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3-(1-ADAMANTYL)FURAZANS

A. B. Sheremetev[1]*, A. M. Kozeev[1], N. S. Aleksandrova[1],

M. I. Struchkova[1], and K. Yu. Suponitsky[2]

The reactivity of 3-(1-adamantyl)-4-aminofurazan was studied. Upon treatment with oxidizing reagents the amino group is oxidized to azo, azoxy, and nitro groups. The nitration of 3-(1-adamantyl)-4-aminofurazan with nitric acid provided the corresponding nitroamine. The reaction of 3-(1-adamantyl)-4-nitrofurazan with nitrating and bromination agents takes place at the bridgehead position of the adamantane fragment and gives the corresponding nitroxyl and bromo derivatives. An X-ray structural analysis of 4,4'-di(1-adamantyl)azofurazan was undertaken.

Keywords: adamantanes, furazans, electrophilic reactions, X-ray structural analysis.

The synthesis and investigation of compounds in which an adamantane framework is attached to a heterocycle is one of the most active directions in the chemistry of adamantane [1-5]. The geometry and lipophilicity of adamantane are extremely favorable for its transport through biological membranes and have been used widely for the creation of biologically active compounds [6-9]. In particular, a series of adamantane derivatives of 1,2,4- [10-13], 1,3,4- [14-21], and 1,2,5-oxadiazole [7, 22-26] having bactericidal, anti-inflammatory, and antidiarrheal activity and also agents for the treatment of Alzheimer's disease have been obtained.

Despite the fact that the adamantyl derivatives of isomeric oxadiazoles are of potential interest the chemical properties of such compounds have barely been studied at all. There are no published data on the insertion of substituents into an adamantane fragment attached to an oxadiazole ring. The most effective method for modification of the adamantane fragment is electrophilic substitution [27, 28]. In this communication, we disclose investigations of (1-adamantyl)-1,2,5-oxadiazole modifications *via* electrophilic substitution.

It should be noted that 1,2,5-oxadiazole (furazan) is a highly electron-deficient aromatic heterocycle due to the presence of three heteroatoms [29, 30]. For this reason, the reactivity of molecules containing a furazan substituent toward electrophilic reagents is greatly reduced [31-33]. On the other hand, the bulky adamantyl fragment at the *ortho* position to the second substituent in the furazan ring can affect the reactivity of this substituent. It was on account of these facts that the present investigation was undertaken.

*To whom correspondence should be addressed, e-mail: sab@ioc.ac.ru.

[1]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Ave., Moscow 119991, Russia.

[2]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova St., Moscow 119991, Russia; e-mail: kirshik@yahoo.com.

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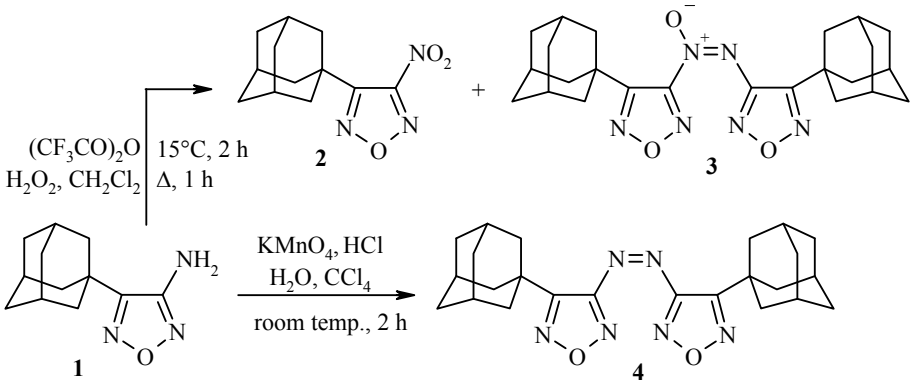
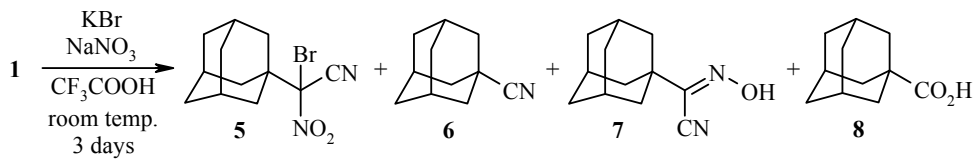
As starting material, we used 3-(1-adamantyl)-4-aminofurazan (**1**) [26], which contains the least electron-withdrawing aminofurazanyl fragment (Taft induction constant σ^* 2.55 [34]).

