RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

A Practical Anodic Oxidation of Aminofurazans to Azofurazans: an environmentally friendly route†

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Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Nickel oxyhydroxide, NiOOH, anode has been shown to be effective tools for the oxidation of aminofurazans to azofurazans in *ca* 1% aqueous alkali at room temperature. The electrochemical reaction is simple and convenient, eliminating the use of expensive and toxic organic or inorganic oxidants. The green economic preparations of desired azo compounds are very clean, producing only H_2 as a result of cathodic reduction.

Introduction

Green chemical processes play a crucial role in sustainable development, and atom-economical strategies for the enhancement of molecular complexity are the key elements for the design of new environmentally favorable synthetic processes. According to the trend, we have focused our effort on the development of a safe and efficient methods to prepare furazan (1,2,5-oxadiazole) derivatives.

Furazan chemistry has extended over a period of about 140 years, and many useful derivatives have been synthesized and investigated. Applications of these compounds are highly diverse, ranging from medicinal chemistry to explosive and propellant ingredients.[1] In this family, azofurazan structural motif is present in a range of crown ether analogs[2] and biologically active molecules that inhibit the NO-dependent activation of the soluble guanylate cyclase.[3] However, compounds incorporated azofurazan framework with a high nitrogen content and large positive heats of formation have been most extensively studied as energetic materials.[4] 4,4'-Diaminoazofurazan **1**,[4c,5] 3,4-di(4-nitrofurazan-3-azo)furazan **2**,[4a,6] 4,4'-di(5-tetrazolyl)-azofurazan**3**,[7] 4,4-dinitrodiazenoxyazofurazan **4**,[8] and *tetrakis*(furazano)[3,4-c:3',4'-g:3",4"-k:3"',4"']-[1,2,5,6,9,10,13, 14]-octaazacyclohexa-decine **5**[4c,9] are examples of the energetic compounds (Fig. 1). Given their utility, the development of synthetic methodology to access azofurazan derivatives is continually warranted.

Azofurazans are typically prepared from aminofurazans by an oxidation reaction. Traditionally, this has been carried out using such reagents as $KMnO_4/H^+$,[10] $CrO_3/AcOH$,[11] $(NH_4)_2S_2O_8$,[12] NaOCl or NaOBr,[13] nitronium tetrafluoroborate,[14] Br_2/H_2O,[15] or a variety of organic reagents (dibromoisocyanuric acid[16] and trichloroisocyanuric acid).[4e,17] These procedures, however, require the use of hazardous, corrosive or expensive reagents. In a chemical oxidation, stoichiometric amounts or excess of an oxidant are needed.As a result the corresponding amounts of metal salts or acids are formed as waste. Separation of the products from the waste is often difficult. Our goal was to develop a convenient, economical and environmentally friendly synthetic protocol for a quick assembly of the azofurazan core.

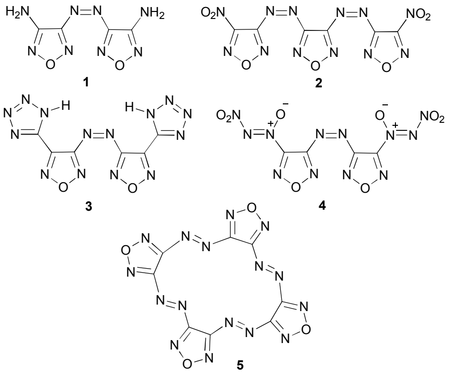

Figure 1 Some high energetic azofurazans.

The growing social pressure for new green technologies and the promise of organic electrosynthesis to deliver them has led to high academic and industrial interest in electrochemical methods.[18] The electron in electrosynthesis is one of the most environmentally friendly reagents, as it produces no waste in contrast to chemical reagents; furthermore, it is the cheapest reagent in chemistry.

Organic electrooxidation has attracted much attention as one of the effective methods in carbon-carbon, carbon-nitrogen, and

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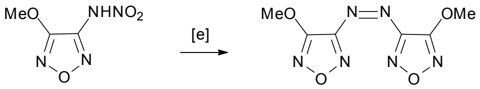
†Electronic Supplementary Information (ESI) available: NMR and X-ray data. See DOI: 10.1039/b000000x/

carbon-oxygen bond formations.[19] At the same time, electrochemical N=N bond formations isnearlyunexplored. Thus, an alkyl azo compound, di(^{t}butyl) diazene, than have been obtained in low yield by electrooxidation of ^{t}butylamine, was described.[20a] The onlyknown electrochemical synthesis of azo-(het)arenes from amino(het)areneis oxidation of anilines to azo-benzenes (3-47% yield; the largest yields were recorded for compounds bearing electron-withdrawing substituents).[20b,20c] However, the electro-oxidation of the aniline nitrogen atom usually resulted in the formation of a radical cation, that can exist in multiple resonance forms.The latter provides an opportunity for three possible couplings: (*i*) nitrogen-nitrogen (head-to-head, HH), (*ii*) nitrogen-arene (head-to-tail, HT) and (*iii*) arene-arene (tail-to-tail, TT). HT and TT coupling occurs predominately, and the polymerization of anilines is a common result.[21]

Recently, we have shown that electrooxidation of 3-methoxy-4-nitraminofurazan **6** leads to the formation of 4,4”-dimethoxyazofurazan **7**in undivided cell in *ca* 40% yield(Scheme 1).[22]This procedure required preparation and the use of hazardous starting nitramine**6**.



