Russian Chemical Bulletin, International Edition, Vol. 60, No. 8, pp. 1703—1711, August, 2011 1703

α-Nitroalkyl-*ONN*-azoxyfurazanes and some of their derivatives

O. A. Luk´yanov,* G. V. Pokhvisneva, T. V. Ternikova, N. I. Shlykova, and M. E. Shagaeva

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
E-mail: L120@ioc.ac.ru

A reaction of aminofurazanes with 2,2-dimethyl-5-nitro-5-nitroso-1,3-dioxane in the presence of dibromoisocyanurate furnished (2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-furazanes. Their reactions with AcCl/MeOH and subsequent transformations led to the first members of substituted mononitroalkyl- and (polynitroalkyl-*ONN*-azoxy)furazanes, *viz.*, 3-(nitromethyl-*ONN*-azoxy)-4-nitrofurazane, 3-(dinitromethyl-*ONN*-azoxy)-4-nitrofurazane, 3-(trinitromethyl-*ONN*-azoxy)-4-nitrofurazane, and some of their derivatives and analogs.

Key words: (2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)furazanes, (nitromethyl-*ONN*-azoxy)furazanes, (halonitromethyl-*ONN*-azoxy)furazanes, 3-(dinitromethyl-*ONN*-azoxy)-4-nitrofurazane, 3-(trinitromethyl-*ONN*-azoxy)-4-nitrofurazane, 3-(fluorodinitromethyl-*ONN*-azoxy)-4-nitrofurazane, nitration, halogenation, deoxymethylation, debromination.

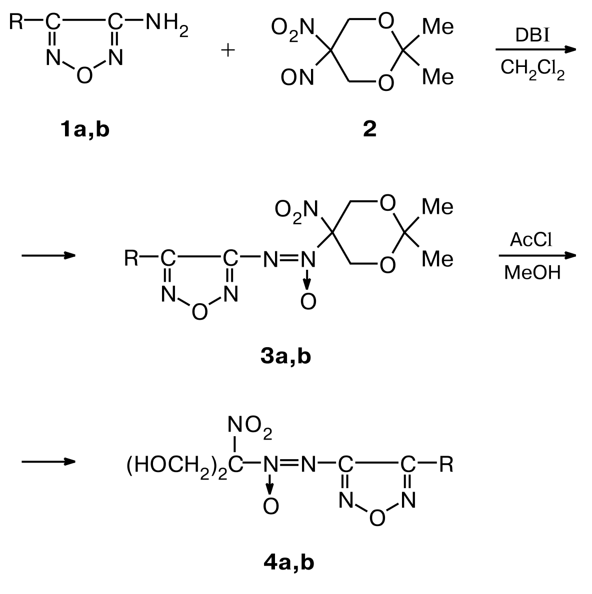
Earlier, it was shown that alkyl- and aryl-*NNO*-azoxy-α-nitro- and polynitroalkanes[1—3] are thermally quite stable compounds and in this property exceed the isomeric aryl-*ONN*-azoxy-α-polynitroalkanes.[4] In this connection, we attempted to synthesize α-nitro- and α-polynitroalkyl-*ONN*-azoxyfurazanes and some of their derivatives. Compounds of this type, when a combination of their composition and properties is favorable, can become very efficient energy-intensive compounds, including the rare enough representatives of stable organic oxidants with the positive enthalpies of formation. In the present work, we used the earlier found approach to the synthesis of aliphatic α-nitroalkyl-*ONN*-azoxy compounds and their derivatives[1] for the preparation of α-nitro- and α-polynitroalkyl-*ONN*-azoxyfurazanes.

In the full agreement with our expectations, 3-amino-4-methylfurazane (**1a**) and 3-amino-4-nitrofurazane (**1b**) smoothly reacted with 2,2-dimethyl-5-nitro-5-nitrosodioxane (**2**) in dichloromethane in the presence of dibromoisocyanurate (DBI) giving rise to the desired 2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxyfurazanes **3a**,**b** in 40—85% yields (Scheme 1).

The acetal fragment in compounds **3** is very labile and upon treatment with acetyl chloride in methanol for a short time is smoothly transformed to the bis-hydroxymethyl fragment, which is a part of (1,3-dihydroxy-2-nitropropyl-2-*ONN*-azoxy)furazanes **4a**,**b** formed by this reaction.

The thus obtained α-nitroalkyl-*ONN*-azoxyfurazane derivatives **3a**,**b** and **4a**,**b** are quite stable liquid (**4a**) or crystalline compounds with not very high (50—90 °C) melting points. Their structures were inferred from the elemental analysis data, IR and NMR spectroscopic data (Table 1), and results of subsequent chemical transformations.

Scheme 1



R = Me (**a**), NO_2 (**b**)

The yields (%): 41 (**3a**), 85 (**3b**), 89 (**4a**), 92 (**4b**).

As earlier,[1] we studied two main approaches to the transformation of dihydroxynitroisopropyl-*ONN*-azoxy compounds to the corresponding nitromethyl-*ONN*-azoxy compounds. The first approach consisted in the sequential

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1678—1686, August, 2011.

Table 1. Melting points, yields, the IR and ^{1}H ($CDCl_3$), ^{13}C, ^{14}N, and ^{19}F NMR spectroscopic data, and elemental analysis data for α-nitroalkyl-*ONN*-azoxyfurazanes and their derivatives