We had previously developed a method for the oxidation of aminofurazans to nitrofurazans with the mixtures based on H_2O_2 containing H_2SO_4, $NaWO_4$, and other inorganic additives [35]. Attempts to use these mixtures for oxidation of the amine **1** proved ineffective: not only the amine **1** did not dissolve in the aqueous oxidizing mixtures, but it is not even at all wetted, which prevented the reaction. The reaction with employment trifluoroperacetic acid as organic solvent, which has also been used for the oxidation of aminofurazans [36, 37], proved to be more effective. Oxidation usually requires no more than 3 hours [38, 39] at 15°C (the usual conditions) to complete, however in our case the reaction mixture remained blue, indicating the presence of an intermediate nitroso compound, even after 24 h. In the present case oxidation is probably prevented due to the steric hindrance. However, it is possible to bring the reaction to completion by refluxing the reaction mixture; the color disappears completely after reflux for an hour. It should be noted that the adamantane framework can undergo oxidative degradation during the action of peracids, giving polar oxygen-containing products [40]. In fact, according to TLC, polar products are also formed in the reaction mixture together with the low-polarity compounds **2** and **3** (R_f 0.71 and 0.27, respectively, eluent 1:1 hexane–$CHCl_3$). When the reaction mixture is washed these substances pass into the aqueous phase. After chromatographic separation of the substances present in the organic phase, 3-(1-adamantyl)-4-nitrofurazan (**2**) and 4,4'-di(1-adamantyl)azoxyfurazan (**3**) were isolated with yields of 32 and 7%. Attempts to isolate individual products from the aqueous phase were unsuccessful.

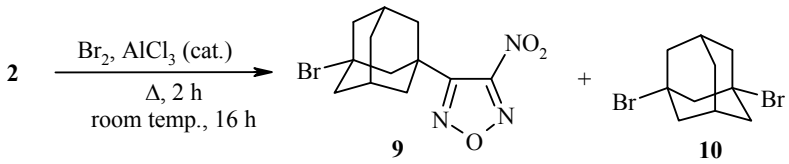


It is known [41-46] that oxidation of aminofurazans by one-electron oxidizing agent, such as $KMnO_4$, in hydrochloric acid usually gives good yields of the corresponding azofurazans. This reagent also proved effective in the case of the amine **1**; oxidation in the two-phase CCl_4–H_2O system took 2 h, and the azo product was formed in 81% yield.

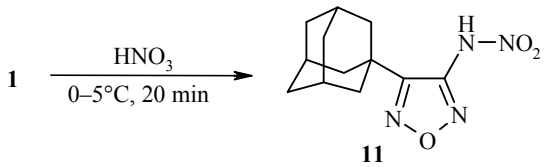
The amine **1** was not changed during the attempts of bromination in CCl_4, while an inseparable mixture of products was formed when it was refluxed in bromine in the presence of $AlCl_3$ [47] or $AlBr_3$ [48]. When a KBr–$NaNO_3$–CF_3CO_2H mixture was used for mild oxidative bromination of adamantanes [49] the adamantane framework of compound **1** was not affected, and decomposition of the furazan ring was observed. Four products were isolated from the reaction mixture: 2-(1-adamantyl)-2-bromo-2-nitroacetonitrile (**5**) (15%); adamantane-1-carbonitrile (**6**) (11%); 2-(1-adamantyl)-2-hydroxyiminoacetonitrile (**7**) (18%); adamantane-1-carboxylic acid (**8**) (14%). A similar type of ring cleavage is characteristic for aminofurazans under diazotization conditions [30, 50, 51].



