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Dedicated to Full Member of the Russian Academy of Sciences I.P. Beletskaya on her jubilee

New Syntheses of [1,2,5]Oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-Dioxide

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Abstract—New methods were developed for the synthesis of [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide from 4-(*tert*-butyl-*NNO*-azoxy)-*N*-nitro-1,2,5-oxadiazol-3-amine or its alkali metal salts and acid anhydrides (or chlorides) in the presence of strong acids. The yield of [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide in acetic anhydride in the presence of sulfuric acid or sulfuric anhydride at 20°C in 20 min attained 83%. A general mechanism was proposed for the reactions under study. Acetyl group behaved for the first time as departing group in the synthesis 1,2,3,4-tetrazine 1,3-dioxides, and [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide was obtained in 47% yield from *N*-[4-(acetyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-yl]acetamide.

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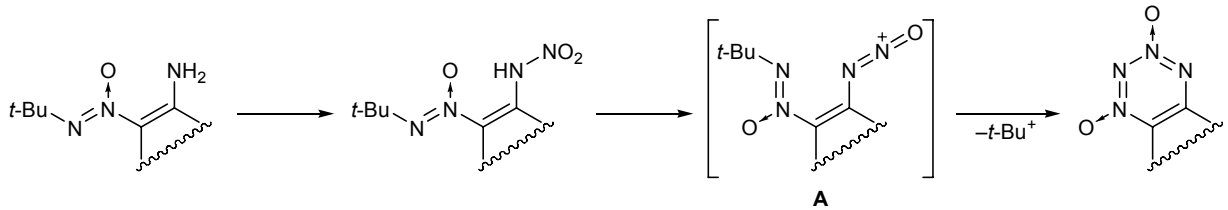
[1,2,5]Oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide (**I**, furazano-1,2,3,4-tetrazine 1,3-dioxide) occupies a specific place among known 1,2,3,4-tetrazine 1,3-dioxides [1]. First, it is the only known representative of five-membered heterocycles fused to a tetrazine dioxide ring. Second, compound **I** is characterized by a high standard enthalpy of formation (158–160.9 kcal× mol^{-1}) [2, 3], which makes it promising as component of energetic compositions [4–6]. Third, the conditions of synthesis of [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide (**I**) differ essentially from those for the preparation of aromatic analogs or tetrazine dioxides fused to a six-membered heteroring.

Tetrazine dioxides are generally synthesized from *o*-(*N*-nitroamino)-*tert*-butylazoxyarenes in which the *tert*-butyl group is the leaving group [1, 7] (Scheme 1). Both ionic systems (NO_2BF_4, HNO_3–H_2SO_4, HNO_3–oleum, PCl_5) and low-polar compounds (N_2O_5, P_4O_{10}) were successfully used to prepare tetrazine dioxides of the aromatic series [1]. It is believed that tetrazine dioxides are formed through intermediate oxodiazonium ion **A**.

Tetrazine dioxide **I** was synthesized in 52% yield from amine **IIa** with the use of NO_2BF_4 (Scheme 2) [1, 8]. In the reaction of *N*-nitroamine **IIIa** with P_4O_{10} in acetonitrile the yield of **I** was poor even when the reaction was carried out under fairly severe conditions (30% at 80°C) [1], whereas *N*-nitroanilines readily reacted with P_4O_{10} at 20°C in 15–40 min to afford 63–88% of the corresponding benzotetrazine dioxides [7].

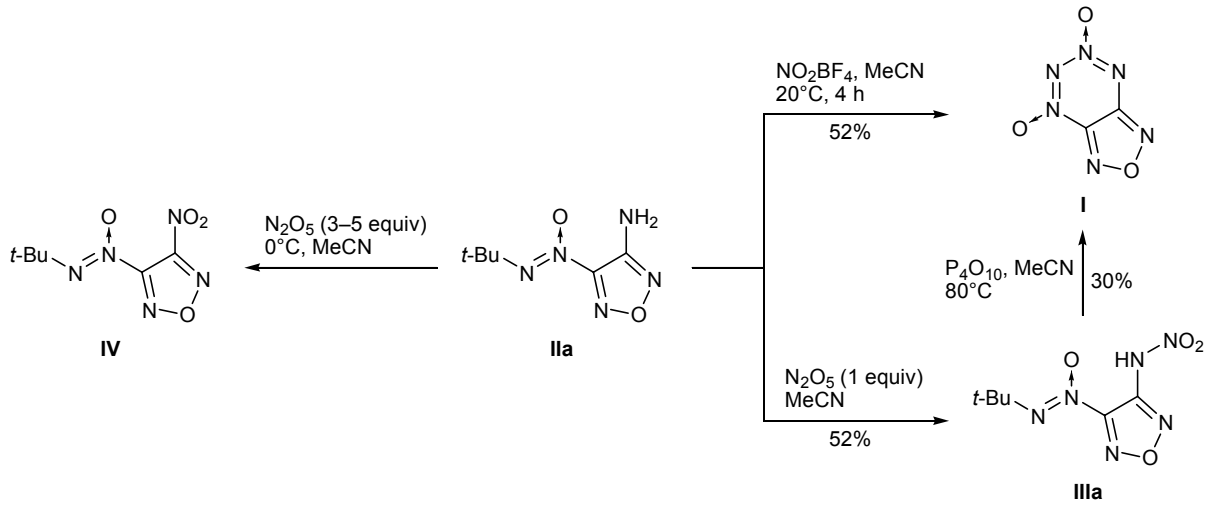
Scheme 1.