6 **7**

Scheme 1

It should be noted that the electrooxidations for N=N bond formation in the syntheses of azocompounds mentioned above[20,21]have been carried out with great expensivePt anode in a non-aqueous medium (acetonitrile).An attractive perspective for synthesis of (het)aromatic azo compounds is electrooxidation of corresponding (het)aryl amines on Ni anode under galvanostatic electrolysis.The basic electrochemical reaction at Ni anode[23] involves the formation of nickel hydroxide $Ni(OH)_2$and itsoxidation in alkaline solution (typical electrolyte is 1*M*$NaOH/H_2O$) to nickel oxyhydroxide NiOOH[24] which is an equivalent to the well-known oxidant, nickel peroxide.[25] Electrochemical synthesis is based on a combination of an electron transfer at the Ni anode with a chemical reaction of electrodeposited NiOOH (Figure3). The electron transfer (re)generates the NiOOH reagent. The anodeis usually used in organic synthesis for oxidation of C-H and C-C bonds of organic compounds.[26] It should be noted that an example of N=N bond formation at the NiOOHanode have been described: 1,1-disubstituted hydrazines were oxidized in good yield to 1,1,4,4-tetrasubstituted tetrazenes.[23] To the best of our knowledge, a synthesis of (het)aryl azo compounds using NiOOH anode has not been reported. We hypothesized that it might be possible to use the anode for oxidation of a (het)aryl amine to the corresponding azo compound.

As a part of a program aimed at the development of ecological synthetic methods for the construction of energetic materials,[27] we now report a facile and reliable electrochemical oxidation of aminofurazans. This clean process allows the synthesis of azofurazansin one step with high atom economy, and driven by loss of environmentally benign hydrogen gas.

Results and discussion

We were gratified to find that this NiOOH electrode was successful in the oxidative preparation of the azofurazans, giving clean reaction profiles (Fig. 3). We started our study by examining the oxidation of 3-amino-4-methylfurazan **8a** to 4,4’-dimethylazofurazan **9a**.Cyclic voltammetry (CV) was used for an initial evaluation of the electrocatalytic process. The typical voltammetric response is exemplified in Fig. 2. Compared to the voltammogram of the Ni^{2+}/Ni^{3+} pair ($E^{1/2}$ = 430 mV) in absence of a substrate (solid line), the peak current increases when amine **8a** was added (dotted line). The observation is similar to that fixed at the electrooxidation urea[28] and alcohols[29] on NiOOH catalyst surface in alkaline medium.

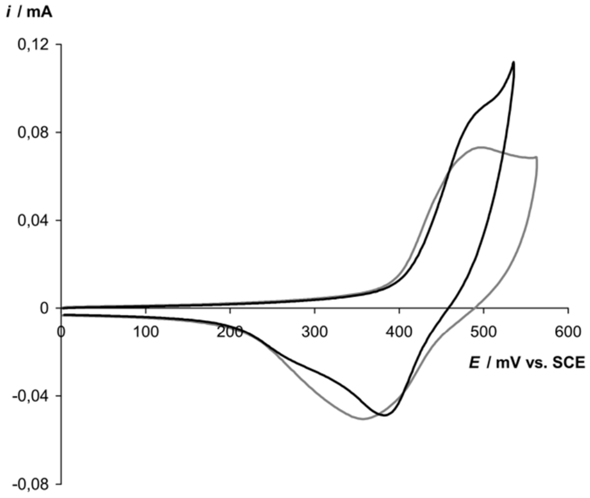
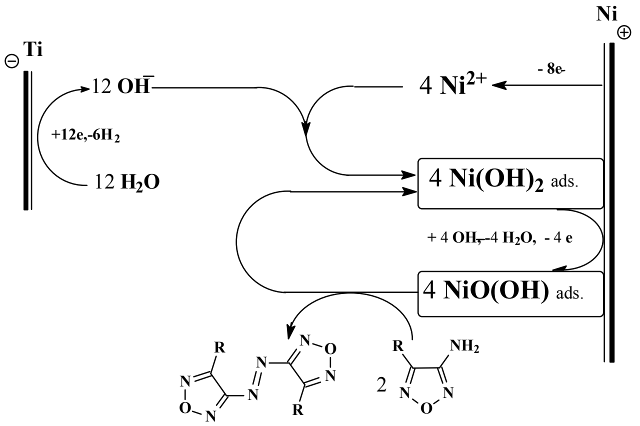


Figure 2. CVs of Ni/NiOOH in 0.2 M NaOH with (black dotted line) and without (gray solid line) amine **8a** (20 mmol L^{-1}, 100 mV s^{-1}).

