 mL) under a dry atmosphere. The mixture was stirred for 0.5 hours at 20°C. The solvents were evaporated to half volume, yielding a suspension that was treated with HCl gas up to pH 2–1 and evaporated. Chromatography was performed on the residue on silica gel. Elution with pentane → CH_2Cl_2 → MeOH yielded five fractions.

The first fraction, 3-azido-4-nitrofurazan (**24**) was obtained as a colorless oil. Based on results from spectroscopy and TLC, the substance corresponded in all respects to the compound described earlier [28]. The second fraction, 3-amino-4-nitrofurazan (**23**) was obtained as yellow crystals, m.p. 123–124°C, (m.p. 125°C [23a], 122.5°C [29], 120°C [10]). The third fraction, 3-amino-4-(4-nitrofurazanyl-*NNO*-azoxy)furazan (**22**) was obtained as yellow crystals, m.p. 130–131°C, (m.p. 131°C [22a]). The fourth fraction, 3-hydroxy-4-nitrofurazan (**7**) was obtained as a yellow oil (m.p. 20–21°C [15]). The fifth fraction was bis-1,3-(3-nitrofurazanyl)triazene (**25**), m.p. 95–96°C. MS *m/z* 275 (M^+), 225 ($M^+ - NO_2$), 179 ($M^+ - 2NO_2$), 151 ($M^+ - 2NO_2 - N_2$), 142, 87, 68, 54, 46. IR: $\nu = 3300\ cm^{-1}$, 1625, 1590, 1545, 1490, 1450, 1425, 1400, 1365, 1340, 1235, 1190, 1160, 1065, 1045, 965, 935. $C_4H_1N_9O_6$ (271.11): Calcd: C, 17.72; H, 0.37; N, 46.50. Found: C, 17.53; H, 0.47; N, 46.30.

REFERENCES

[1] Sheremetev, A. B.; Shatunova, E. V. In Combustion and Detonation, Proceedings of the 28th International Annual ICT-Conference, Karlsruhe, Germany, June 24–June 27, 1997, 94, 1–8.

[2] Sheremetev, A. B.; Yudin, I. L.; Aleksandrova, N. S.; Andrianov, V. G.; Starchenkov, I. B. In Proceedings of the 23rd International Pyrotechnics Seminar, Tsukuba, Japan, September 30–October 4, 1997, 377–388.

[3] Batog, L. V.; Konstantinova, L. S.; Rozhkov, V. Yu.; Lebedev, O. V.; Epishina, M. A.; Makhova, N. N.; Ovchinnikov, I. V.; Khmelnitskii, L. I. In Energetic Materials—Production, Processing and Characterization, Proceedings of the 29th International ICT-Conference, Karlsruhe, Germany, June 30–July 3, 1998, 55, 1–10.

[4] Sheremetev, A. B.; In Energetic Materials—Production, Processing and Characterization, Proceedings of the 29th International ICT-Conference, Karlsruhe, Germany, June 30–July 3, 1998, 58, 1–13.

[5] Afanasev, G. T.; Arhipov, V. I.; Gogulya, M. F.; Sovko, A. A. In Energetic Materials—Production, Processing and Characterization, Proceedings of the 29th International ICT-Conference, Karlsruhe, Germany, June 30–July 3, 1998, 72, 1.

[6] Sinditskii, V. P.; Dong, H. W.; Serushkin, V. V.; Fogelzang, A. E.; Sheremetev, A. B. In Energetic Materials—Production, Processing and Characterization, Proceedings of the 29th International ICT-Conference, Karlsruhe, Germany, June 30–July 3, 1998, 170, 1–11.

[7] Sheremetev, A. B.; Semenov, S. E.; Kuzmin, V. S.; Strelenko, Yu. A.; Ioffe, S. L. Chem—Eur J 1998, 4, 1023–1026.

[8] Sheremetev, A. B.; Kulagina, V. O.; Aleksandrova, N. S.; Dmitriev, D. E.; Strelenko, Yu. A.; Lebedev, V. P.; Matyushin, Yu. N. Propellants, Explosives, Pyrotechnics 1998, 23, 142–149.

[9] Zelenin, A. K.; Trudell, M. L. J Heterocycl Chem 1997, 34, 1057.

[10] Zelenin, A. K.; Trudell, M. L.; Gilardi, R. D. J Heterocycl Chem 1998, 35, 151–155.

[11] Boyer, J. H. Nitroazoles; VCN: Deerfield Beach, Florida, 1986; 341–344.

