New *N*-nitrosoamines
2.* Transformations of tetrahydro-1,3-oxazines into nitrates of *N*-nitrosoamino alcohols

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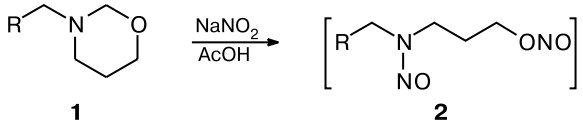
The reactions of HNO_3 with tetrahydro-1,3-oxazines **1a—c** produced by aminomethylation of diketopiperazine, isatin, and succinimide, respectively, afforded nitrates of amino alcohols $[RCH_2NH_2(CH_2)_3ONO_2]^+NO_3^-$ (**4a—c**) whose subsequent *N*-nitrosation ($NaNO_2$, AcOH) gave nitrates of *N*-nitrosoamino alcohols $RCH_2N(NO)(CH_2)_3ONO_2$ (**5a—c**). The structures of compound **5b**,**c** were established by X-ray diffraction analysis.

Key words: heterocyclic α-carbonyl-containing NH-acids, amides, tetrahydro-1,3-oxazines, destructive nitration, *N*-nitrosation, nitrates of amino alcohols and *N*-nitrosoamino alcohols, X-ray diffraction analysis.

Earlier, we have described a procedure for the synthesis of new *N*-nitrosoamines[1] containing heterocyclic fragments. This method is based on the preparation and nitrosative cleavage of tertiary amines, *viz.*, Mannich derivatives of heterocyclic NH-acids and methylamine or ethylenediamine. However, attempts to extend the nitrosative cleavage reaction to derivatives of the same NH-acids and 3-aminopropanol, *viz.,* tetrahydro-1,3-oxazines (**1**) (Scheme 1), were unsuccessful because the reactions gave complex mixtures of compounds from which we failed to isolate the expected nitroso compounds **2**.

Scheme 1



1 **2**

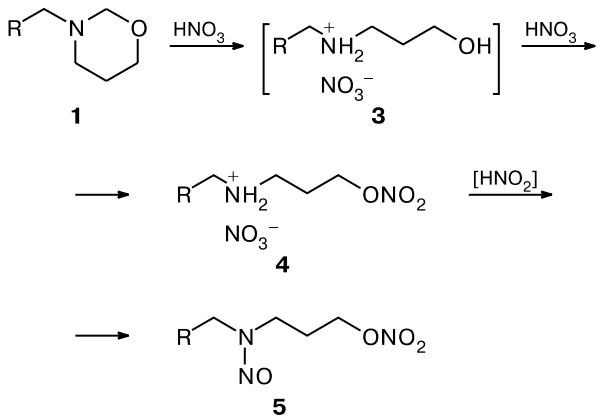
R is a residue of NH-acid

Nevertheless, compounds **2** are, in our opinion, of certain interest. One would expect that compounds containing simultaneously a particular heterocycle, the highly reactive[2] nitrosoamino group, and the nitrite group, which can generate nitrogen monoxide under certain conditions[3,4] (the latter is of vital importance for living organisms[5]) would exhibit high biological activities (for example, cardiac or antitumor activities).

The nitrate group can also generate nitrogen monoxide,[3,4] nitrates being superior to nitrites in chemical stability.

The aim of the present study was to examine the possibility of transforming tetrahydro-1,3-oxazines **1** into ni-

Scheme 2



1 **3** **4** **5**

R is a residue of NH-acid

* For Part 1, see Ref. 1.

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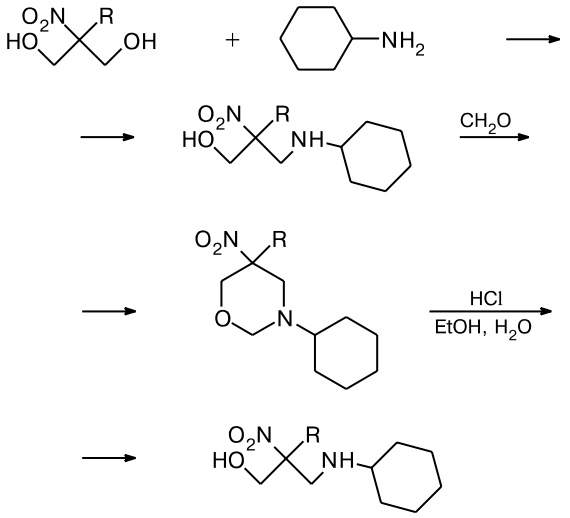
trates of *N*-nitrosoamino alcohols **5** by successive destructive nitration and *N*-nitrosation (Scheme 2).

