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3,4-Bis(4′-nitrofurazan-3′-yl)furoxan: a Melt Cast Powerful Explosive and a Valuable Building Block in 1,2,5-Oxadiazole Chemistry

Andrei I. STEPANOV*, Dmitry V. DASHKO
and Alexander A. ASTRAT'EV

Special Design and Construction Bureau SDCB "Technolog", Sovetsky prosp. 33-A, 192076 Saint Petersburg, Russia
**E-mail: stepanoff@pisem.net*

Abstract: The results of our studies on the reactivity of 3,4-bis(4′-nitrofurazan-3′-yl)furoxan (BNFF), with some O- and N-nucleophiles are presented. It is shown that both nitro groups of BNFF can be easily replaced by nucleophiles. Depending on the identity of the nucleophile, BNFF may be transformed into two types of 1,2,5-oxadiazole derivatives, notably 4-R substituted bis(4-R-furazan-3-yl) furoxanes or 7-R substituted 7*H*(7R)-tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*] azepine-1-oxides − a new heterocyclic system comprised of an azepine ring annelated with three 1,2,5-oxadiazole rings.

Keywords: 3,4-bis(4′-nitrofurazan-3′-yl)furoxan, furazan, furoxan, 1,2,5-oxadiazole, azepine

Introduction

4,4″-Dinitro[3,3′:4′,3″]tris[[1,2,5]oxadiazole]-2′-oxide (3,4-bis(4′-nitrofurazan-3′-yl)furoxan, DNTF, BNFF) (1) represents one of the most successful examples of a practical embodiment of the idea of the nitro-1,2,5-oxadiazole moiety being used for the design of novel, high density, high energy materials. The synthesis of BNFF was first described more than 30 years ago in Russia (Special Design and Construction Bureau SDCB "Technolog", Saint Petersburg), within the scope of searching for new, powerful, high-density, energetic materials. Modern qualification standards for melt cast explosives

[1] have caused a recent, substantial growth of interest [2, 3] in BNFF. The combination of performance [4] (168.4% TNT), which is essentially equal to that of HMX, along with a relatively low (108-110 °C) melting point, allows BNFF to be considered as an ingredient in melt-pour formulations [5]. BNFF forms eutectic mixtures with TNT (m.p. 58 °C; 37.86 mol% BNFF) [5], PETN (m.p. 95.7 °C; 68.2 mol% BNFF) [6], and TNAZ (m.p. 78.9 °C; 40.49 mol% BNFF) [7], and also ternary mixtures [8]: TNT/TNAZ/BNFF (m.p. 76.5-76.7 °C; 52.3/27.3/20.4 mol%), TNAZ/BNFF/RDX (m.p. 47-50 °C; 54.9/39.6/5.5 mol%). It has been shown that addition of BNFF and its eutectics with TNT and TNAZ results in improvement in the mouldability of plastic-bonded explosives [9]. The addition of 2,4-dinitroanisole (DNAN) to BNFF resulted in decreased shock sensitivity [10].

Table 1. Some properties of BNFF

$\Delta H^0_{298,f}$, kJ·mol^{-1}	ρ, g·cm^{-3}	D, km·s^{-1}	Impact sensitivity (10 kg, 25 cm, %)	Friction sensitivity (kg·cm^{-2}, %)
- 706.1	1.937	9250	94	1000/0; 2000/6; 3000/20

To date, in spite of the known relevant, significant energetic characteristics of BNFF, very little attention has been paid to the question of its chemical properties.

Results and Discussion

Recently we have demonstrated that BNFF is rather sensitive towards the action of N- and O- nucleophiles [11-13]. Specifically we have ascertained that, two types of products are possible (Figures 1 and 2), depending on the nature of the nucleophilic reagent used. With univalent nucleophiles, incapable of forming two new chemical bonds, the replacement of both nitro groups by two molecules of the nucleophile is expected to occur. For example, reaction with NaN_3 or highly-basic secondary amines, such as N,N-diethylamine, morpholine, piperidine, N-methylpiperazine, 2-methylaminoethanol, results in the corresponding terminal diazide (2) or diamine (3-7) formation. In the latter case, it should be pointed out, that both strongly electron withdrawing nitro groups are displaced by the soft, amine nucleophiles demonstrating the significant electron withdrawing effect of the three linked 1,2,5-oxadiazole rings. This is in contrast to the analogous 3,4-dinitrofurazan in which only one nitro group can be replaced by an amino group under similar, mild conditions [14]).