However, preparative-scale evaluation is crucial in order to establish the actual performance and efficiency of the Ni^{2+}/Ni^{3+} catalytic systems under synthetic conditions. Preparative electrolysis of compound **8a** under galvanostatic conditions involved using a four-neck jacketed flask as an undivided cell, a cylindrical Ni anode, a cylindrical net Ti cathode, and an aqueous solution of an alkali as the supporting electrolyte.



9 **8**

Figure3. Schematic illustration of the possible electrochemical mechanism for the oxidation of aminofurazans on $Ni(OH)_2$.

Anodic oxidations of amine **8a** were carried out at stirring under various conditions. The reactions were generally clean when monitored by NMR, only target azo compound **9a** and unreacted starting materialhave been identifiable components. Details on the experimental protocol are summarized in Table 1.

Table 1. Electrooxidative coupling[a] 3-amino-4-methylfyrazan **8a** on NiOOH anode[b]

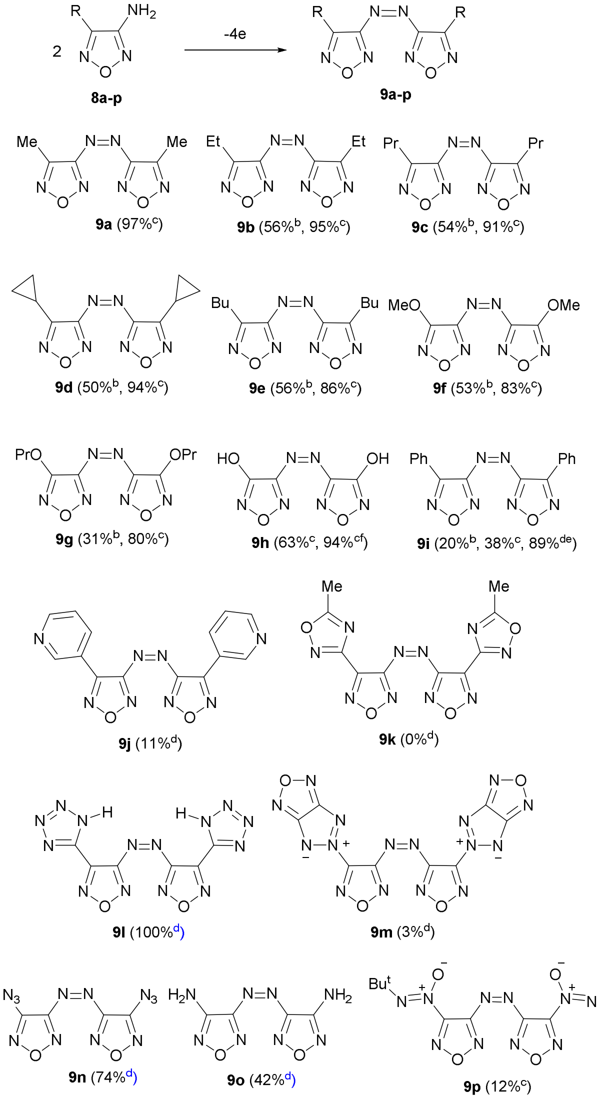
Entries	Base (concentration, mol×L^{-1})	Current density (mA×cm^{-2})	Electricity passed, Q/Q_{theor}[c]	Time (min)	Yield (%)[d]	
					9a	Recovery of **8a**
1	LiOH (0.1)	6	1	22	57	42.0
2	NaOH (0.1)	6	1	22	59	39.5
3	KOH (0.1)	6	1	22	46	52.5
4	NaOH (0.2)	6	1	22	76 (74)	22 (20)
5	NaOH (0.3)	6	1	22	67	31.0
6	NaOH (0.5)	6	1	22	61	38.0
7[e]	NaOH (0.2)	6	1	22	73[e]	25.5
8	NaOH (0.2)	2	1	66	59	39.5
9	NaOH (0.2)	3	1	45	53	45.5
10	NaOH (0.2)	4	1	34	65	33.0
11	NaOH (0.2)	8	1	17	58	41.0
12	NaOH (0.2)	16	1	8.5	64	33.5
13	NaOH (0.2)	6	1.5	33	83	17
14	**NaOH (0.2)**	**6**	**2**	**44**	**97 (95)**	1.5
15	NaOH (0.2)	7	1	19	66	33.0

[a] Reactions were run under galvanostatic conditionson 2 mmol scale of compound **8a** in 100 ml of H_2O (0.02 mol×L^{-1}) at room temperature. [b] Before the experiment, the Ni anode (*ca*. 48 cm^2) was activated according to the next procedure:[24] A thin NiOOH surface layer was deposited on the anode at preliminary electrolysis in a solution 0.1 M $NiSO_4$, 0.1 M NaOAc, and 0.005 M NaOH, at j_a = 1 mA×cm^{-2} with periodical reverse of the electrode polarization. [c] Here Q is the amount of electricity (F), and Q_{theor} = 2F per a mole of compound **8a**. [d] Determined by ^1H NMR spectroscopy using 4,4'-dimethoxyazofurazan as an internal standardadded after the reaction (averages of two runs); isolated yields are shown in parentheses. [e] Reaction conducted at 70°C.

