Heteroatom Chemistry
Volume 25, Number 4, 2014

Dinitrogen Trioxide–Mediated Domino Process for the Regioselective Construction of 4-Nitrofuroxans from Acrylic Acids

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Received 23 December 2013; revised 14 March 2014

ABSTRACT: *4-Nitrofuroxans (4-nitro-1,2,5-oxadiazole 2-oxides) were prepared by a dinitrogen trioxide–mediated domino reaction of acrylic acids under the action of $NaNO_2$ excess in AcOH at room temperature. The reaction proceeds completely regioselectively and presents a new, simple, general, and safe method for the preparation of both 3-aryl- and 3-alkyl-4-nitrofuroxans available with difficulty before. A mechanism for the furoxan ring construction through a four-step one-pot protocol is proposed. The synthesized nitrofuroxans have been characterized by multinuclear NMR spectroscopy and X-ray powder diffraction.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:226–237, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21166

INTRODUCTION

A synthesis of the first representatives of furoxans (1,2,5-oxadiazole 2-oxides) dates back to the late 19th century when pioneering methods of the furoxan ring formation such as oxidation of vicinal glyoximes [1a], cyclodimerization of nitrile oxides [1b], and dehydration of α-nitrooximes [1c] were described. Furoxan chemistry has been vigorously evolving for the past 100-year period due to its unique properties that distinguish it from other azoles [2]. First of all, furoxan is used as a building block containing a "hidden" nitro group or two nitroso groups. In the course of its chemical transformation, the nitro group can be released in such reactions as the Boulton–Katritzky rearrangement of benzo- and monocyclic furoxans [3] and, in other cases, a reaction, primarily under action of nucleophiles, may involve nitroso groups (e.g., the Beirut reaction of benzofuroxans [4] and aminofuroxans rearrangement to triazol-1-oxides [5]). Another unique property of furoxans is their susceptibility to thermal isomerization in which the exocyclic oxygen atom transfers from one nitrogen atom to the other [6]. The reaction can be described as a direct opening of the furoxan ring, resulting in a dinitrosoethylene intermediate to be followed by direct cyclization to another isomer without involving any other particles and without generating any additional intermediate complexes—so-called "no mechanism reaction." Equal reaction rates in different solvents are used as the evidence [6b]. The preference in generating a particular isomer depends on the electronic

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Contract grant sponsor: Russian Academy of Sciences (the program OKhNM-04).

Contract grant sponsor: Russian Foundation for Basic Research.

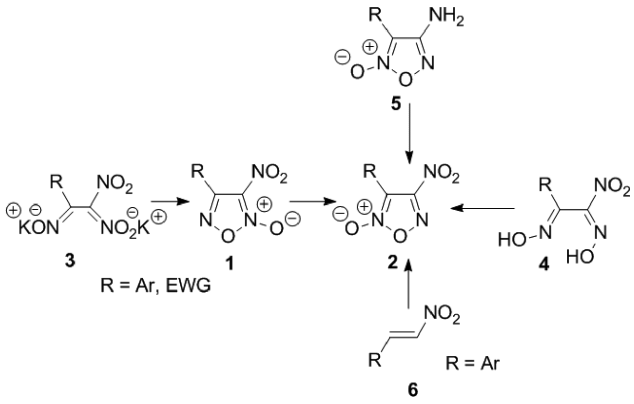
Contract grant numbers: 12-03-12012 OFNM and 12-03-31560.

effects of substituents at C(3) and C(4) atoms of the furoxan ring. Furoxans chemical behavior differs from *N*-oxides of other nitrogen heterocycles: In spite of their capability of reduction to corresponding furazans under the action of various agents such as PCl_3, phosphines, phosphites, $SnCl_2$, or Zn in AcOH [7], attempts to prepare furoxans by oxidation of furazans have failed. Symmetrically substituted furoxans can dissociate under heating into two nitrile oxides as a result of cycloreversion. In the reaction conditions, the latter can either be captured as cycloadducts by means of an interaction with various dipolarophiles or isomerize to respective isocyanates [8].

Continuous investigations revealed key potential applications of furoxans. It has been found that furoxan derivatives have a broad range of biological activity [9]—they act as nitric oxide (NO) donors [10] and as neuroprotective and procognitive agents [11] as well as delay cytotoxic [12], antihelmintic [13a], antibacterial [13b], and fungicidal [13c] activities. In addition, the furoxan ring is of interest as a structural unit for designing energetic compounds owing to positive enthalpy of formation and the presence of two active oxygen atoms inside the ring [14]. This makes nitrofuroxans especially attractive since the nitro group adds two active oxygen atoms to the molecule. Some nitrofuroxan derivatives (e.g., 4,4′-dinitro-3,3′-diazenofuroxan) have high explosive performance [15]. In addition, nitrofuroxans are efficient NO donors [16]. Furthermore, they are very useful as sources of polyfunctional derivatives prepared by nucleophilic substitution of the nitro group under the action of N-, O-, S-nucleophiles or hydride ion, by reductive condensation to azo- and azoxyderivatives, etc. [2a].

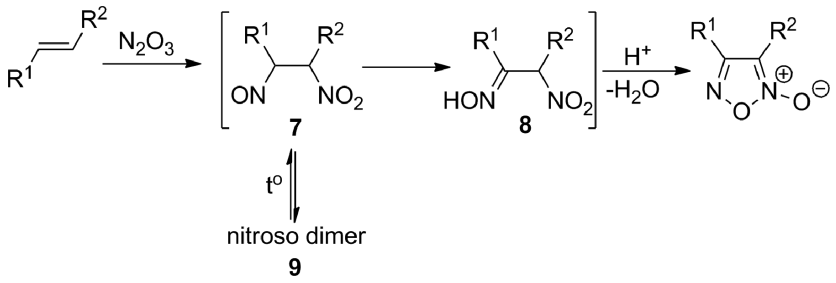
Several representatives both of 3-nitrofuroxans **1** and of 4-nitrofuroxans **2** prepared by different synthetic routes are described. Most of them have been developed in past few years. In particular, our research team developed a method for the synthesis of 3-nitro-4-R-furoxans **1** (R = Ar, COMe, CO_2Et) based on nitrosation of dipotassium salts of 2-R-2-hydroximino-1,1-dinitroethanes **3** [17]. By refluxing in toluene, 3-nitroisomers **1** isomerize quantitatively to thermodynamically preferable 4-nitroisomers **2**. 4-Nitrofuroxans **2** can also be prepared by oxidative cyclization of the *amphi*-form of corresponding nitroglyoximes **4** [18], as well as by means of the amino group oxidation in 4-aminofuroxans [19] **5** and of the β-nitrostyrenes interaction with $NaNO_2$ in AcOH [20] **6** (Scheme 1).

Unfortunately, all the methods have serious disadvantages. The preparation of 4-nitrofuroxans **2** by oxidation of nitroglyoximes **4** or aminofuroxans **5** is restricted because of an insufficient set of starting compounds. Moreover, to oxidize the latter rather strong oxidative mixtures are needed. Low yields of 4-nitrofuroxans **2** are typical for their synthesis from β-nitrostyrenes **6** and nitrosation of dipotassium salts of 2-R-2-hydroximino-1,1-dinitroethanes **3** runs successfully exclusively with aromatic or electron-withdrawing substituents. In addition, dipotassium salts per se and their precursors—dinitromethane sodium or potassium salt—are high explosives. In regard to isomeric alkylnitrofuroxans, methods of their synthesis actually have not been developed and just their individual representatives have been described so far. Therefore, a search for a new general as well as simpler and safer approach to the synthesis of nitrofuroxans remains relevant.