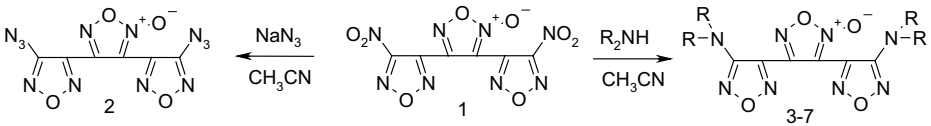


Figure 1. Reaction of BNFF with NaN_3 and secondary amines (R_2NH = $HNEt_2$ (3); $N(C_2H_4)_2O$ (4); $HN(CH_2)_5$ (5); $HN(C_2H_4)NMe$ (6); $HN(Me)CH_2CH_2OH$ (7)).

The reaction of BNFF with NaN_3 seems to be a more convenient, synthetic route to the diazide (2) than that suggested earlier from 3-aminofurazan-4-chlorocarboxamidoxime by the process of diazotization, azidation and dimerization [15, 16]. Insertion of two azide groups appreciably decreases the density of the compound (2). A low melting point, good thermal stability, and high detonation velocity allows one to consider 3,4-bis(4′-azidofurazano-3′-yl) furoxan (2) (DAZTF) as a potential candidate for use as an ingredient in melt-pour formulations (Table 2).

Table 2. Some properties of DAZTF [16]

ρ, $g \cdot cm^{-3}$	D, $km \cdot s^{-1}$	Q, $kJ \cdot kg^{-1}$	Impact sensitivity (10 kg, 25 cm, %)	Friction sensitivity 3.92 MPa, 90°
1.743	8525	6162	86-100	86-100

A geometrical, structural peculiarity of the BNFF molecule, in which both furazan rings are turned towards each other [17, 18], allows the synthesis of not only typical linear products like (3-7), but also previously unknown, tetracyclic systems in which three annelated 1,2,5-oxadiazole moieties form a 7-membered heterocyclic ring. It is noteworthy that the highly pre-organized BNFF molecule sets up the favorable structural prerequisites for the cyclic substitution product formation, wherein both nitro groups of BNFF are replaced by only one molecule of a bivalent nucleophile. For example, with compounds containing primary amino group (amines, ammonia and hydrazine) BNFF forms 7R-substituted 7*H*-tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine 1-oxides (8-12) (Figure 2).

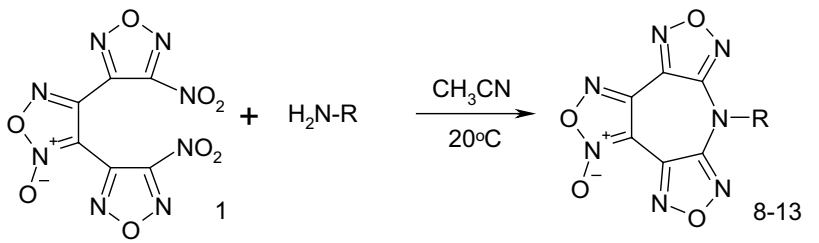


Figure 2. Reaction of BNFF with ammonia, hydrazine and primary amines [R = H (**8**), NH_2 (**9**), CH_3 (**10**), CH_2CH_2OH (**11**), CH_2Ph (**12**), *cyclo*-C_7H_{13} (**13**)].

The structures of the products obtained were established by physicochemical analysis [11-13] and supported by their chemical properties. The structure of compound (**8**) was also confirmed by X-ray diffraction analysis (Figure 3).