The results in Table 1 indicate that in the electrooxidation, all of the bases (entries 1–3) favored the formation of azo compound **9a** with comparable selectivity. It appeared that NaOH is optimum with respect to overall yield and cost. We found that the use of 0.1 *M* NaOH in H_2O at 22°C under an air atmosphere produced **9a** after 22 min in 59% yield with a moderate conversion of **8a** (Table 1, entry 2). Using 0.2 *M* NaOH as a basic medium, the conversion was enhanced, but the resultingyield of **9a** remained below 80% (Table 1, entry 4). Increase of the temperature (entry 7) or prolongation of the reaction time (entry 8) did not lead to an improvement in the yield. However, an excellent result was obtained when doublequantityof electricity waspassed; a 97% yield of azo compound **9a** and almost complete conversion of amine **8a** were observed (Table 1, entry 14).

Next, the scope of this oxidation was examined (Table 2). It was found that the solubility of aminofurazans in water is a key parameter to the success of the electrochemical process. Thus, the solubility of alkyl and alkoxy compounds **8a-g** is much better than that of aryl **8i** and hetarylfurazans **8j**, **8k**, and **8m**. As a result, a variety of groups, including Me (**a**), Et (**b**), Pr (**c**), Bu (**e**), cyclopropyl (**d**), MeO (**f**), PrO (**g**), and OH (**h**) were perfectly tolerated under these reaction conditions to produce the corresponding azofurazans **9a-h** in excellent yields. On the other hand, aminofurazans bearing aryl and pyridyl substituents showed little conversion into the desired azofurazans **9i** and **9j**. Aminofurazan **8k** with 1,2,4-oxadiazolyl group is insoluble in water. As a result, attempts to oxidize this amine to azocompound **9k** were unsuccessful and only unreacted starting material was observed. On the other hand, tetrazolylfurazanylamine **8l** have higher water solubility and produced the desired azo compound **9l** in excellent yield. Obviously, this protocol could be feasible for large scale production of the product **9l**.

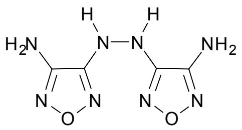
Table 2 Electrooxidative synthesis of azofurazans from aminofurazans on NiOOHanode.[a]



[a] Reaction conditions: substrate **8** (2 mmol), 0.2 M NaOH in H_2O (100 ml), 25°C, current density j_a= 6 mA cm^{-2}, Q_{theor} = 2F per a mole of compound **8**, NiOOH coated anode, Ti cathode. General procedure was used. Isolated yields are an average of three runs; in all cases where the reaction was unsuccessful or the yield of azo compound **9** was low, significant amounts of starting material were recovered. [b] Electricity passed: Q/Q_{theor} = 1. [c] Electricity passed: Q/Q_{theor} = 2.5. [d] Electricity passed: Q/Q_{theor} =3. [e] Reaction was performed at 70 °C. [f] 3-Amino-4-nitrofurazan **8r** was used in place of 3-amino-4-hydroxyfurazan **8h**.

The electrooxidation of an amino group in 3,4-diaminofurazan **8o** was first expected to provide the desired azo compound **9o**. An amino group of this product can further react with itself or with the amino group of remaining starting amine **8o** to generate oligomeric azofurazan byproducts. The easiest way to remove these impurities is via crystallization, thus giving diaminoazofurazan **9o** in acceptable yields (42%, Table 2).

It is significant that 1,2-bis(3-aminofurazan-4-yl)hydrazine **10** is nearly quantitatively converted to azocompound **9o** in 0.2*M* NaOH/H_2O at electro oxidation on NiOOH anode with $Q = Q_{theor}$ = 2F per a mole for *ca* 20 min at room temperature. In contrast, there is a report that bubbling of air through methanol solution convert hydrazine **10** to azo compound **9o** in good yield (92%);[5a] however, the reaction takes up to 20 h to complete.

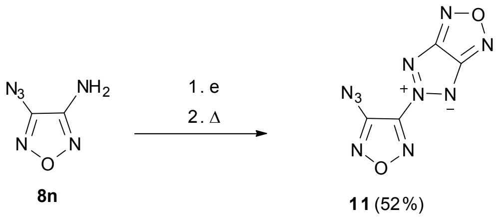


10

Attempted electrooxidation of 3-amino-4-nitrofurazan (**8r**, R = NO_2) resulted exclusively in the formation of hydroxyl product **9h** instead of the desired 4,4-dinitroazofurazan (**9r**, R = NO_2), which was undetectable. Hydrolysis of the nitro group proceeded cleanly to provide the hydroxy derivative **9h** in 94% yield; in contrast, only 63% yield of compound **9h** was obtained from oxidation of 3-amino-4-hydroxyfurazan **8h**.