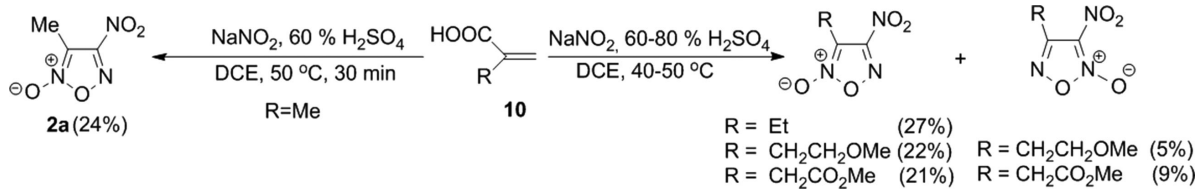


SCHEME 1 Known synthetic routes to nitrofuroxans.

In search for such approach, we paid our attention to furoxan ring formation methods based on the interaction of unsaturated compounds with nitrosating agents having been in focus of many investigations for a long time. The first synthesis of 4-aryl-3-methylfuroxans involving the treatment of arylmethylethylene with $NaNO_2$ in AcOH medium was published by Angeli back in 1892 [1c]. Later on, other authors replicated this reaction and examined the action of the same nitrosating system on some other disubstituted ethylenes, including structures with functional substituents, such as cinnamic alcohol [21a] or methylformylethylene [21b]. It was established that the first reaction step was the N_2O_3 addition to the double bond of starting olefin that gave pseudonitrosite **7**. Its nitroso fragment isomerizes to the oxime fragment at heating, and only after that the furoxan ring forms through dehydration of α-nitrooxime **8**. To effectively transform pseudonitrosite **7**, which forms nitroso dimer **9**, to α-nitrooxime **8** heating in polar aprotic solvents (dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide) is required and, for



SCHEME 2 Mechanism for the formation of the furoxan ring by means of the α-nitrooxime dehydration.



SCHEME 3 Known examples for the synthesis of nitrofuroxans from acrylic acids.

dehydration, most effective appeared to be heating of α-nitrooxime **8** in sulfuric or polyphosphoric acid [21c] (Scheme 2). For dialkylpseudonitrosites, the proposed synthetic method was based on passing of the NO and O_2 gaseous mixture through an ether solution of disubstituted ethylenes [21c].

Recently [22], the preparation of a mixture of isomeric 3(4)-R-4(3)-arylfuroxans from the β-R-substituted styrenes under the action of $NOBF_4$ under basic or even almost neutral reaction conditions has been reported. Since the reaction yields a mixture of the isomers, the authors suppose that the intermediate product is a dinitrosoethylene derivative rather than α-nitrooxime.

Few efforts of using a reaction between unsaturated compounds and nitrosating agents with the view of preparing nitrofuroxans have been described. A successful synthesis of 4-nitro-3-phenylfuroxan from styrene has been reported; however, authors failed to introduce substituted styrenes into the reaction [23]. As mentioned above (Scheme 1), we succeeded in preparing 3-aryl-4-nitrofuroxans **2** from β-nitrostyrenes in low yields [20]. An inseparable mixture of isomeric 4(3)-methyl-3(4)-nitrofuroxans **1a** and **2a** (ratio 1:13) was isolated in a minor yield (3.3%) after 2-methylmaleic acid nitration and characterized by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy [24].

A principal possibility to synthesize 3-methyl-4-nitrofuroxan **2a** in 24% yield by an interaction between methacrylic acid **10a** and $NaNO_2$ in a two-phase system 60% H_2SO_4–dichloroethane (DCE) at low heating (50°C) was for the first time shown in [25]. Later on, we extended this approach to some other 2-alkylacrylic acids [20]. Corresponding nitrofuroxans were prepared in low yields and in most cases as a mixture of 3- and 4-nitroisomers (Scheme 3).

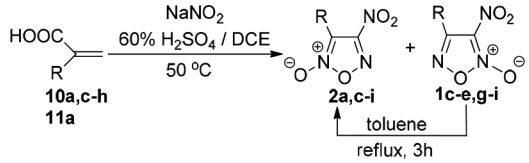
RESULTS AND DISCUSSION

Since both 2-alkyl- and 2-arylsubstituted acrylic acids are readily available compounds, we decided to study in detail their behavior under the action of different nitrosating systems. To do that, we presynthesized a representative set of 2-alkyl- and 2-arylacrylic acids **10b–g** and **11a–d** by known methods [26]. 2,9-Dimethylenedecanedioic acid (**10h**) unknown before was prepared from malonic ester and α,ω-dibromohexane in a similar manner.

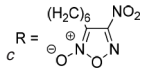
At first, we investigated a possibility of using the conditions described in [20, 25] ($NaNO_2$ in a two-phase system: 60% H_2SO_4–DCE, 50°C) to prepare nitrofuroxans **1** and **2** with different substituents. We managed to synthesize 3-methyl-4-nitrofuroxan **2a** in the proposed conditions [25] even in higher yield—36%. Furthermore, we found this approach to be general for the synthesis of other alkylnitrofuroxans from 2-alkylacrylic acids **10c–h**, which reacted irrespective of the alkyl substituent structure (Method A). However, the actually inseparable mixture of 3- and 4-nitrofuroxans **1c–e,g,h** and **2c–e,g,h** (Table 1) in most cases (with the exception of entries 1 and 5) was obtained in moderate yields. The method also proved to be suitable for the synthesis of nitrophenylfuroxan from 1-phenylacrylic acid **11a,** yet still as a mixture of two isomers **1i** and **2i.**

The ratio of isomers **1** and **2** was estimated on the basis of the integral intensity ratio of proton signals in the ^{1}H NMR spectra and signals from NO_2

TABLE 1 Synthesis of 3-R-4-Nitrofuroxans **2** by Means of Method A



Entry	R	Chemical Shift of the NO_2 Group in ^{14}N NMR (ppm)		Ratio[a] 2/1	Yield[b] 2 (%)
		1	2		
1	Me (**10a**)	–	–34.89	99:1	**2a** (36)
2	*n*Pr (**10c**)	–38.25	–34.73	9:1	**2c** (39)
3	*i*Pr (**10d**)	–38.16	–34.19	10:1	**2d** (34)
4	*n*Bu (**10e**)	–38.25	–34.76	12:1	**2e** (39)
5	Cy (**10f**)	–	–34.11	99:1	**2f** (39)
6	Bn (**10g**)	–38.95	–35.42	11:1	**2g** (12)
7	 (**10h**)	–38.25	–32.60	5:1	**2h**[c] (28)
8	Ph (**11a**)	–39.88	–35.32	11:1	**2i** (24)

[a]Determined by the integral intensity ratio of proton signals in the ^1H NMR spectra.
[b]Isolated yield.
[c] 

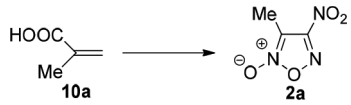
groups in the ^{14}N NMR spectra since positions of the substituents in nitrofuroxans derivatives can be unambiguously determined on the basis of the ^1H, ^{14}N, and ^{13}C NMR spectra (Table 1).

