Generation of oxodiazonium ions
1. Synthesis of [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-oxides

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Methods for the synthesis of [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-oxides, which include the reaction of 3-nitramino-4-(R-phenyl)furazans or their *O*-methyl derivatives with electrophilic agents, have been developed. Unsubstituted [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-oxide was synthesized from 3-nitramino-4-phenylfurazan upon the action of phosphorus anhydride or oleum, as well as from *O*-methyl derivative of 3-nitramino-4-phenylfurazan upon the action of H_2SO_4, $MeSO_3H$, CF_3CO_2H and $BF_3 \cdot Et_2O$, while 6-, 7-, 8-, and 9-nitro-substituted [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-oxides — from the corresponding 3-nitramino-4-(nitrophenyl)furazans upon the action of the H_2SO_4-HNO_3 nitrating mixture. A suggestion has been made that an oxodiazonium ion is formed in these reactions from nitramines or their *O*-methyl derivatives upon the action of electrophilic agents, which is further involved into the intramolecular reaction of electrophilic aromatic substitution (S_EAr) with the aryl group. The structure of [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxides was confirmed by ^1H, ^{13}C, and ^{14}N NMR spectra. Theoretical studies by the B3LYP/6-311G(d,p) method of combined molecular system (*O*-methylated 3-nitramino-4-phenylfurazan + $[H_3SO_4]^+$) resulted in calculation of thermodynamic parameters of the sequence of cascade elementary reactions leading to the formation of [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-oxide.

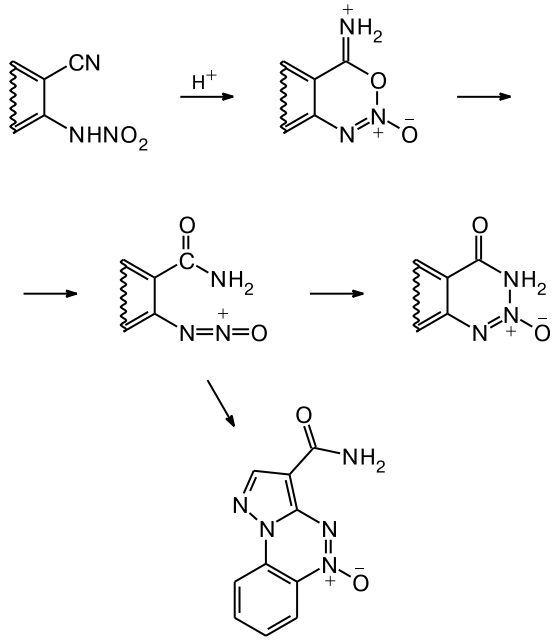
Key words: cinnolines, furazans, azoxy compounds, nitramines, oxodiazonium ion, electrophilic aromatic substitution, quantum chemical calculations, ^1H, ^{13}C, ^{14}N NMR spectroscopy.

Oxodiazonium ions $[Ar—N=N=O]^+$ have structures isoelectronic to a nitronium ion, however, unlike for the latter, method for the generation of oxodiazonium ions bound to an aryl group have been discovered only recently. Two independent groups of researchers[1,2] suggested that the mechanism of formation of annulated 1,2,3-triazin-4-one 2-oxides from nitramines containing an *ortho*-cyano group includes intermediate formation of an oxodiazonium ion (Scheme 1), and this was confirmed by its intramolecular trapping with the phenyl substituent.

We have considered a possibility of the intermediate formation of an oxodiazonium ion in the synthesis of annulated 1,2,3,4-tetrazine 1,3-dioxides (see Review 3 and references cited therein). It was suggested that this ion was formed by the intermolecular reaction of nitramines $Ar—NHNO_2$ with some electrophilic agents. At the same time, other mechanisms for the formation of 1,2,3,4-tetrazine 1,3-dioxides can be suggested, which do not involve oxodiazonium cation as a kinetically independent species.

The main purpose of the present work is to confirm formation of the oxodiazonium cation in the reactions of primary aromatic nitramines with electrophilic agents by its trapping with the phenyl ring. 3-Nitramino-4-phenyl-

Scheme 1



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furazan and its nitrophenyl derivatives have been chosen as model compounds.

Results and Discussion

Synthesis of starting compounds. The reaction of aminofurazan **1a** with 1 equiv. of KNO_3 in H_2SO_4 (Scheme 2) results in nitration of the phenyl ring to form all three possible isomers **1b**, **1c**, and **1d** in 34, 28, and 27% yields, respectively, which were separated by preparative TLC.

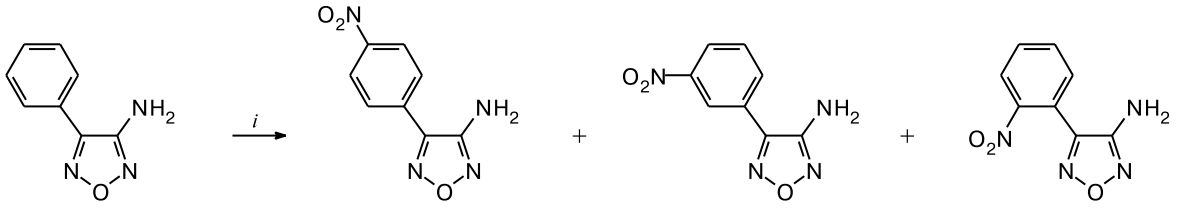
Nitration of aminofurazans **1a** and **1b** with nitronium tetrafluoroborate at low temperature in MeCN leads to *N*-nitramines **2a** and **2b**, respectively (Scheme 3). Nitramine **2b** in the pure form (m.p. 104—109 °C, decomp.) is more stable than **2a** (m.p. 69—71 °C, decomp.). Methylation of nitramine **2a** with diazomethane in diethyl ether leads to a mixture of *O*- and *N*-methyl derivatives **3a** and **4a** in the ratio 1.8 : 1 (see Scheme 3) in quantitative yield, which were separated by preparative TLC.

The structures of amines **1b—d**, nitramines **2a,b**, and methylated nitramines **3a** and **4a** were confirmed by the ^1H, ^{13}C, and ^{14}N NMR spectra. Full assignment of the signals in the ^{13}C NMR spectra of these compounds was made using the $^1H—^{13}C$ (HMBC and HSQC) two-dimensional correlations. According to the ^1H and ^{13}C NMR spectroscopy, *O*-methyl compound **3a** is a single stereoisomer. Similarly to the *O*-methylated nitramines,[4] the *E*-configuration can be assigned to the azoxy fragment of this compound.

Generation of oxodiazonium ions from *N*-nitramines and their *O*-methyl derivatives upon the action of protic acids or $BF_3 \cdot Et_2O$. Nitration of primary amines (direct reaction) and the corresponding to this process denitration of primary *N*-nitramines (reverse reaction) have been studied well enough (see Review 5). Protonation at the N atom with the formation of the intermediate **A** (Scheme 4, Eq. (1)) takes place during the denitration of nitramines, which decomposes with regeneration of the amine.

At the same time, protonation at the O atom with the formation of the intermediate **B** can be also suggested during the reaction of nitramine with acids, which could have eliminated H_2O to lead to the oxodiazonium ion **C** (see Scheme 4, Eq. (2)). Such a direction of protonation in the aliphatic compounds is considered as probable during decomposition of primary nitramines in acidic medium.[6] While studying heterocyclic compounds, we made a suggestion that similar reactions take place to explain the transformation of a primary *N*-nitramine group to a nitroso group[7] ($—NHNO_2 \rightarrow —N=O$). In addition, we studied a possibility of the $—O—NH—NO_2 \rightarrow \rightarrow [—O—N=N=O]^+$ transformation in the acid-catalyzed decomposition of *N*-nitrohydroxylamines.[8]

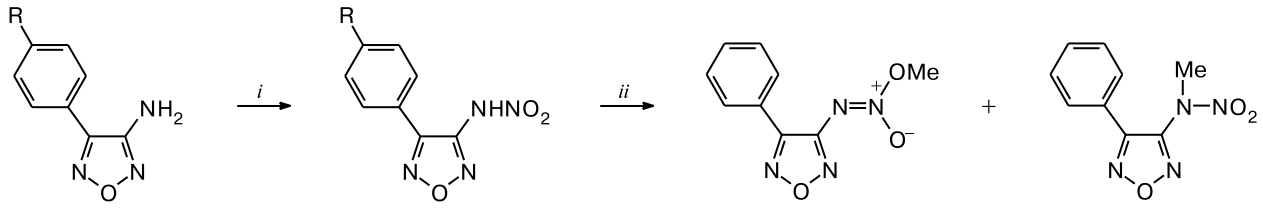
Scheme 2



1a **1b** (34%) **1c** (28%) **1d** (27%)

i. KNO_3 (1 equiv.)/H_2SO_4, 20 °C, 10 min, 89%.