[12] Sheremetev, A. B. Ross Khim Zhurn (Zhurn Ross Khim Ob-va im D I Mendeleeva) 1997, 41(2), 43–54 (in Russian); Mendeleev Chem J (Engl Trans) 1997, in press.

[13] Sheremetev, A. B.; Mantseva, E. V.; Aleksandrova, N. S.; Kuzmin, V. S.; Khmelnitskii, L. I. Mendeleev Commun 1995, 25–27.

[14] Sheremetev, A. B.; Strelenko, Yu. A.; Novikova, T. S.; Khmelnitskii, L. I. Tetrahedron 1993, 49, 5905–5914.

[15] Sheremetev, A. B.; Kharitonova, O. V.; Nesterova, E. V.; Kulagina, V. O.; Shatunova, E. V.; Aleksandrova, N. S.; Melnikova, T. M.; Ivanova, E. A.; Dmitriev, D.

E.; Eman, V. A.; Kuzmin, V. S.; Novikova, T. S.; Lebedev, O. V. Zh Org Khim 1999, in press (in Russian).
[16] Sheremetev, A. B.; Novikova, T. S.; Khmelnitskii, L. I. The Conference on Aromatic Nucleophilic Substitution, Novosibirsk, USSR, June 13–15, 1989, 175 (in Russian).
[17] Sheremetev, A. B.; Nesterova, E. V. The First All-Union Conference on Theoretical Organic Chemistry, Volgograd, USSR, September 29–October 5, 1991, 120 (in Russian).
[18] Sheremetev, A. B.; Kulagina, V. O.; Ivanova, E. A. The Fifteenth International Congress of Heterocyclic Chemistry, Taipei, Taiwan, August 6–11, 1995, PO1-010.
[19] Sheremetev, A. B.; Kharitonova, O. V.; Melnikova, T. M.; Novikova, T. S.; Kuzmin, V. S.; Khmelnitskii, L. I. Mendeleev Commun 1996, 141–143.
[20] Sheremetev, A. B.; Kulagina, V. O.; Ivanova, E. A. J Org Chem 1996, 61, 1510–1511.
[21] Sheremetev, A. B.; Aleksandrova, N. S. Mendeleev Commun 1998, 238–239.
[22] Sheremetev, A. B.; Aleksandrova, N. S.; Novikova, T. S.; Khmelnitskii, L. I. Izv Akad Nauk SSSR Ser Khim 1989, 749 (in Russian), Bull Acad Sci USSR Div Chem Sci 1989, 38, 678.
[23] (a) Novikova, T. S.; Melnikova, T. M.; Kharitonova, O. V.; Kulagina, V. O.; Aleksandrova, N. S.; Sheremetev, A. B.; Pivina, T. S.; Khmelnitskii, L. I.; Novikov, S. S.; Mendeleev Commun 1994, 138–140; (b) Gunasekaran, A.; Trudell, T. L.; Boyer, J. H.; Heteroatom Chem 1994, 441–445; (c) Churakov, A. M.; Semenov, S. E.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovskii, V. A. Mendeleev Commun 1995, 102–103.
[24] Sheremetev, A. B.; Kharitonova, O. V.; Yudin, I. L.; Myasnikov, V. A.; Novikova, T. S.; Khmelnitskii, L. I.; Shitov, O. P.; Tartakovskii, V. A. Pat USSR 1752734, 1992, Chem Abst 1993, 119, 271166.
[25] Yudin, I. L.; Sheremetev, A. B.; Myasnikov, V. A.; Nesterova, E. V.; Shitov, O. P. Second Moscow Conference on Phase Transfer Catalysis, Moscow, Russia, 1994, 72 (in Russian).
[26] Myasnikov, V. A.; Yudin, I. L.; Sheremetev, A. B.; Shitov, O. P.; Tartakovskii, V. A.; Novikova, T. S.; Khmelnitskii, L. I. Pat USSR 1715808, 1992, Chem Abst 1992, 117, 234041.
[27] Myasnikov, V. A.; Yudin, I. L.; Sheremetev, A. B.; Shitov, O. P.; Tartakovskii, V. A.; Novikova, T. S.; Khmelnitskii, L. I. Pat USSR 1715809, 1992; Chem Abst 1992, 117, 191867.
[28] Churakov, A. M.; Ioffe, S. L.; Strelenko, Yu. A.; Tartakovsky, V. A. Tetrahedron Lett 1996, 37, 8577–8580.
[29] Solodyuk, G. D.; Boldyrev, M. D.; Gidaspov, B. V.; Nikolaev, V. D. Zh Org Khim 1981, 17, 861–866 (in Russian); Russ J Org Chem (Engl Transl) 1981, 17, 756–760.