Compound	M.p. /°C	Yield (%)	Found / Calculated (%)				Molecular formula	IR ν/cm^{-1}	Solvent	NMR (δ, *J*/Hz)
			C	H	N	Br				
3a	54	41 (58*)	37.46 37.63	4.65 4.57	23.82 24.39	—	$C_9H_{13}N_5O_6$	—	Acetone-d_6	^{1}H: 1.52, 1.55 (both s, 3 H each, 2 Me); 2.47 (s, 3 H, Me)
3b	48—49 (from hexane)	85	30.14 30.20	2.69 3.17	26.04 26.41	—	$C_8H_{10}N_6O_8$	1384, 1584 (NO_2); 1204, 1504 (N_2O)	$CDCl_3$	^{1}H: 1.52, 1.54 (both s, 3 Heach, 2 Me); 4.82, 4.83 (both s, 2 H each, 2 CH_2)
4a	Oil	89	30.16 29.14	4.01 3.64	—	—	$C_6H_9N_5O_6$	—	Acetone-d_6	^{1}H: 2.42 (s, 3 H, Me); 4.65 (s, 4 H, 2 OCH_2); 5.25 (s, 2 H, 2 OH)
4b	87—89	92	21.48 21.59	1.78 2.17	29.14 30.22	—	$C_5H_6N_6O_8$	1352, 1572 (NO_2); 1056, 1524 (N_2O); 3312 (OH)	Acetone-d_6	^{1}H: 4.66 (d, 4 H, 2 CH_2, *J* = 5.4); 5.20 (t, 2 H, 2 OH, *J* = 5.4)
5a*	Oil	90	—	—	—	—	—	1340, 1565 (NO_2); 1055, 1500 (N_2O); 3100—3600 (OH)	CD_3CN	^{1}H: 2.30 (s, 3 H, Me); 4.82—3.7 (m, 3 H, CH_2OH); 6.69 (t, 1 H, $CHNO_2$, *J* = 6)
5b*	Oil	58, 74	—	—	—	—	—	—	$CDCl_3$	^{1}H: 2.79 (t, 1 H, OH); 4.69 (m, 2 H, CH_2); 6.60 (t, 1 H, CH)
6a	78—79	66.7	25.70 25.66	2.35 2.67	37.46 37.43	—	$C_4H_5N_5O_4$	—	$CDCl_3$	^{1}H: 2.52 (s, 3 H, Me); 6.45 (s, 2 H, CH_2)
6b	87—88	76—77	16.89 16.52	0.72 0.92	38.72 38.54	—	$C_3H_2N_6O_6$	—	$CDCl_3$ Acetone-d_6 DMSO-d_6	^{1}H: 6.5 (s, 2 H, CH_2); 7.25 (s, 2 H, CH_2) ^{13}C: 98.0; 125.5; 149.6
7a	68—69	88.7	14.21 13.91	0.85 0.86	20.24 20.29	46.04 46.37	$C_4H_3Br_2N_5O_4$	1320, 1600 (NO_2); 1204, 1524 (N_2O)	Acetone-d_6	^{1}H: 2.52 (s, 3 H, Me)
7b	Oil	74	9.89 9.59	—	22.15 22.36	42.53 42.52	$C_3Br_2N_6O_6$	—	$CDCl_3$	^{13}C: 129.4; 148.5; 155.0 ^{14}N: −45.8; −39.23; −24.71
7c	64.5—66.5	14.3	18.91 18.77	1.08 1.18	27.54 27.36	28.67 27.70	$C_4H_3N_5O_4Cl_2$	—	$CDCl_3$	^{1}H: 2.52 (s, 3 H, Me)
8b*	Oil		—	—	—	—	—	—	$CDCl_3$	^{1}H: 3.65 (br.m, 1 H, OH);4.82 (d, 2 H, CH_2)
10	Oil	27, 59	20.80 20.70	1.81 1.74	36.68 26.21	—	$C_4H_4N_6O_6$	—	$CDCl_3$	^{1}H: 2.29 (d, 3 H, Me, *J* = 6.3); 6.60 (q, 1 H, CH, *J* = 6.3)
11	Oil	30	24.29 24.40	2.63 2.46	34.53 34.19	—	$C_5H_6N_6O_6$	1376, 1576 (NO_2); 1076, 1508 (N_2O)	$CDCl_3$	^{1}H: 2.35 (s, 6 H, 2 Me)
13	Oil	18, 39	17.44 17.33	0.93 1.08	35.23 35.38	—	$C_4H_3N_7O_8$	—	$CDCl_3$	^{1}H: 2.91 (s, 3 H, Me)
16	70—71	80	13.72 13.69	0.35 0.38	37.18 37.26	—	$C_3HN_7O_8$	1344, 1596, 1608 (NO_2); 1184, 1520 (N_2O)	$CDCl_3$	^{1}H: 7.86 (s, 1 H, CH) ^{14}N: −39.67 (s, 2 NO_2); −39.60 (s, NO_2); −64.90 (br.s, N_2O)
K-**16**	157 (decomp.)	95	12.36 11.96	—	32.04 32.56	—	$C_3N_7O_8K$	1128, 1168, 1200, 1296, 1312, 1476, 1500, 1532, 1580	$CDCl_3$	
NH_4-**16**	129 (decomp.)	91	12.97 12.86	1.40 1.44	39.43 40.00	—	$C_3H_4N_8O_8$	1352, 1576 (NO_2); 1288, 1500 (N_2O)	—	—
17a	51—53	20	15.52 15.45	0.92 0.97	26.52 27.03	25.26 25.69	$C_4H_3N_6O_6Br$	1620 (NO_2) 1044, 1520 (N_2O)	$CDCl_3$	^{1}H: 2.43 (s, 3 H, Me)

(*to be continued*)

Table 1 (*continued*)

Compound	M.p. /°C	Yield (%)	Found / Calculated (%) C	H	N	Br	Molecular formula	IR ν/cm^{-1}	Solvent	NMR (δ, *J*/Hz)
17b	Oil	34	10.92 10.54	—	28.23 28.67	23.42 23.37	$C_3N_7O_8Br$	—	$CDCl_3$	^{13}C: 121.62; 147.62; 155.07 ^{14}N: –36.11 (2 NO_2); –40.24 (NO_2); –57.84 (N_2O)
18	Oil	48	12.81 13.10	—	34.88 34.86	—	$C_3N_7O_8F$	—	$CDCl_3$	^{13}C: 114.0 (d, $J_{^{13}C,F}$ = 324.85; 147.0 (s, C(3)); 155.1 (t, C(4), *J* = 18.3); ^{14}N: –65.85 (br.s, N→O); –41,63 (s, 1 N, NO_2); –41.10 (s, 2 N, 2 NO_2); ^{19}F: –91.20 (s, F)
19	Oil	84	—	—	36.31 36.36	—	$C_3N_8O_{10}$	—	$CDCl_3$	^{13}C: 118.52 (br.); 147.02; 155.14 ^{14}N: –40.31 (NO_2); –48.65 (3 NO_2); –70 (br., N_2O)

* Unstable compounds.

dehydroxymethylation. For this purpose, the diols **4a**,**b** were treated with one equivalent of NaOH or KOH in anhydrous EtOH, which led to the isolation of low stable yellow salts of 3-(2-hydroxy-1-nitroethyl-1-*ONN*-azoxy)-4-methylfurazane Na-**5a** or 4-nitrofurazane (K-**5b**) in ~80% yield.