Scheme 3

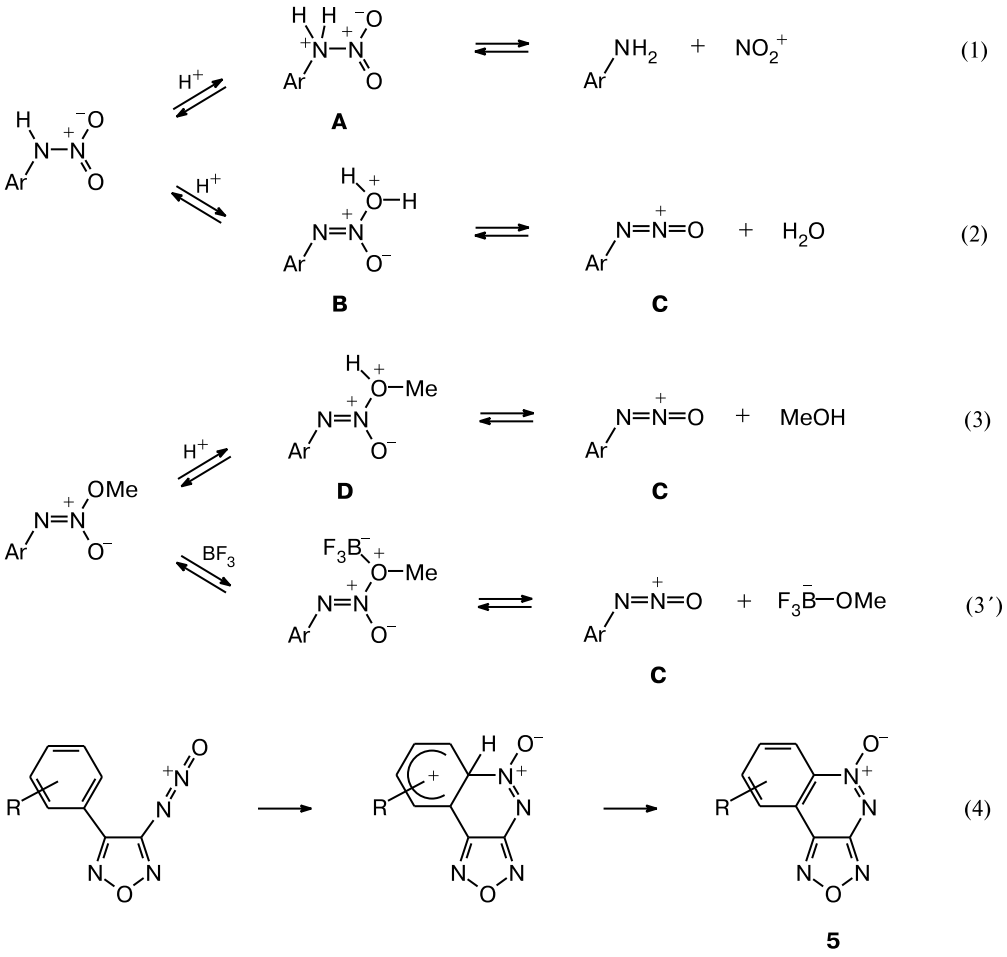


1a,b **2a,b** **3a** **4a**

i. NO_2BF_4, MeCN, $-30 \rightarrow -10$ °C; *ii*. CH_2N_2, Et_2O, 20°C.

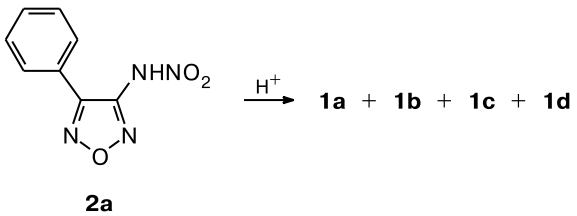
R = H (**1a**, **2a**), NO_2 (**1b**, **2b**)

Scheme 4



The reaction of nitramine **2a** with an excess of sulfuric acid or trifluoromethanesulfonic acid for 5 min leads to a mixture of aminofurazans **1a—d** (Scheme 5, Table 1). Obviously, the reaction proceeds as a denitration process according to Eq. (1) (see Scheme 4) with subsequent nitration of amine **1a** at the phenyl ring with the liberated nitric acid. It is obvious that no formation of oxodiazonium ion by Eq. (2) occurs (see Scheme 4).

Scheme 5



The denitration process can be avoided, if the nitramine is exchanged with its *O*-methyl derivative, for example, **3a** (see Scheme 4, Eq. (3)). The protonated form **D** could have eliminated MeOH with the formation of oxodiazonium ion **C**, which can react with the phenyl ring to give furazano[3,4-*c*]cinnoline 5-oxides (FCO) **5** (see Scheme 4, Eq. (4)). Note that the detailed quantum chemical studies of the reaction (3) (see Scheme 4) showed that protonation of *O*-methyl compound **3a** with $[H_3SO_4]^+$

Table 1. Reactions of nitramine **2a** with acids

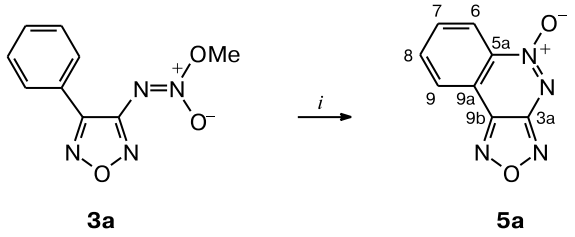
Acid (concentration (%))	Ratio acid : H_2O (mol)	Molar ratio of products (%)*			
		1a	**1b**	**1c**	**1d**
H_2SO_4 (100)	1 : 0	17	35	21	27
H_2SO_4 (93)	1 : 0.4	3	45	22	30
CF_3SO_3H (100)	1 : 0	9	35	31	25

* The molar ratios of products were determined from the ^{1}H NMR spectra. Nitramine **2a** was completely converted within 5 min at 20 °C. The total yield of products **1a—d** is close to quantitative.

leads to a complex consisting of oxodiazonium ion, molecule of methanol, and molecule of H_2SO_4 (for more details see the last section of the paper).

It was found that compound **3a** in solutions of concentrated acids is converted to FCO **5a** in good yields (Scheme 6, Table 2). The rate of cyclization strongly depends on the acid strength. For example, in H_2SO_4 (the Hammett acidity function $H_0 = -11.94$)[9] compound **3a** completely disappears within 5 min (TLC monitoring), in weaker $MeSO_3H$ ($H_0 = -7.74$)[10] within 30 min, and in CF_3COOH ($H_0 = -2.71$)[11] the reaction comes to completion within 3 days.

Scheme 6



3a **5a**

i. H^+ or $BF_3 \cdot OEt_2$, 20 °C.

For the transformation of compound **3a** to FCO **5a**, a Lewis acid can be also used, for example, $BF_3 \cdot OEt_2$ (see Scheme 6, Table 2). However, the yield of FCO **5a** is considerably lower than when acids were used.

Generation of oxodiazonium cation from *O*-methyl compound **3a** upon the action of $BF_3 \cdot Et_2O$ is likely to proceed according to Scheme 4 (Eq. (3′)).

Another approach, which allows one to accomplish generation of oxodiazonium cation from nitramine upon the action of acids, consists in that as to make the denitration process of nitramine reversible. This can be achieved, if exclude a possibility of nitration of the phenyl substituent by the use of nitramine **2b** as a model, which contains an electron-withdrawing nitro group in the ring. After this nitramine was kept in 93% H_2SO_4 during 1 h, approximately equal amounts of amine **1b** and nitramine **2b**, as well as small amount of FCO **5b**, are observed in the reaction mixture (Scheme 7, Table 3, the last line). About the same proportion of products is observed after 1 h, if amine **1b** and 1 equiv. of conc. HNO_3 are taken in the reaction instead of nitramine **2b** (Scheme 7, Table 3).