The reactions of tetrahydro-1,3-oxazines with HNO_3 have not been described earlier, whereas their transformations under the action of other mineral acids were studied. For example, it was demonstrated[6] that heating of tetrahydro-1,3-oxazines, which were prepared by aminomethylation of mononitroalkanes, with hydrochloric acid in an aqueous-ethanolic solution led to their degradation accompanied by elimination of CH_2O to give amino alcohols. The latter are intermediates in the formation of these tetrahydrooxazines (Scheme 3).

Scheme 3



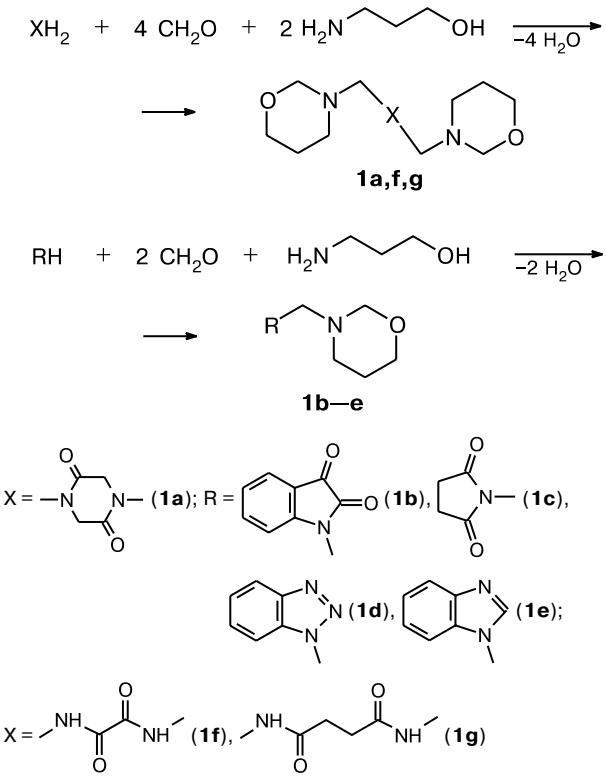
Taking into account these data, one would expect that the reactions of HNO_3 with tetrahydrooxazines **1** (see Scheme 2) will begin with protonation of the tertiary nitrogen atom and elimination of CH_2O to form amino alcohol **3**, which will undergo O-nitration giving rise to nitrate **4**. The latter, apparently, can be subjected to nitrosation according to one of the known procedures[2] to prepare the target nitrate of *N*-nitrosoamino alcohol **5**. Actually, this process did occur in some cases described below.

Results and Discussion

We used derivatives of diketopiperazine **1a**, isatin **1b**, succinimide **1c**, benzotriazole **1d**, benzimidazole **1e**, oxalic acid amide (**1f**), and succinic acid amide (**1g**), which were readily prepared by aminomethylation,[7] as the starting tetrahydrooxazines **1** (Scheme 4).

These compounds showed different behavior in destructive nitration and can be divided into two groups. The first group includes compounds containing the amide fragment, *i.e.*, derivatives of acid amides or imides