It is obvious, that in a similar reaction of BNFF with aliphatic diamines it is possible to obtain coupling products of one or both amino groups. The result of reaction of BNFF with ethylenediamine strongly depends upon the order of addition of the reagents (Figure 4). The slow addition of ethylenediamine to a solution of BNFF in acetonitrile allows both amino groups to participate in the nucleophilic substitution reaction and results in the formation of 1,2-bis[[1-oxide 7*H*-tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine]-7-yl]] ethane (14). In the case of addition of the reagents in the reverse order, i.e. in which BNFF was slowly added to an excess of a solution of ethylenediamine in acetonitrile, only 7-(2-aminoethyl-7*H*-tris[1,2,5]oxadiazolo[3,4-*b*:3,4′-*d*:3″,4″-*f*]azepine 1-oxide was isolated (15).

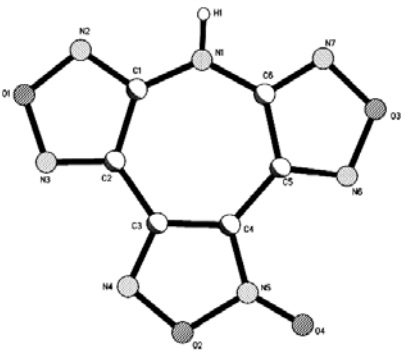


Figure 3. Molecular structure of compound **8**.

Carrying out a similar reaction with hexamethylenediamine ($H_2N(CH_2)_6NH_2$), possessing no appreciable inductive effect between the two amino groups, we always obtained mixtures of the two possible coupling products, independently of the order of addition (1,6-bis[[1-oxide 7*H*-tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine]-7-yl]] hexane (16) and 7-(6-aminohexyl)-7*H*-tris[1,2,5] oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine 1-oxide (17)).

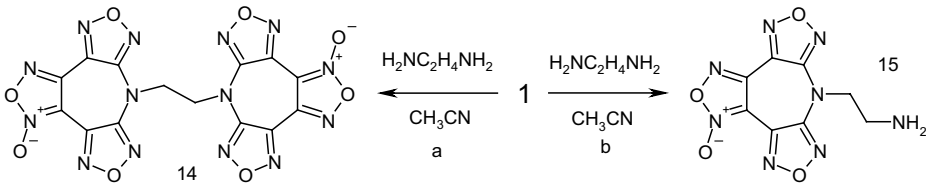
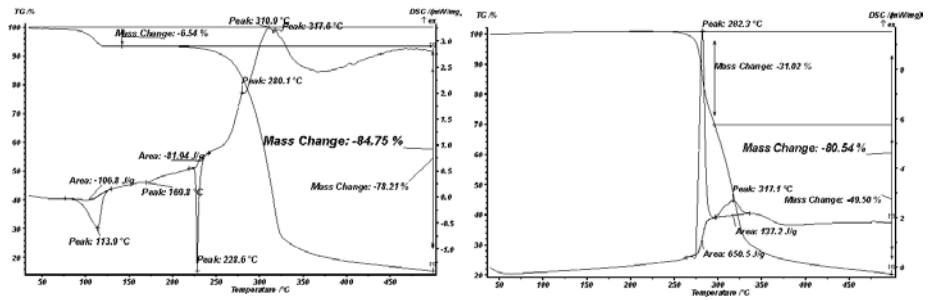


Figure 4. Reaction of BNFF with ethylenediamine.

7*H*-Tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine 1-oxide (**8**) and its 7-amino derivative (**9**) possess high, calculated densities 1.86-1.97 g×cm^{-3} and good thermostability (Figure 5), and therefore may be of interest as energetic materials.

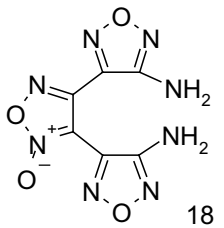


7*H*-Tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*] azepine 1-oxide (**8**) monohydrate

7-Amino-7*H*-tris[1,2,5]oxadiazolo [3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine 1-oxide (**9**)

Figure 5. TG/DSC thermal decomposition behavior of compounds **8** and **9**.