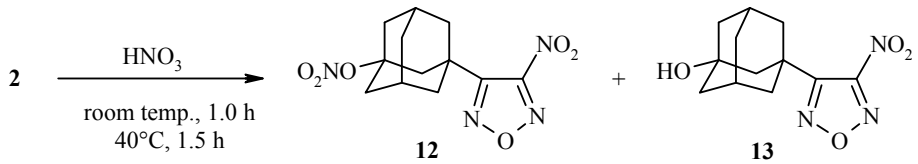
The problems arising during bromination are probably due to the presence of the amino group in compound **1**. Although it contains the more electron-withdrawing nitrofurazan fragment (Taft induction constant σ* 2.88 [34]) compound **2** can actually be fully brominated with the Br_2–$AlCl_3$ mixture in 2 h. It should be noted that under these conditions [47, 48] four bromine atoms may be substituted in reaction with unsubstituted adamantane, however only monobromination occurs with compound **2**. Compound **9** was isolated in a 62% yield, while 1,3-dibromoadamantane (**10**) was formed as a side product (19%).



There are several potential centers capable of reacting with nitrating reagents in the structure of the amine **1**. On the one hand, it is known [52-57] that the amino group in the furazan ring can be converted into a nitramino group, and on the other, nitro [58-60] or nitroxy [61] groups can be inserted in the adamantane framework. If the amine **1** is treated with concentrated nitric acid at 0°C selective N-nitration can occur, and the nitramine **11** is formed in a 78% yield. If 56% nitric acid is used the yield of the product **11** is reduced to 11%, while the use of HNO_3–H_2SO_4, HNO_3–CF_3CO_2H, and HNO_3–$(CF_3CO)_2O$ mixtures at temperatures between 10 and 50°C give mixtures that according to TLC contain more than 10 products.



As in the case of bromination, nitration of the derivative **2** takes place in a more well-defined manner. Whereas the reaction does not occur at room temperature, if compound **2** is heated in concentrated nitric acid at 40°C nitroxylation of adamantane is complete after 1.5 h. After dilution of the reaction mixture with water, extraction, and chromatographic purification, the nitrate ester **12** was obtained in a 55% yield. The hydroxyadamantane **13** (yield 18%), formed during isolation of compound **12** as a result of hydrolysis, was isolated as a side product.



The structure of the synthesized adamantylfurazans was confirmed by elemental analysis, IR and NMR spectroscopy, and EI mass spectrometry (Table 1). An X-ray structural analysis was undertaken for compound **4** (Fig. 1).

The mass spectra of most of the compounds contain signals for the low-intensity molecular ions, while the signal of the most intense ion corresponds to the adamantyl radical. The fragmentation under EI arises from the functional groups that are present. Thus, in the case of the nitro derivative **2** and the nitramine **11** the nitro group is removed first, and $[M\text{-}NO_2]^+$ ions are formed. For the nitro derivative **10**, which contains a bromoadamantyl fragment, although the low-intensity $[M\text{-}NO_2]^+$ ion is recorded the main direction of fragmentation results from loss of bromine, and the strongest ion is $[M\text{-}Br]^+$. For the azoxy compound **3** loss of the oxygen of the azoxy group with formation of the ion $[M\text{-}O]^+$ is the primary dissociation event during EI.

A characteristic feature for the nitrofurazans **2**, **10**, **12**, and **13** is the presence in the ^{14}N NMR spectra of a narrow ($\Delta\nu_{1/2}$ = 18-25 Hz) singlet for the nitrogen atom of the nitro group at 30.3-32.8 ppm. In the ^{13}C NMR spectra the signal of the carbon atom attached to the nitro group is greatly broadened as a result of $^{13}C–^{14}N$ coupling, which facilitates assignment of the signals. The JMODXH.AU software, with which it is possible to distinguish between the signals of the CH, CH_2, and CH_3 groups and the quaternary carbon atoms, and the data from two-dimensional $^{1}H–^{13}C$ heteronuclear correlation spectra through one bond (HMQC) and through 2-3 bonds (HMBC) were used for assignment of the signals in the ^{13}C NMR spectra. The spectral data of related compounds were taken into account during analysis of the spectra [62-64].