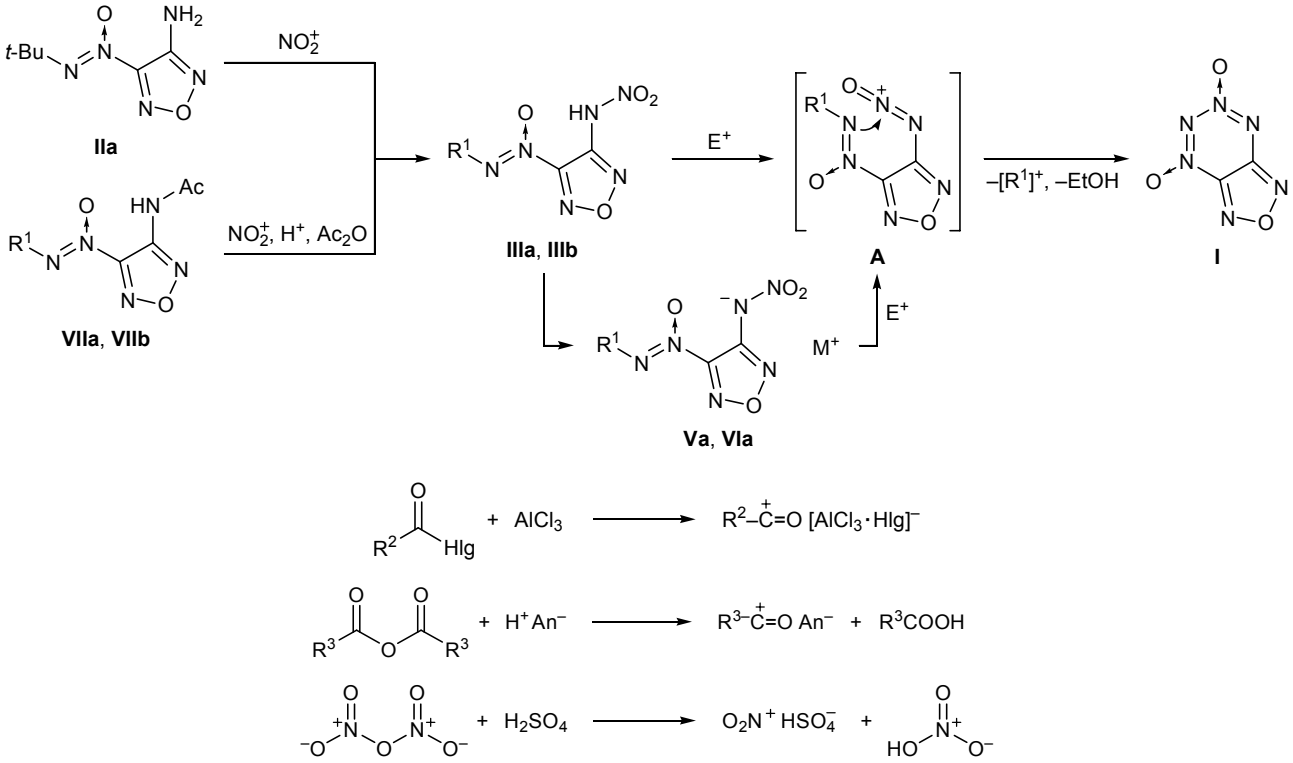
Even more contrasting results were obtained in syntheses with N_2O_5. Anilines reacted with nitric anhydride to form 51–83% of tetrazine dioxides [9], whereas the reaction of N_2O_5 with **IIa**, which is obviously mediated by *N*-nitroamine **IIIa**, gave only the oxidation product, nitro derivative **IV** [10] (Scheme 2). No reasonable explanation was given to the observed pattern.

The goals of the present study were to develop efficient procedures for the synthesis of [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide (**I**), elucidate reasons for considerably different reaction paths of nitric anhydride with *N*-nitroamine **IIIa** and aromatic analogs, and estimate the effect of some factors on the synthesis of compound **I**.

Scheme 2.



Scheme 3.



R^1 = *t*-Bu (**a**), Ac (**b**); $E^+ = NO_2^+$, $R^2C(O)^+$, $R^3C(O)^+$, SO_3, P_4O_{10}; R^2 = Me; Hlg = Cl, Br; R^3 = Me, Et, Ph; $H^+An^- = HClO_4$, H_2SO_4, HBF_4, H_3PO_4; **Va**, M = Na; **VI**, M = K.

Table 1. Synthesis of tetrazine dioxide **I** from *N*-nitroamine **IIIa**

Run no.	Acid (Lewis acid)[a]	Solvent	Temperature, °C	Reaction time,[b] h	Yield of **I**, %
1	$AlCl_3$	AcCl	5–10	0.25	30
2	$ZnCl_2$	Ac_2O	25	2	3
3[c]	$HClO_4$	Ac_2O	20	0.25	55
4	H_2SO_4	Ac_2O	20	0.33	83
5[c]	HBF_4	Ac_2O	20	7	56
6[d]	H_3PO_4	Ac_2O	20	48	3
7	H_2SO_4	$(EtCO)_2O$	20	0.33	55
8[e]	Oleum (60% SO_3)	AcOH	22	30	53
9	SO_3	$ClCH_2CH_2Cl$	–10 to –5	0.25	57
10	SO_3	Ac_2O	25	0.25	82
11	P_4O_{10}	Ac_2O	10	0.5	60
12[f]	H_2SO_4–$(PhCO)_2O$	$MeNO_2$	20	7	23

[a] Molar ratio acid–**IIIa** 2 : 1, unless otherwise stated.
[b] The reaction time was determined by the disappearance of initial compound **IIIa** according to the TLC data.
[c] The required amount of acid was added to excess Ac_2O, and AcOH was then removed under reduced pressure.
[d] Anhydrous acid was preliminarily prepared by adding a required amount of P_2O_5 to 82% H_3PO_4.
[e] 6.2 mol of SO_3 per mole of **IIIa**.
[f] Molar ratio $(PhCO)_2O$-**IIIa** 2 : 1.

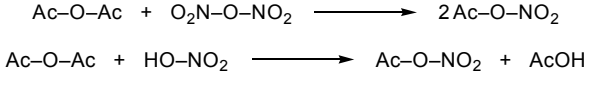
We have developed new methods of synthesis of compound **I**, the first communication being reported in 2004 [11]. Tetrazine dioxide **I** was obtained by reactions of *N*-nitroamines **IIIa** and **IIIb** or their salts **Va** and **VIa** with organic acid anhydrides and chlorides in the presence of strong mineral acids as ionizing agents, as well as with mineral acid anhydrides in the absence (SO_3, P_4O_{10}) or in the presence of strong acid (N_2O_5) (Scheme 3).

It is advisable to use polar solvents having no basic properties. Strong Brønsted ($HClO_4$, H_2SO_4, HBF_4, H_3PO_4) or Lewis acid ($AlCl_3$, $BF_3 \cdot Et_2O$, $ZnCl_2$) promotes ionization of weakly polar anhydride (acid halide) to form an ion pair E^+An^- (Scheme 3). Attack by electrophilic species E^+ on *N*-nitroamine molecule yields intermediate oxodiazonium ion **A** which undergoes cyclization to tetrazine dioxide **I** via elimination of *tert*-butyl or acetyl cation. The conditions of synthesis and yields of compound **I** from *N*-nitroamine **IIIa** are collected in Table 1.

The reaction time in acetic anhydride and the yield of **I** (Table 1, run nos. 3–6) depended on the strength of the added acid. In the presence of strong acids such as H_2SO_4 (H_0 = –11.94 [12]) or $HClO_4$ (H_0 = –10.31 for 78.6% $HClO_4$ [12]), *N*-nitroamine **IIIa** disappeared completely in 15–20 min (TLC), whereas considerably longer time was necessary to complete the reaction catalyzed by less strong acids, 7 h in the presence of HBF_4 and 48 h in the presence of H_3PO_4 (H_0 = –5.2 [12]). Strong acids ($HClO_4$, H_2SO_4, HBF_4) ensured a good yield of **I** (55–83%), while the yield was close to zero with the use of weaker acids such as H_3PO_4 (3%) and CF_3COOH (~0.1%; H_0 = –2.71 [13]).

