Organic Chemistry

Synthesis and structure of di(*NON*-azoxy)formals and some related *N*-alkyl-*N'*-alkoxydiazene *N*-oxides

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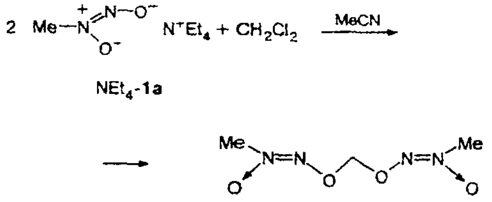
A series of di(*NON*-azoxy)formals and some related *N*-alkyl-*N'*-alkoxydiazene *N*-oxides were prepared by the reaction of *N*-nitrosohydroxylamine salts with dihaloalkanes. The dependence of the yield of di(methyl-*NON*-azoxy)formal on the reaction conditions and the nature of the cation was studied. The structure of di(methyl-*NON*-azoxy)formal and di(phenyl-*NON*-azoxy)formal as well as of the copper *tert*-butylnitrosohydroxylaminate was established by X-ray diffraction analysis.

Key words: di(*NON*-azoxy)formals, *N*-alkyl-*N'*-alkoxydiazene *N*-oxides, *N*-nitrosohydroxylamines, X-ray diffraction analysis, synthesis.

N'-Alkoxydiazene *N*-oxides (ADO) have been known since the end of the previous century and in recent decades they have been studied fairly comprehensively. A number of compounds of this class, di(alkoxy-*NNO*-azoxy)methanes and their derivatives, are relatively easy to obtain.[1] However, structural isomers of these compounds, *viz.*, di(*NON*-azoxy)formals (DAF), have not been known previously. Recently[2] we synthesized the first representative of DAF, di(methyl-*NON*-azoxy)formal (**2a**) in a yield of 28% by the reaction of the tetraethylammonium salt of methylnitrosohydroxylamine (NEt_4-**1a**) with CH_2Cl_2 (Scheme 1).

Scheme 1



NEt_4-**1a**

2a

In this work, we studied the effects of the solvent, the reaction conditions, and the nature of reagents on the yield of formal **2a**; the results obtained are presented in Table 1. It can be seen that in the case of salt NEt_4-**1a** (entries *1—9*), the nature of the solvent and CH_2XY have no significant effect on the yield of **2a**, but the reactions with CH_2Cl_2 or in MeOH occur much more slowly than those with CH_2XBr in bipolar aprotic solvents. Salt NEt_4-**1a** is fairly hygroscopic, and we were not able to isolate it in a pure state. Therefore, we prepared the previously unknown potassium salt (K-**1a**), which is much more convenient to work with (it is not

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Table 1. Yield of formal **2a** as a function of reaction conditions and the nature of reagents

$$2\underset{\mathbf{1a}}{MeN_2O_2^-Kat^+} + CH_2XY \rightarrow \mathbf{2a}$$

Entry	Cat	CH_2XY (moles per 2 moles of **1a**)	Solvent (*V*/mL per mole of **1a**)	Reaction temperature/°C (reaction duration/h)	The yield of **2a** (%)
1	NEt_4	CH_2Cl_2 (33.2)	CH_2Cl_2 (1065)	Reflux (10)	20[a]
2	NEt_4	CH_2Cl_2 (1.35)	MeCN (385)	H.[b] + reflux (1) + ~20 (72)	28[a,c]
3	NEt_4	CH_2Cl_2 (2.29)	DMF (355)	H. 40 (0.5) + ~20 (24)	24[d]
4	NEt_4	CH_2BrCl (2.3)	DMF (355)	H. 110 (0.5) + ~20 (24)	22[d]
5	NEt_4	CH_2Br_2 (1.88)	DMF (355)	H. (0.5) + 20 (24)	27[d]
6	NEt_4	CH_2Br_2 (1.04)	DMF (355)	H. 30 (0.5) + ~20 (24) + reflux (0.5)	25[d]
7	NEt_4	CH_2Cl_2 (1.22)	MeOH (463)	~20 (24) + reflux (6)	3[d](23[e])
8	NEt_4	CH_2BrCl (1.08)	MeOH (463)	~20 (24) + reflux (6)	16[d] (21[e])
9	NEt_4	CH_2Br_2 (1.08)	MeOH (463)	~20 (24) + reflux (6)	24[d]
10	Na	CH_2Cl_2 (1.05)	H_2O[f] (60)	Reflux (5)	0
11	Na	CH_2Br_2 (2.13)	HMPA (530)	~20 (120) + 70 (96)	9[g]
12	K	CH_2Br_2 (1.77)	DMSO (2325)	~20 (1 month)	14[g]
13	K	CH_2Br_2 (2.02)	DMSO (283)	50—55 (0.5) + 70—80 (1.5)	32[g]
14	K	CH_2Br_2 (1.48)	DMSO—H_2O, 20 : 1 (267)	70—75 (1.5) + 90 (1)	32[g]
15	K	CH_2Br_2 (2.00)	DMSO (1240)	63—78 (0.5) + ~20 (24)	33[a]
16	K	CH_2Br_2 (2.03)	MeOH (448)	Reflux (18)	23[g]
17	K	CH_2Br_2 (2.03)	MeOH (448)	Reflux (48)	32[g]
18	K	CH_2Br_2 (1.77)	EtOH (1650)	76—77 (18)	23[g]
19	Cu	CH_2Br_2 (1.05)[h]	DMSO (340)[h]	100—110 (6)	0[g,i]