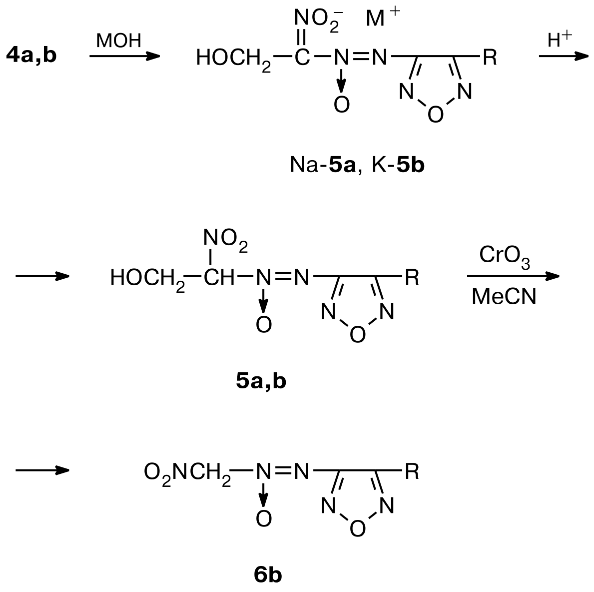
Treatment of the thus obtained salts with aqueous mineral acids or gaseous HCl in anhydrous diethyl ether (until a precipitate became colorless) led to the isolation of the corresponding 3-(2-hydroxy-1-nitroethyl-1-*ONN*-azoxy)furazanes **5a**,**b**, which are dense low stable oils. Their structures were inferred from the IR and ^{1}H NMR spectroscopic data (Table 1) and results of subsequent transformations (Scheme 2).

Compound **5b** was taken as an example to establish that such nitro alcohols are smoothly enough oxidized by the Jones reagent, apparently, to the corresponding unstable carboxylic acid, whose decarboxylation results in the desired 3-(nitromethyl-*ONN*-azoxy)-4-nitrofurazane (**6b**) in 77% yield.

The second approach to the synthesis of nitromethyl-*ONN*-azoxyfurazanes consisted in the sequential exhaustive bromination of dihydroxynitroisopropyl-*ONN*-azoxy compounds **4a**,**b** in alkaline medium and debromination of the thus formed dibromonitromethyl-*ONN*-azoxyfurazanes **7a**,**b**.

It was found that both dihydroxynitroisopropyl-*ONN*-azoxyfurazanes **4a**,**b** and the products of their monodehydroxymethylation **5a**,**b**, as well as their salts, can be used as the starting compounds for the synthesis of the desired dihalonitromethyl-*ONN*-azoxyfurazanes **7a**,**b** (Scheme 3).

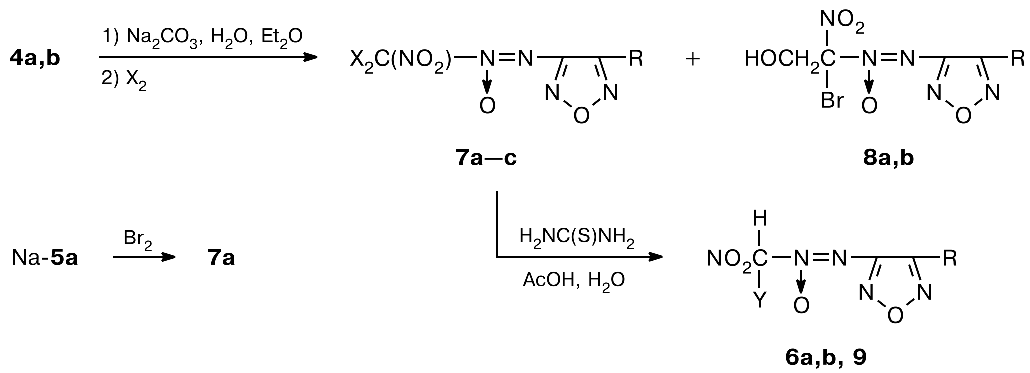
Scheme 2



M = Na, K
R = Me (Na-**5a**, **5a**), NO_2 (K-**5b**, **5b**, **6b**)

The yields (%): 90 (**5a**), 58 (**5b**), 77 (**6b**).

Scheme 3



R = Me (**6a**, **7a,c**, **8a**), NO_2 (**6b**, **7b**, **8b**, **9**); X = Br (**7a,b**), Cl (**7c**); Y = H (**6a,b**), Br (**9**)

The yields (%): 89 (**7a**), 74 (**7b**), 14.3 (**7c**), 66.7 (**6a**), 76 (**6b**)

Elementary bromine or chlorine in the presence of inorganic bases were used as halogenating agents. Treatment of **4b** with an excess of Na_2CO_3 in the water—diethyl ether two-phase system and subsequent reaction with bromine gave, depending on the conditions, either 3-(dibromonitromethyl-*ONN*-azoxy)-4-nitrofurazane (**7b**) or its mixture with the product of the preceding step, *i.e.*, 3-(1-bromo-2-hydroxy-1-nitroethyl-*ONN*-azoxy)-4-nitrofurazane (**8b**), as the major reaction products. Predominant (or in a number of cases, exclusive) formation of dibromide **7b** was facilitated by the increase in the reaction time of **4b** with the base, as well as by the increase in the temperature of bromination to 25—30 °C. The yield of **7b** reached 70—74% with the virtually complete absence of monobromide **8b** among the reaction products (Table 2).

In principle, the same picture was observed in the bromination of **4a** under similar conditions, however, the maximum yield of **7a** was only 30%. At the same time, if a preliminary isolated sodium salt of 3-(2-hydroxy-1-nitroethyl-1-*ONN*-azoxy)-4-methylfurazane Na-**5a** was used for the bromination in water in the presence of a three-fold excess of Na_2CO_3, the dibromide **7a** was formed in 89% yield.

Table 2. Yields of 3-(dibromonitromethyl-*ONN*-azoxy)-4-nitrofurazane (**7b**) and 3-(1-bromo-2-hydroxy-1-nitroethyl-*ONN*-azoxy)-4-nitrofurazane (**8b**) on bromination of 3-(1,3-dihydroxy-2-nitropropyl-2-*ONN*-azoxy)-4-nitrofurazane **4b** in the presence of Na_2CO_3

Na_2CO_3 : **4b** mol/mol	*T*/°C	*t*/min	*T*´/°C	Yield (%)	
				7b	**8b**
10 : 1	0	10	0—5	28	37
—	20	15	20	34	15
—	5—8	180	20	35	—
—	5—8	20	10	48	21
—	17	25	20	51	—
12 : 1	7—10	20	25—30	68	—
11 : 1	7—10	20	20—30	74	—

Note. *T* is the temperature of the reaction of **4b** with Na_2CO_3, *t* is the reaction time, *T*´ is the temperature of the reaction with bromine.