The proposed structure was confirmed unambiguously by X-ray structural analysis of compound **4** (Fig. 1). The symmetrically independent part of the unit cell contains half of the molecule of compound **4**, which is at a special position at the center of symmetry and has the *ap-sp-sp* conformation (according to the system of notation [68, 66] based on the geometry of the central C−N=N−C fragment, which can be either *anti*- or *syn-peri*-planar, *ap* or *sp* respectively, and also on the orientation of the C=N bonds of the furazan ring in relation to the central N=N fragment). It should be noted that the overwhelming majority of the azofurazans studied by X-ray structural analysis are characterized in the crystal by the *ap-ap-ap* conformation [54, 69]. In the case of compound **4**, however, such conformation is sterically unfavorable on account of the repulsion between the hydrogen atoms of the adamantane and the azo bridge.

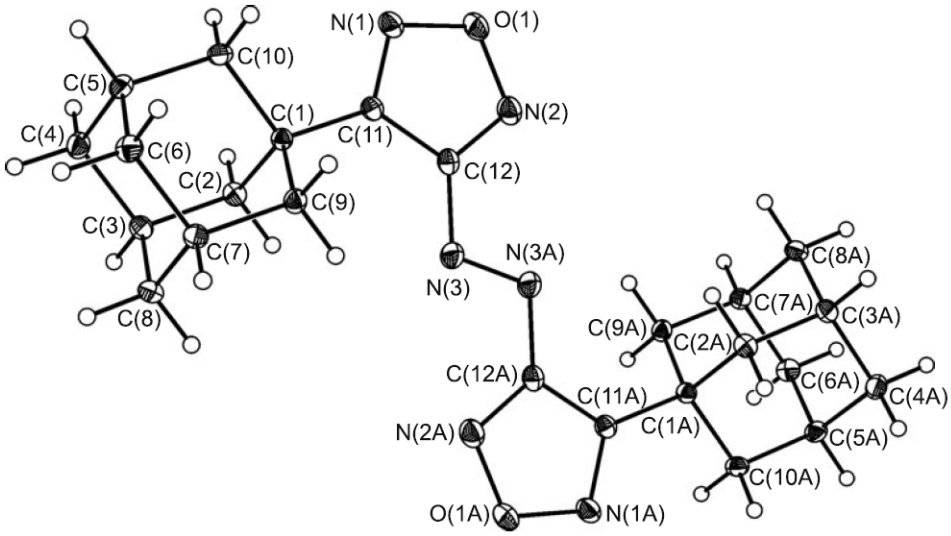
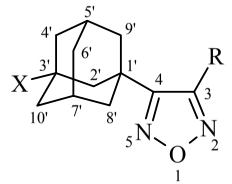


Fig. 1. A general view of the molecule of compound **4** with the atoms represented by thermal vibration ellipsoids of 50% probability.

The geometry of compound **4** is described well in terms of the effect of the donor and acceptor groups on the furazan ring [67]. The N−O bonds of the furazan ring at the azo group are shorter than at the adamantane substituent, while the lengths of the N(3)−C(12) and N(3)−N(3A) bonds (Table 2) indicate conjugation between the furazan ring and the azo bridge. (The average length of the C−N and N=N bonds is 1.431 and 1.222 Å, respectively [70].) Similar relationships were found earlier for the compounds presented in Table 2.

TABLE 1. Spectral Characteristics of 3-R-4-(3-X-Adamantan-1-yl)furazans **2-4**, **10-13**