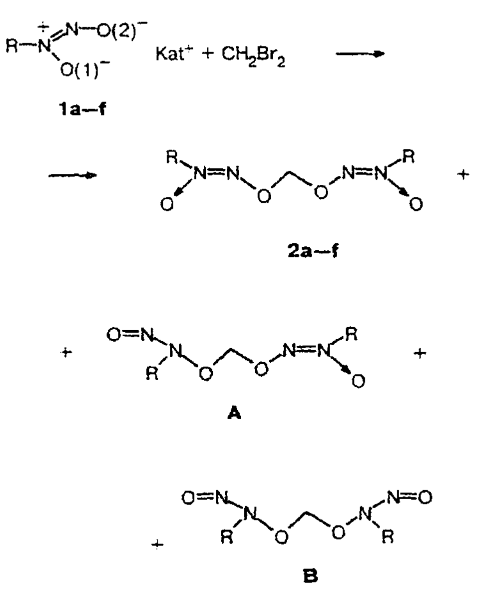
[a] Isolation: concentration *in vacuo*, dilution with water, filtration, washing with water, and drying. [b] H. is spontaneous heating. [c] In Ref. 2 a yield of 35% was mistakenly presented. [d] Isolation: cooling (−18 °C), filtration, washing with water, and drying. [e] The mother liquor was refluxed for 8 h with excess CH_2Br_2, overall yield. [f] Under conditions of phase transfer catalysis by Et_4NBr (0.02 mol per mole of **1a**). [g] Isolation: dilution with water, cooling (−18 °C), filtration, washing with water, drying. [h] Recalculated for g-equivalent of Cu-**1a**. [i] CuBr was isolated (65%).

hygroscopic at a relative humidity of ≤50 %). Salt K-**1a** is much less reactive in aprotic solvents than NEt_4-**1a** (*cf.* entries *5*, *6*, and *13—15*, Table 1); however, we found conditions under which the yield of **2a** in its reaction with CH_2Br_2 in DMSO is as high as 32—33% (entries *13—15*). The yield of **2a** does not decrease when MeOH, in which salt K-**1a** is readily soluble (~30%), is used instead of DMSO (entry *17*). As should be expected, chelate (Cu-**1a**) does not enter into this reaction (entry *19*). Unexpectedly, the reactivity of salt Na-**1a** proved to be low both in HMPA and under conditions of phase transfer catalysis (entries *10* and *11*). Unlike K-**1a**, salt Na-**1a** is virtually insoluble in MeOH and DMSO.

As a result, a convenient procedure for the preparation of formal **2a** by the reaction of salt K-**1a** with CH_2Br_2 in MeOH or DMSO was developed. Using this procedure, we synthesized a series of DAF (**2a—f**) by the reaction of salts of nitrosohydroxylamines (NHA) (**1a—f**) with CH_2Br_2 (Scheme 2).

The yields of other aliphatic DAF are, as a rule, higher than that of **2a** even without optimization (42—47% against 32—33%). This is apparently due to the steric restrictions to the reactions at the O(1) atoms in anions **1b—f**, which decrease the proportion of unstable nitrosohydroxylamines **A** and **B** formed as by-products. Vigorous decomposition of compounds **A** and **B** was

Scheme 2

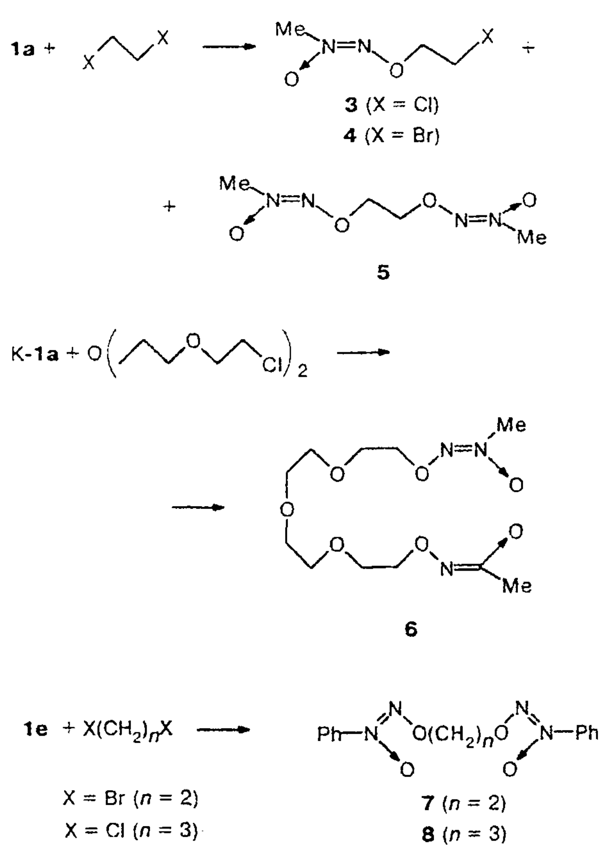


R = Me (**a**), Bu^t (**b**), Bu^i (**c**), *n*-C_5H_{11} (**d**), Ph (**e**), $PhCH_2$ (**f**), 2-$FC_6H_4CH_2$ (**g**)
Cat = K, NH_4, NMe_4 NEt_4

observed when the reaction mixture resulting from the synthesis of **2a** in DMSO was diluted with water. In MeOH, gas evolution caused by decomposition of products **A** and **B** occurred during the reaction. Previously, one of the authors has shown that a nitrosohydroxylamine related to compounds **A** and **B** is formed as the major product in the reaction of salt NEt_4-**1a** with allyl bromide; it was isolated in a pure state.[3] In the syntheses of DAF **2f** and **2g**, benzaldehyde and 2-fluorobenzaldehyde, respectively, were isolated from the reaction mixtures as dinitrophenylhydrazones in yields of 4—5%. These aldehydes result apparently from the decomposition of by-products **A** and **B**. The low yields of **2e** (3.2—4.4%) compared to those of aliphatic DAF are probably due to the facts that the salts of aromatic NHA are less stable than those of aliphatic NHA[4] and that the cupferron anion is less nucleophilic than anions of aliphatic NHA (pK_a for cupferron is 4.10—4.11, and that for hexahydrocupferron is 5.58 [4]).