Scheme 4



Scheme 5

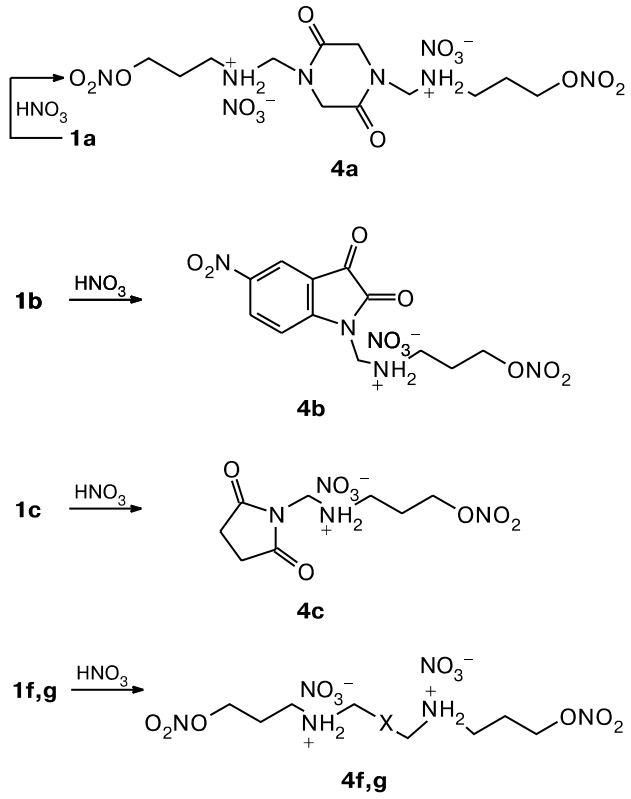


Table 1. Characteristics of nitrates of amino alcohols

Compound	Found / Calculated (%)			Molecular formula	^{1}H NMR (DMSO-d_6), δ (*J*/Hz)	IR, (ν/cm^{-1})
	C	H	N			
4a	28.44 28.58	4.72 4.79	22.68 22.22	$C_{12}H_{24}N_8O_4$	2.08 (br.m, 4 H, CCH_2C); 3.03 (br.m, 4 H, $NHCH_2$); 4.27 (br.s, 4 H, NCH_2CO); 4.59 (br.m, 4 H, NCH_2NH); 4.66 (br.m, 4 H, CH_2ONO_2); 9.13 (br.s, 4 H, $NH_2^+NO_3^-$)	3000, 2780 (NH_2^+); 1673 (C=O); 1615, 1277, 860 (ONO_2); 1385 (NO_3^-)
4b	37.14 37.88	4.11 4.33	18.00 18.08	$C_{12}H_{13}N_5O_{10}$	—	3000, 2750 (NH_2^+); 1772, 1757 (C=O); 1628, 1280 (ONO_2), 1529, 1343 (NO_2); 1385 (NO_3^-)
4c	32.88 32.66	4.93 4.80	19.58 19.04	$C_8H_{14}N_4O_8$	2.04 (br.m, 2 H, CH_2); 2.71 (s, 4 H, CH_2C=O); 3.10 (br.t, 2 H, $NH_2^+CH_2$, *J* = 6.8); 4.59 (t, 2 H, CH_2ONO_2, *J* = 5.8); 4.62 (s, 2 H, NCH_2N); 9.28 (br.s, 2 H, $NH_2^+NO_3^-$)	2830, 2720 (NH_2^+); 1784, 1724 (C=O); 1619, 1613, 1277 (ONO_2); 1385 (NO)
4f	25.27 25.11	4.61 4.64	23.50 23.43	$C_{10}H_{22}N_8O_{14}$	2.05 (br.quint, 4 H, CH_2, *J* = 5.6); 3.06 (br.m, 4 H, $NH_2^+CH_2$); 4.50 (br.d, 4 H, NCH_2N, *J* = 5.6); 4.61 (br.t, 4 H, CH_2ONO_2, *J* = 5.6); 9.00 (br.s, 4 H, $NH_2^+NO_3^-$); 9.83 (br.t, 2 H, CONH, *J* = 5.6)	3328, 1514 (NH); 3229 (NH_2^+); 1631, 1283, 872 (ONO_2); 1385 (NO_3^-); 1700, 1628 (C=O)
4g	28.40 28.46	4.87 5.17	22.20 22.13	$C_{12}H_{26}N_8O_{14}$	2.01 (br.quint, 4 H, CCH_2C, *J* = 5.7); 2.49 (s, 4 H, CH_2CO); 2.97 (br.t, 4 H, CH_2N, *J* = 5.7); 4.34 (d, 4 H, NCH_2N, *J* = 5.7); 4.58 (t, 4 H, CH_2ONO_2, *J* = 5.7); 8.71 (br.s, NH_2^+); 8.99 (br.t, 2 H, CONH, *J* = 5.7)	3329, 1526 (NH); 2933, 2774 (NH_2^+); 1673 (C=O); 1622, 1280, 872 (ONO_2)

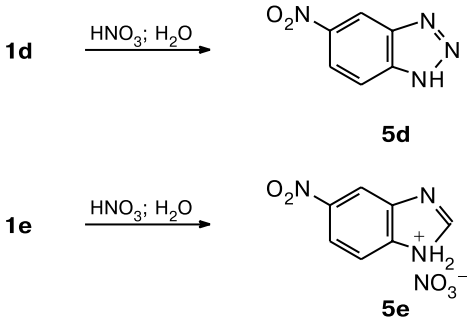
1a—c,f,g. The second group comprises derivatives of benzotriazole **1d** and benzimidazole **1e** devoid of the carbonyl group adjacent to the N atom. In compounds of the first group, only the tetrahydrooxazine ring is subjected to destruction (at the N—C—O bonds), like in the reactions studied earlier,[6] to give the expected nitrates of alcohols (as nitric acid salts) **4a—c,f,g**. It should be noted that nitrolysis of the isatin derivative was accompanied by nitration of the benzene ring at position 5 (Scheme 5).

Nitrates **4a—c,f,g** were prepared as stable crystalline compounds, which can be isolated in pure form by dilution of the reaction mixtures with water (Table 1).

Compounds of the second group undergo deeper destruction resulting in the cleavage not only of the tetrahydrooxazine ring but also of the N—C—N bond between two rings with the result that only 5-nitro derivatives of the starting NH-acids **5d,e** were isolated after dilution of the reaction mixtures with water (Scheme 6).