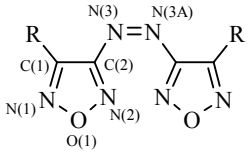
Compound	R	X	IR spectrum (KBr), ν, см$^{-1}$	^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)	^{13}C NMR spectrum ($CDCl_3$), δ, ppm									^{14}N NMR spectrum ($CDCl_3$), δ, ppm	Mass spectrum, *m/z*
					C-3	C-4	C-1'	C-2'	C-3'	C-4',10'	C-5',7'	C-6'	C-8',9'		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
2	NO_2	H	2911, 2855, 1567, 1535, 1454, 1339, 1184, 1054, 1015, 843	1.80 (6H, s, 4',6',10'-CH_2); 2.10 (6H, s, 2',8',9'-CH_2); 2.12 (3H, s, 3',5',7'-CH)	159.8	155.8	34.8	39.5	27.8	36.0				-30.3 (NO_2)	249 $[M]^+$, 203, 176, 135
3	–NN(O)–	H	2908, 2850, 1549, 1486, 1475, 1453, 1389, 1378, 1367, 1343, 1237, 1167, 1059, 1016, 1007, 922	1.81 (12H, s, 4',6',10'-CH_2); 2.13 (6H, br. s, 3',5',7'-CH); 2.14 (12H, br. s, 2',8',9'-CH_2)	158.0; 153.3	159.4; 156.3	34.7; 34.3	40.0; 39.7	27.8; 27.7	36.2; 35.9				-69.7 (N→O)	450 $[M]^+$, 434, 135
4	–N=N–	H	2934, 2907, 2850, 1541, 1452, 1400, 1368, 1343, 1244, 1182, 1109, 1062, 1008, 974, 901, 832	1.83 (12H, s, 4',6',10'-CH_2); 2.15 (6H, s, 3',5',7'-CH); 2.19 (12H, s, 2',8',9'-CH_2)	162.8	160.1	34.7	40.7	28.02	36.3					—

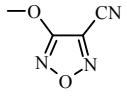
TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
10	NO_2	Br	2934, 2910, 2854, 1566, 1453, 1369, 1339, 1290, 1261, 1184, 1055, 1015, 975, 929, 843	1.81 (2H, s, 6'-CH_2); 2.12 (4H, s, 8',9'-CH_2); 2.33 (2H, s, 5',7'-CH); 2.46 (4H, s, 4',10'-CH_2); 2.70 (2H, s, 2'-CH_2)	158.8	153.3	38.4	50.0	61.2	47.6	31.4	34.1	37.6	-32.8 (NO_2)	329, 327 $[M]^+$, 283, 281, 248
11*	$NHNO_2$	H	3136, 2930, 2912, 2855, 1597, 1544, 1540, 1410, 1330, 1310, 1265, 1241, 1016, 990, 897, 862	1.72 (6H, s, 4',6',10'-CH_2); 1.96 (6H, s, 2',8',9'-CH_2); 2.02 (3H, s, 3',5',7'-CH); 9.72 (1H, s, NH)	159.9	148.2	33.6	39.8	27.8	35.7				-30.8 (NO_2)	264 $[M]^+$, 218, 188, 135
12	NO_2	ONO_2	2935, 2915, 2860, 1612, 1563, 1452, 1371, 1338, 1276, 1182, 1050, 1010, 974, 924, 865, 840	1.78 (2H, br. s, 6'-CH_2); 2.06 (2H, d, ^2J = 7.7) и 2.13 (2H, d, ^2J = 7.7, 8',9'-CH_2); 2.21 (4H, s, 4',10'-CH_2); 2.51 (2H, s, 5',7'-CH); 2.52 (2H, s, 2'-CH_2)	159.6	154.0	38.1	41.4	87.9	38.5	30.1	34.4	38.0	-32.1 (NO_2) -43.2 (ONO_2)	—
13	NO_2	OH	3370-3220, 2932, 2908, 2852, 1562, 1453, 1368, 1340, 1260, 1185, 1102, 1014, 976, 930, 843	1.69 (2H, s, 6'-CH_2); 1.80 (4H, s, 4',10'-CH_2); 2.01 (4H, s, 8',9'-CH_2); 2.06 (2H, s, 2'-CH_2); 2.38 (2H, s, 5',7'-CH); 3.55 (1H, br. s, OH)	157.8	154.5	37.7	46.8	67.8	43.9	30.0	34.5	38.2	-31.3	—

*The ^1H, ^{13}S, and ^{14}N NMR spectra were recorded in DMSO-d_6.