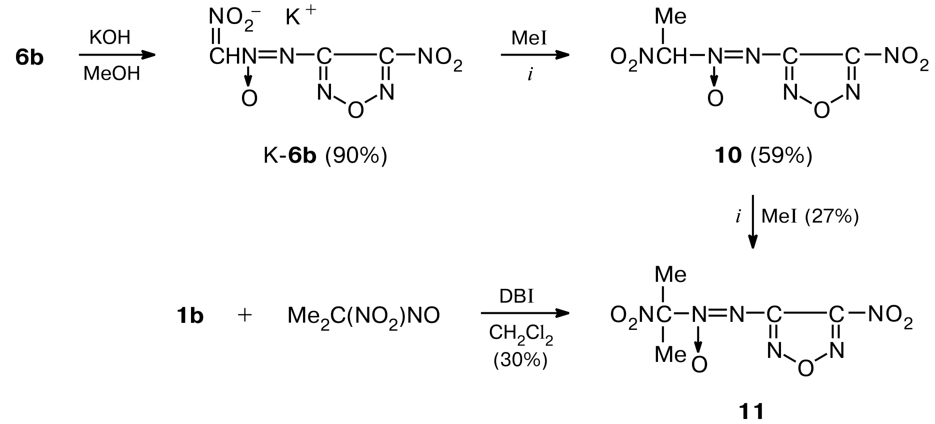
When a reduction reaction of the described above bromonitroalkyl-*ONN*-azoxyfurazanes with thiourea in AcOH was studied, it was found that this reactant is an excellent reducing agent for these compounds and allows one to obtain the products of debromination **6a,b** in more than 70% yield (see Scheme 3).

When the dibromide **7b** was reduced, an instantaneous disappearance of the starting compound from the reaction mixture and formation of the product **6b** (isolated in 76% yield) were observed already after addition of the equimolar amount of thiourea at 20 °C in aqueous acetic acid. Note that the formation of the intermediate 3-(bromonitromethyl-*ONN*-azoxy)-4-nitrofurazane (**9**) was detected only when 0.5 mol of thiourea per 1 mol of the starting compound **7b** was used. Compound **9** is a crystalline substance. Its structure was inferred from the ^{1}H NMR spectral data and the fact of its transformation to nitrofurazane **6b** upon the action of thiourea.

Comparison of the two considered approaches to the preparation of compound **6** allows one to conclude on the preference of the bromide version, since the total yield of **6** from the diol **4** in this case exceeded 50%, while in the synthesis of compounds **6** with oxidation of the intermediate monool **5**, the yield is around 35%.

The thus obtained nitromethyl-*ONN*-azoxyfurazanes **6a**,**b** are relatively stable crystalline compounds; they manifest chemical properties typical of polynitro compounds with labile α-hydrogen atom, though significant differences also exist. For instance, treatment of **6b** with potassium hydroxide in methanol leads to potassium salt of 3-(nitromethyl-*ONN*-azoxy)-4-nitrofurazane (K-**6b**) in more than 90% yield (Scheme 4).

Scheme 4



i. 18-Crown-6.

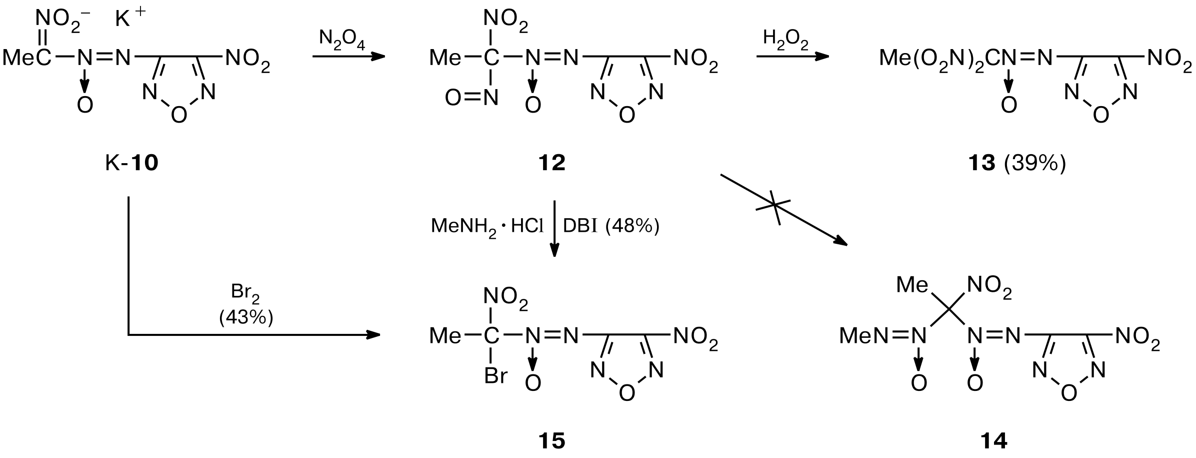
This salt undergoes methylation by the excess of methyl iodide in the presence of 18-crown-6, and the result strongly enough depends on the reaction time. After the first four hours, the major reaction product is 3-(1-nitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (**10**) (60% yield), whereas after 16 h, the reaction gives a mixture of **10** and 3-(2-nitropropyl-2-*ONN*-azoxy)-4-nitrofurazane (**11**), resulted from further methylation of **10**. The structure of compound **11** was confirmed by its alternative synthesis from isopropylpseudonitrol and **1b** in the presence of DBI (see Scheme 4).

Compound **10**, similarly to primary nitro compounds, form relatively stable salts upon the action of inorganic bases, including NH_3. Treatment of the potassium salt K-**10** with N_2O_4 leads to the low stable dark blue 3-(1-nitro-1-nitrosoethyl-1-*ONN*-azoxy)-4-nitrofurazane **12**, which can be oxidized with H_2O_2 to 3-(1,1-dinitroethyl-1-*ONN*-azoxy)-4-nitrofurazane **13** (Scheme 5).