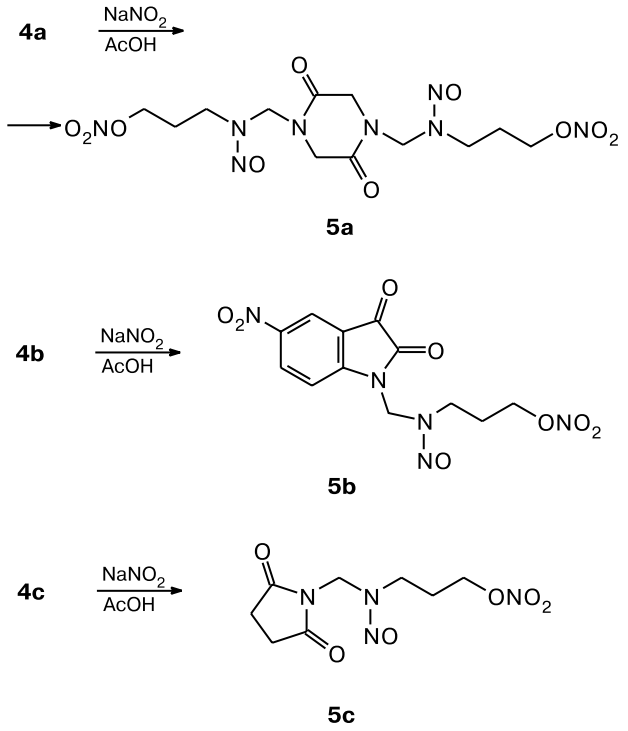
The most commonly used procedure for the preparation of *N*-nitrosoamines is based on the reactions of solutions of secondary amines in acids (hydrochloric, sulfuric, and acetic acids) with alkali metal nitrites.[2] The reactions of nitrates of amino alcohols **4a—c** with $NaNO_2$ in AcOH afforded the target nitrates of *N*-nitrosoamino alcohols **5a—c** in high yields (Scheme 7, Table 2).

Scheme 6



The structures of nitrates of *N*-nitrosoamino alcohols **5b,c** were studied by X-ray diffraction analysis (Figs. 1 and 2; Tables 3—5). As in the case of *N*-nitrosoamines studied earlier,[1,8] the NNO group in compounds **5b,c** is nonlinear (N—N, 1.341(11) Å in **5b** and 1.316(9) Å in **5c**; N—O, 1.181(13) Å in **5b** and 1.221(8) Å in **5c**; N—N—O, 116.0(7)° in **5b** and 115.8(7)° in **5c**) due to the presence of the free lone electron pair of the nitrogen atom of the nitroso group. However, due to the electron-withdrawing properties, this group is involved in a rather strong interaction with the lone electron pair of the second N atom

Scheme 7



bound to this group. As a result, the second N atom has an almost planar-trigonal configuration and only slightly deviates from the plane formed by the nearest carbon and nitrogen atoms (the deviation of the N atom from the CCN plane is only 0.038 Å in **5b** and 0.032 Å in **5c**). The nitro group attached to the benzene ring is characterized by the following parameters: C—NO_2, 1.458(11) Å; N—O, 1.199(12) and 1.210(12) Å; the O—N—O angle, 122.2(9)°.

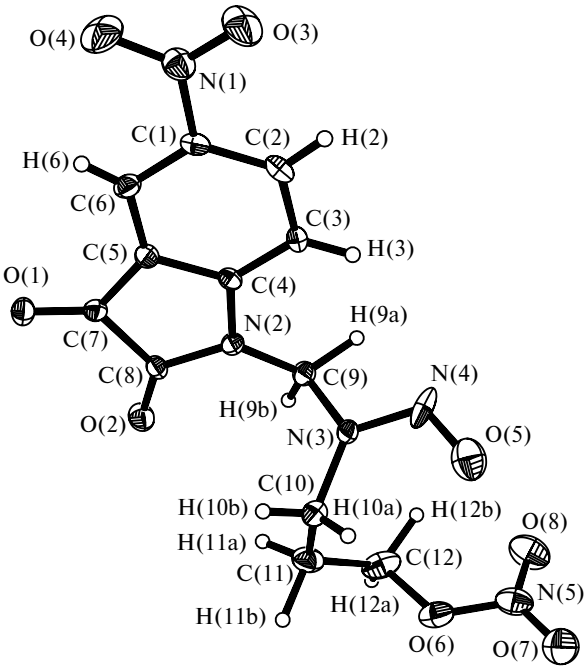


Fig. 1. Molecular structure of compound **5b**.