TABLE 2. Some Bond Lengths (Å) in the Molecules of Compound **4** and Other Azofurazans



R	O(1)–N(1)	O(1)–N(2)	N(3)–C(2)	N(3)–N(3A)
–Ad (**4**)	1.399(10)	1.374(10)	1.413(11)	1.254(14)
$-NH_2$ [65]	1.406(2)	1.355(2)	1.399(3)	1.266(3)
$-NHNO_2$ [54]	1.411(2)	1.356(2)	1.400(2)	1.255(2)
–OMe [66]	1.394(2)	1.360(2)	1.404(2)	1.244(2)
 [67]	1.390(3)	1.370(3)	1.410(4)	1.248(3)

Thus, it was shown that electrophilic reagents can be used for modification of the adamantylfurazans skeleton of the molecule. Despite the fact that the furazan ring reduces the reactivity of the adamantane fragment of the molecule these reactions make it possible to obtain compounds that are unavailable by other methods. The rich possibilities of the chemistry of bromo-, nitroxy-, and hydroxyadamantanes make it possible to hope that the obtained compounds will be effective in targeted syntheses.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Bruker Alpha-T spectrometer. The ^{1}H, ^{13}C, and ^{14}N NMR spectra at the natural contents of the isomers were recorded on a Bruker AM-300 spectrometer (300, 75, and 30 MHz, respectively) in DMSO-d_6 (compounds **7**, **11**) or in $CDCl_3$ (the other compounds). The chemical shifts in the ^{14}N NMR spectra were determined with reference to $MeNO_2$ as external standard. The two-dimensional spectra were recorded on a Bruker Avance 600 spectrometer by the standard Bruker procedure. The mass spectra were recorded on a Varian MAT-311A instrument, EI (70 eV). Elemental analysis was conducted on a CHNS/O Analyser 2400 (Perkin-Elmer Instruments Series II). The melting points were determined on Gallenkamp melting point apparatus and were not corrected. The reactions and the purity of the products were monitored by TLC on Sorbfil plates with a fixed layer, and silica gel SiO_2 40/100 was used for preparative chromatography. The starting 3-(1-adamantyl)-4-aminofurazan (**1**) was obtained by the published method [26].

3-(1-Adamantyl)-4-nitrofurazan (2) and 4,4'-Di(1-adamantyl)azoxyfurazan (3). 85% H_2O_2 (2 ml, 2.33 g, 58.2 mmol) was added dropwise to a mixture of CH_2Cl_2 (40 ml) and trifluoroacetic anhydride (14 ml, 21.00 g, 0.10 mol) cooled to 8°C. Amine **1** (2.00 g, 9.12 mmol) was then added to the obtained solution portionwise with stirring so that the temperature did not exceed 15°C. The reaction mixture was stirred at 15°C for 2 h and was then refluxed for 1 h. After cooling, H_2O (50 ml) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×15 ml). The combined extracts were washed with water (3×20 ml) and dried over $MgSO_4$. The solvent was removed at reduced pressure, and the remaining oil was separated by column chromatography with gradient elution with hexane → 1:1 hexane–$CHCl_3$.

The first fraction (R_f 0.71, hexane–$CHCl_3$, 1:1) was **compound 2**. Yield 0.73 g (32%), light-yellow oil, n_D^{24} 1.513. Found, %: C 57.91; H 6.12; N 16.78. $C_{12}H_{15}N_3O_3$. Calculated, %: C 57.82; H 6.07; N 16.86.

The second fraction (R_f 0.27, hexane–$CHCl_3$, 1:1) was **compound 3**. Yield 0.14 g (7%), fine colorless crystals, mp 211-212°C (hexane). Found, %: C 64.06; H 6.79; N 18.79. $C_{24}H_{30}N_6O_3$. Calculated, %: C 63.98; H 6.71; N 18.65.

4,4'-Di(1-adamantyl)azofurazan (4). Conc. HCl (6 ml) was added to a solution of the amine **1** (0.50 g, 2.28 mmol) in CCl_4 (12 ml). A solution of $KMnO_4$ (0.54 g, 3.42 mmol) in H_2O (30 ml) was added to the obtained two-phase mixture with vigorous stirring. The reaction mixture was then stirred for a further 2 h at room temperature and diluted with CCl_4 (30 ml). Oxalic acid was then added in portions until the reaction mixture was colorless. The organic layer was separated, washed with water (3×20 ml), and dried over $MgSO_4$, and the obtained solution was passed through a thin layer of silica gel on a Schott filter. The solvent was removed at reduced pressure, and the residue was recrystallized from $CHCl_3$. Yield 0.40 g (81%), orange crystals, mp 263-264°C. Found, %: C 66.39; H 7.03; N 19.23. $C_{24}H_{30}N_6O_2$. Calculated, %: C 66.34; H 6.96; N 19.34.