As shown in [20,24], chemical shifts of protons of CH_2 fragments at C(3) carbon atoms in the ^1H NMR spectra of 3-alkyl-4-nitrofuroxans **2** are located more upfield as compared to the analogous group of signals at the C(4) carbon atom of the furoxan ring in 4-alkyl-3-nitrofuroxans **1** ($\Delta\delta = \sim 0.2$ ppm). The nitro group position at the furoxan ring referring to the *N*-oxide fragment can also be determined using ^{14}N NMR spectra data for isomeric arylnitrofuroxans [17a,b]—the signal of the 3-nitro group moved upfield by 3.7–4.7 ppm relative to the 4-nitro group signal. A close difference in chemical shifts of the signals from the nitro groups ($\Delta\delta = 3.3$ ppm) is also observed in isomeric methylnitrofuroxans **1a** and **2a**. The signals of C(3) and C(4) carbon atoms in the ^{13}C NMR spectra of isomeric arylnitrofuroxans are varied in a similar manner [17a,b]: The chemical shift of the C(3) carbon atom in 4-aryl-3-nitrofuroxans occurs upfield by ~20–25 ppm in comparison with that of the C(4) carbon atom in 3-aryl-4-nitrofuroxans. Synthesized 4-alkyl-3-nitrofuroxans **1c–e,g,h** were not isolated and were isomerized to 3-alkyl-4-nitrofuroxans **2c–e,g,h** by refluxing of the prepared mixtures of isomers in toluene for 3 h. Isomeric nitrophenylfuroxans **1i** and **2i** were separated by column chromatography on SiO_2. The characteristics of the isolated isomers were completely in agreement with the literature [17b]. In addition, 3-nitroisomer **1i** was isomerized to 4-nitroisomer **2i** by refluxing of the mixture in toluene in the same conditions (Table 1).

To increase the yields of the final products, we have performed a wide search of reaction conditions by the example of methacrylic acid **10a** varying a nitrosating reagent ($NaNO_2$, N_2O_4), its amount (3–9 mol for 1 mol of initial acrylic acid), reaction medium (H_2SO_4–DCE, ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulfate ([emim]HSO_4), AcOH), temperature (0–100°C), and reaction time (0.5–120 h) (Table 2).

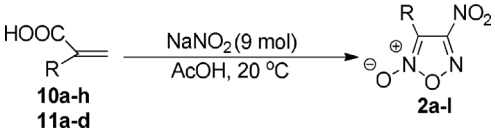
According to the data from Table 2, conditions for the synthesis of 3-methyl-4-nitrofuroxan **2a** in Method B (entry 5) proved to be the best. Those were extended to the other 2-substituted acrylic acids. It appeared that the reaction of all synthesized 2-alkylacrylic acids **10b–h** as well as 2-arylacrylic acids **11a–d** with the $NaNO_2$ excess in AcOH at room temperature proceeded completely regioselectively and resulted in only 3-R-4-nitrofuroxans **2a–l** in moderate and high yields (Table 3). Important advantages of the developed method include easy isolation of synthesized 4-nitrofuroxans and the absence of impurities. To isolate the final products, it is just needed to pour the reaction mixture in water and either filter them or extract with CH_2Cl_2 followed by evaporation of the solvent.

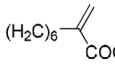
TABLE 2 Optimization of the Reaction Conditions for the Synthesis of 3-Methyl-4-nitrofuroxan **2a**



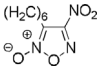
Entry	*Nitrosation Reagent (mol)*	*Reaction Medium*	*Temperature (°C)*	*Time (h)*	*Yield 2a (%)*
1	$NaNO_2$ (3.5)	60% H_2SO_4–DCE	50	0.5	36
2	$NaNO_2$ (3)	[emim][HSO_4]	20	120	0
3	$NaNO_2$ (3)	[emim][HSO_4]	100	120	0
4	N_2O_4 (5)	Et_2O	0	3	10
5	$NaNO_2$ (9)	AcOH	20	72	51
6	$NaNO_2$ (9)	CF_3COOH	20	72	8

TABLE 3 Synthesis of 3-R-4-Nitrofuroxans **2** by Means of Method B



Entry	*R*	*Time (h)*	*Yield[a] 2 (%)*
1	Me (**10a**)	72	**2a** (51)
2	$MeOCH_2CH_2$ (**10b**)	72	**2b** (32)
3	*n*Pr (**10c**)	72	**2c** (52)
4	*i*Pr (**10d**)	72	**2d** (55)
5	*n*Bu (**10e**)	72	**2e** (54)
6	Cy (**10f**)	72	**2f** (57)
7	Bn (**10g**)	72	**2g** (41)
8	 (**10h**)	120	**2h**[b] (70)
9	Ph (**11a**)	72	**2i** (36)
10	Naphthalen-1-yl (**11b**)	72	**2j** (71)
11	*p*-MeC_6H_4 (**11c**)	72	**2k** (35)
12	*p*-ClC_6H_4 (**11d**)	72	**2l** (33)

[a]Isolated yield.

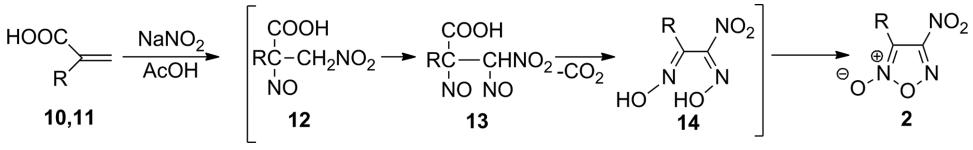
[b] R = 

To explain the regioselective formation of 3-R-4-nitrofuroxans **2** from acrylic acids **10a–h** and **11a–d** and the $NaNO_2$ excess in AcOH, we proposed a hypothetic Scheme 4, which differs from Scheme 2 for the formation of furoxan ring by means of the α-nitrooxime dehydration. Most likely, this reaction represents the dinitrogen trioxide–mediated domino process and involves four sequential steps. The first step is similar to the first step of Scheme 2 and results in the pseudonitrosite **12** formation by addition of N_2O_3 generated from $NaNO_2$ in AcOH, to the double bond of acrylic acids **10** or **11**. Furthermore, the methylene group of intermediate **12** is nitrosated under the action of N_2O_3 resulting in a dinitroso derivative **13**. The latter undergoes decarboxylation with simultaneous isomerization of both nitroso groups to the oxime ones to give *amphi*-glyoximes **14**, which are oxidized to 4-nitrofuroxans **2** under the action of the same nitrogen oxides. The appearance of the mixture of isomeric nitrofuroxans by Method A may be explained by the formation of the mixture of isomeric *amphi*-glyoximes at heating in the presence of H_2SO_4.

The structure of the synthesized compounds was established by a totality of elemental and spectral analysis data (^1H, ^{13}C, ^{14}N NMR spectroscopy, mass spectrometry, and IR), and the structure of compound **2h** was additionally supported by powder X-ray diffraction data.