We attempted to obtain derivative of nitroethyl-1-bis(*ONN*-azoxy)furazane **14** by sequential treatment of K-**10** with N_2O_4 and then $CH_3NH_2 \cdot HCl$ and DBI. However, only 3-(1-bromo-1-nitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (**15**) was isolated from the reaction products instead of compound **14**. The question on the exclusive pathway for the formation of **15** remains yet open, since it is easy formed by bromination of K-**10**, whereas the pseudonitrol **12** was not isolated in the individual state because of its low stability. At the same time, a possibility of substitution for the nitroso group in pseudonitrol by bromine in the reactions involving DBI has been already reported earlier.[5]

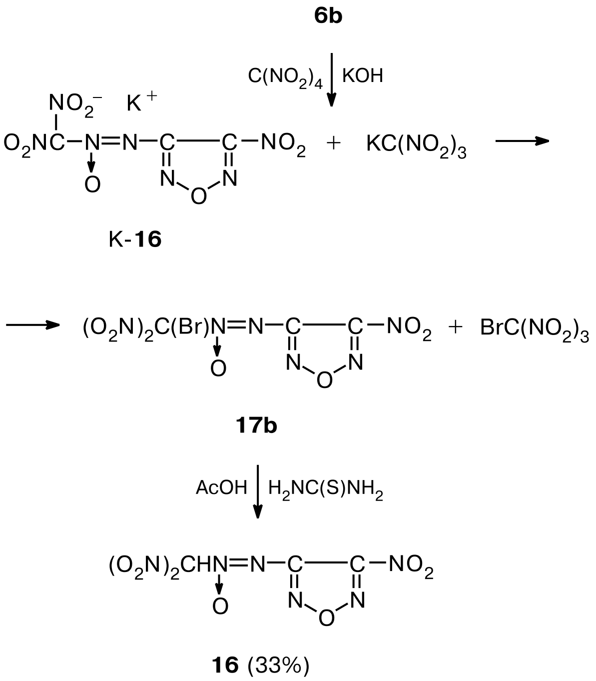
The method for the preparation of 3-(1,1-dinitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (**13**) described above cannot be used for the synthesis of 3-(dinitromethyl-*ONN*-azoxy)-4-nitrofurazane (**16**) as the first member in the series of 3-(dinitroalkyl-*ONN*-azoxy)-4-R-furazanes. For the synthesis of furazane **16** we used the reaction of alkaline nitration of nitro compounds with tetranitromethane. The reaction conditions were the same as in the nitration of 2-methyl-1-nitromethyldiazene 1-oxide used earlier,[1]

Scheme 5



i.e., tetranitromethane and then KOH in methanol were sequentially added to a solution of the starting **6b** in methanol with cooling by ice. However, in the case of 2-methyl-1-nitromethyldiazene 1-oxide nitration took place already at 0 °C with the rapid formation of a precipitate of the dinitro compound potassium salt, in the case of nitration of **6b**, right after mixing the starting reactants a poorly soluble in methanol potassium salt of **6b** (K-**6b**) formed a precipitate, and its complete nitration required approximately 1 day at room temperature. Addition of acetonitrile to the reaction mixture dissolved the salt, that considerably accelerated the nitration. A direct isolation of the dinitro compound from the reaction mixture seemed quite difficult because of the parallel formation of the trinitromethane salt, therefore, the reaction products were subjected to bromination and the thus obtained bromodinitromethylazoxy product **17** was isolated by TLC in 34% yield (Scheme 6).

Scheme 6



It should be noted that, together with **17**, a dibromonitro compound **7b** was also isolated, however, only in 2% yield, that indicates that the starting compound **6b** was almost completely involved into the reaction.

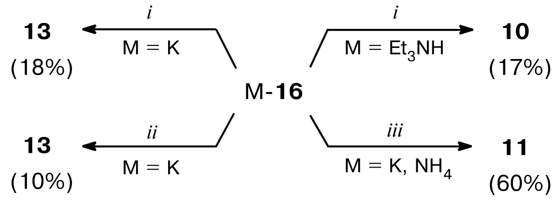
Treatment of bromide **17** with thiourea in acetic acid instantly reduced it to give the desired dinitromethylazoxy compound **16**, the latter is a crystalline compound with m.p. 70—71 °C (33% yield).

We studied some chemical properties of **16**. As it was expected, this compound readily forms comparably stable bright orange salts with NH_3, KOH, and other bases. These salts, similarly to the salts of gem-dinitro compounds, can be involved into methylation reactions, but results of such transformations have proved poorly predictable. When potassium, triethylammonium, or morpholinium salts of **16** (the latter two salts were obtained *in situ*) were treated with methyl iodide in methanol, acetonitrile, or dichloromethane for 1 day at 20 °C, formation of methylation products in only trace amounts was observed, however, methylation of K-**16** in acetonitrile for 8 days leads to the formation of dinitroethyl derivative **13** in 18% yield. Another result was observed in methylation of triethylammonium salt of **16** (**16** • Et_3NH); in this case, **13** was obtained only in trace amount, whereas the denitrated **10** was the major reaction product in 17% yield.

On the solvent-free methylation of K-**16** or NH_4-**16** with methyl iodide taken in excess amount in the presence of 18-crown-6, the reaction came to completion within few hours giving a nitropropyl derivative **11** as the product (60% yield).

To sum up, for obtaining a primary methylation product of **16**, the reaction with methyl iodide should be carried out in solvents, however, the yield of the desired dinitro derivative **13** does not exceed 20%. Yet less satisfactory result was obtained when dimethyl sulfate was used as a methylating agent: after heating of compound K-**16** with $(CH_3O)_2SO_2$ in acetone at 50 °C for 3 days, the product **13** was obtained in ~10% yield (Scheme 7).

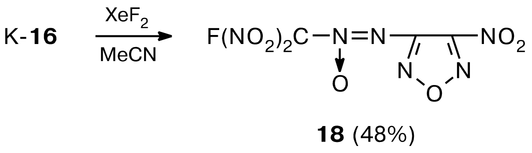
Scheme 7



Conditions: *i.* MeI, MeCN; *ii.* Me_2SO_4, Me_2CO; *iii.* MeI, 18-crown-6.

Halogenation reactions of salts **16** proceed significantly more rapidly and selectively. Even with xenon difluoride, the process comes to completion after heating at 50 °C for 4 h and subsequent storage at 20 °C for 15 h. The yield of the thus obtained 3-(fluorodinitromethyl-*ONN*-azoxy)-4-nitrofurazane (**18**) was 48% (Scheme 8). It was a quite stable oilish product.

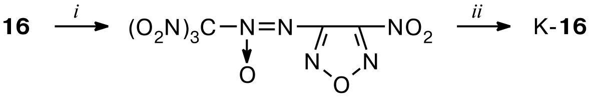
Scheme 8



18 (48%)

The nitration reaction of **16** to 3-(trinitromethyl-*ONN*-azoxy)-4-nitrofurazane (**19**) proceeds even smoother, it requires heating of **16** with the H_2SO_4—HNO_3 mixture for 2 h at 70 °C and gives the product in 84% yield (Scheme 9).

Scheme 9



19 (84%)

Reagents and conditions: *i.* HNO_3, H_2SO_4, 70 °C, 2 ч; *ii.* KOH.

The latter is also a liquid compound; its structure was inferred from the elemental analysis and IR spectral data, as well as based on its transformation to K-**16** upon the action of KOH.