It is significant to note that the N-amino derivative **9** is structurally rather similar to 3,4-bis(4-aminofurazan-3-yl)furoxane (BAFF (18)) (Figure 6), which was recently suggested as a low sensitivity explosive [19] with detonation velocity 8100 m·s^{-1}(1.795 g·cm^{-3}). However, compound **9**, as opposed to BAFF, possesses higher friction and shock mechanical sensitivity, probably due to the effect of the weak hydrazine N-N bond (compare with the unsubstituted azepine, **8**) (Table 3).



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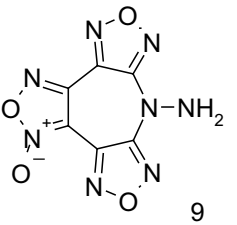

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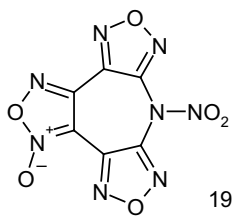
Figure 6. Comparison of chemical structures of BAFF (18) and N-aminoazepine **9**.

Unfortunately, azepine **8** appears to be hygroscopic and crystallizes from water, alcohol or diluted nitric acid as a stable monohydrate that loses water upon heating to 136 °C (Figure 5). The monohydrate of **8** has crystal density 1.817 g·cm^{-3} (X-ray) with measured detonation velocity 7900 m·s^{-1} (1.80 g·cm^{-3}).

Table 3. Sensitivity parameters of BAFF (18) and azepines **8**, **9**

Compound No.	Shock sensitivity (10 kg, 25 cm)	Friction sensitivity (kg·cm^{-2})
18	32	4300
8	8	3146
9	88	2178

The fairly negative oxygen balance of azepine **8** (-57.8%) could be increased to -34.3% by nitro group substitution, forming 7-nitro-7*H*-tris[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*d*:3″,4″-*f*]-azepine 1-oxide (19) which is structurally similar to the well-known, powerful, hydrogen free explosive BTF [20] (**20**) (Figure 7).



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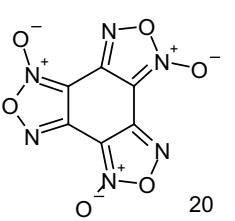
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Figure 7. Comparison of the chemical structures of conjectural nitramine **19** and BTF (**20**).

Unexpectedly, by studying the behavior of azepine **8** in various nitrating systems we obtained rather unusual results. Compound **8** was unreactive in

concentrated nitric acid and in Ac_2O/NH_4NO_3 system (a). However, in such typical nitrating systems as HNO_3/Ac_2O, HNO_3/H_2SO_4, HNO_3/oleum, HNO_3/TFAA (b), instead of the expected formation of the nitramine function we observed "oxidative dimerization" of the parent compound **8** with a new N(7)-N(7′) bond formation (Figure 8).

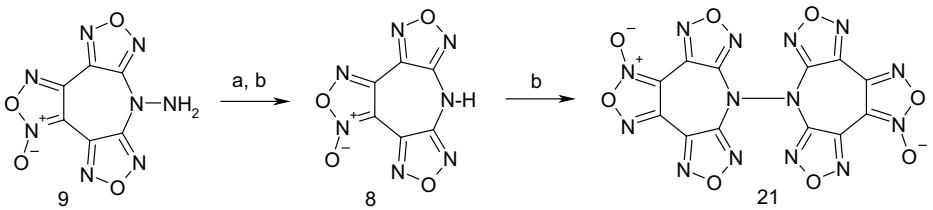

Figure 8. "Oxidative dimerization" of azepin **8** (a: 35%-H_2O_2/H_2SO_4, 1:1.5 by vol., 50 °C; $KMnO_4$/AcOH, 40 °C; HNO_3, 10 °C; NH_4NO_3/Ac_2O, 70 °C; b: HNO_3/Ac_2O, 1:1 by vol., 0-5 °C; HNO_3 / TFAA, 1:1 by vol., - 10 °C).