Table 2 illustrates a generalized protocol implemented for the synthesis of azo compounds of interest in the energetic material chemistry arena such as 4,4-dihydroxyazofurazan **9h**,[4d,30] 4,4'-di(5-tetrazolyl)-azofurazan**9l** (identical with compound **3** from Fig.1),[7] compound **9m**,[4c] 4,4'-diaminoazofurazan **9o**(identical with compound **1** from Fig.1),[4c,5] and compound **9p**[31](the latter is an intermediate in the synthesis of nitrodiazenoxides, R'-N(O)=N-NO_2[8]).

Notably, these electrochemical conditions provide access to the products derived from 3-amino-4-azidofurazan **8n**.[32] At room temperature, highly sensitive azo compound **9n** can be made in 74% yield (Table 2). On the other hand, at higher temperatures, energetic pentalene **11**[33] (Scheme 2) was synthesized in good yield.

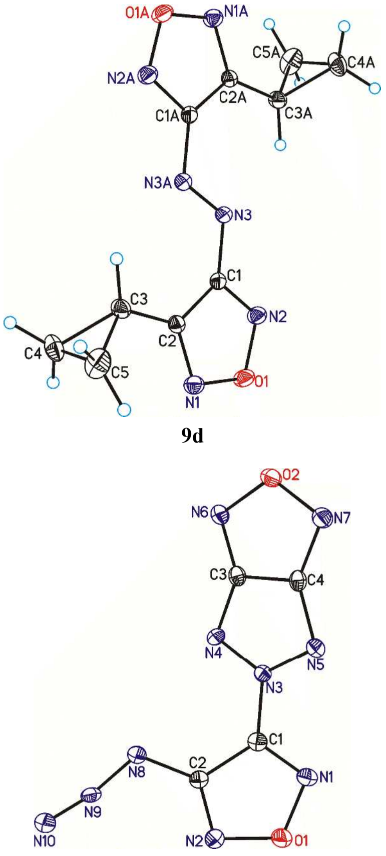


Scheme 2

The products were identified from their characteristic spectroscopic properties by comparison with those of similar compounds in the literature. Their ^{13}C NMR data are all consistent with the presence of the azofurazan corein the proposed structures. In particular, the δ_C values for $\underline{C}$-N=N (155-163 ppm), and C-R (148-151 ppm) are typical of azofurazans.[34] The structures of 4,4-dicyclopropylazofurazan **9d** and 5-(4-azidofurazan-3-yl)-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazol-5-ium-4-ide **11** were established by X-ray crystallography(Fig. 4).[35]

An asymmetric unit cell of azo compound **9d** contains half of the molecule located at the center of symmetry which adopts planar structure and *ap-ap-ap* conformation that is typical for azofurazans.[10i,36]

An asymmetric unit cell of fused furazan **11** contains one molecule, and this structure is characterized by high density (1.859 g·cm^{-3} at 100K). The molecule is somewhat nonplanar probably due to steric repulsion between substituents at the furazan ring. For the analysis of the crystal packing we used combination of the common visual analysis of the crystal packing based on consideration of the close contacts and the approach based on intermolecular pair energies[37] for which the M052X/aug-cc-pvdz level of approximation was utilized. Both methods and the basis set were successfully applied in our recent studies on isolated molecules and their aggregates.[38] The details of the crystal packing analysis are given as electronic supporting information (ESI).



9d

11

Fig.4 General view of the structures **9d** and **11** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Conclusions

In summary, we have reported a novel, efficient, and easy to perform green method for N=N bond formation to the synthesis of azofurazans. Key features of the approach include the electrooxidation of aminofurazans in *ca* 1% aqueous alkalion NiOOH anodewithout the use of inorganic/organic oxidants or other solvents. The process run in water produces from good to excellent yields of the azofurazans, promising candidates for energetic material formulations. Given the high yield, "greenness", and possibility of scaling-up, the process has considerable potential for adoption by pilot plant.

Current research from this laboratory is directed towards developing new applications of the electrooxidation in azoheterocycle synthesis.

Experimental section

Caution! Some substances prepared herein are highly energetic compounds and sensitive to various stimuli. Safety precautions, such as face shields, a leather apron, gloves, and hearing protection should be employed. These compounds should be handled with great care.