New ADO (**3—8**) were synthesized by the reactions with α,ω-dihaloalkanes (Scheme 3).

Scheme 3



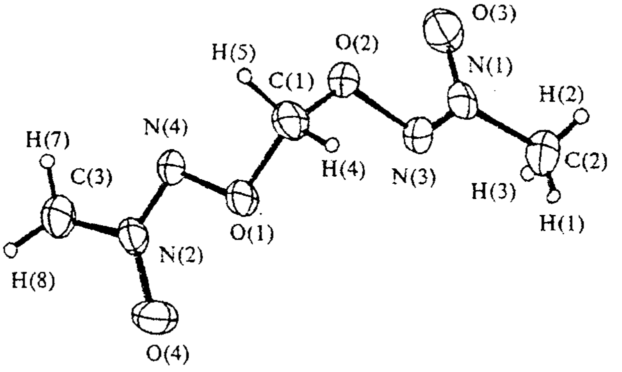


Fig. 1. Structure of molecule **2a**.

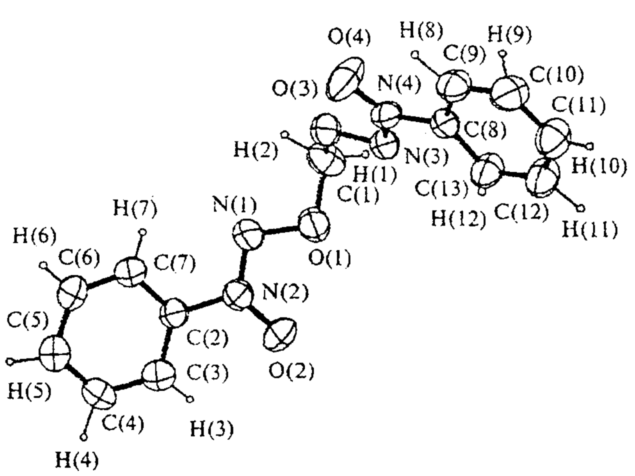


Fig. 2. Structure of molecule **2e**(*a*).

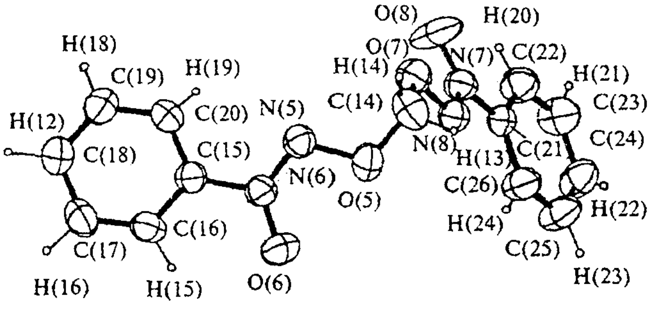
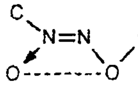


Fig. 3. Structure of molecule **2e**(*b*).

As in the case of DAF, the yields of aromatic ADO **7** and **8** are lower than those of **3—6**. The high yield of compound **6** (60%) is apparently due to the podand catalysis both by the compound **6** itself and by the intermediate monoalkylation product.

The structures of DAF, unlike those of the isomeric geminal di(alkoxy-*NNO*-azoxy)methanes, have not been studied earlier. In this work, we determined the structures of DAF **2a** and **2e** and also of one of the intermediate products, salt Cu-**1b**. Molecule **2a** has a *Z,Z*-configuration (Fig. 1). Nonhydrogen atoms of the two halves of molecule **2a** lie in the C(1)O(1)N(4)N(2)O(4)C(3) and C(1)O(2)N(3)N(1)O(3)C(2) planes, the angle between these planes being 75.5°. The unit cell in the structure of the crystal of **2e** contains two crystallographically independent molecules: *a* (Fig. 2) and *b* (Fig. 3). The bond lengths and angles in their diazene-oxide moieties are listed in Tables 2 and 3. The N(1)C(2)O(1)N(2)O(2)C(1) and O(3)C(8)N(3)N(4)O(4)C(1) groups of atoms in molecule *a* are located in two planes arranged at an angle of 69.1°, while in molecule *b*, the N(5)C(15)O(5)O(6)N(6)C(14) and O(7)C(21)O(8)N(8)N(7)C(14) planes form an angle of 68.5°. The benzene rings in both molecules deviate from the planes of the diazene-oxide fragments: the N(1)C(2)O(1)N(2)O(2)C(1) and C(2)C(3)C(4)C(5)C(6)C(7) planes in molecule *a* form an angle of 11.7°, and the angle between the O(3)C(8)N(3)N(4)O(4)C(1) and C(8)C(9)C(10)C(11)C(12)C(13) planes is 12.2°; in molecule *b*, the N(5)C(15)O(5)O(6)N(6)C(14) and C(15)C(16)C(17)C(18)C(19)C(20) planes are arranged at an angle of 11.1°, and the O(7)C(21)O(8)N(8)N(7)C(14) and C(21)C(22)C(23)C(24)C(25)C(26) planes form an angle of 11.2°. The CON=N$^+$(O$^-$)C fragments in ADO molecules are planar and exist in a *Z*-configuration stabilized by p—π- and n—σ*-conjugation.[5–7] A specific feature of DAF **2a** and **2e** that distinguishes them from di(alkoxy-*NON*-azoxy)methanes is that the C—O bonds in them are shorter, while the =N—O— bonds are longer (see Table 2). This may be due to the fact that the n_π(O)—σ*(C—O)-orbital interaction through the central carbon atom is stronger in the former case. Another possible explanation of this feature is the negative induction effect of the geminal N$^+$(O$^-$)=NO groups in DAF, which is manifested as a decrease in the contributions of two resonance structures (**E** and **F**) of the four structures (**C**—**F**) describing the p—π-conjugation in the N_2O_2-group[5] (Scheme 4).