In conclusion, it should be noted that the new procedure for the preparation of nitrates of *N*-nitrosoamino alcohols bearing the α-carbonyl-containing nitrogen heterocycle in *N*-substituents can, apparently, be extended to other compounds of this series. It should be emphasized that a broad spectrum of known α-carbonyl-containing nitrogen heterocycles were involved in aminomethylation reactions. As examples, we can mention benzooxazolin-2-ones,[9] oxazolidin-2-ones,[10] 1,3,4-oxadiazol-2-ones,[11] benzimidazol-2-ones,[12] thiazolidin-2,4-diones,[13] hydantoins,[14] uracil,[14] and pyridazin-6-ones.[15]

Table 2. Characteristics of nitrates of *N*-nitrosoamino alcohols

Compound	Found / Calculated (%)			Molecular formula	^{1}H NMR (solvent), δ (*J*/Hz)	IR, (ν/cm^{-1})
	C	H	N			
5a	32.91 33.03	4.24 4.62	25.96 25.68	$C_{12}H_{20}N_8O_{10}$	(CD_3CN) 1.92 (quint, 4 H, CCH_2C, *J* = 6.4); 3.67 (t, 4 H, NCH_2C, *J* = 6.4); 4.07 (s, 4 H, NCH_2CO); 4.42 (t, 4 H, CH_2ONO_2, *J* = 6.4); 5.72 (s, 4 H, NCH_2N)	1664 (C=O); 1634, 1280, 857 (ONO_2); 1490, 1313, 1052 (NNO)
5b	40.64 40.80	3.19 3.14	20.17 19.83	$C_{12}H_{11}N_5O_8$	(DMSO-d_6) 1.91 (quint, 2 H, CCH_2C, *J* = 6.0); 3.65 (t, 2 H, NCH_2C, *J* = 6.0); 4.44 (t, 2 H, NCH_2ONO_2, *J* = 6.0); 6.25 (s, 2 H, NCH_2N); 7.41 (dd, 1 H, H(6), ^3J = 8.0, ^4J = 2.0); 8.34 (d, 1 H, H(7), *J* = 8.0); 8.58 (d, 1 H, H(4), ^4J = 2.0)	1751 (C=O); 1616, 1283 (ONO_2); 1553, 1340 (NO_2); 1034, 1307 (NNO)
5c	36.71 36.93	4.86 4.65	21.79 21.53	$C_{16}H_{24}N_8O_{12}$	(CD_3CN) 1.87 (dt, 2 H, CCH_2C, *J* = 5.8; *J* = 6.9); 2.69 (s, 4 H, CH_2CO); 3.61 (t, 2 H, NCH_2C; *J* = 6.9); 4.38 (t, 2 H, CH_2ONO_2, *J* = 5.8); 5.72 (s, 2 H, NCH_2N)	1772 w, 1709 s (C=O); 1640, 1280, 872 (ONO_2); 1352 (NNO)

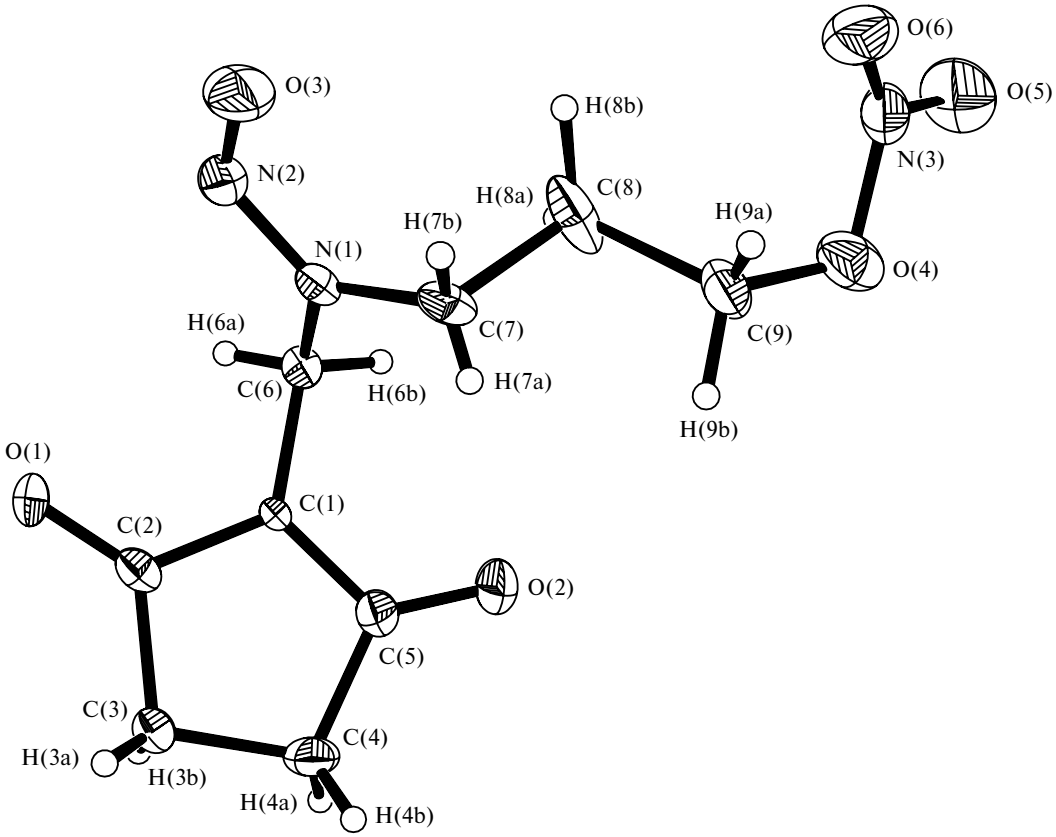


Fig. 2. Molecular structure of compound **5c**.