Nitration of N-aminoazepine **9** in various systems was accompanied by oxidative elimination of the N-amino group and formation of compound **8**, which, depending on the nitrating system used, either remained unchanged (HNO_3, 10 °C; NH_4NO_3/Ac_2O, 70 °C), or «dimerized» to bis-azepine **21** (HNO_3/Ac_2O, 0-5 °C; HNO_3 / TFAA, - 10 °C). Some of our attempts to oxidize the N-amino group in **8** also resulted in deamination. Unlike the precursor azepines **8** and **9**, compound **21** is only slightly soluble in nitric, trifluoroacetic and acetic acid, or in alcohol, chlorobenzene, even at elevated temperatures, but is soluble in diethyl carbonate and N,N-dimethylformamide (**DMF**). Heating of a solutions of **21** in DMF above 100 °C is accompanied by N(7)-N(7′) bond cleavage and formation of the parent azepine **8**. Despite its high thermal stability (Figure 9), due to the known weakness of an N-N bond compound **21** is rather sensitive (shock sensitivity is 100% (10 kg, 25 cm)).

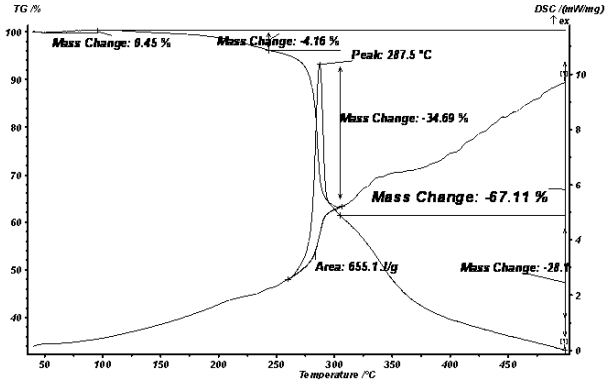

Figure 9. TG/DSC thermal decomposition behavior of N(7)-N(7′) diazepinyl **21**.

The unusual behavior of the azepines **8** and **9** under various nitrating conditions is similar to certain unsuccessful efforts in the nitration of 4,8-dihydrobisfurazano[3,4-*b,e*]pyrazine (**BFP**) [21], and also to some of the peculiar chemical properties of the corresponding 4,8-diamino derivative [22]. The failure to form the N-nitro derivative of BFP [23] could be explained by the formation of a stable biradical which is stabilized by the mesomeric effect of two annelated furazan rings and formation of a 14-π electron aromatic system [24]. Similarly, the observed dimerization of azepine **8** proceeds through a radical intermediate stabilized by the three 1,2,5-oxadiazole rings. The radical either dimerizes to **21** or abstracts an atom of hydrogen from solvent with the formation of azepine **8**.

The hydrogen atom of the imino group in azepine **8**, due to the strong electron-withdrawing action of the two furazan rings, has conspicuous acid character and so compound **8** is readily soluble in aqueous alkaline solutions. In contrast to 3,4-bis(4′-aminofurazan-3′-yl)furoxan (18) or common 3-aminofurazan derivatives, compound **8** is unreactive to acylating agents (acetic or propionic anhydrides, benzoyl chloride), but may be alkylated with common alkylating reagents (Figure 10).

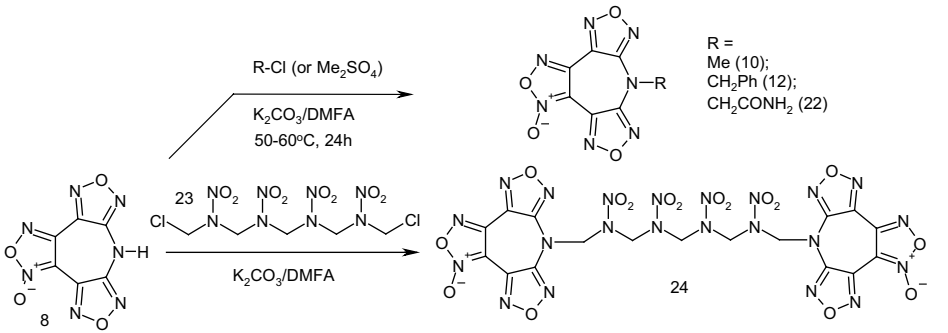

Figure 10. Alkylation of azepine **8**.