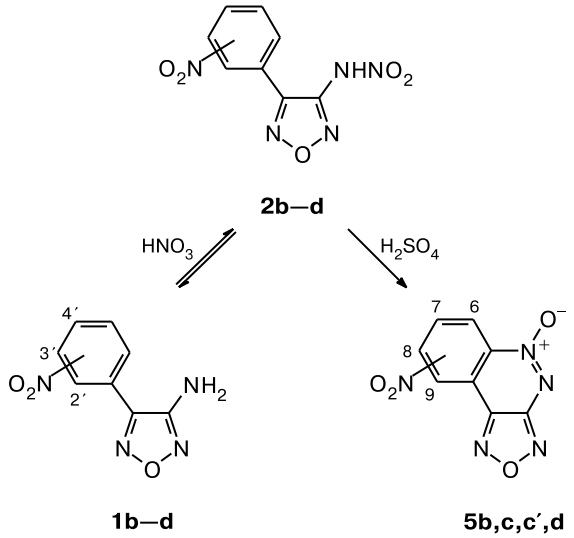
Table 2. Formation of FCO **5a** by the reaction of compound **3a** with acids or $BF_3 \cdot Et_2O$

Acid (concentration (%))	Ratio acid : H_2O (mol)	Reaction time	Yield of FCO **5a** (%)[a]
H_2SO_4 (100)	1 : 0	5 min	78
H_2SO_4 (93)	1 : 0.4	5 min	70
CH_3SO_3H (100)	1 : 0	30 min	83
CF_3COOH (100)	1 : 0	3 days	79
$BF_3 \cdot Et_2O$ (100)	1 : 0	1 days	31[b]

[a] The yields of FCO **5a** were determined from the ^1H NMR spectra. Conversion of compound **3a** was complete.

[b] The yield of FCO **5a** is calculated for the isolated product.

Scheme 7



2b—d

1b—d **5b,c,c′,d**

Position of the NO_2 group: 4′ (**1b**, **2b**), 3′ (**1c**, **2c**), 2′ (**1d**, **2d**), 7 (**5b**), 8 (**5c**), 6 (**5c′**), 9 (**5d**).

If the reaction time is increased to 24 h, almost complete conversion of nitramine is observed, and the yield of FCO **5b** reaches 77%. An increase in concentration of H_2SO_4 to 96% accelerates the reaction, whereas an increase to 100% somewhat slows it down (see Table 3).

For evaluation of comparative rates of cyclization of compounds with different positions of the nitro group in the benzene ring, aminofurazans **2b—d** were involved into the reaction with HNO_3 under the same conditions (100% H_2SO_4, 1 equiv. of conc. HNO_3, 20 °C, 10 h). The reaction products were analyzed by ^1H NMR spectroscopy. Conversion of the compounds (a degree of transformation of amine **1** and nitramine **2** into the reaction products: FCO **5** and unidentified products, was from 16 to 31% with respect to FCO **5**) was determined using ^1H NMR spectroscopy. For the 4-, 3-, and 2-nitrophenyl-substituted compounds, the conversion was 61, 54, and 20%, respectively. Apparently, the low rate of cyclization of 2-nitrophenyl-substituted nitramine **2d** is due to the steric reasons. Significant amount of unidentified by-products does not allow one to evaluate the relative rates of cyclization more accurate.

A plausible mechanism of the formation of FCO **5** is shown in Scheme 4 (see Eqs (2) and (4)). At the same time, one cannot completely exclude an alternative mechanism either, which includes nitration of nitramine with

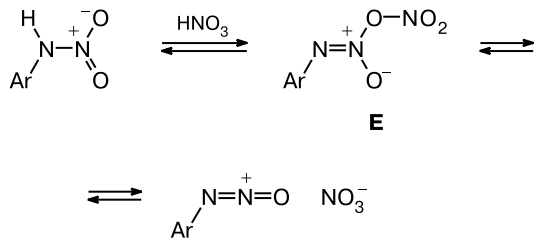
Table 3. Formation of FCO **5b** from aminofurazan **1b** and nitraminofurazan **2b** in the presence of 1 equiv. of HNO_3

Starting compound	Concentration of H_2SO_4 (%)	Ratio H_2SO_4 : H_2O (mol)	t^a/h	Molar ratio (%)[b]			
				1b	**2b**	**5b**	P^c
1b	93	1 : 0.4	1	32	39	11	18
1b	93	1 : 0.4	24	0	3	77	20
1b	96	1 : 0.23	24	2	7	79	12
1b	100	1 : 0	24	9	19	62	10
2b[d]	93	1 : 0.4	1	29	37	6	28

[a] Reaction time.
[b] The molar ratios of products were determined from the ^{1}H NMR spectra.
[c] Unidentified products.
[d] In the absence of HNO_3.

nitric acid at the O atom to form the intermediate **E** (Scheme 8). Nitric acid can be liberated in the process of denitration (see Scheme 4, Eq. (1)). The intermediate **E** is able to dissociate with the formation of oxodiazonium cation (see Scheme 8). We considered such a mechanism in the preceding work[12] for the generation of oxodiazonium cation from nitramines upon the action of N_2O_5 in organic solvents.

Scheme 8



Generation of oxodiazonium ions from *N*-nitramines upon the action of H_2SO_4—HNO_3 nitrating mixture. As it was shown above, cyclization of 3-amino-4-(nitrophenyl)-furazans **1b—d** to FCO **5b—d** takes place upon the action of 1 equiv. of conc. HNO_3 in sulfuric acid. However, the rate of the reaction is low under such conditions and a prolonged time is required to reach high conversion of aminofurazans. In this case, if 24 h is required for the synthesis of 7-nitro derivative **5b** in ~80% yield, then for obtaining 9-nitro derivative **5d** in the same yield already a few days are needed. In order to develop convenient preparative procedure, a 10-fold excess of the nitrating agent was used in the reaction. To simplify the procedure, conc. HNO_3 was replaced with the corresponding amount of KNO_3. Such a method allowed us to synthesize FCO **5b—d** in 92—95% yields (Table 4). 3-Amino-4-(*m*-nitrophenyl)furazan **1c** gave a mixture of isomeric 8-nitro- and 6-nitro derivatives **5c** and **5c´**, respectively, which was separated by preparative TLC. Apparently, oxodiazonium cation in this case was formed in accordance with Scheme 8.

Position of the nitro group in the phenyl ring of the starting compounds significantly affects the rate of the ring closure. The cyclization is the fastest in the case of *p*-nitro-substituted compound **1b** (2 h), *o*-nitro-substituted compound **1d** cyclizes slower (5 h), the lowest rate of the reaction is observed for *m*-nitro-substituted compound **1c** (7 h). Apparently, these differences in the reaction rates are due to the different thermodynamic stability of the corresponding σ-complexes **6b**, **6d**, **6c**, and **6c´** formed

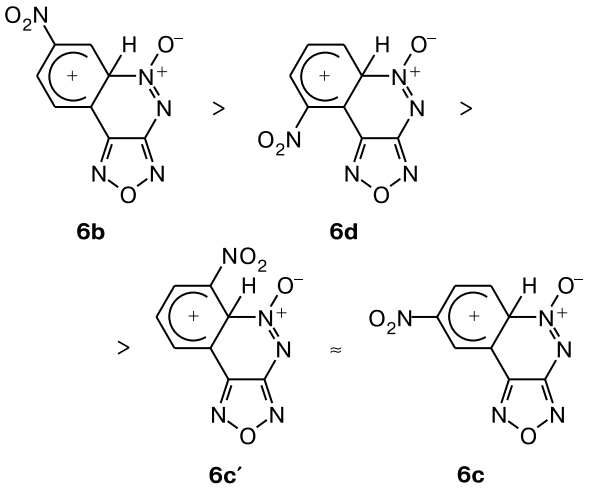


Table 4. Synthesis of nitro-substituted FCO **5b—d**

Starting compound	τ^a/h	FCO	Position of substituent NO_2 to FCO **5**	Yield of FCO **5** (%)[b]
1b	2	**5b**	7	95
1c	7	**5c**	8	42
		5c´	6	51
1d	5	**5d**	9	92

[a] Reaction time.
[b] The yields of FCO **5b—d** were determined from the ^{1}H NMR spectra. Conversion of compounds **1b—d** were complete.