In conclusion, we developed methods for the synthesis of 3-(nitromethyl-*ONN*-azoxy)-, dinitromethyl-*ONN*-azoxy)-, or 3-(trinitromethyl-*ONN*-azoxy)-4-R-furazanes, as well as some of their derivatives and analogs.

Experimental

The reaction progress was monitored by TLC on Silufol UV-254 plates. IR spectra were recorded on a UR-20 spectrometer. ^1H NMR spectra were recorded on a Bruker-AM-300 spectrometer. Melting points were determined on a Kofler heating stage. Dibromoisocyanurate,[6] 2,2-dimethyl-5-nitro-5-nitroso-1,3-dioxane (**2**),[7] 3-amino-4-methylfurazane (**1a**),[8] and 3-amino-4-nitrofurazane (**1b**)[9] were synthesized according to the described procedures. Physicochemical characteristics for the compounds obtained are given in Table 1.

3-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-4-methylfurazane (3a). A solution of compound **1a** (1.53 g, 15 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **2** (2 g, 10.5 mmol) and DBI (6.08 g, 21 mmol) in anhydrous CH_2Cl_2 (27 mL) at 20 °C over 1 h, then the mixture was stirred for 1 h, a precipitate was separated, the filtrate was washed with aqueous Na_2CO_3, dried with Na_2SO_4, and the solvent was evaporated. The residue was diluted with a small amount of diethyl ether, a precipitate of unreacted **2** (0.58 g) was separated, the filtrate was subjected to column chromatography on silica gel (benzene) to isolate **3a** (1.19 g, 41%).

3-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)-4-nitrofurazane (3b). The compound **1a** (2 g, 15.38 mmol) and DBI (5.3 g, 18.47 mmol) were added to a solution of **2** (2.92 g, 15.38 mmol) in anhydrous CH_2Cl_2 (50 mL) at 20 °C. The reaction mixture was stirred for 24 h at 20 °C, passed through the layer of SiO_2, additionally washed with CH_2Cl_2, the solvent was evaporated, and the residue was crystallized by rubbing under the layer of hexane. The yield was 4.16 g (85%).

3-(1,3-Dihydroxy-2-nitropropyl-2-*ONN*-azoxy)-4-methylfurazane (4a). Acetyl chloride (6.86 mL) was added dropwise to a solution of **3a** (1.08 g, 3.76 mmol) in MeOH (17.5 mL) at 20 °C, the mixture was stirred for 1 h, the volatile products were removed *in vacuo*. The residue was subjected to preparative TLC to isolate **4a** (0.83 g, 89%) as an oil.

3-(1,3-Dihydroxy-2-nitropropyl-2-*ONN*-azoxy)-4-nitrofurazane (4b). Acetyl chloride (11 mL, 12.16 g, 15.5 mmol) was added to a solution of **3b** (3.24 g, 10.19 mmol) in MeOH (50 mL), the mixture was stirred for 0.5 h at 20 °C, the volatile products were removed *in vacuo*. The residue was crystallized by rubbing under the layer of CCl_4 to yield compound **4b** (2.6 g, 92%), m.p. 87—89 °C.

3-(2-Hydroxy-1-nitroethyl-1-*ONN*-azoxy)-4-methylfurazane (5a). A solution of NaOH (0.056 g, 1.4 mmol) in EtOH (20 mL) was added dropwise to a solution of **4a** (0.35 g, 1.41 mmol) in anhydrous EtOH (15 mL). A precipitate that formed was filtered off and washed with diethyl ether to obtain Na-**5a** (0.28 g, 84%), m.p. 185—190 °C (with decomp.). ^1H NMR (D_2O), δ: 2.22 (s, 3 H, Me); 4.82 (s, 2 H, CH_2). A dry gaseous HCl was bubbled through a suspension of the salt in anhydrous diethyl ether with cooling until the yellow precipitate turned colorless. The filtrate was concentrated to yield **5a** (0.23 g, 90%) as a dense yellowish oil.

3-(2-Hydroxy-1-nitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (5b). A solution of KOH (0.16 g, 2.86 mmol) in EtOH (2 mL) was added to a solution of **4b** (0.8 g, 2.88 mmol) in EtOH (4 mL) at 5—7 °C. An orange salt that formed was filtered off, washed with diethyl ether, dissolved in H_2O (4 mL), acidified with concentrated H_2SO_4 to pH ~1. The colorless solution was extracted with CH_2Cl_2 (3×3 mL), the extracts were dried with $MgSO_4$ and the solvent was evaporated to obtain **5b** (0.41 g, 58%) as an oil, which was used for oxidation.

3-(Nitromethyl-*ONN*-azoxy)-4-methylfurazane (6a). A solution of thiourea (0.1 g, 1.3 mmol) in H_2O (4.5 mL) was added to a solution of **7a** (0.45 g, 1.3 mmol) in AcOH (2.25 mL) at 20 °C and the reaction mixture was stirred for 30 min, followed by dilution with water (10 mL) and extraction of the product with CH_2Cl_2 (3×10 mL). The extracts were dried with Na_2SO_4, the volatile products were removed *in vacuo*, and the residue was subjected to preparative TLC on silica gel (benzene—acetone, 6 : 1) to isolate **6a** (0.16 g, 66.7%), m.p. 78—79 °C (from CCl_4).

3-(Nitromethyl-*ONN*-azoxy)-4-nitrofurazane (6b). ***A.*** The Jones reagent (1 mL) (prepared from 7 g of CrO_3, 50 mL of H_2O, 6 mL of conc. H_2SO_4) was added to a solution of **5b** (0.55 g) in MeCN (10 mL) and the reaction mixture was stirred for 3—4 h at 50 °C until **5b** disappeared (TLC monitoring). The solution was filtered, the filtrate was concentrated to dryness, the residue was dissolved in H_2O (10 mL), extracted with CH_2Cl_2 (3×6 mL), dried with $MgSO_4$, concentrated to dryness, treated with hexane, and filtered to obtain **6b** (0.37 g, 77%), m.p. 87—88 °C (with decomp., from hexane).

B. A solution of thiourea (0.15 g, 1.97 mmol) in H_2O (10 mL) was added to a solution of **7b** (0.73 g, 1.94 mmol) in glacial AcOH (5 mL) at 20 °C. The reaction mixture was stirred for 10 min, diluted with H_2O (20 mL), and extracted with CH_2Cl_2 (3×20 mL). The extracts were dried with $MgSO_4$, concentrated to dryness, treated with hexane, and filtered to obtain **6b** (0.32 g, 76%), which was identical to the sample described above.