By alkylation of **8** with 1,9-dichloro-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane (23) we obtained a very thermally stable N-nitroamine derivative **24** (see Figure 10), which was stable up to 300 °C.

The result of the reaction of BNFF with weak bases depends on the solvent choice. Allowing BNFF to react with aqueous solutions of alkali metals carbonates leads to complete destruction of the molecule. Carrying out similar reactions in anhydrous alcohols however allows the preparation of the corresponding terminal dialkoxy derivatives of 3,4-bis(4′-R-furazan-3′-yl)furoxan **25**, **26**. In acetonitrile, the formation of the cyclic ether **27** was observed. In the latter case, the reaction is accompanied by the elimination of nitrogen oxides (Figure 11). It is believed that the reaction mechanism is initiated by the carbanion of acetonitrile, which facilitates the nitro group to undergo an intramolecular rearrangement to the nitrous acid ester [25]. The nitrite ester loses NO and undergoes an intermolecular nucleophilic substitution reaction with the other nitro group of the molecule, forming cyclic ether **27**.

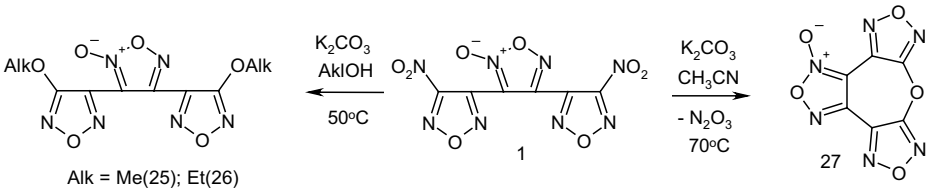

Figure 11. Reaction of BNFF with K_2CO_3.

Oxepino[2,3-*c*:4,5-*c'*:6,7-*c''*]tris[1,2,5]oxadiazole 1-oxide (27) has a negative oxygen balance of – 54.2%. Because of its explosive characteristics [26] and its moderate melting point (Table 4), oxepine **27** may be of interest as a low sensitivity, melt cast explosive. Like unsubstituted azepin **8** compound **27**

crystallize from aqueous acetonitril in monohydrate form [27].

Table 4. Some properties of oxepine **27** [26]

ρ, $g \cdot cm^{-3}$	D, $m \cdot s^{-1}$	Q, $kJ \cdot kg^{-1}$	Shock sensitivity (10 kg, 25 cm)	Friction sensitivity	H_{50}, cm (5 kg)	m.p., °C
1.866	8256	6162	12%	0% (3.92MPa, 90°); 4600 $kg \cdot cm^{-2}$*	57.7	91-92

* our data

Unlike azepines **8-15**, oxepine **27** easily undergoes ring opening reactions of the 7-membered ring by the action of nucleophilic reagents (*e.g.* K_2CO_3/MeOH, NH_3, morpholine) with the formation of a mixture of isomeric 4-hydroxy-4′-R- and 4′-hydroxy-4-R-derivatives of [3,3′;4′,3″]tris[[1,2,5]oxadiazole] 2′-oxide.

Hitherto the azepine heterocyclic system has been considered rather chemically inert. Therefore, for the most part, the observed chemical transformations of compounds like **8-15** routinely involve only transformations of the side chain functional groups. Nevertheless, it is well known that furoxanes are rather interesting ring systems, capable of miscellaneous chemical transformations [28], so reactions of the furoxane ring was of particular interest. We have found that the reduction of azepines **8-15** in ethanol by hydrazine in the presence of Pearlman's catalyst (5%-Pd/C) leads to the opening of the furoxan ring and the formation of two vicinal amino-groups. The use of catalytic hydrogenation to effect the reduction gave higher yields of the diamines **28-34**, up to 75-85% (Figure 12). Diamines **28-34** are poorly soluble in alcohols and can be separated by filtration.