Table 5. ^{1}H and ^{14}N NMR spectra of FCO **5a—d** in acetone-d_6

Compound[a]	^{1}H NMR, δ (*J*/Hz)				^{14}N NMR, δ ($\Delta\nu_{1/2}$/Hz)
	H(6)	H(7)	H(8)	H(9)	
5a[b]	8.66 (dd, *J* = 8.6, *J* = 1.1)	8.16 (ddd, *J* = 8.6, *J* = 7.5, *J* = 1.3)	8.22 (ddd, *J* = 7.8, *J* = 7.5, *J* = 1.1)	8.59 (dd, *J* = 7.8, *J* = 1.3)	−50 (N→O, $\Delta\nu_{1/2}$ = 12)
5b (7)	9.33 (d, *J* = 2.0)	—	8.99 (dd, *J* = 8.6, *J* = 2.0)	8.94 (d, *J* = 8.6)	−17 (C—NO_2, $\Delta\nu_{1/2}$ = 100), −52 (N→O, $\Delta\nu_{1/2}$ = 20)
5c (8)	8.95 (d, *J* = 9.3)	8.90 (dd, *J* = 9.3, *J* = 2.4)	—	9.33 (d, *J* = 2.4)	−13 (C—NO_2, $\Delta\nu_{1/2}$ = 80), −48 (N→O, $\Delta\nu_{1/2}$ = 12)
5c´ (6)	—	8.43 (dd, *J* = 7.8, *J* = 1.1)	8.48 (t, *J* = 7.8)	8.92 (dd, *J* = 7.8, *J* = 1.1)	−11 (C—NO_2, $\Delta\nu_{1/2}$ = 50), −57 (N→O, $\Delta\nu_{1/2}$ = 15)
5d (9)	9.00 (d, *J* = 8.5)	8.40 (t, *J* = 8.2)	8.67 (dd, *J* = 8.0, *J* = 1.0)	—	−13 (C—NO_2, $\Delta\nu_{1/2}$ = 60), −53 (N→O, $\Delta\nu_{1/2}$ = 20)

[a] Position of NO_2 group is given in parentheses.
[b] The ^{1}H—^{1}H COSY was used to assign the signals.

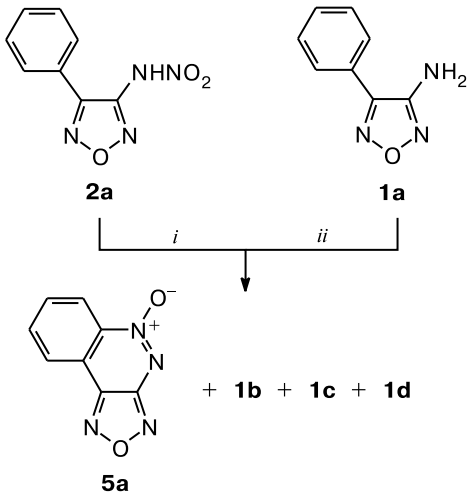
upon the attack of oxodiazonium cation on the phenyl ring, which is determined by both the electronic and steric factors.

Furazano[3,4-*c*]cinnoline 5-*N*-oxides **5** are representatives of a new heterocyclic system. Their structure was confirmed by ^{1}H, ^{14}N (Table 5), and ^{13}C NMR spectroscopy (Table 6), IR spectroscopy, and mass spectrometry. The full assignment of signals for the compounds in the ^{13}C NMR spectra was performed using the ^{1}H—^{13}C two-dimensional correlations.

The method of generation of oxodiazonium ions from nitramines upon the action of nitrating agents (see Scheme 7) does not allow one to synthesize FCO **5a**, the compound containing no electron-withdrawing substituents in the benzene ring. In this connection, we studied a possibility of generation of oxodiazonium cations by the reaction of *N*-nitramines with SO_3 and P_4O_{10}.

Generation of oxodiazonium ion from *N*-nitramine upon the action of SO_3. The reaction of nitramine **2a** with oleum of different concentrations was studied (Scheme 9, Table 7). The reagents were mixed with cooling (0 °C) to avoid for the reaction mixture to be strongly heated and turn black. The reaction is complete within 5 min. It turned out that when the molar ratio **2a** : SO_3 = 1 : 8, 3-amino-4-(nitrophenyl)furazans **1b—d** are the main reaction products, whereas FCO **5a** is formed in the trace amounts (3%). Apparently, the small excess of SO_3 mainly gives irreversible denitration of nitramine **2a**.

Scheme 9



i. Oleum, 0 → 20 °C, 5 min; *ii*. 1 equiv. of conc. HNO_3, 14% oleum, 0 → 20 °C, 5 min.

Table 6. ^{13}C NMR spectra of FCO **5a—d** in acetone-d_6[a]

Compound[b]	δ							
	C(3a)	C(5a) (br.s)	C(6)	C(7)	C(8)	C(9)	C(9a)	C(9b)
5a	157.5	141.8	123.9	134.7	135.9	126.2	119.5	138.2
5b (7)	158.1	142.3	119.7	151.6 (br.s)	130.0	128.7	124.5	138.0
5c (8)	157.0	143.4	125.6	128.0	150.6 (br.s)	120.9	120.0	137.3
5c´ (6)	156.6	131.2	144.1 (br.s)	128.4	136.4	128.0	121.1	137.0
5d (9)	156.9	141.1	127.0	134.4	129.5	146.4 (br.s)	112.6	134.3

[a] The ^{1}H—^{13}C (HMBC and HSQC procedures) two-dimensional correlations were used to assign the signals.
[b] Position of NO_2 group is given in parentheses.

Table 7. Formation of FCO **5a** from nitramine **2a** in oleum

Starting compound	Content of SO_3 in oleum (wt.%)	Ratio **2a** (**1a**) : SO_3 (mol)	Molar ratio[a] (%)				
			5a	**1b**	**1c**	**1d**	**1a**
2a	1.5	1 : 8	3	30	30	24	13
	4	1 : 20	23	21	31	22	3
	7	1 : 35	52	17	12	19	0
	14	1 : 70	70	10	11	9	0
1a[b]	14	1 : 70	0	35	41	24	0

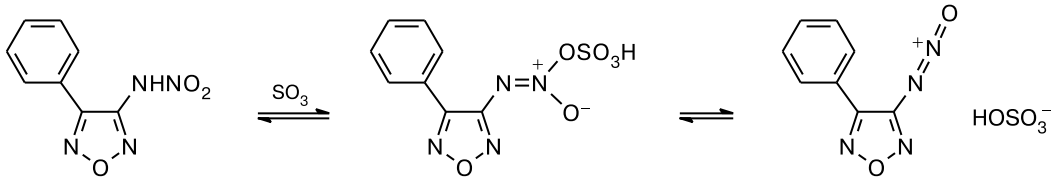
[a] The molar ratios of products were determined from the ^{1}H NMR spectra. Conversion of the starting compounds was complete.
[b] HNO_3 was added as a reagent.

An increase in concentration of SO_3 in the reaction mixture leads to the increase in the yield of FCO **5a**, and for the molar ratio **2a** : SO_3 = 1 : 70 it reaches 70%. If aminofurazan **1a** is taken instead of nitramine **1a** and added to a solution of equivalent amount of conc. HNO_3 in 14% oleum, no FCO **5a** is formed, rather nitration of the phenyl ring takes place, that leads to a mixture of amines **1b**—**d** (see Table 7). It is obvious that the *C*-nitration takes place significantly faster than the *N*-nitration under these conditions.

It is probable that under conditions of sulfation, the oxodiazonium cation is formed from nitramine *O*-sulfo derivative **F** (Scheme 10).

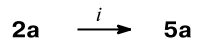
Generation of oxodiazonium ion from *N*-nitramine upon the action of P_4O_{10}. Earlier,[3] we have described the reactions of 2-(*tert*-butyl-*NNO*-azoxy)(*N*-nitramino)benzene and 3-(*tert*-butyl-*NNO*-azoxy)-4-(*N*-nitramino)furazan with P_4O_{10} in MeCN as a solvent leading to annulated 1,2,3,4-tetrazine 1,3-dioxides. Supposedly, the course of these reactions includes transformation of the —$NHNO_2$ group to the $[—N=N=O]^+$ cation. To confirm this suggestion, we carried out the reaction of nitramine **2a** with P_4O_{10} under similar conditions. Heating nitramine **2a** in anhydrous MeCN with a 20-fold excess of P_4O_{10} gave FCO **5a** in 66% yield (Scheme 11). The by-products formed in this reaction can be easily separated by chromatography on silica gel. Apparently, under phosphorylation conditions the oxodiazonium cation is generated from *O*-phosphorylated nitramine **G**.