General: All the reagents and solvents were of analytical grade, purchased from commercial sources, and used as received. Alkylfurazan **8a-e**,[39] alkoxy- and hydroxyfurazans **8f-h**,[40] aryl derivatives **8i** and **8j**,[41] 1,2,4-oxadiazole **8k**,[42] tetrazole **8l**,[43] compound **8m**,[44] and ^{t}butylazoxy derivative **8p**[45] were synthesized by using previously reported methods. Infrared spectra were determined in KBr pellets on a Perkin-Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311A instrument. High resolution mass-spectra (HRMS) were measured on the Bruker micrOTOF II instrument using electrospray ionization (ESI).The ^{1}H, ^{13}C and ^{15}N (external standard: CH_3NO_2) spectra were recorded at 300.13, 75.47 and 50.7 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the solvent-*d* or to external standard without correction nitromethane (^{15}N). Analytical TLC was performed using commercially precoated silica gel plates (Silufol UV_{254}), and visualization was effected with short wavelength UV light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected.

Electrolysis. Electrochemical experiments were performed on a galvanostatic mode using the direct current source B5-8 in an 200 mL 4-neck jacketed flask as an undivided cell equipped with a cylindrical Ni anode (S = 48 cm^2) and a cylindrical Ti cathode (S = 20 cm^2). The distance between the electrodes was 1.1 cm. During the electrolysis, the reaction mixture was stirred with a magnetic stir bar at constant temperature (thermostat U-1). Before the experiment, the Ni anode was activated according to the procedure described earlier:[24] preliminary electrolysis was carried out in the solution containing 0.1 M $NiSO_4$, 0.1 M NaOAc, and 0.005 M NaOH, at j_a = 1 mA cm^{-2} with periodical reverse of the electrode polarization. This procedure is necessary for the formation of multi-layer coating containing NiOOH on the Ni anode surface.

Electrooxidation of 3-amino-4-methylfurazan 8a (General procedure). A 0.2 Msolution of NaOH (100 mL) and amine **8a** (0.2 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 2 F per mole of starting amine of electricity were passed (Q = 386 C), the solution usually changed from colorless to red-orange and the electrolysis was stopped. Then the reaction mixture was stirred for 15 min. Product was extracted with CH_2Cl_2 (3×30 mL). The combined extract was washed with water, dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by recrystallization.

4,4'-Dimethylazofurazan (9a): Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 108-109 °C (lit.[46]mp 107 °C); ^{1}H and ^{13}C NMR spectra are identical with those reported in the literature.[34a]

By analogous methodology were obtained azofurazans**9b-9g**, **9i-9j, 9l-9n** and **9p**.

4,4'-Diethylazofurazan (9b). Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 59-60°C (hexane); IR (KBr) ν/cm^{-1}: 2987, 2930, 1562, 1460, 1425, 1387, 1324, 1205, 1035, 979, 916, 800, 738, 719, 618; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.98 (t, J = 7.4 Hz, 6H, CH_3), 2.98 (k, J = 7.4 Hz, 4H, CH_2); ^{13} C NMR (75,5 MHz, DMSO-d$_6$): δ 10.9 (s, CH_3), 18.1 4 (s, CH_2), 150.7 (s, C-R), 162.5 (s, $\underline{C}$-N=N); Anal.Calcd for $C_8H_{11}N_6O_2$(222.40): C 43.24, H 4.54, N 37.82; found: C 43.28, H 4.50, N 37.76. HRMS (ESI-TOF) cacld for $C_8H_{10}N_6NaO_2^+$ ([M + Na$^+$]) = 245.0763, found 245.0779.

4,4'-Dipropylazofurazan (9c). Orange oil, R_f = 0.62 (1:1 hexane/CH_2Cl_2); IR (KBr) ν/cm^{-1}: 2967, 2937, 2877, 1559, 1463, 1245, 1201, 1092, 1027, 918, 806, 720, 616; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, J = 7.4 Hz, 6H, CH_3), 1.76 (k, J = 7.4 Hz, 4H, CH_2), 2.95 (t, J = 7.4 Hz, 4H, CH_2); ^{13}C NMR (75,5 MHz, $CDCl_3$): δ 13.5 (s, CH_3), 20.2 (s, CH_2), 26.3 (s, CH_2), 148.3 (s, C-R), 162.6 (s, $\underline{C}$-N=N); Anal.Calcd for $C_{10}H_{14}N_6O_2$(250.26): C 47.99, H 5.64, N 33.58; found: C 48.01, H 5.60, N 33.46.

4,4'-Dicyclopropylazofurazan (9d). Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 108-110°C (MeOH); IR (KBr) ν/cm^{-1}:1557, 1461, 1413, 1341, 1213, 1177, 1094, 1064, 1025, 925, 885, 819, 724, 617, 607; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (m, 4H, CH_2), 2.37 (m, 1H, CH); ^{13} C NMR (75,5 MHz, $CDCl_3$): δ 5.5 (s, CH), 10.0 4 (s, CH_2), 151.5 (s, C-R), 162.9 (s, $\underline{C}$-N=N); Anal.Calcd for $C_{10}H_{10}N_6O_2$(246.23): C 48.78, H 4.09, N 34.13; found: C 48.82, H 4.02, N 34.02. HRMS (ESI-TOF) cacld for $C_{10}H_{10}N_6NaO_2^+$ ([M + Na$^+$]) = 269.0763, found 269.0765.