Table 2. Bond lengths (*d*/Å) in the diazene oxide fragments

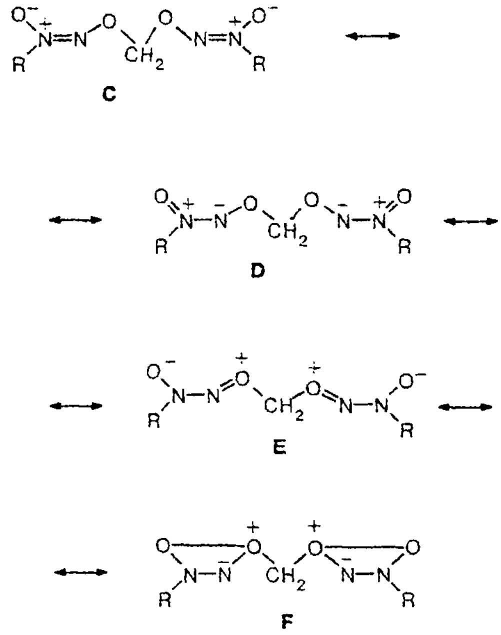


in compounds **2a** and **2e**

Compound	C—O	N—O	N=N	N→O	C—N	O...O
2a	1.415(4)	1.399(4)	1.263(5)	1.259(5)	1.473(6)	2.474(10)
	1.423(4)	1.390(6)	1.271(6)	1.260(5)	1.466(4)	2.450(10)
2e(*a*)	1.422(6)	1.387(5)	1.298(6)	1.241(6)	1.450(6)	2.443(10)
	1.441(7)	1.408(6)	1.273(6)	1.248(6)	1.469(6)	2.455(10)
2e(*b*)	1.398(7)	1.395(6)	1.268(6)	1.248(6)	1.454(6)	2.449(10)
	1.428(7)	1.408(6)	1.278(6)	1.233(6)	1.484(6)	2.435(10)
Literature data[a]	1.452	1.363	1.272	1.260	1.491	2.476

[a] Averaged over three $R^1R^2C[N^+(O^-)=NOMe]_2$ compounds, where $R^1 = R^2 = H$ [8]; $R^1 = H$, $R^2 = Me$[5] and $R^1 = R^2 = Me$ [5].

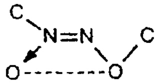
Scheme 4



Owing to the smaller contribution of structures **E** and **F**, the band corresponding to the π—π*-transition in the UV spectrum of azoxyformal **2a** shifts to shorter wavelengths with respect to these bands in the spectra of other ADO (229 and 234—237 nm [9]).

The large range of variation of the bond lengths for the two halves of the independent molecules of compound **2e** (see Table 2) is apparently due to the π—π-conjugation between the phenyl and N_2O_2 groups, which does occur despite the fact that the planes of these groups are rotated with respect to each other (11—12°). Owing to this conjugation, the electron density is easily redistributed over the common π-system depending on the requirements of the steric strain in the molecule and on the packing of the molecules in the crystal.

Table 3. Bond angles (ϕ/deg) in the diazene oxide fragments



in compounds **2a** and **2e**

Compound	CN→O	CN=N	O←N=N	N=NO	N=NC
2a	118.6(5)	114.5(5)	126.9(5)	108.1(5)	107.9(5)
	118.8(5)	115.6(5)	125.4(5)	108.1(5)	108.8(5)
2e(*a*)	118.9(4)	113.8(4)	127.3(4)	106.6(4)	106.4(4)
	120.5(4)	114.9(4)	124.5(4)	107.7(4)	109.6(4)
2e(*b*)	119.3(4)	114.5(4)	126.2(4)	106.5(4)	105.7(4)
	119.6(4)	115.5(4)	124.9(4)	108.8(4)	111.1(4)
Literature data[a]	118.9	113.9	127.1	108.2	108.3

[a] Averaged over three $R^1R^2C[N^+(O^-)=NOMe]_2$ compounds, where $R^1 = R^2 = H$ [8]; $R^1 = H$, $R^2 = Me$[5] and $R^1 = R^2 = Me$[5].

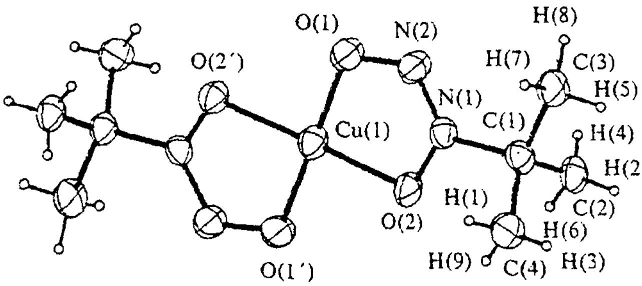


Fig. 4. Structure of complex Cu-**1b**.

The copper atom in molecule Cu-**1b** (Fig. 4) is located in a center of symmetry, which accounts for its strictly planar environment; the oxygen atoms form a rectangle with the sides O(1)...O(2) 2.510 Å and O(1)...O(2′) 2.884 Å. The lengths of the Cu—O(1), Cu—O(2), O(1)—N(2), N(1)—N(2), N(1)—O(2), and N(1)—C(1) bonds are 1.911(3), 1.912(3), 1.301(3), 1.270(3), 1.324(4), and 1.494(4) Å, respectively; these values are typical[10,11] of copper complexes of other NHA.