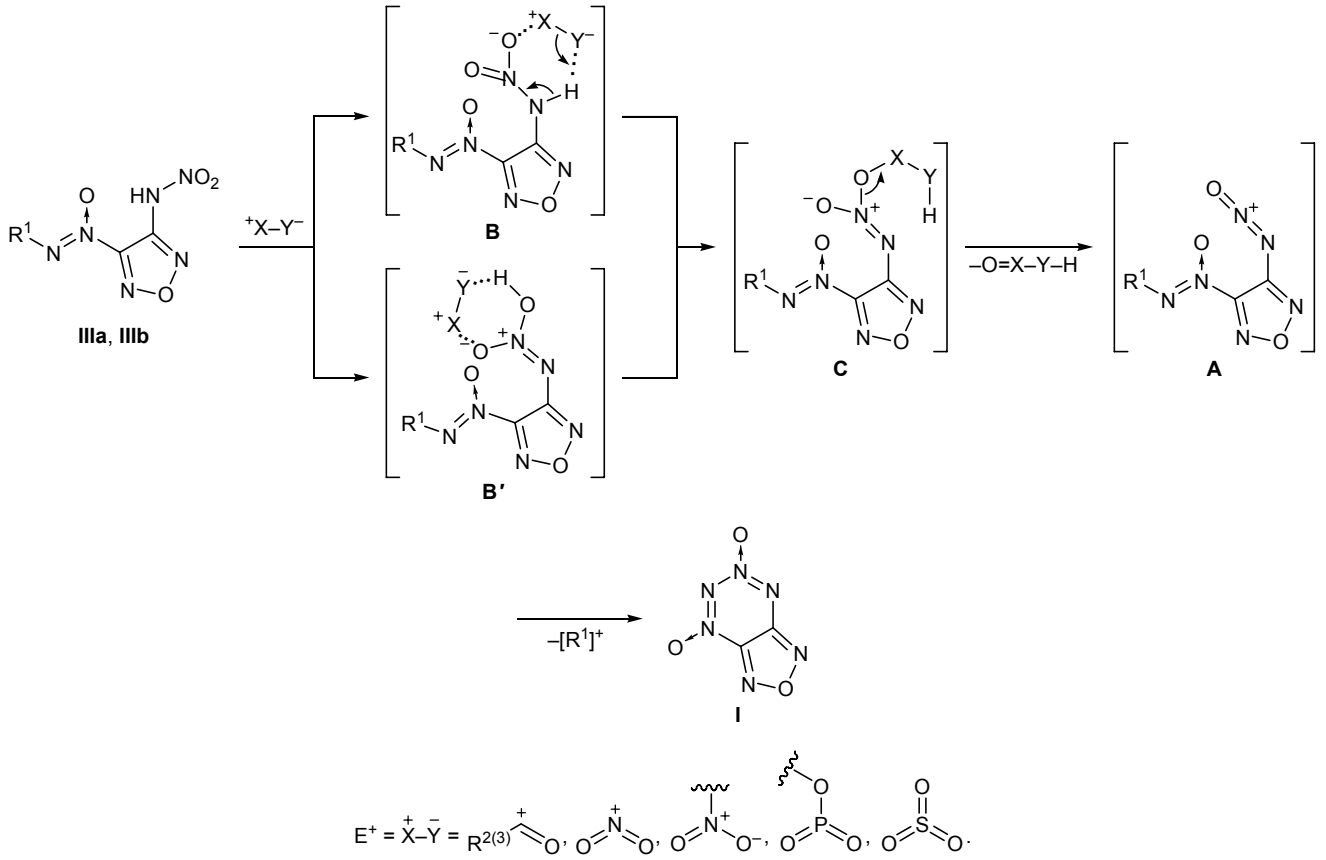
Presumably, the high yield of **I** in Ac_2O in the presence of P_4O_{10} (Table 1, 60%) or SO_3 (82%; cf. run no. 9) is favored by the additive effect of anhydrides ionized by the acid liberated during the reaction. Unlike acids, the reaction of N_2O_5 with Ac_2O gives weakly polar mixed anhydride, acetyl nitrate [14] (Scheme 4). Strong acid (HNO_3) that may be formed via abstraction of hydroxide ion from *N*-nitroamine **IIIa** reacts with Ac_2O to produce very weak acid (AcOH) and acetyl nitrate [15]. The lack of a strong electrophile is responsible for the failure to obtain tetrazine dioxide **I** in the reaction of *N*-nitroamine **IIIa** with N_2O_5 in Ac_2O.

Scheme 4.



We presume that the strength of the added acid determines the ionic character of the acylium (nitronium) ion–anion couple (E^+An^-) and cation **A**–anion

Scheme 5.



couple (Scheme 5) and thus affects the reaction time and the yield of **I**.

The role of the inductive (+*I*) or mesomeric (+*M*) effect of the substituent R^3 in the anhydride should be noted (Scheme 3; Table 1, run nos. 4, 7, 12). The substituents rank as follows with respect to their efficiency: Me > Et > Ph. Obviously, the yield of compound **I** increases in parallel with the electrophilicity of the reagent generated from the anhydride and H_2SO_4. Increased negative charge on the oxygen atom also favors the reaction. Potassium salt **VIa** reacted with NO_2BF_4 in MeCN (Table 2) at an appreciably higher rate as compared to *N*-nitroamine **IIIa**, and the yield of **I** was higher (2 h, 52%) [7]. The synthesis of **I** from *N*-nitroamine salts **Va** and **VIa** (Scheme 3, Table 2) in the system Ac_2O–H_2SO_4 almost does not differ from the reaction with *N*-nitroamine **IIIa** since the salts in acid medium are rapidly converted into free *N*-nitroamine **IIIa**.

Aminofurazans are considerably weaker bases (pK_{BH^+} of 4-nitrofurazan-3-amine is –4.4 [16]) than monosubstituted *o*-nitroanilines (pK_{BH^+} = –0.3 [17]), and their basicity approaches that of dinitroanilines (pK_{BH^+} = –5.4) [17]. Obviously, the difference in the basicity of *N*-nitro derivatives of *o*-nitroaniline and *N*-nitroaminofurazan **IIIa** should be similar to the difference in the basicity of the initial amines. Therefore, the results of the reactions with the same non-ionized

Table 2. Synthesis of tetrazine dioxide **I** from salts **Va** and **VIa** at 20°C

Salt	Reagent	Solvent	Reaction time, min	Yield of **I**, %
Va, **VIa**[a]	H_2SO_4–Ac_2O	Ac_2O	20	82–83
VIa[b]	NO_2BF_4	MeCN	20	68
VIa[a]	BF_3·Et_2O–Ac_2O	Ac_2O	17 h	36

[a] Molar ratio acid–salt 3 : 1.
[b] Molar ratio NO_2BF_4–salt 2 : 1, 25°C.

electrophile (e.g., N_2O_5 or P_4O_{10}) under analogous conditions differ so strongly: the reaction with *N*-nitroaminofurazan **IIIa** either requires more severe conditions than with aromatic analogs or gives no tetrazine dioxide **I**.