3-(Nitromethyl-*ONN*-azoxy)-4-nitrofurazane potassium salt (K-6b). A solution of KOH (0.112 g, 2.0 mmol) in MeOH (2 mL) was added dropwise to a solution of **6b** (0.4 g, 1.83 mmol) in MeOH (2 mL) cooled with ice. An orange precipitate that formed was filtered, washed with anhydrous diethyl ether, and dried in air to obtain K-**6b** (0.42 g, 90%). ^{1}H NMR ($CDCl_3$), δ: 8.5 (s, 1 H, CH).

3-(Dibromonitromethyl-*ONN*-azoxy)-4-methylfurazane (7a). Bromine was added to a solution of Na salt of **5a** (0.37 g, 1.54 mmol) and Na_2CO_3 (0.48 g, 4.5 mmol) in H_2O (18 mL) with stirring until discoloring stopped. The reaction mixture was extracted with CH_2Cl_2, the extracts were washed with water, dried with Na_2SO_4, and subjected to preparative TLC on silica gel (benzene) to isolate **7a** (0.47 g, 88.7%), m.p. 68—69 °C (from hexane).

3-(Dibromonitromethyl-*ONN*-azoxy)-4-nitrofurazane (7b). A solution of Na_2CO_3 (8.4 g, 79 mmol) in H_2O (50 mL) was added to a solution of **4b** (2 g, 7.2 mmol) in diethyl ether (50 mL) at 7—10 °C. The reaction mixture was stirred at 10—15 °C for 20 min, then Br_2 was added dropwise at 20—30 °C until discoloring stopped. The ethereal layer was separated, the aqueous layer was extracted with diethyl ether (20 mL). The ethereal layers were combined, passed through a column with silica gel, and concentrated to obtain **7b** (2 g, 74%) as an oil.

3-(Dichloronitromethyl-*ONN*-azoxy)-4-methylfurazane (7c). An aq. NaOH (0.27 g, 7 mmol) was added to a solution of **4a** (0.27 g, 0.1 mmol) in diethyl ether (7 mL), followed by bubbling Cl_2 through the emulsion with vigorous stirring until it turned colorless. The ethereal layer was separated, the aqueous was extracted with diethyl ether, the ether was evaporated, and the residue was subjected to preparative TLC on silica gel (benzene—hexane, 2 : 1) to isolate **7c** (0.04 g, 14.3%), m.p. 64.5—66.5 °C.

3-(1-Nitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (10). 18-Crown-6 (0.09 g of the complex with acetonitrile) was added to a suspension of (K-**6b**) (0.094 g) in MeI (10 mL) and the mixture was stirred for 4 h at 20 °C. Compound **10** was isolated by preparative TLC (0.05 g, 59%).

3-(1-Nitroethyl-1-*ONN*-azoxy)-4-nitrofurazane potassium salt (K-10). Finely powdered KOH (0.025 g, 0.45 mmol) was added to a solution of **10** (0.1 g, 0.43 mmol) in MeCN (15 mL) at 20 °C and the reaction mixture was stirred for 30 min, followed by filtration. The filtrate was concentrated to dryness and washed with anhydrous diethyl ether to obtain K-**10** (0.099 g, 85%).

3-(2-Nitroisopropyl-2-*ONN*-azoxy)-4-nitrofurazane (11). ***A.*** 3-Amino-4-nitrofurazane (0.2 g, 1.54 mmol) and DBI (0.5 g, 1.74 mmol) were added to a solution of 2-nitro-2-nitrosopropane (0.18 g, 1.52 mmol) in MeCN (10 mL) at 20 °C and the reaction mixture was stirred for 4 h. A precipitate was filtered off, the filtrate was concentrated, and the residue was subjected to preparative TLC on silica gel (benzene—hexane, 2 : 1) to isolate **11** (0.13 g, 30%).

B. 18-Crown-6 (0.04 g of the complex with acetonitrile) was added to a suspension of K-**6b** (0.04 g) in CH_3I (5 mL). The reaction mixture was stirred for 16 h at 20 °C, concentrated to dryness, dissolved in CH_2Cl_2 (10 mL), washed with saturated aq. Na_2SO_3 (2 mL) and water, dried with $MgSO_4$, and subjected to preparative TLC in benzene to isolate **11** (0.01 g, 27%) and **10** (0.01 g, 30%).

3-(1,1-Dinitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (13). ***A.*** Methyl iodide (0.2 mL, 0.45 g, 3.2 mmol) was added to a solution of K-**16** (60 mg, 0.2 mmol) in MeCN (5 mL). The reaction mixture was stirred for 8 days at 20 °C, diluted with water, and extracted with CH_2Cl_2 (2×5 mL). The extracts were dried with $MgSO_4$ and subjected to preparative TLC to isolate **13** (10 mg, 18%).

B. A solution of N_2O_4 in CH_2Cl_2 (0.03 mL, containing 0.08 mmol of N_2O_4) was added to a suspension of K-**10** (10 mg, 0.037 mmol) in CH_2Cl_2 (3 mL) at −40 °C. The mixture was stirred for another 30 min at −40 °C, then the cooling was removed, a few drops of 35% aq. H_2O_2 was added, and the mixture was stirred until the blue color disappeared. The organic layer was subjected to preparative TLC to isolate **13** (4 mg, 39%).

3-(1-Bromo-1-nitroethyl-1-*ONN*-azoxy)-4-nitrofurazane (15). ***A.*** A saturated aq. Na_2CO_3 was added to a solution of K-**10** (0.04 g, 0.15 mmol) in H_2O (2 mL) to pH ~8—9, followed by addition of Br_2 (0.01 mL, 0.03 g, 0.2 mmol). The reaction mixture was stirred for 30 min at 20 °C, extracted with CH_2Cl_2 (2×3 mL), the extract was dried with $MgSO_4$, concentrated, and subjected to preparative TLC in benzene to isolate **15** (0.02 g, 43%) as an oil.

B. A solution of N_2O_4 (0.02 g, 0.22 mmol) in CH_2Cl_2 was added to a suspension of K-**10** (0.06 g, 0.22 mmol) in CH_2Cl_2 (3 mL) at −40 °C, the reaction mixture was stirred for 30 min at −40 °C and filtered, followed by addition of DBI (0.065 g, 0.23 mmol) and $MeNH_2 \cdot HCl$ (0.02 g, 0.3 mmol) to the blue filtrate containing **12**. The cooling was removed, the reaction mixture was stirred for 30 min, filtered through the layer of silica gel, and concentrated to dryness. The residue was subjected to preparative TLC to isolate **15** (0.033 g, 48%).