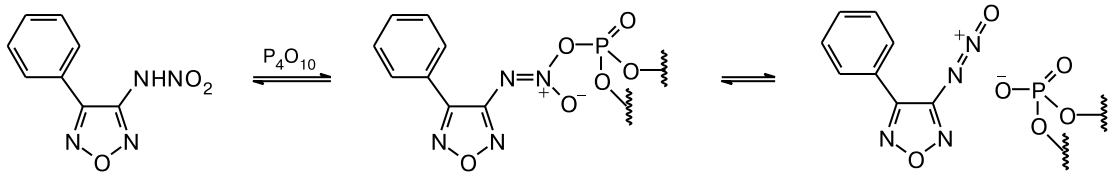
Scheme 10



F

Scheme 11





G

i. P_4O_{10}, MeCN, 70 °C, 10 h (66%).

Theoretical study of generation of oxodiazonium ion from *O*-methyl compound 3a in H_2SO_4 by the B3LYP functional density method. To confirm existence of oxodiazonium ion as a kinetically independent species, we studied the potential energy surface (PES) of combined molecular system *O*-methylated 3-nitramino-4-phenylfurazan (**3a**) + $[H_3SO_4]^+$ in the gas phase by the B3LYP/6-311G(d,p) functional density method.[13,14] For the confirmation of local minima on the PES, we performed calculations of vibrational spectra of the species studied.

Taking into account acidity of the reaction medium, we considered a protonated molecule of sulfuric acid $[H_3SO_4]^+$ as a protonating agent. Earlier,[15,16] it has been shown that ions $[H_3SO_4]^+$ can exist in 100% sulfuric acid in the form of complexes containing one or two molecules of H_2SO_4. It is known that protonation of alkyl sulfates promotes formation of carbenium ions.[17]

The study of PES (Fig. 1) showed that protonation of *O*-methyl compound **3a** at the O atom of the MeO group with $[H_3SO_4]^+$ leads to a nonactivated elongation of the N...O(H)Me bond with the formation of the complex consisting of oxodiazonium ion, molecule of methanol, and molecule of H_2SO_4 (Fig. 2, Table 8), in which the N...O(H)Me bond length is 1.923 Å. As it follows from the calculated Mulliken effective charges, the —N=N=O fragment in the oxodiazonium ion (Fig. 3) is characterized by a positive total charge (0.37 e) and, therefore, tends to be involved into intramolecular electrostatic interaction with the phenyl fragment. In addition, according to the calculated data the LUMO localized on the —N=N=O fragment can efficiently interact with the HOMO localized on the phenyl fragment. To sum up, in the framework of the molecular orbitals perturbation theory, proceeding from the geometrical and electronic structure of the considered oxodiazonium ion, one can predict the readiness of the corresponding reaction leading to the formation of the σ-complex of phenyl group with oxodiazonium ion.

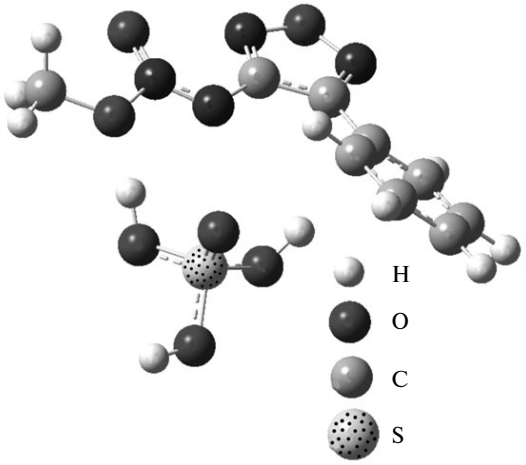


Fig. 1. The initial geometry of the complex used in the study of PES of combined molecular system **3a** + $[H_3SO_4]^+$.

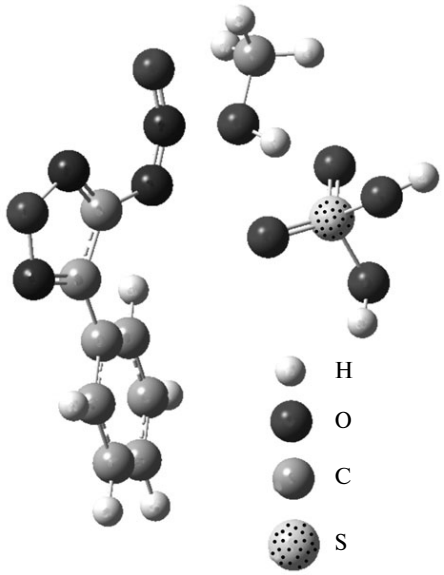


Fig. 2. Geometry of the complex oxodiazonium cation + MeOH + + H_2SO_4 optimized by the DFT/B3LYP method and obtained in the study of PES of combined molecular system **3a** + $[H_3SO_4]^+$.

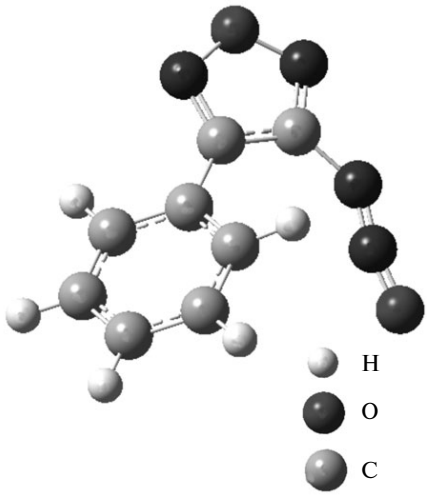


Fig. 3. Geometry of oxodiazonium cation optimized by the DFT/B3LYP method.

Results of calculation of cationic σ-complex by the B3LYP method with full optimization of geometrical parameters (Fig. 4) indicates its stability, though thermodynamically it is less favorable (endothermicity of the reaction of its formation is equal to 2.3 kcal mol^{-1} at T = 298 K) than the corresponding oxodiazonium ion. The final elementary reaction of the proton transfer from this σ-complex to the molecule of sulfuric acid leading to the formation of FCO **5a** (Fig. 5) is exothermic ($\Delta H = -15.6$ kcal mol^{-1} at T = 298 K). To sum up, the calculated data obtained

Table 8. Selected geometric parameters (bond lengths and bond angles) calculated by the B3LYP/6-311G(d,p) method for the fragment C—N=N=O in the complex oxodiazonium ion + MeOH + H_2SO_4 (see Fig. 2) (I) and in the "free" oxodiazonium ion (see Fig. 3) (II)

Parameter	I	II	Parameter	I	II
Bond length	*d*/Å		Bond angle	ω/deg	
C—N	1.406	1.386	N—N—O	151	169
N—N	1.202	1.147			
N—O	1.180	1.150			
N...OH*	1.923	—			

* The distance between the central nitrogen atom of the fragment C—N=N=O and the oxygen atom of MeOH in the complex.

allows one to suggest a plausible mechanism of the formation of FCO **5a** from *O*-methyl compound **3a** as a sequence of the elementary reactions (Scheme 12).

Scheme 12

3a + $[H_3SO_4]^+$ ⟶ $[Ar—N=N=O]^+$ + MeOH + H_2SO_4 (*a*)

($\Delta H = -6.7$ kcal mol^{-1})

$[Ar—N=N=O]^+$ ⟶ $[\sigma\text{-Complex}]^+$ (*b*)

($\Delta H = +2.3$ kcal mol^{-1})

$[\sigma\text{-Complex}]^+ + H_2SO_4$ ⟶ **5a** + $[H_3SO_4]^+$ (*c*)

($\Delta H = -15.6$ kcal mol^{-1})

The calculated data indicate that the reactions (*a*) and (*c*) are strongly exothermic, whereas the reaction (*b*) is weakly endothermic. The sequence of these reactions results in irreversible formation of FCO **5a** (at $T = 298$ K

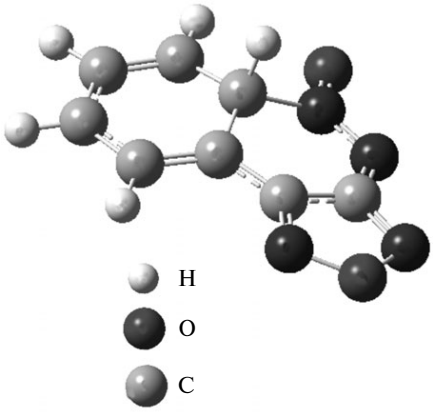


Fig. 4. Geometry of the σ-complex optimized by the DFT/B3LYP method.