Experimental

The starting tetrahydrooxazines **1a—g** were synthesized according to a procedure described earlier.[7] Destructive nitration was carried out using freshly distilled HNO_3 (d 1.51 g cm^{-3}). The ^{1}H NMR spectra were recorded on an NMR spectrometer equipped with a superconducting magnet (294 MHz); the instrument was developed and built at the Institute of Problems of Chemical Physics in Chernogolovka of the Russian Academy of Sciences. The IR spectra were recorded on a Specord M-82 spectrophotometer in KBr pellets.

Synthesis of compounds 4a—c,f,g and 5d,e (general procedure). Tetrahydrooxazine (10 mmol) was added portionwise to HNO_3 (0.15—0.28 mol) with stirring and cooling to 0—4 °C. The reaction mixture was kept at 0—2 °C for 0.5—1.5 h and poured onto ice. The resulting mixture was stirred at ~20 °C for 3 h and cooled to a temperature from 0 to −5 °C. The precipitate that formed was filtered off, washed with water, dried, and purified as described below.

1,4-Bis(5-nitroxy-2-azoniapentyl)piperazine-2,5-dione dinitrate (4a). Reagents and conditions: HNO_3 (0.20 mol), 30 min. The yield was 58%, m.p. 149—150 °C (with decomp.). After reprecipitation with water from HNO_3, m.p. 150—151 °C (with decomp.).

5-Nitroindoline-1-(5-nitroxy-2-azoniapentyl)-2,3-dione nitrate (4b). Reagents and conditions: HNO_3 (0.15 mol), 1.5 h. The yield was 64%, m.p. 117—118 °C (with decomp.). After reprecipitation with water from HNO_3, m.p. 120—122 °C (with decomp.).

1-(5-Nitroxy-2-azoniapentyl)pyrrolidine-2,5-dione nitrate (4c). Reagents and conditions: 0.15 mol HNO_3, 30 min. The yield was 60%, m.p. 126—128 °C (with decomp.). After reprecipitation with water from HNO_3, m.p. 126—128 °C (with decomp.).

***N,N´*-Bis(5-nitroxy-2-azoniapentyl)oxamide dinitrate (4f).** Reagents and conditions: HNO_3 (0.22 mol), 40 min. The yield was 59%, m.p. 157—159 °C (with decomp.). After recrystallization from 5% HNO_3, m.p. 162—163 °C (with decomp.).

***N,N´*-Bis(5-nitroxy-2-azoniapentyl)succindiamide dinitrate (4g).** Reagents and conditions: HNO_3 (0.28 mol), 40 min. The reaction mixture was poured onto ice. The resulting solution was concentrated *in vacuo* at 20—25 °C. Methanol (5 mL) and Pr^{i}OH (2 mL) were added to the residue and the mixture was kept at 0 °C for 3 h. The precipitate that formed was filtered off and washed with a mixture of the same alcohols. The yield was 59%, m.p. 99—100 °C (with decomp.). After recrystallization from a 1 : 2.5 Pr^{i}OH—MeOH mixture, m.p. 103—105 °C (with decomp.).

5-Nitrobenzotriazole (5d). Reagents and conditions: HNO_3 (0.15 mol), 1.5 h. The yield was 49%, m.p. 187—190 °C (with decomp.). After recrystallization from 5% HNO_3, m.p. 214—215 °C (with decomp.; *cf.* lit. data[16]: m.p. 211 °C). ^{1}H NMR (DMSO-d_6), δ: 3.90 (br.s, 1 H, NH); 8.10 m, 1 H,