The powder diffraction pattern (see the Experimental section) of **2h** was indexed using TOPAS 4.2 software [27] in the orthorhombic crystal system, with the *Pbca* space group judged from the cell volume (expected $Z' = 0.5$) and the systematic absences. The lattice parameters (after Rietveld refinement) are $a = 13.86225(22)$ Å, $b = 10.20307(14)$ Å, $c = 10.33897$ (14) Å, and $V = 1462.32(4)$ Å^3.

The crude molecular geometry for the structure solution was obtained using the MM approach as implemented in Marvin (Marvin 5.8.1, 2012; ChemAxon, http://www.chemaxon.com). Since we expected $Z' = 0.5$, half of the molecule (see Fig. 3) was used as a model for structure solution in direct



SCHEME 4 Proposed mechanism for the formation of 3-R-4-nitrofuroxans **2** from 1-R-acrylic acids **10** and **11**.

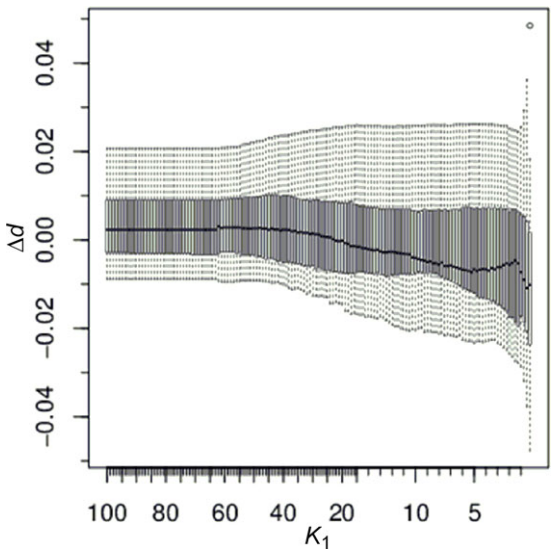


FIGURE 1 Box-and-whisker plots for bond length deviation (Δd) distributions in Rietveld refinements of **2h** at varied values of global penalty function weighting (K1).

space using the Parallel Tempering method as implemented in FOX [28]. Indeed, in the solution found the molecule lies around the inversion center.

Further Rietveld refinement was performed using breakable restraints based on previously published the "Morse" restraint model [29] and was applied during the Rietveld refinement in TOPAS (see the Experimental section). The analysis of the deviations of refined bond lengths from the defined values within this restraint model has been shown to validate Rietveld refined structures: The structures containing no outliers in bond Δd distribution are considered correct. The restraints for the refinement initially were prepared basing on a PBE/L2 [30] calculation of **2h** using PRIRODA software [31]. However, the calculated geometry of the furoxan ring in this model has been problematic, with O2–N2 distance of 1.7 Å and model showed outliers in the refinement. We assume that such discrepancy is caused by the incorrect description of polar bonds by PBE functional: The ring geometry in the calculated model deviated significantly from the published crystal structure of **2a** [32]. Thus, the restraints for the final refinement were prepared on the basis of the structure of **2a** for the furoxan ring and a PBE/L2 for the alkyl chain.

After 150 refinements in TOPAS with the decreasing penalty function weight (K_1; see the Experimental section), there were not outliers in the bond length deviation (Δd) distribution (see Fig. 1), supporting the correctness of the refined structure. At $K_1 = 3$, the refinement converged to $R_p/R_P'/R_{WP}/R_{WP}'/R_{Bragg}$ values of 2.269/9.703/3.259/8.274/1.653 with R_{exp}/R_{exp}' values of 0.681/1.729, $\chi^2 = 4.786$, and rms Δd of 0.015 Å.

Synthesized alkylnitrofuroxans are either low-melting compounds (**2a,f,g,i–l**) or stable distillable liquids (**2c–e**). They incorporate four active oxygen atoms in the molecule and are challenging as promising ingredients (e.g., plasticizers) for energetic formulations. The density of the liquids **2c**, **2d**, and **2e** was measured with a pycnometer and found to be 1.266, 1.300, and 1.180 g cm^{-3}, respectively. The heat of formation ($\Delta_f H^o$) is very important parameter in evaluating the performance of energetic materials. This characteristic can be calculated for furoxan derivatives by various quantum chemical methods [33]. However, recently it has been shown that for furoxans a simple prediction of $\Delta_f H$ can be performed with good accuracy by using the additive method based on the values of the group contribution and the intramolecular interaction [34]. The calculated values for 4-nitro-3-propyl- and isopropylfuroxans **2c,d** and 3-butyl-4-nitrofuroxan **2e** are –8.57 and –15.44 kcal mol^{-1}, respectively.

CONCLUSIONS

In summary, our investigations have resulted in a development of simple, general, efficient, and safe method for the synthesis of 3-alkyl- and 3-aryl-4-nitrofuroxans. This method is based on the N_2O_3-mediated domino reaction of corresponding acrylic acids with $NaNO_2$ excess in AcOH at room temperature. A four-step *one-pot* route of the reaction is described. The target nitrofuroxans are formed completely regioselectively with moderate and good yields. It is especially important that the developed method allows preparing earlier hardly accessible 3-alkyl-4-nitrofuroxans. Synthesized alkylnitrofuroxans are either low-melting compounds or stable distillable liquids with sufficiently high density and enthalpy of formation. They incorporate four active oxygen atoms in the molecule and show promise as ingredients of energetic formulations.

EXPERIMENTAL

General

All reactions were carried out in well-cleaned glassware with magnetic stirring. All starting materials were purchased from commercial sources. Melting points were measured on a Gallenkamp Sanyo apparatus and are not corrected. Elemental analyses were performed on the CHN analyzer Perkin–Elmer 2400. The IR spectra (ν, cm^{-1}) were measured using a Bruker "Alpha" spectrometer. Mass spectra were

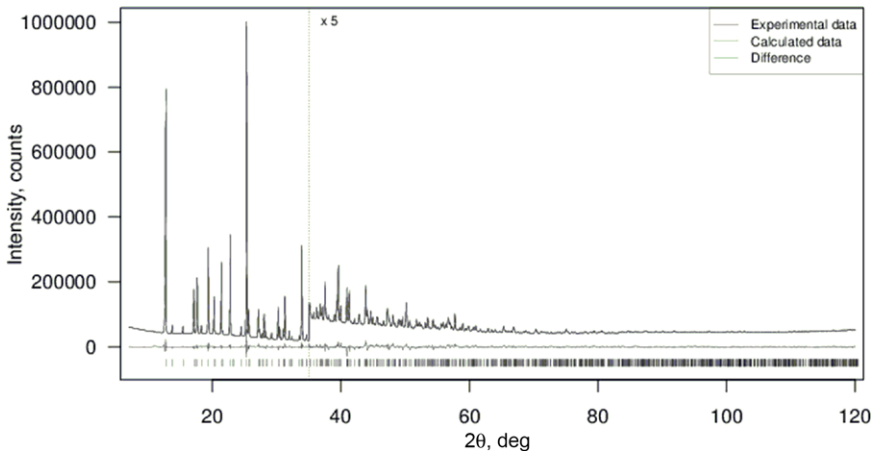


FIGURE 2 Experimental and calculated powder patterns for **2h** at K1 = 3 and their difference.

measured using a Finnigan MAT INCOS-50 instrument. The NMR spectra of all compounds were measured using a Bruker AC200-31 spectrometer at 200 MHz for ^{1}H and 50.3 MHz for ^{13}C spectra and a Bruker AM-300 spectrometer at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C spectra and 21.5 MHz for ^{14}N spectra in $CDCl_3$ or [D_6]DMSO. ^{1}H and ^{13}C spectra were recorded using TMS as an internal standard. ^{14}N spectra were measured using CH_3NO_2 (δ_{14N} = 0.0 ppm) as an external standard. Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminum sheets. The X-ray powder diffraction (XRD) of **2h** was measured on a Bruker D8 Advance Vario diffractometer with a LynxEye detector and Ge (111) monochromator, λ(Cu Kα1) = 1.54060 Å, $\Theta/2\Theta$ scan from 7° to 120°, stepsize 0.018338° (see Fig. 2). The measurement was performed in the transmission mode, with **2h** deposited between two Kapton films.