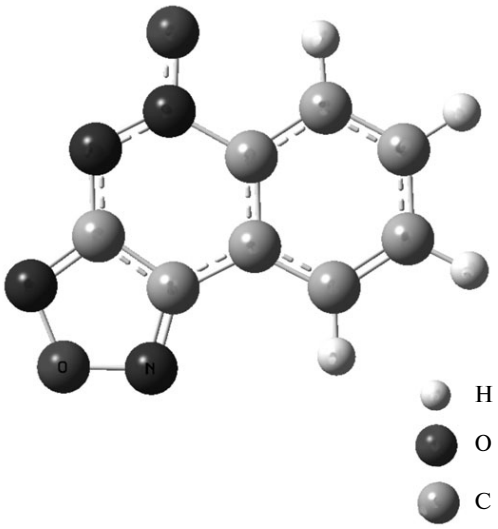


Fig. 5. Geometry of FCO **5a** optimized by the DFT/B3LYP method.

$\Delta H = -20.0$ kcal mol^{-1}, $\Delta G = -29.5$ kcal mol^{-1}). When concentrated, but not 100%, sulfuric acid is used, an oxonium ion $[H_3O]^+$ can also be the protonating species. However, if comparable values of proton affinity for the molecules of water and sulfuric acid are taken into account,[18] then the thermodynamics of the process of formation of FCO **5a** from *O*-methyl compound **3a** can change within 3 kcal mol^{-1}.

In conclusion, transformation of nitramines **2a—d** to FCO **5a—d** upon the action of nitrating, phosphorylating, and sulfating agents is a serious argument in favor of the intermediate formation of oxodiazonium cation $[—N=N=O]^+$. The ability of this cation to be involved into intramolecular reaction of aromatic electrophilic substitution with the phenyl ring containing no substituents, as well as with deactivated aromatic ring containing nitro groups in *ortho*-, *meta*-, and *para*-positions were demonstrated.

A new method for the generation of oxodiazonium ion from methoxy(oxido)diazenyl group —N=N(O)OMe upon the action of acids was developed. Theoretical studies of the mechanism of this reaction by the B3LYP functional density method were performed.

Experimental

^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13, 125.76, and 36.14 MHz, respectively) in acetone-d_6. Chemical shifts are given relatively to Me_4Si (^{1}H, ^{13}C) or $MeNO_2$ (^{14}N, external standard, the high-field chemical shifts have negative values). IR spectra were recorded on a Specord M-80 spectrometer (KBr pellets), mass spectra were recorded on a Kratos MS-300 instrument (EI, 70 eV). Reaction progress was monitored by TLC (Silufol UV-254

and Merck 60 F_{254}). Column chromatography on silica gel was used. 3-Amino-4-phenyl-1,2,5-oxadiazole[19] and ethereal solution of diazomethane[20] were obtained according to the known procedures. Distilled colorless HNO_3, $d = 1.5$ g cm^{-1}, was used.

3-Nitramino-4-phenyl-1,2,5-oxadiazole (2a). The compound NO_2BF_4 (0.23 g, 1.72 mmol) was added in small portions to a solution of 3-amino-4-phenyl-1,2,5-oxadiazole **1a** (0.2 g, 1.24 mmol) in anhydrous acetonitrile (6 mL) with vigorous stirring at −30 °C. The cooling bath was removed and the stirring was continued until the temperature reached −10 °C, then the reaction mixture was poured into the aqueous solution of $NaHCO_3$ (0.5 g in 20 mL). The aqueous layer was separated, washed with Et_2O (2×10 mL), and acidified with 10% aq. HCl to pH 2, then extracted with CH_2Cl_2 (5×10 mL). The extract was dried with $MgSO_4$ and concentrated *in vacuo* to obtain nitramine **2a** (176 mg, 69%) as yellowish crystals, after recrystallization from light petroleum m.p. 69—71 °C (decomp.). Found (%): C, 46.53; H, 2.87; N, 26.91. $C_8H_6N_4O_3$. Calculated (%): C, 46.61; H, 2.90; N, 27.18. IR, ν/cm^{-1}: 1280, 1312, 1324, 1404, 1468, 1504, 1616, 3308. ^{1}H NMR, δ: 7.61—7.64 (m, 3 H, H(3′), H(4′), H(5′)); 7.88 (dd, 2 H, H(2′), H(6′), $J = 7.3$ Hz, $J = 2.2$ Hz); 9.25 (br.s, 1 H, NH). ^{13}C NMR, δ: 125.5 (C(1′)); 128.3 (C(2′), C(6′)); 130.3 (C(3′), C(5′)); 132.3 (C(4′)); 149.0 (C(3)); 152.8 (C(4)). The HMBC and HSQC experiments were used to assign the signals. ^{14}N NMR, δ: −37 (N—$\underline{N}O_2$, $\Delta\nu_{1/2}$ = 20 Hz). MS, *m/z*: 206 $[M]^+$.

Reaction of compound 2a with diazomethane. A solution of diazomethane, obtained from *N*-methyl-*N*-nitrosourea (0.2 g), in Et_2O (3 mL) was added dropwise to a stirred solution of nitramine **2a** (90 mg, 0.44 mmol) in Et_2O (3 mL) at 20 °C until evolution of the gas was ceased and the solution turned slightly yellowish. Then the solvent was evaporated *in vacuo* to obtain a mixture of *O*- and *N*-methyl derivatives **3a** and **4a** (94 mg, 98%) as yellowish crystals. The mixture was separated by preparative TLC on silica gel (eluent: light petroleum—AcOEt (4 : 1)) to yield *O*-methyl compound **3a** (60 mg, 63%) and *N*-methyl compound **4a** (34 mg, 35%).

***E*-3-[Methoxy(oxido)diazenyl]-4-phenyl-1,2,5-oxadiazole (3a)**, m.p. 72—73 °C (from MeOH). Found (%): C, 49.33; H, 3.70; N, 25.21. $C_9H_8N_4O_3$. Calculated (%): C, 49.09; H, 3.66; N, 25.45. IR, ν/cm^{-1}: 1240, 1300, 1452, 1544, 1556. ^{1}H NMR, δ: 4.23 (s, 3 H, Me); 7.53—7.59 (m, 3 H, H(3′), H(4′), H(5′)); 7.96 (dd, 2 H, H(2′), H(6′), $J = 7.8$ Hz, $J = 1.9$ Hz). ^{13}C NMR, δ: 59.1 (Me); 124.8 (C(1′)); 128.3 (C(2′), C(6′)); 129.1 (C(3′), C(5′)); 131.1 (C(4′)); 150.6 (C(4)); 153.1 (C(3)). The HMBC and HSQC experiments were used to assign the signals. ^{14}N NMR, δ: −50 (N→O, $\Delta\nu_{1/2}$ = 90 Hz). MS, *m/z*: 220 $[M]^+$, 189 $[M - OMe]^+$.

3-[Methyl(nitro)amino]-4-phenyl-1,2,5-oxadiazole (4a), m.p. 69—71 °C (from light petroleum). Found (%): C, 49.27; H, 3.69; N, 25.13. $C_9H_8N_4O_3$. Calculated (%): C, 49.09; H, 3.66; N, 25.45. IR, ν/cm^{-1}: 1292, 1424, 1452, 1480, 1568. ^{1}H NMR, δ: 3.95 (s, 3 H, Me); 7.54—7.60 (m, 3 H, H(3′), H(4′), H(5′)); 7.78 (dd, 2 H, H(2′), H(6′), $J = 7.7$ Hz, $J = 1.3$ Hz). ^{13}C NMR, δ: 40.0 (Me); 124.7 (C(1′)); 127.2, 127.3 (C(2′), C(6′)); 129.4, 129.5 (C(3′), C(5′)); 131.4 (C(4′)); 152.0 (C(4)); 152.4 (C(3)). The HMBC and HSQC experiments were used to assign the signals. ^{14}N NMR, δ: −35 (N—$\underline{N}O_2$, $\Delta\nu_{1/2}$ = 30 Hz). MS, *m/z*: 220 $[M]^+$.