Electrophile E^+ (or X–Y in Scheme 5) is a polarized molecular entity consisting of atoms with different electronegativities, and its coordination with *N*-nitroamine **III** is governed by electrostatic interactions. In this context, the known syntheses of **I** by reactions with NO_2BF_4 [7] and P_4O_{10} in MeCN [1] may be regarded as particular cases of the proposed mechanism. We presume that the initial step in the reaction of electrophile E^+ with *N*-nitroamine **IIIa** or **IIIb** is formation of two-center associate **B** or **B′** which is converted into tetrazine dioxide **I** through intermediate *O*-adduct **C** and diazonium oxide **A**. The contribution of structure **B** or **B′** may depend on the ionic strength of the reaction medium and the form of *N*-nitroamine (nitroamine, *aci*-nitro form or its salt). The lifetime of covalent *O*-adduct **C** is determined by the rate of ionization and dissociation of the N–OX bond in intermediate **B** (**B′**). We believe that the reaction of *N*-nitroamine with electrophile E^+ is a version of β-elimination [18] and that the proposed mechanism is appropriate for all known methods of synthesis of tetrazine dioxides.

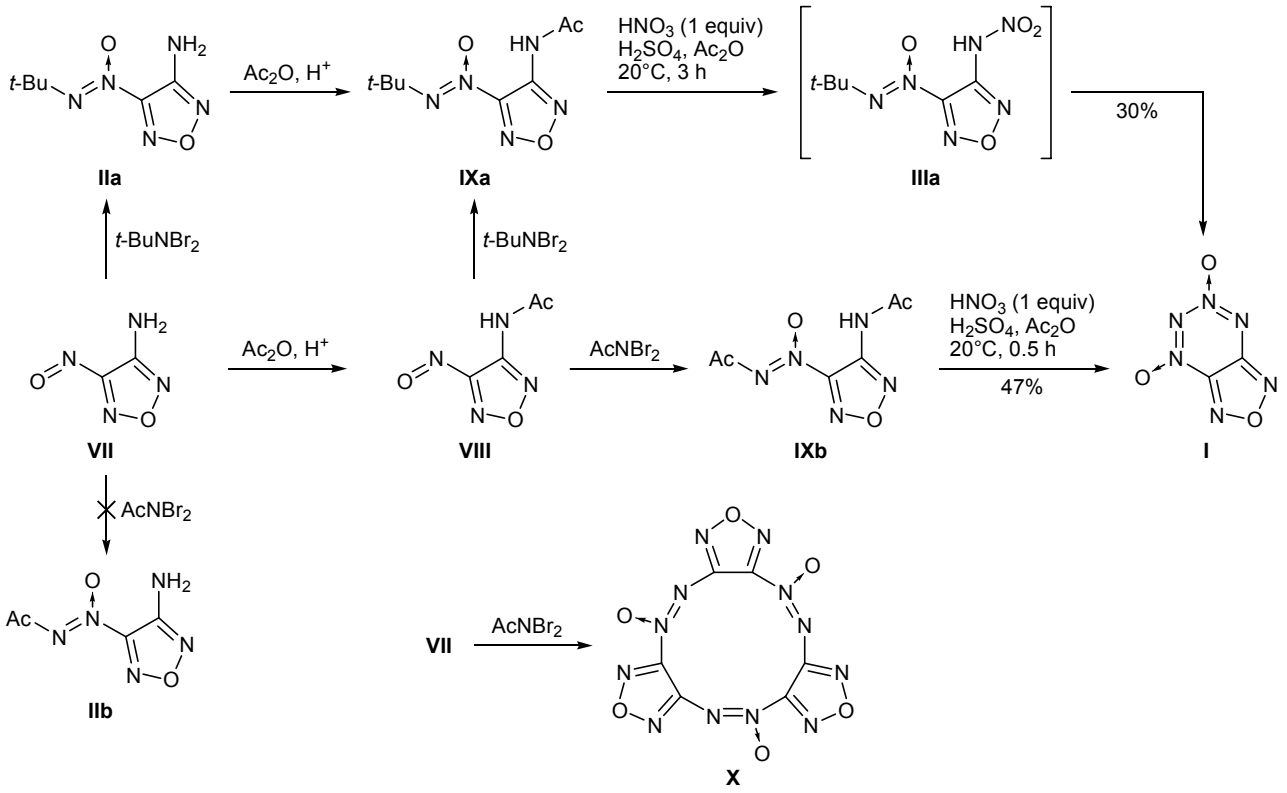
We previously [19] developed a procedure for the preparation of NO_2BF_4 from N_2O_5 and Bu_4NBF_4 (Scheme 6). Addition of nitric acid to the reaction mixture (in methylene chloride) initiates ion exchange leading to precipitation of NO_2BF_4. The presence of an acid increases the polarity of the medium, and weakly polar N_2O_5 molecule undergoes ionization to give $NO_2^+NO_3^-$ couple.

Scheme 6.

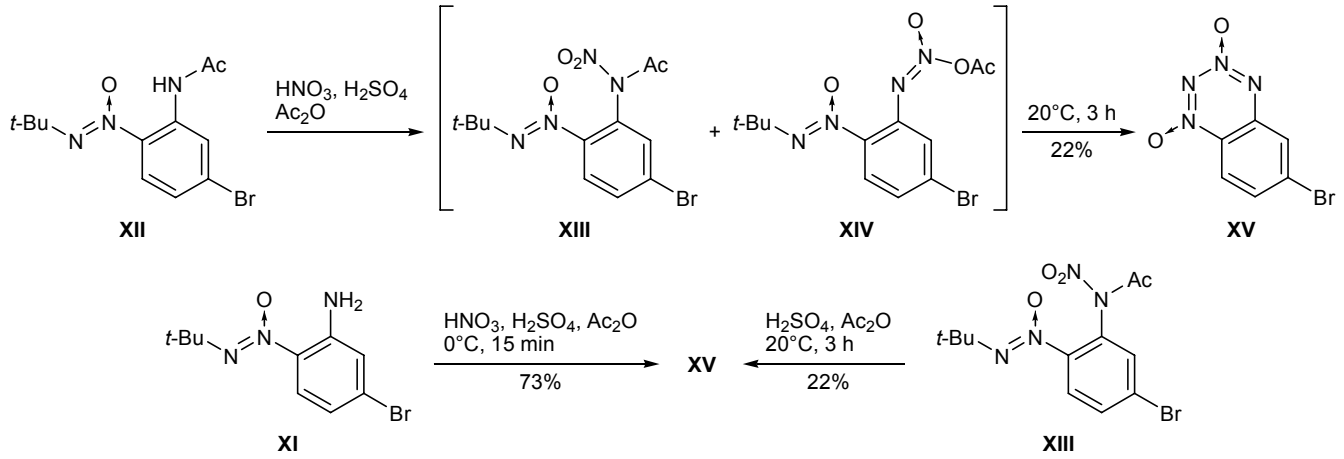
$$Bu_4N^+BF_4^- + NO_2^+NO_3^- \xrightarrow{HNO_3,\ CH_2Cl_2} NO_2^+BF_4^-\downarrow + Bu_4N^+NO_3^-$$

This procedure was utilized in the synthesis of tetrazine dioxide **I**. The latter is not formed in the reaction of N_2O_5 with *N*-nitroamine **IIIa** in MeCN (Scheme 2) [9], as well as in Ac_2O. Addition of 1 equiv of moderately strong HNO_3 (d_{20} = 1.5 g/cm^3) (65% HNO_3, H_0 = –3.78, 20°C [12]) to a solution of N_2O_5 in an inert polar solvent ($MeNO_2$) ensured formation of 2% of **I** (0°C, 48 h, molar ratio **IIIa**–N_2O_5–HNO_3 1:3:1). Under analogous conditions, the

Scheme 7.