Experimental

IR spectra were recorded on UR-20 and Specord 75-IR instruments, UV spectra were obtained on Specord UV-VIS and Specord M-40 spectrophotometers, and ^{1}H NMR spectra were measured using tetramethylsilane as the internal standard on an NMR spectrometer with a cryogenic magnet (294 MHz) developed and produced at the Institute of Chemical Physics in Chernogolovka of the RAS. Mass spectra were recorded on an MX-1320 mass spectrometer. The individual state of compounds was checked by TLC on Silufol UV-254 plates using C_6H_6—AcOEt (3 : 1) as the eluent. For quick purification from resins and salts, silica gel 40—100 μm from Chemapol was used. Compounds **2e**, **5**, **7**, and **8** were isolated by flash-chromatography on a dry column (FC)[12] filled with Silpearl sorbent using C_6H_6—AcOEt as the eluent. Cupferron was purified by recrystallization from EtOH.

Sodium methylnitrosohydroxylaminate (Na-1a) was obtained from the copper salt (Cu-**1a**) similarly to the tetraethylammonium salt NEt_4-**1a**.[3] It was purified by precipitation with ethanol from a concentrated aqueous solution. Yield 80%, m.p. 306—308 °C (decomp.). UV (0.1 *M* NaOH), λ_{max}/nm: 247 (ε 9360) (*cf.* Ref. 13), (0.1 *N* H_2SO_4): 227 (ε 7720). IR (paste with CCl_4), ν/cm^{-1}: 2945, 2900, 1475, 1435, 1420, 1385, 1365, 1300, 1245, 1120, 1050. Found (%): C, 15.10; H, 3.76; N, 29.70. $CH_3N_2NaO_2$. Calculated (%): C, 12.25, H, 3.08, N, 28.57 (similar deviations have been observed in a previous study[13]).

Potassium methylnitrosohydroxylaminate (K-1a) was prepared in a similar way and purified by precipitation with DMF from a solution in MeOH followed by washing with acetone; yield 95%, m.p. 224—227 °C; after recrystallization from EtOH, m.p. 228—229 °C. The salt is non-hygroscopic at a relative humidity below 50%, and when humidity is above 70%, the compound runs. Its UV spectrum coincides with that of salt Na-**1a**.

Tetramethylammonium *tert*-butylnitrosohydroxylaminate (NMe_4-1b) was prepared from the copper salt (Cu-**1b**)[9] similarly to NEt_4-**1a** [3] and recrystallized from MeCN. Yield 48%, m.p. 199 °C (decomp.).

Potassium and copper isobutylnitrosohydroxylaminates (K-1c and Cu-1c). At −15 to −25 °C, dry NO was passed through an vigorously stirred solution of the Grignard reagent prepared from Mg (0.3 mol) and Bu^{i}Cl (0.3 mol) in 300 mL of Et_2O at such a rate that the gas was almost entirely absorbed. The reaction was completed after 1.5 h. The reaction mixture was purged with Ar, and a mixture of MeOH (15 mL) and Et_2O (30 mL) was gradually added to it at −10—0 °C. Then the mixture was acidified with 5 *M* HCl, the ethereal layer was separated, and the aqueous layer was extracted with Et_2O (2×80 mL). The combined ethereal solutions were extracted with an excess of 10% KOH, neutralized with 5 *M* HCl with respect to phenolphthalein, and concentrated *in vacuo*. Toluene (20 mL) was added, and the mixture was concentrated to dryness and dissolved in hot Pr^{i}OH (30 mL). The precipitate of KCl was filtered off, anhydrous Et_2O (100 mL) was added to the filtrate, and the precipitate was filtered off and washed with Et_2O. Hygroscopic colorless crystals (*cf.* Ref. 14) were dried *in vacuo* at 150 °C. Yield 8.90 g (19%), m.p. 240—250 °C (decomp.). The reaction of the mother liquor with $CuSO_4$ gave an additional 10.30 g (23%) of the copper salt Cu-**1c**, m.p. 82—82.5 °C (EtOH—H_2O) (*cf.* Ref. 14: m.p. 81—82 °C). Overall yield 42%.

Potassium and copper *n*-pentylnitrosohydroxylaminates (K-1d and Cu-1d) were obtained similarly to K-**1c** and Cu-**1c**; the yield of K-**1d** was 26%, it decomposed at 210—260 °C; the yield of Cu-**1d** was 13%, m.p. 82—83 °C (EtOH).

Potassium phenylnitrosohydroxylaminate (K-1e). 5 *M* HCl (250 mL) was added with stirring and cooling (7—14 °C) to a suspension of cupferron (101.9 g, 0.602 mol) in 650 mL of water and 35 mL of aqueous NH_3. The mixture was stirred for 1.5 h at 5—10 °C, the precipitate of phenylnitrosohydroxylamine was filtered off, washed with water (1 L), and suspended in 200 g of ice water, and the mixture was neutralized by 5 *M* KOH (0.56 mol) with respect to phenolphthalein. The solution was mixed with activated carbon (50 g), left for 2 days in a refrigerator, filtered, extracted with $CHCl_3$ (2×50 mL), and concentrated *in vacuo*. Yield 86.8 g (82%).