Nitration of 3-amino-4-phenyl-1,2,5-oxadiazole (1a) with the H_2SO_4—HNO_3 mixture. A solution of KNO_3 (188 mg, 1.86 mmol) in 93% aq. H_2SO_4 (1 mL) was added dropwise to a solution of aminofurazan **1a** (0.3 g, 1.86 mmol) in 93% aq. H_2SO_4 (4 mL) with vigorous stirring at 20 °C. The reaction mixture was stirred for 10 min and then poured onto finely crushed ice (15 g). A suspension formed was extracted with CH_2Cl_2 (5×10 mL). The combined organic layer was washed with brine (2 mL), dried with $MgSO_4$, and concentrated *in vacuo* to obtain a mixture of 3-amino-4-(nitrophenyl)-1,2,5-oxadiazoles **1b—d** (345 mg, 90%), which was separated by preparative TLC on silica gel (eluent: light petroleum—AcOEt (2 : 1)). Compound **1b** (132 mg, 34%), compound **1c** (107 mg, 28%), and compound **1d** (104 mg, 27%) were finally obtained.

3-Amino-4-(4′-nitrophenyl)-1,2,5-oxadiazole (1b), m.p. 173—175 °C. Found (%): C, 46.47; H, 2.95; N, 26.85. $C_8H_6N_4O_3$. Calculated (%): C, 46.61; H, 2.93; N, 27.18. IR, ν/cm^{-1}: 1312, 1348, 1476, 1516, 1604, 1632, 3328, 3452. ^{1}H NMR, δ: 5.80 (br.s, 2 H, NH_2); 8.15 (d, 2 H, H(2′), H(6′), $J = 9.0$ Hz); 8.44 (d, 2 H, H(3′), H(5′), $J = 9.0$ Hz). ^{13}C NMR, δ: 125.1 (C(3′), C(5′)); 130.1 (C(2′), C(6′)); 133.5 (C(1′)); 146.8 (C(4)); 150.0 (br.s, C(4′)); 156.3 (C(3)). ^{13}C NMR (DMSO-d_6), δ: 124.0 (C(3′), C(5′)); 129.1 (C(2′), C(6′)); 131.8 (C(1′)); 145.6 (C(4)); 148.2 (C(4′)); 155.3 (C(3)). The HMBC and HSQC experiments were used to assign the signals. ^{14}N NMR (acetone-d_6), δ: −13 (NO_2, $\Delta\nu_{1/2}$ = 130 Hz). MS, *m/z*: 206 $[M]^+$, 176 $[M - NO]^+$.

3-Amino-4-(3′-nitrophenyl)-1,2,5-oxadiazole (1c), m.p. 123—125 °C (from MeOH). Found (%): C, 46.78; H, 2.89; N, 27.01. $C_8H_6N_4O_3$. Calculated (%): C, 46.61; H, 2.93; N, 27.18. IR, ν/cm^{-1}: 1308, 1320, 1352, 1472, 1516, 1532, 1636, 3316, 3412. ^{1}H NMR, δ: 5.81 (br.s, 2 H, NH_2); 7.91 (t, 1 H, H(5′), $J = 8.1$ Hz); 8.27 (d, 1 H, H(6′), $J = 7.3$ Hz); 8.43 (dd, 1 H, H(4′), $J = 8.1$ Hz, $J = 1.5$ Hz); 8.66 (t, 1 H, H(2′), $J = 1.5$ Hz). ^{13}C NMR, δ: 123.6 (C(2′)); 125.8 (C(4′)); 128.8 (C(1′)); 131.7 (C(5′)); 134.9 (C(6′)); 146.7 (C(4)); 149.7 (br.s, C(3′)); 156.2 (C(3)). The HMBC and HSQC experiments were used to assign the signals. ^{14}N NMR, δ: −13 (NO_2, $\Delta\nu_{1/2}$ = 100 Hz). MS, *m/z*: 206 $[M]^+$, 176 $[M - NO]^+$.

3-Amino-4-(2′-nitrophenyl)-1,2,5-oxadiazole (1d), m.p. 113—114 °C (from MeOH) (*cf.* Ref. 21: m.p. 111—112 °C). Found (%): C, 46.74; H, 2.95; N, 26.99. $C_8H_6N_4O_3$. Calculated (%): C, 46.61; H, 2.93; N, 27.18. IR, ν/cm^{-1}: 1312, 1352, 1476, 1524, 1532, 1632, 3340, 3444. ^{1}H NMR, δ: 5.63 (br.s, 2 H, NH_2); 7.75 (dd, 1 H, H(6′), $J = 7.3$ Hz, $J = 2.2$ Hz); 7.91 (td, 1 H, H(4′), $J = 7.3$ Hz, $J = 2.2$ Hz, $J = 1.5$ Hz); 7.98 (td, 1 H, H(5′), $J = 7.3$ Hz, $J = 1.5$ Hz); 8.34 (dd, 1 H, H(3′), $J = 8.1$ Hz, $J = 1.5$ Hz). ^{13}C NMR, δ: 121.8 (C(1′)); 126.2 (C(3′)); 132.9 (C(4′)); 133.6 (C(6′)); 135.2 (C(5′)); 147.2 (C(4)); 149.4 (br.s, C(2′)); 156.8 (C(3)). The HMBC and HSQC experiments were used to assign the signals. ^{14}N NMR, δ: −12 (NO_2, $\Delta\nu_{1/2}$ = 85 Hz). MS, *m/z*: 206 $[M]^+$, 176 $[M - NO]^+$.

3-Nitramino-4-(4′-nitrophenyl)-1,2,5-oxadiazole (2b). The compound NO_2BF_4 (32 mg, 0.24 mmol) was added in small portions to a solution of compound **1b** (38 mg, 0.18 mmol) in anhydrous acetonitrile (3 mL) with vigorous stirring at −30 °C. The cooling bath was removed and the stirring was continued until the temperature reached 0 °C. Then, a solution of K_2CO_3 (0.1 g) in water (0.5 mL) was added to the reaction mixture, which was stirred for another 30 min at 0 °C. The mixture obtained was concentrated at 0 °C. The residue was thoroughly triturated and washed with Et_2O (5 mL) with vigorous stirring over 30 min. The washing was repeated another 2 times. A pre-

cipitate was dissolved in H_2O (10 mL) and the aqueous layer was washed with Et_2O (2×5 mL). Then, the aqueous layer was acidified with 10% aq. H_2SO_4 to pH 2 and extracted with AcOEt (3×5 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated *in vacuo* to obtain nitramine **2b** (32 mg, 69%) as yellowish crystals, m.p. 104—109 °C (decomp.). Found (%): C, 38.19; H, 2.07; N, 27.62. $C_8H_5N_5O_5$. Calculated (%): C, 38.26; H, 2.01; N, 27.88. IR, ν/cm^{-1}: 1280, 1292, 1328, 1344, 1520, 1604, 1616, 3316. ^{1}H NMR, δ: 8.17 (d, 2 H, H(2′), H(6′), J = 8.6 Hz); 8.44 (d, 2 H, H(3′), H(5′), J = 8.6 Hz). ^{13}C NMR, δ: 124.3 (C(3′), C(5′)); 129.0 (C(2′), C(6′)); 130.8 (C(1′)); 148.5 (C(3)); 149.6 (br.s, C(4′)); 150.7 (C(4)). The HMBC experiment was used to assign the signals. ^{14}N NMR, δ: −12 (C—NO_2, $\Delta\nu_{1/2}$ = 150 Hz); −37 (N—$\underline{N}O_2$, $\Delta\nu_{1/2}$ = 25 Hz). MS, *m/z*: 251 $[M]^+$, 206 $[M - NO_2]^+$.