Scheme 8.



stronger sulfuric acid converted N_2O_5 into $NO_2^+HSO_4^-$; and tetrazine dioxide **I** was obtained in a good yield (57%, 0°C, 0.5 h). It should be noted that *N*-nitroamine **IIIa** failed to react with N_2O_5 in the presence of anhydrous HCl (4 days, 0 to 20°C). This result may be expected, for N_2O_5 is known to react with HCl yielding NO_2Cl and HNO_3. Nitrosyl chloride NO_2Cl (μ = 0.42) is less polar than N_2O_5 (μ = 1.39) [20], and it tends to undergo homolytic dissociation [21], i.e., the degree of ionization of the N–Cl bond is low. Thus the electrophilicity of E^+ species (Scheme 3) generated from nitric or acetic anhydride is directly related to the strength of the added acid.

Tetrazine dioxide **I** was also synthesized in 62% yield (Scheme 3) by one-pot reaction of **IIa** with the system HNO_3–H_2SO_4 (molar ratio 1:2)–Ac_2O.

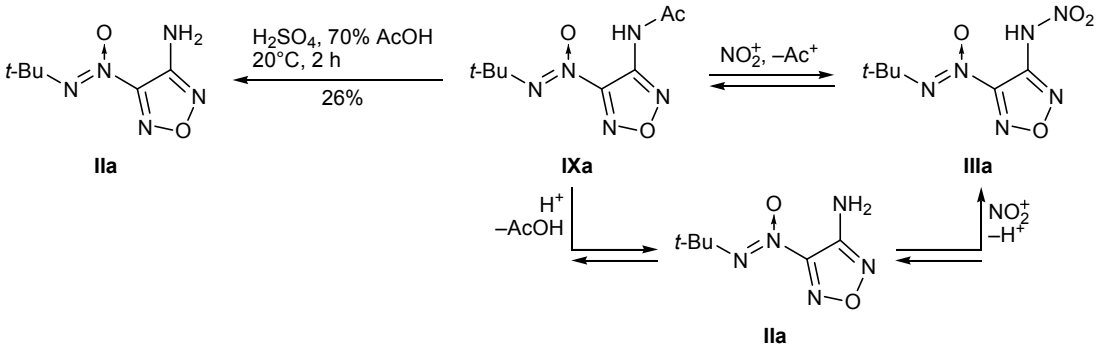
With a view to elucidate the effect of the distal substituent (azoxy group) on the synthesis of tetrazine dioxide **I** we have developed alternative methods for its preparation from acetamides **IXa** and **IXb** (Scheme 7). We failed to obtain acetyldiazene oxide **IIb** by the Kovacic reaction [22] from amine **VII**; instead, compound **VII** was oxidized with *N*,*N*-dibromoacetamide to macrocycle **X**. Therefore, nitrosofurazanamine **VII** was initially converted into acetamide **VIII**, and treatment of the latter with *N*,*N*-dibromo-2-methylpropan-2-amine or *N*,*N*-dibromoacetamide afforded the corresponding diazene oxides **IXa** and **IXb**. *N*-[4-(Acetyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-yl]acetamide (**IXb**) in the system HNO_3–H_2SO_4–Ac_2O (20°C, molar ratio **IXb**–HNO_3–H_2SO_4 1:1:2) was converted in 0.5 h into tetrazine dioxide **I** (yield 47%). Increase of the reaction time to 3 h reduced the yield to 28%.

Under analogous conditions, the yield of **I** from amide **IXa** was 30% (3 h, 20°C), and 63% of unreacted initial compound was recovered from the reaction mixture. The reaction with **IXa** was slower than with amine **IIa** (0.4 h, 0 to 20°C, 62%), the reactant ratio being the same. Comparison of the results of synthesis of compound **I** from **IXa** and **IXb** shows that acetyl group in the azoxy fragment is a better leaving group than *tert*-butyl.

Aniline **XI** reacted with HNO_3–H_2SO_4–Ac_2O to give 73% of benzotetrazine dioxide **XV** in 15 min at 0°C (Scheme 8) [23]. Analogous reaction with acetamide **XII** occurred at a considerably lower rate, and the yield of **XV** was poor (3 h, 20°C, 22%). After 5 min, the reaction mixture contained *N*-nitro-*N*-acetyl derivative **XIII** and only a small amount of tetrazine dioxide **XV**. Insofar as the syntheses of benzotetrazine dioxide **XV** from both acetamide **XII** and pure compound **XIII** in H_2SO_4–Ac_2O ensured similar yields in similar reaction times, we presumed [21] that the cyclization involves *O*-acetyl derivative **XIV** rather than *N*-acetyl-*N*-nitroamine **XIII** as intermediate. The synthesis of **I** from acetamide **IXa** (Scheme 7) also required a longer time, and the yield was lower (3 h, 20°C, 30%) than in the reaction with amine **IIa** (0.4 h, 0 to 20°C, 62%), but no *N*-nitro-*N*-acetyl derivative was detected in the reaction mixture (TLC). It is known that *N*-nitration is a reversible process [17]. Presumably, the initial step is reversible deacylation–nitration of amide **IXa** with formation of *N*-nitroamine **IIIa**; theoretically, this process may follow two alternative paths, with or without participation of proton (Scheme 9).

The yield of tetrazine dioxide **I** did not change (30%) when the amount of H_2SO_4 was increased threefold (20°C, 3 h, **IXa**–HNO_3–H_2SO_4 1:1:6; Scheme 7). However, raising the concentration of HNO_3 by a fac-

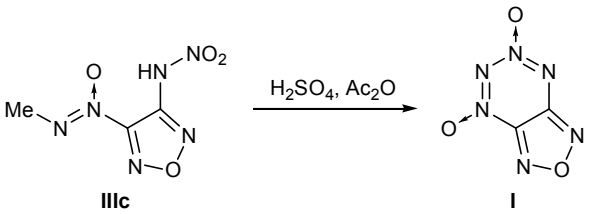
Scheme 9.



tor of 6 (**IXa**–HNO_3–H_2SO_4 1:6:2), other conditions being equal, increased the yield of **I** to 42%, which is very consistent with Scheme 9. Amine **IIa** was obtained from acetamide **IXa** in 70% aqueous AcOH in the presence of H_2SO_4 (Scheme 9). These findings indicate fairly ready deacylation of acetamidofurazans in acid medium.