Potassium benzylnitrosohydroxylaminate semihydrate and copper benzylnitrosohydroxylaminate (K-1f and Cu-1f). The reaction of $PhCH_2MgCl$ (1 mol) with NO was carried out similarly to the reaction of Bu^{i}MgCl. The alkaline extract was acidified with 5 *M* HCl with vigorous stirring and cooling to −5 °C. The precipitate of benzylnitrosohydroxylamine was washed with water, and the remaining water was squeezed out. A small sample of the product was recrystallized from aqueous MeOH, m.p. 77.5—78 °C (*cf.* Ref. 15: m.p. 77—78 °C). The wet product was dissolved in an appropriate quantity of 10% KOH, so that the pH became 8—9. The mixture was concentrated *in vacuo*, and the residue (108 g) was recrystallized from EtOH (200 mL), and dried in air. Yield 80 g, dehydration temperature 110—115 °C, m.p. 211—214 °C (decomp.). Upon heating (1 h) *in vacuo* at 110—145 °C, a sample of the air-dried salt (10.5547 g) lost 0.4838 g, *i.e.*, 0.507 moles of H_2O per mole of anhydrous salt was removed. An additional 14 g of the air-dried product was precipitated with Et_2O (250 mL) from the mother liquor concentrated to 50 mL. The yield of K-**1f** was 94 g (47%). The reaction of the mother and wash liquors with $CuSO_4$ gave an additional 9.1 g (5%) of the copper salt Cu-**1f**, m.p. 157—158 °C (decomp.). Overall yield 52%.

Potassium 2-fluorobenzylnitrosohydroxylaminate monohydrate and copper 2-fluorobenzylnitrosohydroxylaminate (K-1g and Cu-1g) were prepared similarly to K-**1f** and Cu-**1f**. The yield of K-**1g** was 52%, and the temperature of dehydration was 140 °C; m.p. 190—198 °C (decomp.). ^{1}H NMR (15% in DMSO-d$_6$), δ: 3.69 (s, 2 H, H_2O); 4.99 (s, 2 H, CH_2); 7.15 (m, 2 H, Ar); 7.35 (distorted qd, 1 H, Ar, J_q = 6.9 Hz, J_d = 1.5 Hz); 7.64 (td, 1 H, Ar, J_t = 7.5 Hz, J_d = 1.5 Hz). Upon drying *in vacuo* (1 h) at 110—160 °C, a sample of the salt dried in air (6.7502 g) lost 0.5382 g, *i.e.*, 1.003 mole of H_2O per mole of the anhydrous salt. The yield of Cu-**1g** was 14%, m.p. 164—165 °C (decomp.). Overall yield 66%.

Di(methyl-*NON*-azoxy)formal (2a). *A*. CH_2Br_2 (2.6 mL) was added at 50 °C to a suspension of salt K-**1a** (8.09 g, 0.0707 mol) in DMSO (20 mL), the mixture was stirred for 0.5 h at 50—55 °C, an additional 2.4 mL of CH_2Br_2 was added (altogether 0.0713 mol), and the mixture was stirred at 70—80 °C for 1.5 h. At 60 °C, 20 mL of H_2O was gradually added. Intense gas evolution was observed. Then the mixture was heated until the precipitate dissolved (105 °C), cooled to ~20 °C, and allowed to stand at −18 °C for 24 h. The precipitate of **2a** was filtered off and washed with ice water (15 mL), cold EtOH (20 mL), and Et_2O (10 mL). The yield of **2a** was 1.87 g (32.2%); m.p. 195—197 °C (*cf.* Ref. 2: m.p. 199—200 °C).

B. A solution of salt K-**1a** (5.73 g, 0.0502 mol) and CH_2Br_2 (8.84 g, 0.0508 mol) in anhydrous MeOH (33 mL) was refluxed for 18 h and cooled to −18 °C; the precipitate was filtered off and washed with ice water, cold MeOH, and Et_2O. The yield of **2a** was 0.94 g (22.8%). The mother liquor was refluxed for 30 h, and an additional 0.37 g of compound **2a** was isolated in a similar way; overall yield 32%.

Di(*tert*-butyl-*NON*-azoxy)formal (2b). A solution of salt NMe_4-**1b** (0.5 g, 2.61 mmol) and CH_2Br_2 (0.3 mL, 4.3 mmol) in 2 mL of MeOH was kept at ~20 °C for 2 months. Then the solution was concentrated *in vacuo*, H_2O (10 mL) was added, and the product was extracted with $CHCl_3$ (3×10 mL). The extract was passed through a layer of SiO_2 (1 g) on a filter and concentrated *in vacuo*. The yield of **2b** was 0.16 g (49%), m.p. 137—143 °C; after recrystallization from EtOH, m.p. 151—151.5 °C, R_f 0.21. Found (%): C, 44.68; H, 7.80; N, 23.28. $C_9H_{20}N_4O_4$. Calculated (%): C, 43.55; H, 8.12; N, 22.57. UV (H_2O), λ_{max}/nm: 229 (ε 17800). ^{1}H NMR ($CDCl_3$), δ: 1.58 (s, 18 H, Me); 5.89 (s, 2 H, CH_2).

Di(isobutyl-*NON*-azoxy)formal (2c). Potassium carbonate (0.56 g) was added to a solution of salt K-**1c** (4.85 g, 0.031 mol) and CH_2Br_2 (2.2 mL, 0.031 mol) in MeOH (5 mL), and the mixture was refluxed with stirring for 22 h and concentrated *in vacuo*. Water (20 mL) was added, the mixture was concentrated *in vacuo*, water (30 mL) was added, and the product was extracted with $CHCl_3$ (3×30 mL). The extract was passed through a layer of SiO_2 (10 g) on a filter, washed with CH_2Cl_2 (100 mL), and concentrated *in vacuo*. The residue was recrystallized from a CCl_4—hexane mixture to give 2.06 g of **2c**; m.p. 58—58.5 °C, R_f = 0.29. An additional 0.20 g of product **2c** was extracted from mother liquor; m.p. 55—58 °C. Overall yield 57%. ^{1}H NMR (10% in CCl_4), δ: 0.97 (d, 12 H, Me, J = 6.7 Hz); 2.35 (nonete, 2 H, CH); 3.86 (d, 4 H, CH_2N, J = 7.2 Hz); 5.72 (s, 2 H, OCH_2O).