Oxidative Bromination of Amine 1. KBr (0.238 g, 2 mmol) and $NaNO_3$ (0.170 g, 2 mmol) were added to a solution of the amine **1** (0.440 g, 2 mmol) in trifluoroacetic acid (6 ml). The mixture was stirred at room temperature for 3 days and was then poured into H_2O (20 ml). The precipitate was filtered off and dried. The obtained mixture was separated on a column, gradient elution with hexane–$CHCl_3$, 5:1 → $CHCl_3$ → Et_2O.

The first fraction (R_f 0.63, hexane–$CHCl_3$, 5:1) was **2-(1-adamantyl)-2-bromo-2-nitroacetonitrile (5)**. Yield 0.09 g (15%), colorless crystals, mp 99-100°C (CCl_4). IR spectrum, ν, cm^{-1}: 3449, 2935, 2914, 2855, 1572, 1447, 1332, 1304, 1189, 1090, 1055, 976, 869, 849, 824, 773, 754. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.17 (3H, s, 3',5',7'-CH); 1.77 (6H, s, 2',8',9'-CH_2); 1.69 (6H, s, 4',6',10'-CH_2). ^{13}C NMR spectrum, δ, ppm: 111.8; 91.8; 42.8; 37.2; 35.6; 28.0. ^{14}N NMR spectrum, δ, ppm: -18.8. Mass spectrum, *m*/*z* (for ^{79}Br isotope): 298 $[M]^+$, 252 $[M\text{-}NO_2]^+$, 172 $[M\text{-}NO_2\text{-}Br]^+$, 144. Found, %: C 48.27; H 5.09; N 9.25. $C_{12}H_{15}BrN_2O_2$ (299.17). Calculated, %: C 48.18; H 5.05; N 9.36.

The second fraction (R_f 0.49, hexane–$CHCl_3$, 5:1) was **adamantane-1-carbonitrile (6)**. Yield 0.035 g (11%), colorless crystals, mp 194-195°C (mp 193-194°C [71]). The substance corresponded fully to an authentic sample.

The third fraction (R_f 0.05, hexane–$CHCl_3$, 1:1) was **2-(1-adamantyl)-2-hydroxyiminoacetonitrile (7)**. Yield 0.073 g (18%), colorless amorphous substance, mp 143-144°C (mp 142-143°C [72]). The substance corresponded fully to an authentic sample. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 12.92 (1H, s, NOH); 2.02 (3H, s, 3',5',7'-CH); 1.77 (6H, s, 2',8',9'-CH_2); 1.69 (6H, s, 4',6',10'-CH_2). ^{13}C NMR spectrum, δ, ppm: 144.8; 114.8; 44.3; 42.0; 40.7; 32.3.

The fourth fraction (R_f 0.30, EtO_2) was **adamantane-1-carboxylic acid (8)**. Yield 0.05 g (14%), colorless amorphous substance, mp 183-184°C (mp 181-183°C [73]). The substance corresponded fully to an authentic sample.

Bromination of Nitrofurazan 2. A catalytic amount of anhydrous $AlCl_3$ was added to a solution of nitrofurazan **2** (0.40 g, 1.60 mmol) in Br_2 (3.4 ml, 10.5 g, 66.0 mmol) with stirring, and the mixture was refluxed for 2 h. It was then left overnight at room temperature. The bromine was distilled, and the residue was dissolved in $CHCl_2$ (30 ml). The obtained solution was washed with H_2O (2×10 ml) and dried over $MgSO_4$. The oily residue after distillation of the solvent (0.85 g) was chromatographed on a column, gradient elution with hexane → hexane–$CHCl_3$, 10:1 → hexane–$CHCl_3$, 5:1 → $CHCl_3$.