The penalty function in the breakable restrained refinement is defined as follows:

$$P = K_1 \sum_i \kappa_i [1 - e^{-a_i |D_i - d_i|}]^2$$

where P is a penalty function, K_1 is a global penalty function weighting, κ_i is the weighting of the individual bond penalty, a_i is a coefficient corresponding to the bond force constant, D_i is the defined length of a given bond, and d_i is its refined length at the current minimization step. It is a modification of "Morse" restraint model, which does not suffer from asymmetry of the bond potential.

*2,9-Dimethylenedecanedioic acid (***10h***).* Diethylamine (70.8 mmol) and paraformaldehyde (106 mmol) were added to a solution of octane-1,1,8,8-tetracarboxylic acid [26a] (35.4 mmol) in EtOAc (80 mL) at 5–10°C, and the mixture was refluxed

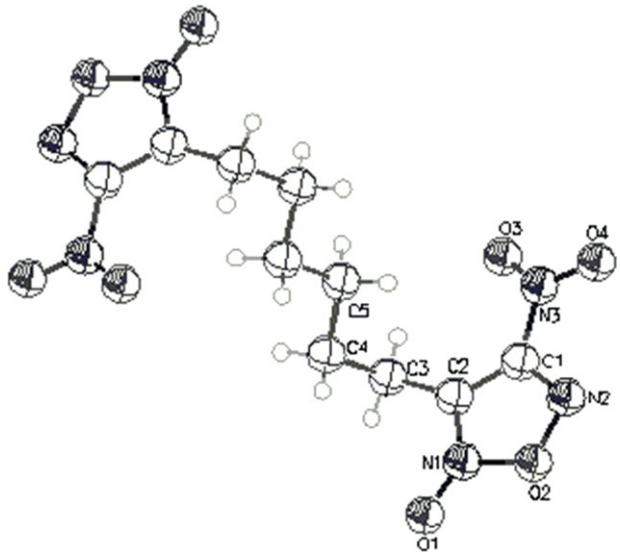


FIGURE 3 Molecular structure of **2h** in crystal. Atoms are represented by spheres indicating their isotropic thermal displacements (ρ = 50%). Only symmetry independent atoms are labeled.

with stirring for 3 h. After cooling down to room temperature, water (20 mL) was added and the resulting mixture was acidified with 3 N aqueous HCl until pH 1. An organic layer was separated, washed twice with water and with brine, dried over $MgSO_4$. The solution was filtered, and the solvent was evaporated under reduced pressure to give the desired product as a white solid. Yield 5.75 g (72%); mp 135–136°C; IR (KBr): ν = 1627, 1692, 2877, 2904, 2922 cm^{-1}; ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.22–1.26 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_2$), 1.37 (t, J = 6.2 Hz, 4H, $CH_2CH_2CH_2CH_2CH_2CH_2$), 2.17 (t, J = 7.8 Hz, 4H, $CH_2CH_2CH_2CH_2CH_2CH_2$), 5.40 (s, 2H, 2C*H*), 6.01 (s, 2H, 2C*H*), 8.9–10.1 (br s, 2H, 2 COO*H*); ^{13}C NMR (75.5 MHz,

[D_6]DMSO): $\delta = 27.91$ (s, $CH_2CH_2CH_2CH_2CH_2CH_2$), 28.37 (s, $CH_2CH_2CH_2CH_2CH_2CH_2$), 31.27 (s, $CH_2CH_2CH_2CH_2CH_2CH_2$), 123.96 (s, 2 × C=CH_2), 141.19 (s, 2 × C=CH_2), 168.09 (s, 2 × COOH); MS (70 eV): *m/z* (%): 226 (12) $[M]^+$, 181 (29) $[M - COOH]^+$, 136 (41) $[M - 2COOH]^+$; elemental analysis calcd for $C_{12}H_{18}O_4$: C 63.70; H 8.02; found: C 63.66; H 7.99.

Method A: 4-Nitrofuroxans **2a,c–i** *from 2-Acrylic Acids and $NaNO_2$ in a Two-Phase System H_2SO_4–dichloroethane (DCE).*

General Procedure. $NaNO_2$ (70 mmol, 4.83 g) was added portionwise to a mixture of 6 mL of 60% H_2SO_4 and a solution of appropriate acrylic acid (20 mmol) in 20 mL DCE at 50°C for 30 min, and the mixture was vigorously stirred at this temperature for additional 30 min. Then the organic layer was separated and washed with 3% Na_2CO_3 aqueous solution until the organic phase was completely became colorless, washed with water, and dried over $MgSO_4$. The solution was filtered, and the solvent was evaporated under reduced pressure to give the product as a mixture of 3- and 4-nitroisomers, which were analyzed by multinuclear NMR spectroscopy. All obtained mixtures were dissolved in toluene (3 mL) and refluxed for 3 h. Then the solvent was evaporated under reduced pressure to give quantitatively the corresponding 4-nitrofuroxans. In addition, isomers **1i** and **2i** were separated by column chromatography (eluent: CCl_4–$CHCl_3$, 3:1).

Method B: 4-Nitrofuroxans **2a–g,i–l** *from 2-Acrylic Acids and $NaNO_2$ in Acetic Acid.*

General Procedure. To a stirred solution of an appropriate acrylic acid (10 mmol) in a mixture of acetic acid (50 mL) and water (5 mL), $NaNO_2$ (30 mmol, 2.07 g) was added at room temperature. Stirring was continued at room temperature overnight. The residual amount of $NaNO_2$ (60 mmol, 4.14 g) was divided into six equal portions; each portion was added to a reaction medium every 10 h. Then water (300 mL) was added. If the solid formed, it was filtered, washed with water, and dried in air. If the solid was not formed, the solution was extracted with CH_2Cl_2 (4×30 mL). Combined organic layers were washed with saturated $NaHCO_3$ solution (2×60 mL), then with water and dried over $MgSO_4$. Organic solution was filtered, and the solvent was evaporated under reduced pressure to afford a pure furoxan compound.