4,4'-Dibutylazofurazan (9e). Orange oil, R_f = 0.62 (1:1 hexane/CH_2Cl_2); IR (KBr) ν/cm^{-1}: 2962, 2935, 2875, 1558, 1466, 1382, 1238, 1197, 1102, 1031, 917, 766, 730, 656, 616; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 7.3 Hz, 6H, CH_3), 1.44 (m, J= 7.4 Hz, 4H, CH_2), 1.72 (m, J = 7.3 Hz, 4H, CH_2), 2.99 (t, J = 7.4 Hz, 4H, CH_2); ^{13} C NMR (75,5 MHz, $CDCl_3$): δ 13.7 (s, CH_3), 22.2 (s, CH_2), 24.2 (s, CH_2), 29.0 (s, CH_2), 148.6 (s, C-R), 162.7 (s, $\underline{C}$-N=N); Anal.Calcd for $C_{12}H_{18}N_6O_2$ (278.31): C 51.79, H 6.52, N 30.20; found: C 51.82, H 6.47, N 30.08. HRMS (ESI-TOF) cacld for $C_{12}H_{18}N_6NaO_2^+$ ([M + Na$^+$]) = 301.1383, found 301.1421.

4,4'-Dimethoxyazofurazan (9f). Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 180-182 °C (EtOH) (lit.[40] mp 177-178 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 (s, 3H, OMe); ^{13} C NMR (75,5 MHz, $CDCl_3$): δ 60.0 (s, OCH_3), 155.0 (s, C-R), 158.8 (s, $\underline{C}$-N=N); Anal.Calcd for $C_6H_6N_6O_4$ (226.15): C 31.87, H 2.67, N 37.16; found: C 31.91, H 2.62, N 37.02. IR spectra are identical with those reported in the literature.[40]

4,4'-Dipropoxyazofurazan (9g). Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 52-53°C (hexane); ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.02 (t, J = 7.4 Hz, 6H, CH_3), 1.78 (k, J = 7.4 Hz, 4H, CH_2), 4.45 (t, J = 7.4 Hz, 4H, OCH_2); Anal.Calcd for $C_{10}H_{14}N_6O_4$ (282.26): C 42.55, H 5.00, N 29.77; found: C 42.59, H 4.55, N 29.52. HRMS (ESI-TOF) cacld for $C_{10}H_{14}N_6NaO_4^+$ ([M + Na$^+$]) = 305.0974, found 205.0977.

4,4'-Diphenylazofurazan (9i). Yellow solid, R_f = 0.62 (1:1

hexane/CH_2Cl_2); mp 134-135°C (hexane), (lit.[47] mp 134-135°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[47]

4,4’-Di-4-(pyridin-3-yl)-azofurazan (9j). Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 145-146°C (hexane); IR (KBr) ν/cm^{-1}: 1593, 1576, 1531, 1476, 1465, 1416, 1383, 1337, 1283, 1133, 1074, 1028, 993, 917, 872, 827, 732, 707, 688, 621, 587; ^1H NMR (300 MHz, DMSO-d$_6$): 7.48 (dd, J = 4.8, 1H, C$\underline{H}$), 8.10 (d, J = 7.9, 1H, C$\underline{H}$), 8.74 (d, J = 4.6, 1H, C$\underline{H}$), 8,91 (s, 1H, C$\underline{H}$); ^{13}C NMR (75,5 MHz, DMSO-d$_6$): δ 120.4, 123.7, 136.8, 148.7 (s, C-R), 149.2, 152.0, 161.8 (s, $\underline{C}$-N=N); Anal.Calcd for $C_{14}H_8N_8O_2$(320.27): C 52.50, H 2.52, N 34.99; found: C 52.53, H 2.49, N 34.85.

4,4’-Bis(4-(1H-tetrazol-5-yl)-azofurazan(9l). Yellow solid, mp 249-250°C (lit.[7] mp 238°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[7]

4,4’-[1,2,3]Triazolo[4,5-c][1,2,5]oxadiazol-azofurazan (9m). Orange solid, R_f = 0.80 (CH_2Cl_2); mp 128-130°C (dec), (lit.[33] mp100-102°C (dec)); ^{13}C NMR spectra are identical with those reported in the literature.[32]

3,3’-Diazidoazofurazan (9n). Yellow solid, R_f = 0.5 (1:1 hexane/CH_2Cl_2);dec *ca* 70°C, (lit.[44] dec 68°C); ^{13}C NMR (75,5 MHz, $CDCl_3$): δ 147.5(s, C-N_3), 156.6 (s, $\underline{C}$-N=N); ^{15}N NMR ($CDCl_3$, 30,4 MHz): -143.8, -136.8, 19.5, 44.3, 49.4, 141.9; ^{13}C NMR spectra are identical with those reported in the literature.[44]