3-(Dinitromethyl-*ONN*-azoxy)-4-nitrofurazane (16). A solution of thiourea (6 mg, 0.08 mmol) in H_2O (1 mL) was added to a solution of **17b** (40 mg, 0.12 mmol) in AcOH (0.5 mL) at 20 °C. After 5 min, the reaction mixture was diluted with water (5 mL) and extracted with CH_2Cl_2 (4×3 mL). The extracts were dried with $MgSO_4$, concentrated to dryness, diluted with CCl_4, and again concentrated to dryness. The residue was subjected to preparative TLC to isolate **16** (0.01 g, 30%), m.p. 70—71 °C.

3-(Dinitromethyl-*ONN*-azoxy)-4-nitrofurazane potassium salt (K-16). ***A.*** Finely powdered KOH (0.021 g, 0.38 mmol) was added to a solution of **16** (0.1 g, 0.38 mmol) in anhydrous MeCN (3 mL). The mixture was stirred at 20 °C until **16** disappeared (TLC, 20 min), filtered, the solvent was evaporated, and the yellow crystals of K-**16** were washed with anhydrous diethyl ether to yield K-**16** (0.108 g, 95%), m.p. 157 °C (decomp.).

B. Finely powdered KOH (5 mg, 0.089 mmol) was added to a solution of **19** (20 mg, 0.065 mmol) in MeOH, the reaction mixture that obtained was stirred at 20 °C for 5 h, concentrated to dryness, and washed with diethyl ether to obtain K-**16** (19 mg, 97%).

3-(Dinitromethyl-*ONN*-azoxy)-4-nitrofurazane ammonium salt (NH_4-16). A solution of **16** (0.052 g, 0.02 mmol) in CH_2Cl_2 (2 mL) was stirred for 10 min under ammonia atmosphere, a salt that formed was separated and washed with diethyl ether to obtain NH_4-**16** (0.05 g, 91%), m.p. 129 °C (decomp.).

3-(Bromodinitromethyl-*ONN*-azoxy)-4-methylfurazane (17a). Tetranitromethane (0.9 mL, 0.3 mmol) was added to a suspension of potassium salt of **6a** (0.11 g, 0.48 mmol), sodium acetate (0.06 g, 0.7 mmol) and 18-crown-6 • CH_3CN (0.03 g, 0.1 mol) in anhydrous CH_3CN (4 mL) at 0—5 °C, the mixture was stirred for 30 min at 0 °C and 1 h at 20 °C. Then bromine was added until discoloring stopped, CH_3CN was evaporated, and the residue was extracted with CH_2Cl_2. The extract was subjected to preparative TLC in benzene to isolate **17a** (0.03 g, 20%), m.p. 51—53 °C.

3-(Bromodinitromethyl-*ONN*-azoxy)-4-nitrofurazane (17b). Tetranitromethane (0.58 mL, 0.95 g, 4.8 mmol) and a solution of KOH (0.16 g, 2.86 mmol) in MeOH (3 mL) were sequentially added to a solution of potassium salt of **6b** (0.16 g, 0.73 mmol) in MeOH (5 mL) with cooling by ice. The reaction mixture was stirred for 1 h, diluted with MeCN (until the precipitate was dissolved, ~5 mL), and left for 16 h to stand. Then bromine was added until discoloring stopped, the mixture was concentrated to dryness, the residue was extracted with CH_2Cl_2 (10 mL), the extract was washed with water, dried, the solvent was evaporated. The residue was subjected to preparative TLC to isolate **17b** (0.085 g, 34%) as an oil.

3-(Fluorodinitromethyl-*ONN*-azoxy)-4-nitrofurazane (18). A mixture of K-**16** (0.108 g, 0.36 mmol) and XeF_2 (0.012 g, 0.72 mmol) in anhydrous MeCN (2 mL) was stirred for 4 h at 50 °C and kept for 16 h at 20 °C. The solvent was evaporated and the residue was subjected to preparative TLC on silica gel (benzene—hexane, 1 : 1) to isolate **18** (0.048 g, 48%) as an oil.

3-(Trinitromethyl-*ONN*-azoxy)-4-nitrofurazane (19). The compound **16** (0.05 g, 0.19 mmol) was added to a mixture of conc. HNO_3 (0.5 mL) and conc. H_2SO_4 (0.5 mL) with cooling, the reaction mixture was heated for 2 h at 70 °C, cooled and poured on ice, then it was extracted with CH_2Cl_2 (2×5 mL), the extracts were washed with water, dried with $MgSO_4$, the solvent was evaporated. The residue was subjected to preparative TLC on silica gel to isolate **19** (0.049 g, 84%) as an oil.

The authors are grateful to E. D. Lubuzh and M. I. Struchkova for the recording IR and ^{1}H NMR spectra.

References

1. O. A. Luk´yanov, G. V. Pokhvisneva, T. V. Ternikova, N. I. Shlykova, Yu. B. Salamonov, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 2000 [*Russ. Chem. Bull.*, *Int. Ed.*, 2009, **58**, 2063].
2. 2. O. A. Luk´yanov, Y. B. Salamonov, Y. T. Struchkov, Y. N. Burtsev, V. S. Kuz´min, *Mendeleev Commun.*, 1992, 52.
3. O. A. Luk´yanov, Yu. B. Salamonov, A. B. Bass, V. S. Bogdanov, Yu. A. Strelenko, V. S. Kuz´min, Yu. T. Struchkov, Yu. N. Burtsev, *Izv. Akad. Nauk*, *Ser. Khim.*, 1992, 2400 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1992, **41**, 1884].
4. Yu. B. Salamonov, O. A. Luk´yanov, A. B. Bass, Yu. A. Strelenko, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1972 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1994, **43**, 1860].
5. G. A. Smirnov, A. M. Vasil´ev, O. A. Luk´yanov, *Izv. Akad. Nauk, Ser. Khim.*, 1991, 2892 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.* (*Engl. Transl.*), 1991, **40**, 2523].
6. W. Gottardi, *Monat. Chem.*, 1968, **99**, 815.
7. O. A. Luk´yanov, Yu. B. Salamonov, A. B. Bass, Yu. A. Strelenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 1991, 109 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1991, **40**, 93].
8. A. B. Sheremetev, Yu. L. Shamshina, D. E. Dmitriev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1007 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 1032].
9. G. D. Solodyuk, M. D. Boldyrev, B. V. Gidaspov, V. D. Nikolaev, *Zh. Org. Khim.*, 1981, **17**, 861 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1981, **17**].

Received January 21, 2011;
in revised form March 30, 2011