Method B: Furoxan **2h** *from Diacrylic Acid* **10h** *and $NaNO_2$ in Acetic Acid.* To a stirred solution of an diacrylic acid **10h** (10 mmol, 2.26 g) in a mixture of acetic acid (110 mL) and water (11 mL), $NaNO_2$ (60 mmol, 4.14 g) was added at room temperature. Stirring was continued at room temperature overnight. The residual amount of $NaNO_2$ (120 mmol, 8.28 g) was divided into 10 equal portions; each portion was added to a reaction medium every 10 h. Then water (400 mL) was added. The solid formed was filtered, washed with water, and dried in air.

*3-Methyl-4-nitrofuroxan (***2a***) [24].* Pale yellow solid; yield 1.04 g (36%)—method A; 0.74 g (51%)—method B; mp 68–69°C; $R_f = 0.43$ (CCl_4/$CHCl_3$ 2:1); IR (KBr): $\nu = 644, 829, 1057, 1126, 1359, 1385, 1499, 1569, 1628, 2904$ cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.51$ (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 9.01$ (s, CH_3), 107.62 (s, C(3) furoxan), 158.93 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): $\delta = -34.89$ (s, NO_2); MS (70 eV): *m/z* (%): 145 (36) $[M]^+$, 115 (33) $[M - NO]^+$, 99 (16) $[M - NO_2]^+$, 85 (100) $[M - 2NO]^+$, 69 (44) $[M - NO - NO_2]^+$; elemental analysis calcd for $C_3H_3N_3O_4$: C 24.84; H 2.08; N 28.96; found: C 24.90; H 2.10; N 28.90.

*3-(2-Methoxyethyl)-4-nitrofuroxan (***2b***) [20].* Yellow oil; yield 0.60 g (32%); $R_f = 0.34$ (CCl_4/$CHCl_3$ 2:1); IR (KBr): $\nu = 835, 1058, 1105, 1192, 1360, 1433, 1575, 1632, 1642, 2873, 2946, 2970$ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.14$ (t, $J = 5.9$ Hz, 2H, $CH_3OCH_2CH_2$), 3.28 (s, 3H, $CH_3OCH_2CH_2$), 3.63–3.69 (m, 2H, $CH_3OCH_2CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 23.41$ (s, $CH_3OCH_2CH_2$), 58.34 (s, $CH_3OCH_2CH_2$), 66.54 (s, $CH_3OCH_2CH_2$), 108.27 (s, C(3) furoxan), 158.91 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): $\delta = -34.68$ (s, NO_2); MS (70 eV): *m/z* (%): 189 (36) $[M]^+$, 159 (24) $[M - NO]^+$, 143 (11) $[M - NO_2]^+$, 129 (31) $[M - 2NO]^+$, 113 (30) $[M - NO - NO_2]^+$, 83 (100) $[M - 2NO - NO_2]^+$, 59 (61) $[MeOCH_2CH_2]^+$, 45 (26) $[MeOCH_2]^+$; elemental analysis calcd for $C_5H_7N_3O_5$: C 31.75; H 3.73; N 22.22; found: C 31.79; H 3.79; N 22.17.

*4-Nitro-3-propylfuroxan (***2c***).* Yellow oil; yield 1.35 g (39%) as a mixture of regioisomers—method A; 0.90 g (52%)—method B; bp 67–68°C (0.6 mmHg); $R_f = 0.64$ (CCl_4/$CHCl_3$ 2:1); IR (KBr): $\nu = 828, 1030, 1059, 1133, 1225, 1274, 1358, 1431, 1462, 1502, 1571, 1631, 2879, 2939, 2971$ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.03$ (t, $J = 7.4$ Hz, 3H, $CH_3CH_2CH_2$), 1.68–1.86 (m, 2H, $CH_3CH_2CH_2$), 2.87 (t, $J = 7.3$ Hz, 2H, $CH_3CH_2CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 13.30$ (s, $CH_3CH_2CH_2$), 19.14 (s, $CH_3CH_2CH_2$), 24.84 (s, $CH_3CH_2CH_2$), 110.62 (s, C(3) furoxan), 158.71 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$):

δ = –34.73 (s, NO_2); MS (70 eV): *m/z* (%): 173 (27) $[M]^+$, 143 (19) $[M - NO]^+$, 127 (14) $[M^+ - NO_2]^+$, 113 (41) $[M^+ - 2NO]^+$, 97 (29) $[M - NO - NO_2]^+$, 67 (38) $[M - 2NO - NO_2]^+$, 43 (100) $[Pr]^+$. elemental analysis calcd for $C_5H_7N_3O_4$: C 34.69; H 4.08; N 24.27; found: C 34.72; H 4.05; N 24.31.

3-Nitro-4-propylfuroxan (**1c**). ^{1}H NMR (300 MHz, $CDCl_3$): δ (distinguishable peaks) = 1.83–1.88 (m, 2H, $CH_3CH_2CH_2$), 3.01–3.06 (m, 2H, $CH_3CH_2CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (distinguishable peaks) = 17.34 (s, $CH_3CH_2CH_2$), 19.65 (s, $CH_3CH_2CH_2$), 28.75 (s, $CH_3CH_2CH_2$), 127.09 (s, C(3) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ (distinguishable peak) = –38.25 (s, NO_2).

3-Isopropyl-4-nitrofuroxan (**2d**). Yellow oil; yield 1.17 g (34%) as a mixture of regioisomers—method A; 0.95 g (55%)—method B; bp 66–67°C (0.6 mmHg); R_f = 0.57 (CCl_4/$CHCl_3$ 2:1); IR (KBr): ν = 1037, 1281, 1319, 1357, 1391, 1460, 1499, 1568, 1626, 2839, 2882, 2964 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (d, J = 7.1 Hz, 6H, $(CH_3)_2CH$), 3.52–3.61 (m, 1H, CH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.80 (s, 2 × CH_3), 24.09 (s, $(CH_3)_2CH$), 113.19 (s, C(3) furoxan), 157.91 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ = –34.19 (s, NO_2); MS (70 eV): *m/z* (%): 173 (32) $[M]^+$, 143 (24) $[M - NO]^+$, 127 (23) $[M - NO_2]^+$, 113 (49) $[M - 2NO]^+$, 97 (11) $[M - NO - NO_2]^+$, 67 (26) $[M - 2NO - NO_2]^+$, 43 (100) $[^iPr]^+$; elemental analysis calcd for $C_5H_7N_3O_4$: C 34.69; H 4.08; N 24.27; found: C 34.73; H 4.11; N 24.30.

4-Isopropyl-3-nitrofuroxan (**1d**). ^{1}H NMR (300 MHz, $CDCl_3$): δ (distinguishable peak) = 1.45 (d, J = 6.9 Hz, 6 H, $(CH_3)_2CH$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (distinguishable peaks) = 19.80 (s, 2 × CH_3), 27.67 (s, $(CH_3)_2CH$); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ (distinguishable peak) = –38.16 (s, NO_2).