We also examined the transformation of *N*-nitroaminofurazan **IIIc** in the system H_2SO_4–Ac_2O (Scheme 10) in order to estimate the effect of the leaving group R^1. After 24 h at 20°C, only traces of **I** were detected by TLC. Unlike *tert*-butyl or acetyl group, carbocation derived from methyl group is unstable. Therefore, this result may be regarded as an indirect proof for the assumed elimination of R^1 as carbocation.

Scheme 10.



To conclude, we have developed new reaction systems based on acid anhydrides or acid chlorides and strong acids as ionizing agents for the synthesis of tetrazine dioxide **I** from *N*-nitroamine **IIIa** or its salts **Va** and **VIa**. The yield of **I** in acetic anhydride in the presence of SO_3 or sulfuric acid attains 82–83%. Diazene oxide **IXb** with acetyl group as leaving group was used for the first time to synthesize tetrazine dioxides. The developed procedures for the synthesis of compound **I** made it possible to systemize general principles for construction of both five- and six-membered rings fused to tetrazine dioxide. The proposed general mechanism allows for the effects of electrophilicity and structure of the reactants and the nature of leaving group R^1.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 75.47, and 21.69 MHz, respectively; the chemical shifts were measured relative to Me_4Si (^1H, ^{13}C) or $MeNO_2$ (^{14}N, upfield shifts are negative). The IR spectra were obtained on a Bruker Alpha-T spectrometer. The progress of reactions was monitored by TLC on Silica gel 60 F_{254} plates (Merck). Preparative chromatography was performed on silica gel. 4-(*tert*-Butyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-amine [9], *N*,*N*-dibromoacetamide [24], 4-nitroso-1,2,5-oxadiazol-3-amine [25], 4-(methyl-*NNO*-azoxy)-*N*-nitro-1,2,5-oxadiazol-3-amine [26], and 4-(*tert*-butyl-*NNO*-azoxy)-*N*-nitro-1,2,5-oxadiazol-3-amine [26] were synthesized by known methods.

[1,2,5]Oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-dioxide (I). *a*. A solution of 2.30 g (10 mmol) of *N*-nitroamine **IIIa** in 8 ml of acetic anhydride was added under vigorous stirring at 10±1°C to a suspension of 3 g (20 mmol) of P_4O_{10} in 25 ml Ac_2O, and the mixture was stirred for 0.5 h. The mixture was then poured into 150 g of an ice–water mixture, stirred for 0.5 h to hydrolyze Ac_2O, and extracted with benzene (4×50 ml). The combined extracts were evaporated under reduced pressure, and the residue was purified by column chromatography using benzene as eluent. Yield 0.95 g (60%), mp 111–113°C; published data [8]: mp 110–112°C. The ^1H, ^{13}C, and ^{14}N NMR and IR spectra of the product were identical to those of an authentic sample of **I**.

b. Mineral acid, 20 mmol (calculated on 100% acid or H_2SO_4 with d^{20} = 1.83 g/cm^3), was added under stirring at 20±3°C to a solution of 2.30 g (10 mmol) of *N*-nitroamine **IIIa** in 25 ml of liquid acid anhydride (Table 1) or a solution of 10 mmol of **IIIa** in 20 ml of anhydride was added to a solution of mineral acid in 5 ml of anhydride. The mixture was stirred until the

initial compound disappeared (TLC, benzene as eluent) and poured into 150 ml of ice water (if trifluoroacetic or phosphoric acid or zinc chloride was used, the mixture was poured into a cold 3–4% solution of sulfuric acid). The mixture was stirred for 0.5 h to hydrolyze anhydride and extracted with benzene (4×30 ml), the solvent was removed under reduced pressure, and the residue was purified by column chromatography using benzene as eluent. The conditions and yields of **I** are given in Table 1.

c. To 20 ml of acetic acid we added under stirring at 22±2°C 4.5 ml of 60% oleum (62 mmol of SO_3), and 2.30 g (10 mmol) of *N*-nitroamine **IIIa** was then added. The mixture was stirred until the initial compound disappeared (TLC, benzene; Table 1) and poured into 100 ml of ice water, and the product was isolated as described above. Yield 0.83 g (53%).

d. Acetyl chloride, 10 ml, was cooled to 0–8°C, 1.34 g (10 mmol) of $AlCl_3$ was added, and 1.15 g (5 mmol) of *N*-nitroamine **IIIa** was then added. The mixture was stirred for 15 min and poured into 150 g of an ice–water mixture, and the product was isolated as described above. Yield 0.24 g (30%).

e. Benzoic anhydride, 2.26 g (10 mmol), was added under stirring at 20±3°C to a solution of 1.15 g (5 mmol) of *N*-nitroamine **IIIa** in 15 ml of nitromethane, 0.58 ml (10 mmol) of H_2SO_4 (d^{20} = 1.83 g×cm^{-3}) was then added, and the mixture was stirred until the initial compound disappeared (TLC, benzene; Table 1). The mixture was poured into 100 ml of a cold 4% solution of H_2SO_4, stirred for 1 h, and extracted with benzene (4×30 ml). The combined extracts were evaporated under reduced pressure, the residue was diluted with 15 ml of CCl_4–benzene (4:1), the precipitate of benzoic acid was filtered off, and the residue was purified twice by column chromatography on silica gel using benzene as eluent. Yield 0.18 g (23%).

f. A solution of SO_3 in 1,2-dichloroethane was prepared by shaking 60% oleum with the solvent. The mixture was kept for 24 h to settle down, and the organic phase was separated and added dropwise (using a pressure-equalizing dropping funnel) to a solution of 2.30 g (10 mmol) of *N*-nitroamine **IIIa** in 15 ml of 1,2-dichloroethane under stirring at –10 to –5°C until the initial compound disappeared (TLC, benzene; Table 1). The mixture was poured into 50 ml of water and stirred for 5 min, the organic phase was separated, the aqueous phase was extracted with 1,2-dichloroethane (4×20 ml), the extracts were combined with the organic phase, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using benzene as eluent. Yield 0.84 g (54%).

g. A stream of gaseous sulfur trioxide was slowly passed through a solution of 2.30 g (10 mmol) of *N*-nitroamine **IIIa** in 30 ml of acetic anhydride under stirring at 25–28°C (on cooling with an ice–water mixture). When the initial compound disappeared (TLC, benzene; Table 1), the mixture was poured into 150 ml of water, and compound **I** was isolated according to the standard procedure. Yield 1.28 g (82%).