Table 3. Selected geometric characteristics of compound **5b**

Bond	*d*/Å	Angle	ω/deg
O(1)—C(7)	1.206(9)	N(5)—O(6)—C(12)	115.1(7)
O(3)—N(1)	1.199(12)	O(3)—N(1)—C(1)	118.7(8)
O(5)—N(4)	1.181(13)	C(4)—N(2)—C(8)	111.1(5)
O(6)—C(12)	1.457(14)	C(8)—N(2)—C(9)	124.1(7)
O(8)—N(5)	1.185(10)	N(4)—N(3)—C(10)	124.3(7)
N(2)—C(4)	1.414(9)	O(5)—N(4)—N(3)	116.0(7)
N(2)—C(9)	1.447(9)	O(6)—N(5)—N(8)	120.4(10)
N(3)—C(9)	1.442(11)	N(1)—C(1)—C(2)	117.5(8)
C(1)—C(2)	1.363(11)	C(2)—C(1)—C(6)	123.6(7)
C(2)—C(3)	1.401(11)	C(2)—C(3)—C(4)	116.3(7)
C(4)—C(5)	1.403(10)	N(2)—C(4)—C(5)	109.8(6)
C(5)—C(7)	1.453(12)	C(4)—C(5)—C(6)	118.9(7)
C(10)—C(11)	1.506(14)	C(6)—C(5)—C(7)	132.2(7)
O(2)—C(8)	1.206(10)	O(1)—C(7)—C(5)	132.1(6)
O(4)—N(1)	1.210(12)	C(5)—C(7)—C(8)	104.5(6)
O(6)—N(5)	1.379(11)	O(2)—C(8)—C(7)	127.4(7)
O(7)—N(5)	1.209(14)	N(2)—C(9)—N(3)	112.6(6)
N(1)—C(1)	1.458(11)	C(10)—C(11)—C(12)	114.9(8)
N(2)—C(8)	1.382(10)	O(3)—N(1)—C(4)	122.2(9)
N(3)—N(4)	1.341(11)	O(4)—N(1)—C(4)	119.0(8)
N(3)—C(10)	1.473(8)	C(4)—N(2)—C(9)	124.5(6)
C(1)—C(6)	1.356(12)	N(4)—N(3)—C(9)	113.4(5)
C(3)—C(4)	1.368(11)	C(9)—N(3)—C(10)	122.0(7)
C(5)—C(6)	1.408(10)	O(6)—N(5)—O(7)	112.2(7)
C(7)—C(8)	1.564(9)	O(7)—N(5)—O(8)	127.4(10)
C(11)—C(12)	1.498(15)	N(1)—C(1)—C(6)	118.9(7)
		C(1)—C(2)—C(3)	120.8(8)
		N(2)—C(4)—C(3)	127.1(6)
		C(3)—C(4)—C(5)	123.1(7)
		C(4)—C(5)—C(7)	108.8(6)
		C(1)—C(6)—C(5)	117.2(7)
		O(1)—C(7)—C(8)	123.2(7)
		O(2)—C(8)—N(2)	126.9(6)
		N(2)—C(8)—C(7)	105.7(6)
		N(3)—C(10)—C(11)	112.6(7)
		O(6)—C(12)—C(11)	106.3(8)

C(7)H, B portion of the AB spectrum, $^3J_{AB}$ = 8.9 Hz); 8.31 m, 1 H, C(6)H, A portion of the AB spectrum, $^3J_{AB}$ = 8.9 Hz, ^4J = 1.9 Hz); 8.94 (d, 1 H, C(4)H, ^4J = 1.9 Hz).

5-Nitrobenzimidazolium nitrate (5e). Reagents and conditions: HNO_3 (0.15 mol), 45 min. The yield was 30%, m.p. 188—190 °C (with decomp.). After recrystallization from H_2O, m.p. 204 °C (with decomp.). Found (%): C, 36.98; H, 2.76; N, 24.53. $C_7H_6N_4O_5$. Calculated (%): C, 37.18; H, 2.67; N, 24.77. ^{1}H NMR (DMSO-d_6), δ: 8.01 (d, 1 H, C(7)H, J = 9.5 Hz); 8.34 (br.d, 1 H, C(6)H, J = 9.5 Hz); 8.66 (br.s, 1 H, C(4)H); 9.64 (s, 1 H, C(2)H); 13.93 (br.s, 2 H, $NH_2^+NO_3^-$). IR (KBr pellets, ν/cm^{-1}): 3089, 2989, 2943, 1505, 1449, 1432, 897, 30 (Ar); 2791, 2651, 2546 (NH_2^+); 1619 (C=N); 1539, 1318 (NO_2); 1345 (NO_3^-).

Synthesis of compounds 5a—c (general procedure). Sodium nitrite was added portionwise with stirring and cooling to 15—18 °C to a mixture of nitrate of the corresponding amino alcohol (10 mmol) with glacial AcOH during 60 min. The reaction mixture was kept at 10—12 °C for 6 h and then poured into ice water. The precipitate that formed was filtered off, washed with water, dried, and purified by recrystallization from chloroalkanes.