3-Butyl-4-nitrofuroxan (**2e**). Yellow oil; yield 1.46 g (39%) as a mixture of regioisomers—method A; 1.01 g (54%)—method B; bp 73–74°C (0.6 mmHg); R_f = 0.60 (CCl_4/$CHCl_3$ 2:1); IR (KBr): ν = 830, 1052, 1357, 1430, 1466, 1501, 1570, 1629, 2875, 2935, 2963 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.4 Hz, 3H, $CH_3CH_2CH_2CH_2$), 1.36–1.48 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.58–1.75 (m, 2H, $CH_3CH_2CH_2CH_2$), 2.88 (t, J = 7.4 Hz, 2H, $CH_3CH_2CH_2CH_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.52 (s, $CH_3CH_2CH_2CH_2$), 22.22 (s, $CH_3CH_2CH_2CH_2$), 23.00 (s, $CH_3CH_2CH_2CH_2$), 27.69 (s, $CH_3CH_2CH_2CH_2$), 110.74 (s, C(3) furoxan), 159.04 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ = –34.76 (s, NO_2); MS (70 eV): *m/z* (%): 187 (27) $[M]^+$, 157 (19) $[M - NO]^+$, 141 (15) $[M - NO_2]^+$, 127 (51) $[M - 2NO]^+$, 111 (12) $[M - NO - NO_2]^+$, 81 (20) $[M - 2NO - NO_2]^+$, 57 (100) $[Bu]^+$; elemental analysis calcd for $C_6H_9N_3O_4$: C 38.51; H 4.85; N 22.45; found: C 38.56; H 4.89; N 22.41.

4-Butyl-3-nitrofuroxan (**1e**). ^{1}H NMR (200 MHz, $CDCl_3$): δ (distinguishable peaks) = 2.32-2.40 (m, 2H, $CH_3CH_2CH_2CH_2$), 2.98–3.09 (m, 2H, $CH_3CH_2CH_2CH_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ (distinguishable peaks) = 13.87 (s, $CH_3CH_2CH_2CH_2$), 22.36 (s, $CH_3CH_2CH_2CH_2$), 26.42 (s, $CH_3CH_2CH_2CH_2$), 29.51 (s, $CH_3CH_2CH_2CH_2$); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ (distinguishable peak) = –38.25 (s, NO_2).

3-Cyclohexyl-4-nitrofuroxan (**2f**). Yellow solid; yield 1.65 g (39%)—method A; 1.21 g (57%)—method B; mp 80–81°C; R_f = 0.66 (CCl_4/$CHCl_3$ 2:1); IR (KBr): ν = 761, 792, 833, 875, 999, 1074, 1142, 1238, 1282, 1353, 1450, 1496, 1563, 1620, 1736, 2858, 2926, 2941 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27–2.18 (m, 10H, $5CH_2$), 3.14–3.26 (m, 1H, CH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.07, 25.69, 26.28, 33.34 (all s, C_6H_{11}), 112.42 (s, C(3) furoxan), 158.61 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ = –34.11 (s, NO_2); MS (70 eV): *m/z* (%): 213 (11) $[M]^+$, 183 (10) $[M - NO]^+$, 167 (7) $[M - NO_2]^+$, 153 (30) $[M - 2NO]^+$, 137 (14) $[M - NO - NO_2]^+$, 107 (9) $[M - 2NO - NO_2]^+$, 83 (100) $[Cy]^+$; elemental analysis calcd for $C_8H_{11}N_3O_4$: C 45.07; H 5.20; N 19.71; found: C 45.03; H 5.24; N 19.75.

3-Benzyl-4-nitrofuroxan (**2g**). Yellow solid; yield 0.53 g (12%) as a mixture of regioisomers—method A; 0.91 g (41%)—method B; mp 82–84°C; R_f = 0.50 (CCl_4/$CHCl_3$ 2:1); IR (KBr): ν = 715, 770, 832, 1047, 1084, 1189, 1357, 1421, 1456, 1501, 1563, 1631, 2913 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (s, 2H, $C_6H_5CH_2$), 7.34 (s, 5H, $C_6H_5CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 28.80 (s, $C_6H_5CH_2$), 108.78 (s, C(3) furoxan), 128.28, 128.68, 129.18, 132.73 (all s, C_6H_5), 157.12 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ = –35.42 (s, NO_2); MS (70 eV): *m/z* (%): 221 (41) $[M]^+$, 191 (18) $[M - NO]^+$, 175 (16) $[M - NO_2]^+$, 161 (32) $[M - 2NO]^+$, 145 (21) $[M - NO - NO_2]^+$, 115 (29) $[M - 2NO - NO_2]^+$, 91 (100) $[Bn]^+$; elemental analysis calcd for $C_9H_7N_3O_4$: C 48.87; H 3.19; N 19.00; found: C 48.90; H 3.14; N 18.96.

4-Benzyl-3-nitrofuroxan (**1g**). ^{1}H NMR (300 MHz, $CDCl_3$): δ (distinguishable peaks) = 4.43 (s, 2H, $C_6H_5CH_2$), 7.57–7.62 (m, 5H, $C_6H_5CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (distinguishable peaks) = 36.48

(s, Ph*C*H$_2$), 127.36, 128.51, 128.91, 129.19, 133.74 (all s, *C*$_6$H$_5$); ^{14}N NMR (21.5 MHz, CDCl$_3$): δ (distinguishable peak) = –38.95 (s, NO$_2$).

3,3′-(Hexane-1,6-diyl)bis(4-nitrofuroxan) (**2h**). Pale yellow solid; yield 1.93 g (28%) as a mixture of regioisomers—method A; 2.41 g (70%)—method B; mp 124–125°C; R_f = 0.37 (CCl$_4$/CHCl$_3$ 2:1); IR (KBr): ν = 814, 919, 1042, 1059, 1148, 1197, 1356, 1432, 1497, 1567, 1624, 2868, 2937, 2951 cm^{-1}; ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.38 (br s, 4H, CH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_2$CH$_2$), 1.64 (br s, 4H, CH$_2$C*H*$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$), 2.78 (t, *J* = 7.0 Hz, 4H, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$); ^{13}C NMR (75.5 MHz, DMSO-*d*$_6$): δ = 22.75 (s, CH$_2$CH$_2$*C*H$_2$*C*H$_2$CH$_2$CH$_2$), 24.52 (s, CH$_2$*C*H$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 27.85 (s, *C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 111.26 (s, C(3) furoxan), 159.20 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, [D$_6$]DMSO): δ = –32.60 (s, NO$_2$); MS (70 eV): *m/z* (%): 344 (6) [M]$^+$, 314 (7) [M – NO]$^+$, 298 (11) [M – NO$_2$]$^+$, 284 (25) [M – 2NO]$^+$, 268 (21) [M – NO – NO$_2$]$^+$, 254 (17) [M – 3NO]$^+$, 252 (13) [M – 2NO$_2$]$^+$, 238 (9) [M – 2NO – NO$_2$]$^+$, 224 (100) [M – 4NO]$^+$, 162 (10) [M – 3NO – 2NO$_2$]$^+$, 132 (39) [M – 4NO – 2NO$_2$]$^+$; elemental analysis calcd for C$_{10}$H$_{12}$N$_6$O$_8$: C 34.89; H 3.51; N 24.41; found: C 34.93; H 3.57; N 24.38.

4,4′-(Hexane-1,6-diyl)bis(3-nitrofuroxan) (**1h**). ^{1}H NMR (200 MHz, CDCl$_3$): δ (distinguishable peak) = 3.02–3.05 (m, 4H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ (distinguishable peaks) = 23.32 (s, CH$_2$CH$_2$*C*H$_2$*C*H$_2$CH$_2$CH$_2$), 25.19 (s, CH$_2$*C*H$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 29.73 (s, *C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$); ^{14}N NMR (21.5 MHz, CDCl$_3$): δ (distinguishable peak) = –38.25 (s, NO$_2$).