Reaction of 3-nitramino-4-phenyl-1,2,5-oxadiazole (2a) with acids (general procedure). An acid (1 mL) was added in one portion to nitramine **2a** (10 mg, 0.05 mmol) (see Table 1) with vigorous stirring at 20 °C. The reaction mixture was stirred for 5 min, then poured into icy water (3 mL), and extracted with CH_2Cl_2 (5×3 mL). The organic extracts were combined, washed with brine (1 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The yields of products **1a—d** were determined by ^{1}H NMR (see Table 1).

Synthesis of [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxide (5a) from *E*-3-[methoxy(oxido)diazenyl]-4-phenyl-1,2,5-oxadiazole (3a) upon the action of acid (general procedure). An acid (1 mL) was added in one portion to *O*-methyl compound **3a** (10 mg, 0.045 mmol) (see Table 2) with vigorous stirring at 20 °C. The reaction mixture was kept at 20 °C for the time indicated in Table 2, then poured into icy water (3 mL). When the reaction was performed in CF_3COOH, the reaction mixture was concentrated and the residue was analyzed by ^{1}H NMR. After extraction with CH_2Cl_2 (5×3 mL), the organic extracts were combined, washed with brine (1 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The yield of cinnoline 5-*N*-oxide **5a** was determined by ^{1}H NMR (see Table 2).

Synthesis of cinnoline 5-*N*-oxide 5a from *E*-3-[methoxy(oxido)diazenyl]-4-phenyl-1,2,5-oxadiazole (3a) upon the action of $BF_3 \cdot Et_2O$. The compound $BF_3 \cdot Et_2O$ (2 mL) was added in one portion to *O*-methyl compound **3a** (20 mg, 0.09 mmol) at 20 °C under dry Ar. The reaction mixture was kept for 24 h at 20 °C, then poured into water (10 mL), neutralized with $NaHCO_3$ to pH 8, and extracted with CH_2Cl_2 (2×5 mL). The organic extracts were combined, washed with brine (2 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Cinnoline 5-*N*-oxide **5a** was purified by preparative TLC on silica gel (eluent: light petroleum—AcOEt (2 : 1)) to obtain the product (5.3 mg, 31%) identical to that synthesized earlier.

Reaction of 3-amino-4-(nitrophenyl)-1,2,5-oxadiazoles 1b—d with HNO_3 in H_2SO_4 (general procedure). Aminofurazan **1b—d** (5 mg, 0.024 mmol) was added in one portion to a solution of conc. HNO_3 (0.001 mL, 0.024 mmol) in sulfuric acid (0.5 mL) (the concentration of H_2SO_4 see in Table 3) at 20 °C with vigorous stirring. The reaction mixture was stirred until compounds **1b—d** were completely dissolved and kept at 20 °C for the time indicated in Table 3. Then the mixture was poured into icy water (2 mL) and extracted with CH_2Cl_2 (5×2 mL). The organic extracts were combined, washed with brine (1 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Degree of conversion of compounds **1b—d** to cinnoline 5-*N*-oxides **5b—d** and ratios of products were determined by ^{1}H NMR (see Table 3).

Reaction of 3-nitramino-4-(4′-nitrophenyl)-1,2,5-oxadiazole (2b) with 93% H_2SO_4. The reaction was carried out according to the general procedure for the reaction of 3-nitramino-4-phenyl-1,2,5-oxadiazole **2a** with acids. The reaction mixture was kept at 20 °C for 1 h. The molar ratio of products was determined by ^{1}H NMR (see Table 3).

Synthesis of cinnoline 5-*N*-oxides 5b—d (general procedure). A solution of KNO_3 (196 mg, 2 mmol) in 100% H_2SO_4 (2 mL) was added in one portion to aminofurazan **1b—d** (40 mg, 0.2 mmol) at 20 °C with vigorous stirring. The reaction mixture was stirred until compounds **1b—d** were completely dissolved and kept at 20 °C for the time indicated in Table 4. Then the mixture was poured into icy water (5 mL) and extracted with CH_2Cl_2 (5×4 mL). The organic extracts were combined, washed with brine (2 mL), dried with $MgSO_4$ and concentrated *in vacuo*. The yields of products **5b—d** were determined by ^{1}H NMR (see Table 4). Cinnoline 5-*N*-oxides **5b—d** were purified by preparative TLC on silica gel (eluent: $CHCl_3$—AcOEt (4 : 1)).

7-Nitro[1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxide (5b), m.p. 128—130 °C (from MeOH). Found (%): C, 41.36; H, 1.34; N, 29.75. $C_8H_3N_5O_4$. Calculated (%): C, 41.21; H, 1.30; N, 30.04. IR, ν/cm^{-1} (the region 1200—1600 cm^{-1}): 1272, 1348, 1428, 1440, 1472, 1540, 1608. MS, *m/z*: 233 $[M]^+$, 203 $[M - NO]^+$.

8-Nitro[1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxide (5c), m.p. 164—166 °C (from CH_2Cl_2). Found (%): C, 41.08; H, 1.32; N, 30.27. $C_8H_3N_5O_4$. Calculated (%): C, 41.21; H, 1.30; N, 30.04. IR, ν/cm^{-1} (the region 1200—1600 cm^{-1}): 1268, 1348, 1440, 1480, 1552. MS, *m/z*: 233 $[M]^+$.

6-Nitro[1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxide (5c′), m.p. 150—152 °C (from CH_2Cl_2). Found (%): C, 41.38; H, 1.33; N, 29.81. $C_8H_3N_5O_4$. Calculated (%): C, 41.21; H, 1.30; N, 30.04. IR, ν/cm^{-1} (the region 1200—1600 cm^{-1}): 1268, 1376, 1420, 1476, 1552. MS, *m/z*: 233 $[M]^+$.

9-Nitro[1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxide (5d), m.p. 204—207 °C (from acetone). Found (%): C, 41.11; H, 1.28; N, 29.79. $C_8H_3N_5O_4$. Calculated (%): C, 41.21; H, 1.30; N, 30.04. IR, ν/cm^{-1} (the region 1200—1600 cm^{-1}): 1272, 1348, 1408, 1424, 1480, 1544, 1584. MS, *m/z*: 233 $[M]^+$; 203 $[M - NO]^+$.

Reaction of nitramine 2a with oleum of different concentrations (general procedure). Oleum (1 mL) was added in one portion to nitramine **2a** (10 mg, 0.05 mmol) (see Table 7) at 0 °C with vigorous stirring. The reaction mixture was heated to 20 °C over 5 min, then poured into icy water (3 mL), and extracted with CH_2Cl_2 (5×3 mL). The organic extracts were combined, washed with brine (1 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The molar ratios of products were determined by ^{1}H NMR (see Table 7).

Reaction of 3-amino-4-phenyl-1,2,5-oxadiazole (1a) with HNO_3 in 14% oleum. The reaction was carried out according to the general procedure for the reaction of 3-amino-4-(nitrophenyl)-1,2,5-oxadiazoles **1b—d** with HNO_3 in H_2SO_4. The reagents were mixed at 0 °C, then the reaction mixture was heated to 20 °C and kept for 5 min at this temperature. The molar ratios of products were determined by ^{1}H NMR (see Table 7).

Synthesis of [1,2,5]oxadiazolo[3,4-*c*]cinnoline 5-*N*-oxide (5a) from nitramine 2a upon the action of phosphorus pentoxide. The compound P_4O_{10} (0.6 g, 2.1 mmol) was added to a solution of nitramine **2a** (20 mg, 0.1 mmol) in anhydrous MeCN at 20 °C with vigorous stirring. The reaction mixture was heated to 70 °C over 10 h with vigorous stirring, then cooled to 20 °C, poured into water (15 mL), and extracted with CH_2Cl_2 (5×5 mL). The

organic extracts were combined, washed with brine (2 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Cinnoline 5-*N*-oxide **5a** was purified by preparative TLC on silica gel (eluent: light petroleum—AcOEt (2 : 1)) to obtain 12 mg (66%) of this compound as white crystals, m.p. 157—159 °C, after recrystallization from CH_2Cl_2 m.p. 167—169 °C. Found (%): C, 49.91; H, 2.17; N, 29.90. $C_8H_4N_4O_2$. Calculated (%): C, 51.07; H, 2.14; N, 29.78. IR, ν/cm^{-1} (the region 1100—1600 cm^{-1}): 1144, 1240, 1272, 1408, 1436, 1440, 1476, 1584. MS, *m*/*z*: 188 $[M]^+$.

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