h. A solution of 1.63 g (15 mmol) of N_2O_5 in 7 ml of nitromethane was added under stirring at 0±3°C to a solution of 1.15 g (5 mmol) of *N*-nitroamine **IIIa** in 8 ml of nitromethane, and 5 mmol of H_2SO_4 (d^{20} = 1.83 g/cm^3) or HNO_3 (d^{20} = 1.5 g/cm^3) was added at –5 to 0°C. Gaseous hydrogen chloride was prepared by adding dropwise sulfuric acid (d^{20} = 1.83 g/sm^3) from a pressure-equilizing dropping funnel to concentrated hydrochloric acid; the gas was passed through a U-tube charged with anhydrous calcium chloride and bubbled through the reaction mixture at 0±3°C. The mixture was stirred until the initial compound disappeared (in the reactions with HNO_3 and H_2SO_4; TLC, benzene; Table 1) and poured into 100 ml of water, and the product was isolated according to the standard procedure (as in *a*), followed by repeated chromatographic purification using chloroform as eluent. Yield 0.44 g (57%) in the presence of H_2SO_4 and 0.02 g (2%) in the presence of HNO_3. No compound **I** was detected by TLC in the reaction mixture after passing HCl over a period of 100 h.

i. Nitric acid (d^{20} = 1.5 g/cm^3), 0.42 ml (10 mmol), was added under stirring at –10 to 0°C to a solution of 1.85 g (10 mmol) of amine **IIa** in 20 ml of acetic anhydride, a solution of 1.1 ml (20 mmol) of H_2SO_4 (d^{20} = 1.83 g/cm^3) in 10 ml of acetic anhydride was then added at 10–20°C, and the mixture was stirred for 25 min at 20°C, cooled to 0°C, and poured into 150 g of an ice–water mixture. Compound **I** was isolated according to the standard procedure. Yield 0.96 g (62%).

j. Potassium salt **VIa**, 2.94 g (11 mmol), was added under stirring at 18–20°C to a solution of 2.92 g (22 mmol) of NO_2BF_4 in 15 ml of anhydrous acetonitrile. The mixture was stirred for 20 min at 20°C, poured into 45 ml of ice water, and extracted with benzene (3×20 ml). The solvent was removed from the extract under reduced pressure, and the residue was purified by column chromatography using benzene as eluent. Yield 1.17 g (68%).

k. Potassium salt **VIa**, 1.34 g (5 mmol), was dissolved in 15 ml of acetic anhydride, 1.26 ml (10 mmol) of $BF_3 \cdot Et_2O$ was added under stirring at 19–24°C, and the mixture was stirred for 17 h at 18–20°C, poured into 100 g of an ice–water mixture, and treated according to the standard procedure to isolate 0.28 g (36%) of **I**.

l. Salt **Va** or **VIa**, 5 mmol, was added under stirring at 15–20°C to a solution of 1.47 g (15 mmol) of H_2SO_4 (d^{20} = 1.83 g/cm^3) in 15 ml of acetic anhydride, and the mixture was stirred until the initial compound disappeared (20 min; TLC, benzene; Table 2). The mixture was poured into 80 ml of cold water, stirred for 0.5 h, and treated according to the standard procedure to isolate 0.64 g (82%, from **Va**) or 0.65 g (83%, from **VIa**) of compound **I**.

m. Nitric acid (d^{20} = 1.5 g/cm^3), 0.21 ml (0.32 g, 5 mmol), was added under stirring at 10–20°C to a solution of 5 mmol of compound **IXa** or **IXb** in 8 ml of acetic anhydride, a solution of 0.55 ml (10 mmol) of H_2SO_4 (d^{20} = 1.83 g/cm^3) in 2 ml of acetic anhydride was added immediately, and the mixture was stirred for 3 (**IXa**) or 0.5 h (**IXb**) at 20–25°C, poured into 75 ml of cold water, and treated according to the standard procedure. Yield 0.24 g (30%, from **IXa**) or 0.37 g (47%, from **IXb**); in the reaction with **IXa**, 0.72 g (63%) of the unreacted initial compound was also isolated. In the reaction of **IXa** with 30 mmol (1.92 g) of HNO_3 the yield of **I** in 3 h was 0.33 g (42%), and in the reaction with 30 mmol of H_2SO_4 (2.94 g), 0.24 g (30%).

4-(*tert*-Butyl-*NNO*-azoxy)-*N*-nitro-1,2,5-oxadiazol-3-amine sodium and potassium salts Va and VIa (*general procedure*). A solution of 0.1 mol of the corresponding alkali metal hydroxide in 50 ml of methanol was added under stirring at 0–12°C to a solution of 0.1 mol of nitroamine **IIIa** in 50 ml of methanol until pH ~6–7. The solvent was removed under reduced pressure, the residue was dried in air and dissolved in 40 ml of methanol on heating to 60°C, and the solution was poured into 100 ml of anhydrous diethyl ether. After cooling, the precipitate was filtered off.

Sodium salt Va. Yield 21.4 g (85%), mp 212–213°C (decomp.). ^{1}H NMR spectrum (acetone-d_6): δ 1.39 ppm (9H, *t*-Bu). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 25.5 (C**Me**$_3$), 60.5 (**C**Me$_3$), 153.9 (C^3), 156.6 br.s (C^4). ^{14}N NMR spectrum (acetone-d_6), δ_N, ppm: –13 (NO_2, $\Delta\nu_{1/2}$ = 45 Hz), –68 (N→O, $\Delta\nu_{1/2}$ = 90 Hz). Found, %: C 28.29; H 3.57; N 33.03. $C_6H_9N_6NaO_4$. Calculated, %: C 28.58; H 3.60; N 33.33.

Potassium salt VIa. Yield 22.8 g (85%), mp 211–213°C (decomp.) ^{1}H NMR spectrum (acetone-d_6): δ 1.40 ppm (9H, *t*-Bu). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 25.5 (C**Me**$_3$), 60.5 (**C**Me$_3$), 154.3 (C^3), 156.7 br.s (C^4). ^{14}N NMR spectrum (acetone-d_6), δ_N, ppm: –12 (NO_2, $\Delta\nu_{1/2}$ = 40 Hz), –68 (N→O, $\Delta\nu_{1/2}$ = 80 Hz). Found, %: C 27.00; H 3.41; N 31.17. $C_6H_9KN_6O_4$. Calculated, %: C 26.86; H 3.38; N 31.33.

Reaction of 4-nitroso-1,2,5-oxadiazol-3-amine (VII) with *N*,*N*-dibromoacetamide. A solution of 4.64 g (20 mmol) of *N*,*N*-dibromoacetamide in 20 ml of anhydrous acetonitrile was added dropwise under stirring at 20°C to a solution of 1.14 g (10 mmol) of compound **VII** in 20 ml of acetonitrile, and the mixture was stirred for 1.5 h (TLC). The solvent was removed under reduced pressure, and the residue was subjected to column chromatography using dichloroethane as eluent to isolate 0.92 g (82%) of tris[1,2,5]oxadiazolo[3,4-*c*:3′,4′-*g*:3″,4″-*k*][1,2,5,6,9,10]hexaazacyclododecine 4,9,14-trioxide (**X**), mp 186–188°C (from $CHCl_3$); published data [27]: mp 187–188°C; the ^{1}H, ^{13}C, and ^{14}N NMR spectra of the product were identical to those of an authentic sample. IR spectrum (KBr), ν, cm^{-1}: 1560, 1520, 1490, 1460, 1340, 1140.