4-Nitro-3-phenylfuroxan (**2i**) *[17b].* Pale yellow solid; yield 0.77 g (19%)—method A; 0.74 g (36%)—method B; mp 96–97°C; R_f = 0.49 (CCl$_4$/CHCl$_3$ 2:1); IR (KBr): ν = 693, 759, 1284, 1292, 1375, 1469, 1496, 1532, 1576, 1619 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.60 (s, 5H, Ph); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 109.15 (s, C(3) furoxan), 119.51, 128.83, 129.32, 131.98 (all s, *C*$_6$H$_5$), 158.11 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, CDCl$_3$): δ = –35.32 (s, NO$_2$); MS (70 eV): *m/z* (%): 207 (27) [M]$^+$, 177 (25) [M – NO]$^+$, 161 (8) [M – NO$_2$]$^+$, 147 (35) [M – 2NO]$^+$, 131 (37) [M – NO – NO$_2$]$^+$, 101 (37) [M – 2NO – NO$_2$]$^+$, 77 (100) [Ph]$^+$; elemental analysis calcd for C$_8$H$_5$N$_3$O$_4$: C 46.39; H 2.43; N 20.29; found: C 46.43; H 2.39; N 20.24.

3-Nitro-4-phenylfuroxan (**1i**) *[17b].* Pale yellow solid; yield 0.07 g (2%)—method A; mp 109–110°C; R_f = 0.70 (CCl$_4$/CHCl$_3$ 2:1); IR (KBr): ν = 693, 767, 853, 1008, 1273, 1299, 1356, 1417, 1463, 1481, 1525, 1545, 1617, 1656 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.59–7.73 (m, 5H, Ph); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 123.98 (s, C(3) furoxan), 129.04, 129.14, 132.27 (all s, *C*$_6$H$_5$), 151.35 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, CDCl$_3$): δ = –39.88 (s, NO$_2$); MS (70 eV): *m/z* (%): 207 (24) [M]$^+$, 177 (32) [M – NO]$^+$, 161 (19) [M – NO$_2$]$^+$, 147 (31) [M – 2NO]$^+$, 131 (44) [M – NO – NO$_2$]$^+$, 101 (53) [M – 2NO – NO$_2$]$^+$, 77 (100) [Ph]$^+$; elemental analysis calcd for C$_8$H$_5$N$_3$O$_4$: C 46.39; H 2.43; N 20.29; found: C 46.41; H 2.45; N 20.27.

3-(Naphthalen-1-yl)-4-nitrofuroxan (**2j**). Yellow solid; yield 1.83 g (71%); mp 95–96°C; R_f = 0.48 (CCl$_4$/CHCl$_3$ 2:1); IR (KBr): ν = 776, 806, 832, 955, 1044, 1075, 1256, 1285, 1357, 1497, 1514, 1568, 1619 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.42–7.44 (m, 1H, Ar-*H*), 7.56–7.65 (m, 4 H, Ar-*H*), 7.97–8.02 (m, 1 H, Ar-*H*), 8.10–8.14 (m, 1H, Ar-*H*); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 108.83 (s, C(3) furoxan), 116.86, 123.26, 125.21, 127.12, 128.29, 129.43, 129.94, 130.13, 133.02, 133.89 (all s, *C*$_{10}$H$_7$), 158.73 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, CDCl$_3$): δ = –36.17 (s, NO$_2$); MS (70 eV): *m/z* (%): 257 (18) [M]$^+$, 227 (15) [M – NO]$^+$, 211 (21) [M – NO$_2$]$^+$, 197 (35) [M – 2NO]$^+$, 181 (9) [M – NO – NO$_2$]$^+$, 151 (26) [M – 2NO – NO$_2$]$^+$, 127 (100) [Naphthyl]$^+$; elemental analysis calcd for C$_{12}$H$_7$N$_3$O$_4$: C 56.04; H 2.74; N 16.34; found: C 55.99; H 2.78; N 16.31.

4-Nitro-3-(p-tolyl)furoxan (**2k**). Yellow solid; yield 0.77 g (35%); mp 88–89°C; R_f = 0.59 (CCl$_4$/CHCl$_3$ 2:1); IR (KBr): ν = 779, 821, 990, 1074, 1121, 1273, 1288, 1364, 1480, 1523, 1561, 1609, 2922 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.46 (s, 3H, C*H*$_3$), 7.37 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.50 (d, *J* = 7.9 Hz, 2H, Ar-*H*); ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 21.68 (s, *C*H$_3$), 111.98 (s, C(3) furoxan), 116.33, 128.63, 130.03, 142.74 (all s, *C*$_6$H$_4$), 159.44 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, CDCl$_3$): δ = –35.03 (s, NO$_2$); MS (70 eV): *m/z* (%): 221 (33) [M]$^+$, 191 (17) [M – NO]$^+$, 175 (12) [M – NO$_2$]$^+$, 161 (29) [M – 2NO]$^+$, 145 (23) [M – NO – NO$_2$]$^+$, 115 (43) [M – 2NO – NO$_2$]$^+$, 91 (56) [MeC$_6$H$_4$]$^+$, 76 (100) [C$_6$H$_4$]$^+$. elemental analysis calcd for C$_9$H$_7$N$_3$O$_4$: C 48.87; H 3.19; N 19.00; found: C 48.82; H 3.22; N 19.04.

3-(4-Chlorophenyl)-4-nitrofuroxan (**2l**). Yellow oil; yield 0.80 g (33%); R_f = 0.57 (CCl$_4$/CHCl$_3$ 2:1); IR (KBr): ν = 785, 844, 997, 1091, 1146, 1291, 1379, 1480, 1526, 1567, 1615 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.57 (br s, 4H, Ar-*H*); ^{13}C NMR

(50.3 MHz, $CDCl_3$): δ = 108.83 (s, C(3) furoxan), 117.88, 129.73, 130.25, 138.45 (all s, C_6H_4), 157.65 (s, C(4) furoxan); ^{14}N NMR (21.5 MHz, $CDCl_3$): δ = –35.81 (s, NO_2); MS (70 eV): *m/z* (%): 243 (6) $[M + 2]^+$, 241 (16) $[M]^+$, 213 (5) $[M - NO + 2]^+$, 211 (15) $[M - NO]^+$, 197 (4) $[M - NO_2 + 2]^+$, 195 (9) $[M^+ - NO_2]^+$, 183 (11) $[M - 2NO + 2]^+$, 181 (32) $[M - 2NO]^+$, 167 (10) $[M - NO - NO_2 + 2]^+$, 165 (26) $[M - NO - NO_2]^+$, 137 (13) $[M - 2NO - NO_2 + 2]^+$, 135 (40) $[M - 2NO - NO_2]^+$, 113 (21) $[ClC_6H_4 + 2]^+$, 111 (59) $[ClC_6H_4]^+$, 76 (100) $[C_6H_4]^+$; elemental analysis calcd for $C_8H_4ClN_3O_4$: C 39.77; H 1.67; N 17.39; Cl 14.67; found: C 39.81; H 1.63; N 17.34; Cl 14.70.

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