Table 4. Selected geometric characteristics of compound **5c**

Bond	*d*/Å	Angle	ω/deg
O(1)—C(2)	1.211(6)	N(3)—O(4)—C(9)	110.3(12)
O(3)—N(2)	1.221(8)	N(2)—N(1)—C(6)	116.47(6)
O(4)—C(9)	1.476(20)	C(6)—N(1)—C(7)	121.9(5)
O(4)—C(9)	1.440(12)	O(4)—N(3)—O(5)	114.4(13)
O(5)—N(3)	1.257(15)	O(4)—N(3)—O(6)	114.4(10)
O(6)—N(3)	1.217(18)	O(4)—N(3)—O(6)	120.8(8)
N(1)—C(6)	1.439(7)	C(2)—C(1)—C(5)	112.7(4)
C(1)—C(2)	1.403(5)	C(5)—C(1)—C(6)	122.9(4)
C(1)—C(6)	1.443(6)	O(1)—C(2)—C(3)	128.8(4)
C(3)—C(4)	1.530(9)	C(2)—C(3)—C(4)	105.6(4)
C(7)—C(8)	1.516(7)	O(2)—C(5)—C(1)	123.3(5)
C(8)—C(9)	1.525(16)	C(1)—C(5)—C(4)	108.3(4)
O(2)—C(5)	1.219(6)	N(1)—C(7)—C(8)	110.6(5)
O(4)—N(3)	1.404(13)	C(7)—C(8)—C(9)	109.8(6)
O(4)—N(3)	1.312(13)	O(4)—C(9)—C(8)	112.6(11)
O(5)—N(3)	1.070(16)	N(3)—O(4)—C(9)	119.0(9)
O(6)—N(3)	1.265(21)	N(2)—N(1)—C(7)	121.5(5)
N(1)—N(2)	1.316(9)	O(3)—N(2)—N(1)	115.8(7)
N(1)—C(7)	1.460(9)	O(4)—N(3)—O(5)	118.0(11)
C(1)—C(5)	1.396(8)	O(5)—N(3)—O(6)	129.0(12)
C(2)—C(3)	1.498(8)	O(5)—N(3)—O(6)	119.7(12)
C(4)—C(5)	1.502(7)	C(2)—C(1)—C(6)	124.2(5)
C(8)—C(9)	1.617(19)	O(1)—C(2)—C(1)	123.2(5)
		C(1)—C(2)—C(3)	108.0(5)
		C(3)—C(4)—C(5)	105.2(5)
		O(2)—C(5)—C(4)	128.4(6)
		N(1)—C(6)—C(1)	112.6(4)
		C(7)—C(8)—C(9)	107.2(8)
		O(4)—C(9)—C(8)	114.6(13)

Table 5. Crystallographic parameters of compounds **5b** and **5c**

Parameter	**5b**	**5c**
Molecular formula	$C_{12}H_{11}N_5O_8$	$C_9H_{12}N_3O_6$
Space group	$P2_1$	$P2_1$
a/Å	10.887(3)	9.180(3)
b/Å	5.716(2)	6.233(2)
c/Å	12.475(4)	10.730(3)
β/deg	107.33(2)	104.16(2)
V/Å^3	741.1(4)	595.3(3)
Z	2	2
ρ_{calc}/g cm^{-3}	1.583	1.441
θ—2θ Scan range (deg)	2—52	2.5—58
Number of measured reflections	2320	1753
Number of reflections with $I > 4.0\sigma$	1009	1126
Weighting scheme	$w^{-1} = \sigma^2(F) + kF^2$	
k	0.0009	0.0006
R	0.055	0.067
R_w	0.070	0.079

1,4-Bis(2-nitroso-5-nitroxy-2-azapentyl)piperazine-2,5-dione (5a). Reagents and conditions: AcOH (33 mL), $NaNO_2$ (0.1 mol). The yield was 96%, m.p. 116—118 °C (with decomp.). After recrystallization from 1,2-dichloroethane, m.p. 118—119 °C (with decomp.).

5-Nitroindoline-1-(2-nitroso-5-nitroxy-2-azapentyl)-2,3-dione (5b). Reagents and conditions: AcOH (25 mL), $NaNO_2$ (50 mmol). The yield was 86%, m.p. 134—135 °C (with decomp.). After recrystallization from a mixture of $CHCl_3$ and 1,2-dichloroethane (1 : 3), m.p. 136—137 °C (with decomp.).

1-(2-Nitroso-5-nitroxy-2-azapentyl)pyrrolidine-2,5-dione (5c). Reagents and conditions: AcOH (25 mL), $NaNO_2$ (50 mmol). The yield was 75%, m.p. 91—93 °C (with decomp.). After reprecipitation from a mixture of CCl_4 and $CHCl_3$ (1 : 2), m.p. 93—94 °C (with decomp.).

X-ray diffraction study. X-ray diffraction data sets for compounds **5b,c** were collected on a four-circle automated Siemens R3/PC diffractometer (λMo-Kα, λ = 0.71074 Å, T = 22 °C). The unit cell parameters were determined and refined using 24 equivalent reflections with 2θ < 22—26°. Three strong standard reflections with θ < χ > 65° were monitored after each 100 reflections. Since the intensities of these check reflections showed no decrease in the course of X-ray data collection, absorption was ignored. The crystallographic parameters and details of structure refinement are given in Table 5.

The structures of compounds **5b,c** were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All calculations were carried out using the SHELXTL PLUS program package (PC version).[17] The atomic coordinates of compounds **5b,c** were deposited with the Cambridge Structural Database.[18] The selected geometric parameters of the molecules **5b,c** are given in Tables 3 and 4.

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