Di(*n*-pentyl-*NON*-azoxy)formal (2d) was obtained similarly to **2c**. Yield 2.31 g (42%), m.p. 38—39 °C (pentane). ^{1}H NMR (10% in DMSO-d$_6$), δ: 0.86 (t, 6 H, Me, J = 6.7 Hz); 1.26 (m, 8 H, $MeC\underline{H_2}C\underline{H_2}$); 1.80 (quintet, 4H, $C\underline{H_2}CH_2N$); 4.11 (t, 4 H, CH_2N, J = 6.6 Hz); 5.88 (s, 2 H, OCH_2O).

Di(phenyl-*NON*-azoxy)formal (2e). *A*. A solution of cupferron (12.0 g, 0.0709 mol) and CH_2Br_2 (5 mL, 0.718 mol) in DMSO (75 mL) was kept at ~20 °C for 3 days, and DMSO was evaporated *in vacuo*. The residue was diluted with 150 mL of water and extracted with $CHCl_3$ (4×50 mL). The extract was concentrated to 130 mL, diluted with Et_2O (130 mL), passed through a mixture of SiO_2 (90 g) on a filter, washed with Et_2O (200 mL), and concentrated *in vacuo*. FC of the residue (5.8 g) on 90 g of a sorbent in a C_6H_6—Et_2O mixture gave a fraction (0.65 g) containing **2e** (R_f 0.39). The product was recrystallized from a MeOH—H_2O mixture to give 0.45 g of **2e** (yield 4.4%); m.p. 112—117 °C. After additional recrystallization from CH_2Cl_2—Et_2O and recrystallization from MeOH repeated twice, the melting point was 120—120.5 °C. IR (KBr), ν/cm^{-1}: 3110, 3070, 3035, 2980, 2925, 2805, 1490 (N_2O_2), 1485 (N_2O_2), 1445, 1395, 1320, 1295, 1100, 1055, 1035, 1025, 1005, 955, 770, 685, 670. UV (H_2O), λ_{max}/nm: 255 (ε 15600), λ_{min}/nm: 228 (ε 8600). ^{1}H NMR (CD_3CN), δ: 6.20 (s, 2 H, OCH_2O); 7.57 (m, 6 H, 3,4,5-$\underline{H_3}C_6H_2$); 7.97 (d, 4 H, 2,6-$\underline{H_2}C_6H_3$, J = 7.7 Hz).

B. A solution of cupferron (5.06 g, 0.0326 mol) in an equimolar amount of a 20% aqueous solution of Me_4NOH was concentrated *in vacuo*. CH_2Br_2 (2 mL, 0.0287 mol) was added to a solution of the residue in MeCN (25 mL). Gas evolution and slight warming of the mixture were observed. The mixture was stirred for 1 h, concentrated *in vacuo*, and dissolved in $CHCl_3$ (30 mL). The precipitate of Me_4NBr (4.43 g, 89%) was filtered off, and the filtrate was concentrated *in vacuo*. The residue (3.53 g) was worked up as described in *A* to give 0.16 g (3.2%) of product **2e**.

Di(benzyl-*NON*-azoxy)formal (2f). A solution of the semihydrate of salt K-**1f** (19 g, 0.0954 mol) and CH_2Br_2 (9 mL, 0.128 mol) in MeOH (60 mL) was refluxed with stirring for 2 days. The mixture was concentrated *in vacuo*, 50 mL of water was added, and the mixture was concentrated *in vacuo* (azeotropic evaporation of by-products). The residue (8.5 g) was washed with water and recrystallized from MeOH (75 mL). The yield of **2f** was 6.20 g (41%), m.p. 117—118 °C. ^{1}H NMR (10% in DMSO-d$_6$), δ: 5.32 (s, 4 H, CH_2N); 5.97 (s, 2 H, OCH_2O); 7.33—7.45 (m, 10 H, Ph). Benzaldehyde was isolated from the mother liquor as dinitrophenylhydrazone (1.13 g, 4%).

Di(2-fluorobenzene-*NON*-azoxy)formal (2g). *A*. CH_2Br_2 (1.05 mL, 0.015 mol) was added to a suspension of anhydrous

Table 4. Coordinates of atoms (×10^4) in molecule **2a**

Atom	*x*	*y*	*z*
O(1)	1267(1)	3892(1)	6283(1)
O(2)	3115(1)	5035(1)	7559(1)
O(3)	5486(1)	4421(2)	8113(2)
O(4)	683(1)	1846(2)	4349(2)
N(1)	4575(1)	3592(2)	8740(2)
N(2)	1331(1)	3065(2)	3908(1)
N(3)	3326(1)	3753(1)	8573(1)
N(4)	1705(1)	4215(2)	4778(2)
C(1)	1721(2)	5140(2)	7285(2)
C(2)	4959(2)	2261(2)	9766(2)
C(3)	1722(2)	3195(2)	2266(2)
H(1)	4251(22)	1846(27)	10237(28)
H(2)	5645(26)	2550(30)	10215(32)
H(3)	5378(24)	1559(28)	9093(28)
H(4)	1251(19)	4971(23)	8261(23)
H(5)	1609(19)	6171(24)	6774(25)
H(6)	2218(24)	2457(30)	2065(32)
H(7)	2155(24)	4048(30)	2034(30)
H(8)	955(24)	3029(29)	1650(30)