Acylation of aminofurazans. *a*. One drop of H_2SO_4 (~20 mg, 0.2 mmol, d^{20} = 1.83 g/cm^3), was added under stirring at 20°C to a solution or suspension of 10 mmol of aminofurazan in 8–10 ml of acetic anhydride. The initial amine dissolved (if not dissolved before), and the mixture spontaneously warmed up to 30–40°C. It was stirred for 10 min, poured into 100 ml of cold (5–10°C) water, stirred for 0.5–1 h, and extracted with ethyl acetate (3×40 ml). The extract was dried over $MgSO_4$ and evaporated under reduced pressure.

b. Silica-supported sulfuric acid was used as catalyst. Silica gel was mixed with excess 80–85% sulfuric acid, the mixture was stirred for 10–15 min, and the solid material was filtered off and dried for 48 h in a desiccator over P_4O_{10} until free-flowing powder was obtained. The amount of the applied acid was determined by the gain in weight. For acylation of 10 mmol of amine we used 0.5 g of silica-supported sulfuric acid containing 55% of sulfuric acid monohydrate. The mixture was stirred for 10–30 min until the initial compound disappeared, the catalyst was filtered off, excess acetic anhydride and acetic acid were distilled off under reduced pressure, the residue was dissolved

in 50 ml of chloroform or 1,2-dichloroethane, the solution was washed with water (2×5 ml) and dried over $MgSO_4$, and the solvent was removed under reduced pressure.

***N*-(4-Nitroso-1,2,5-oxadiazol-3-yl)acetamide (VIII)** was synthesized from 1.14 g of 4-nitroso-1,2,5-oxadiazol-3-amine **VII** as described in *a* or *b*. Purification by column chromatography (eluent CH_2Cl_2 or $CHCl_3$) gave 1.20 g (77%) of blue oily amide **VIII** which crystallized on storage, mp 88–90°C. IR spectrum (KBr), ν, cm^{-1}: 3280 (NH, dimer), 3240 (NH, monomer), 1690, 1680 (CO), 1590 (δ_{NH}) 1495 (NO, monomer), 1430, 1390, 1370, 1310, 1280, 1265, 1240 (NO, dimer). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 (3H, CH_3), 8.32 (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.9 (**C**H_3CO), 136.8 (C^3), 166.1 (C^4), 168.2 (C=O). Found, %: C 30.72; H 2.49; N 35.96. $C_4H_4N_4O_3$. Calculated, %: C 30.78; H 2.58; N 35.89.

***N*-[4-(*tert*-Butyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-yl]acetamide (IXa).** *a*. From 1.85 g of 4-(*tert*-butyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-amine (**IIa**) we obtained according to method *a* or *b* 2.23 g (98%) of oily amide **IXa** which crystallized on storage, mp 44–50°C. IR spectrum (film), ν, cm^{-1}: 3327 (NH), 2976, 2935 (CH_3), 1725 (CO), 1596 (δ_{NH}), 1539, 1489, 1454, 1398, 1384, 1365 [N(O)=N]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.52 (9H, *t*-Bu), 2.35 (3H, CH_3), 9.43 (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.6 [C(O)**Me**], 25.0 (**Me**$_3$C), 60.9 (Me$_3$**C**), 144.0 (C^3), 151.1 br.s (C^4), 167.2 (C=O). ^{14}N NMR spectrum ($CDCl_3$): δ_N –69 ppm (N→O, $\Delta\nu_{1/2}$ = 80 Hz). Found, %: C 42.38; H 5.84; N 30.64. $C_8H_{13}N_5O_3$. Calculated, %: C 42.29; H 5.77; N 30.82.

b. One drop of H_2SO_4, ~20 mg (0.2 mmol, d = 1.83 g/cm^3), was added under stirring at 20°C to a solution of 0.57 g (5 mmol) of 4-nitroso-1,2,5-oxadiazol-3-amine (**VII**) in 10 ml of acetic anhydride. The mixture was stirred for 10 min, 0.5 g (5 mmol) of Na_2CO_3 was added, and the mixture was stirred for 10 min more. The precipitate was filtered off and washed with 15 ml of benzene on a filter, a solution of 2.35 g (10 mmol) of *N*,*N*-dibromo-2-methylpropan-2-amine in 15 ml of benzene was added to the filtrate under stirring, and the mixture was stirred for 45 min at 20°C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using 1,2-dichloroethane as eluent to isolate 1.00 g (88%) of **IXa** as a light yellow oily liquid which crystallized on storage. The IR and ^1H, ^{13}C, and ^{14}N NMR spectra of the product were identical to those of a sample prepared as described in *a*.

4-(*tert*-Butyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-amine (IIa). Compound **IXa**, 1.04 g (4.6 mmol), was dissolved in 15 ml of 70% aqueous acetic acid, 4.5 g (46 mmol) of H_2SO_4 (d^{20} = 1.83 g/cm^3) was added, and the mixture was stirred for 2 h at 20°C and poured into 80 ml of water. The precipitate was filtered off, washed with water (2×5 ml), and dried. Yield 0.22 g (26%). After prolonged storage (3 days), a solid separated from the mother liquor and was filtered off, washed with water (2×5 ml), and dried. We thus isolated an additional amount, 0.55 g (65%), of amine **IIa**. The product was identical to an authentic sample in ^1H, ^{13}C, and ^{14}N NMR and IR spectra.

***N*-[4-(Acetyl-*NNO*-azoxy)-1,2,5-oxadiazol-3-yl]-acetamide (IXb).** A solution of 0.81 g (3.5 mmol) of *N*,*N*-dibromoacetamide in 20 ml of methylene chloride was added under stirring at 20°C to a solution of 0.55 g (3.5 mmol) of compound **VIII** in 30 ml of methylene chloride. The mixture was stirred for 10 h at 20°C, the solvent was removed under reduced pressure, the residue was dissolved in 15 ml of methylene chloride on heating to 40°C, 15 ml of diethyl ether was added to the solution, and the mixture was left to stand at –20°C for crystallization. Yield 0.32 g (43%). The mother liquor was evaporated under reduced pressure, and repeated crystallization gave additionally 0.31 g (41%) of **IXb**. Overall yield 0.63 g (85%), mp 120–123°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 3332 (NH), 2932 (CH_3), 1755, 1708 (CO), 1594 (δ_{NH}), 1535, 1497 m, 1386, 1358 m, 1321 [N(O)=N]. ^1H NMR spectrum (acetone-d_6), δ, ppm: 2.31 [3H, NHC(O)**Me**], 2.45 [3H, MeC(O)N=N(O)], 10.37 (1H, NH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 22.8 and 23.0 [C(O)**Me**], 145.9 (C^3), 153.5 br.s (C^4), 169.3 (NHCO), 181.3 (=NCO). ^{14}N NMR spectrum (acetone-d_6): δ_N –68 ppm (N→O, $\Delta\nu_{1/2}$ = 55 Hz). Found, %: C 33.92; H 3.22; N 32.76. $C_6H_7N_5O_4$. Calculated, %: C 33.81; H 3.31; N 32.86.

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