The first fraction (R_f 0.53, hexane–$CHCl_3$, 5:1) was **1,3-dibromoadamantane (10)**. Yield 0.089 g (19%), colorless plates, mp 99-101°C (mp 100-103°C [74]). Mass spectrum, *m*/*z*: 293 $[M]^+$. The substance corresponded fully to an authentic sample.

The second fraction (R_f 0.36, hexane–$CHCl_3$, 5:1) was **3-(3-bromoadamantan-1-yl)-4-nitrofurazan (9)**. Yield 0.325 g (62%), colorless powder, mp 68-69°C. Found, %: C 43.99; H 4.34; N 12.72. Calculated, %: C 43.92; H 4.30; N 12.80.

3-(1-Adamantyl)-4-(nitramino)furazan (11). Amine **1** (0.200 g, 0.91 mmol) was added with vigorous stirring to fuming nitric acid (0.3 ml, 0.450 g, 7.20 mmol) (*d* 1.5 g/cm^3) cooled to 0°C. The reaction mixture was

maintained at 0-5°C for 20 min and was then allowed to heat to room temperature. The mixture was diluted with CF_3COOH (2 ml), and the precipitate was filtered off and dried over KOH in a vacuum desiccator. Yield 0.187 g (78%), colorless powder, mp 103°C (decomp.). Found, %: C 54.65; H 6.16; N 21.13. $C_{12}H_{16}N_4O_3$. Calculated, %: C 54.54; H 6.10; N 21.20.

3-(3-Nitroxyadamantan-1-yl)-4-nitrofurazan (12) and 3-(3-hydroxyadamantan-1-yl)-4-nitrofurazan (13). Nitrofurazan **2** (0.35 g, 1.4 mmol) was added to fuming nitric acid (2.35 ml, 3.53 g, 56 mmol) (*d* 1.5 g/cm^3). The obtained solution was stirred at room temperature for 1.0 h. The reaction mixture was then heated to 40°C, maintained at this temperature for 1.5 h, cooled to 15°C, and poured onto ice (30 g). The product was extracted with CH_2Cl_2 (4×20 ml), and the combined extracts were dried over $MgSO_4$ and evaporated. The residue (0.27 g) was separated on a column, gradient elution with CCl_4 → CH_2Cl_2–CCl_4, 1:1 → CH_2Cl_2.

The first fraction (R_f 0.25, CCl_4) was **compound 12**. Yield 0.240 g (55%), yellowish oil, n_D^{24} 1.536. Found, %: C 46.53; H 4.64; N 18.00. $C_{12}H_{14}N_4O_6$. Calculated, %: C 46.45; H 4.55; N 18.06.

The second fraction (R_f 0.02, CCl_4) was **compound 13**. Yield 0.067 g (18%), colorless amorphous substance, mp 82-83°C. Found, %: C 54.44; H 5.75; N 15.77. $C_{12}H_{15}N_3O_4$. Calculated, %: C 54.33; H 5.70; N 15.84

X-ray Crystallographic Analysis of Compound 4. The orange crystals of compound **4** ($C_{24}H_{30}N_6O_2$, *M* 434.55) at 100 K are monoclinic: *a* 10.9952(8), *b* 6.5924(5), *c* 28.939(2) Å; β 99.6260(10)°; *V* 2068.1(3) Å^3; *Z* 8; space group *C*2/*c*; μ 0.092 mm^{-1}; d_{calc} 1.396 g/cm^3. The intensities of 15690 reflections were determined on a SMART APEX2 CCD diffractometer (λ(MoKα) 0.71073 Å, graphite monochromator, ω-scan, 2θ < 66°). The initial set of measured intensities was processed by the SAINT and SADABS software included in the APEX2 package [75]. The structure was solved by the direct method and refined by full-matrix least-squares treatment in anisotropic approximation for the non-hydrogen atoms in F^2_{hkl}. The positions of the hydrogen atoms were calculated geometrically and refined in the "rider" model. During refinement, 3876 independent reflections were used (R_{int} 0.0278). The probability of the refinement in all the unique reflections was wR_2 0.0181 (R_1 0.0391 in 3306 reflections with $I > 2\sigma(I)$). All the calculations were done with SHELXTL software [76]. The structure was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 949778).

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