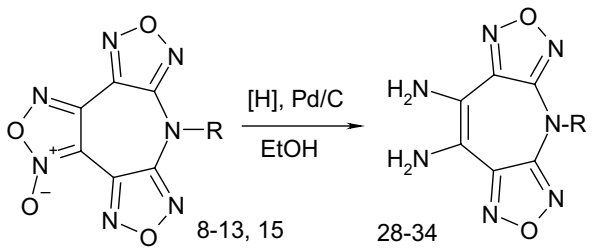

Figure 12. Reductive opening of the furoxan ring in 7-R-7*H*-tris[1,2,5]oxadiazolo[3,4*b*:3′,4′-*d*:3″,4″-*f*]azepine 1-oxides (R = H (**28**), NH_2 (**29**), CH_3 (**30**), CH_3CH_2OH (**31**), CH_2Ph (**32**), *cyclo*-C_7H_{13} (**33**), $CH_2CH_2NH_2$ (**34**)).

The synthetic potential of 4-R-4*H*-bis[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*f*] azepine-8,9-diamines like **28-34** are quite similar to those of *o*-phenylenediamine derivatives and suggest their use in the synthesis of various heterocyclic systems, *e.g.* condensation to imidazole (**35**, Alk = CH_3, C_2H_5) or 1,2,3-triazole derivatives (36) (Figure 13). In case of compounds **29** and **34** amino group of side chain also involves in reaction with acylating agent or nitrous acid (acylation, desamination, respectively).

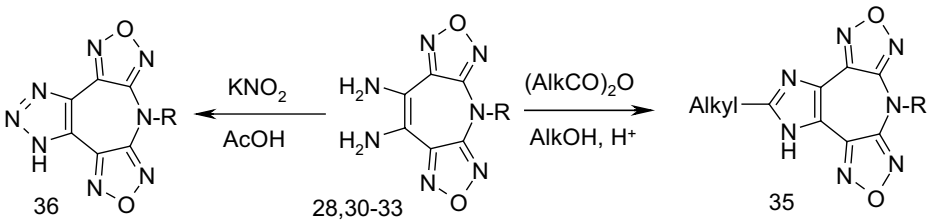

Figure 13. Some reactions of 4-R-4*H*-bis[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*f*]-azepine-8,9-diamines (**28**, **30-33**).

Interestingly, it was found that the nitration of the un-substituted triazole (**36**, R=H), prepared by the reaction of **28** or **29** with nitrous acid in HNO_3/Ac_2O leads to a similar result as for the nitration of azepines **8**, **9**, with the formation of 1*H*,1′*H*-7,7′-dibis[1,2,5]oxadiazolo[3,4-*b*:3′,4′-*f*][1,2,3]triazolo[4,5-*d*]azepine (37) (Figure 14). Compound **37** intensively decomposes (with a flash) at 215 °C (unlike triazole **36**, **R=H**, which starts to sublime at 300 °C and does not melt up to 350 °C).

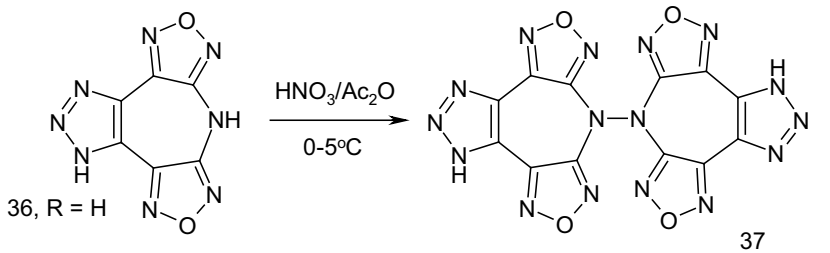

Figure 14. "Oxidative dimerization" of triazole (**36**, R=H) by treatment with HNO_3/Ac_2O.

Conclusions

Herein we have shown that the high synthetic potential of 3,4-bis(4′-nitrofurazan-3′-yl)furoxan (BNFF) is not limited to its application within the framework of energetic compounds. Unlike the majority of known explosives, BNFF is an explosive with attractive energetic properties [29, 30], but also appears to be a valuable building block for a wide range of new 1,2,5-oxadiazole derivatives, including multi-heterocyclic systems.

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