4,4'-*Bis*(*tert*-butyl-*NNO*-azoxy)-3,3'-azofurazan(9p). Orange solid, R_f = 0.60 (1:1 hexane/CH_2Cl_2); mp 128-129°C, (lit.[30] mp 128-129°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[30]

Electrooxidation of 3,4-diaminofurazan (8o). A 0.2 *M*solution of NaOH (100 mL) and amine **8o**(0.2 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6*F* per mole of starting amine were passed (*Q* = 1158 C), the electrolysis was stopped, the reaction mixture was stirred for 15 min. Product was extracted with ethyl acetate (3×80 mL). The combined extract was dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by recrystallization from DMSO/H_2O.**4,4’-Diaminoazofurazan (9o**), yellow-orange solid, mp>300°C (lit.[5a] mp 298°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[5a]

Electrooxidation of 4,4-diaminohydrazofurazan (10). A 0.2 *M* solution of NaOH (100 mL) and amine **10** (0.2 g, 0.001mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 2*F* per mole of starting amine were passed (*Q* = 193 C), the electrolysis was stopped, the reaction mixture was stirred for 15 min. Product was extracted with ethyl acetate (3×80 mL). The combined extract was evaporated in vacuo. The residue was purified by recrystallization from DMSO/H_2O. The yield of **4,4’-diaminoazofurazan 9o** was 61%: mp>300°C (lit.[5a] mp 298°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[5a]

Electrooxidation of 3-amino-4-(tetrazol-5-yl)furazan 8l. A 0.2 *M*solution of NaOH (100 mL) and amine **8l** (0.3 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6*F* per mole of starting amine were passed (*Q* = 1158 C), the electrolysis was stopped, the reaction mixture was stirred for 15 min. After completion of the reaction, concentrated HCl was added (to pH 1) and the mixture was extracted with ether (3×30 mL). The organic phase was dried over Na_2SO_4 and then evaporated. The residue was purified by recrystallization to gave 4,4’-di(5-tetrazolyl)-azofurazan, **(9i)**. Yellow solid, R_f = 0.62 (1:1 hexane/CH_2Cl_2); mp 247-248°C (EtOH/H_2O), (lit. [7] mp 249-250°C); ^1H and^{13}C NMR spectra are identical with those reported inthe literature.[7]

4,4-Dihydroxyazofurazan (9h) was obtained by similarly to compound **9l**: A yellow solid, mp 262-265°C (lit. [4d,40] mp 263-265°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[4d,40]

Electrooxidation of 3-amino-4-nitrofurazan 8r. A 0.2 *M* solution of NaOH (100 mL) and amine **8r** (0.26 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6*F* per mole of starting amine were passed (*Q* = 1158 C), the electrolysis was stopped, the reaction mixture was stirred for 15 min. After completion of the reaction, aqueous HCl solution was added to *pH* 1 and the mixture was extracted with ether (3×30 mL). The organic phase was dried over Na_2SO_4 and then evaporated. The residue was purified by recrystallization to give **4,4-dihydroxyazofurazan (9h)**, mp 262-265°C, (lit.[40] mp 263-265°C); ^1H and ^{13}C NMR spectra are identical with those reported in the literature.[40]

5-(4-Azidofurazan-3-yl)-[1,2,3]triazolo[4,5-c][1,2,5]-oxadiazol-5-ium-4-ide(11).A 0.2 *M*solution of NaOH (100 mL) and amine **8n**(0.26 g, 0.002 mol) were placed in the cell, and electrolysis was carried out at a current of 290 mA and 25°C. After 6*F* per mole of starting amine were passed (*Q* = 1158 C), the electrolysis was stopped, the reaction mixture was diluted with benzene (100 mL) and stirred for 15 min. The benzene extract was dried over $MgSO_4$ and refluxed for 2 h. The solvent was removed under vacuum. The residue was purified by recrystallization to give the product **11**; mp 103-104°C (lit. [33] mp103-104°C); ^{13}C NMR (75,5 MHz, DMSO-d$_6$): δ 147.7(s, C-R), 149.3, 165.6 (s, $\underline{C}$-N=N); ^{15}N NMR (DMSO-d$_6$, 30,4 MHz): -139.7, -135.2, -88.2, -67.9, 23.5, 36.2, 38.8, 43.9; ^1H and ^{13}C NMR spectra are identical with those reported inthe literature. [33]

Acknowledgements

Financial support for this work was provided by The Russian Science Foundation (grant 14-13-01153 to A.B.S., A.M.K. and N.V.P., and 14-13-00884 to K.Y.S.) and the Russian Foundation for Basic Research (grant No. 12-03-00517a to B.V.L.). We are especially grateful to Dr. M. A. Syroeshkin for CV data.

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