Table 5. Coordinates of atoms ($\times 10^5$) in molecule **2e**

Atom	*x*	*y*	*z*
O(1)	60119(3)	4445(3)	57181(5)
O(2)	58703(3)	23376(3)	96837(6)
O(3)	64142(3)	−16242(3)	48941(5)
O(4)	65449(3)	−35282(3)	71255(5)
O(5)	10148(3)	33767(3)	71750(6)
O(6)	8733(3)	14662(4)	92181(6)
O(7)	14147(3)	54471(4)	84158(5)
O(8)	15433(4)	73393(4)	124874(6)
N(1)	68012(4)	8875(4)	76066(5)
N(2)	66229(3)	18866(4)	95785(6)
N(3)	56046(3)	−20840(4)	55233(6)
N(4)	57959(3)	−30570(4)	66875(6)
N(5)	18010(3)	29186(3)	86526(5)
N(6)	16276(2)	19376(3)	95972(5)
N(7)	7984(3)	68750(4)	116348(6)
N(8)	6078(2)	58929(3)	95147(5)
C(1)	61873(4)	−5899(4)	33110(6)
C(2)	73869(5)	24778(4)	117409(7)
C(3)	72515(5)	36215(5)	135032(8)
C(4)	79613(6)	42087(6)	155655(8)
C(5)	87862(5)	36556(6)	159788(8)
C(6)	88842(5)	25057(5)	141707(8)
C(7)	81997(5)	18973(6)	120837(9)
C(8)	50247(5)	−36596(6)	75061(8)
C(9)	51614(5)	−48096(5)	82438(7)
C(10)	44542(6)	−54092(6)	90350(8)
C(11)	36370(6)	−48367(6)	91113(8)
C(12)	35074(6)	−36802(6)	84137(8)
C(13)	42198(6)	−30791(6)	76373(9)
C(14)	11782(7)	44096(7)	58597(9)
C(15)	23821(7)	13425(7)	111918(9)
C(16)	22623(6)	1919(7)	117748(9)
C(17)	29591(6)	−4126(7)	133346(9)
C(18)	37826(5)	1609(6)	142327(8)
C(19)	38862(5)	13255(6)	136525(8)
C(20)	31975(6)	19190(5)	121104(9)
C(21)	251(5)	74774(5)	131214(8)
C(22)	1645(5)	86191(5)	149604(9)
C(23)	−5507(6)	92055(6)	163512(9)
C(24)	−13599(5)	86483(6)	158801(9)
C(25)	−14744(5)	74979(6)	140105(9)
C(26)	−7864(6)	69035(6)	126152(8)
H(1)	56573(15)	−7062(15)	14638(20)
H(2)	68082(15)	−5157(15)	23497(20)
H(3)	66752(15)	40030(15)	128384(20)
H(4)	79306(15)	49887(15)	169350(20)
H(5)	93309(15)	41081(15)	170094(20)
H(6)	94067(15)	20896(15)	146296(20)
H(7)	82561(15)	10829(15)	110244(20)
H(8)	58207(15)	−51823(15)	84693(20)
H(9)	48197(15)	−63540(15)	91911(20)
H(10)	31801(15)	−52294(15)	99694(20)
H(11)	28667(15)	−33696(15)	84673(20)
H(12)	41236(15)	−23134(15)	66088(20)
H(13)	5785(15)	45992(15)	48008(20)
H(14)	16170(15)	44018(15)	50517(20)
H(15)	16765(15)	−1420(15)	108866(20)
H(16)	29165(15)	−12663(15)	137089(20)
H(17)	42584(15)	−3157(15)	154421(20)
H(18)	44287(15)	16827(15)	142569(20)
H(19)	32007(15)	25728(15)	115088(20)
H(20)	7607(15)	88514(15)	156118(20)
H(21)	−4124(15)	100743(15)	177901(20)
H(22)	−19144(15)	89380(15)	166064(20)
H(23)	−20542(15)	72085(15)	134781(20)
H(24)	−8857(15)	60871(15)	114623(20)

salt K-**1g** (4.14 g, 0.02 mol) in DMSO (20 mL), and the mixture was stirred for 2 h at 22 °C. Brine (50 mL) was added, the product was extracted with $CHCl_3$ (3×30 mL), and the extract was washed with brine (20 mL). From the aqueous phase, the starting compound was isolated as the copper salt Cu-**1g** (1.35 g, 34%). The extract was concentrated *in vacuo*, water (20 mL) was added, and the mixture was again concentrated *in vacuo*. The spontaneously crystallized residue was washed with water and recrystallized from MeOH. The yield of **2g** was 0.63 g (18% or 27% based on the reacted salt K-**1g**), m.p. 106—106.5 °C. ^{1}H NMR (10% in DMSO-d_6), δ: 5.42 (s, 4 H, CH_2N); 5.96 (s, 2 H, OCH_2O); 7.22—7.32 (m, 4 H, Ar); 7.45—7.56 (m, 4 H, Ar); (10% in CCl_4), δ: 3.93 (s, 4 H, CH_2N); 5.45 (s, 2 H, OCH_2O); 7.36—8.11 (m, 8 H, Ar).

B. An attempt to carry out the reaction of the monohydrate of salt K-**1g** (11.31 g, 0.05 mol) with CH_2Br_2 (7 mL, 0.1 mol) in MeOH (30 mL) similarly to the synthesis of **2f** (refluxing for 7 days) was unsuccessful (the yield of **2g** was less than 2%). The reaction gave recovered **1g** as salt Cu-**1g** (0.14 g, 1.4%) and 2-fluorobenzaldehyde as dinitrophenylhydrazone (0.86 g, 5.6%), $R_f(C_6H_6)$ 0.38.

***N*-Methyl-*N'*-(2-chloroethoxy)diazene *N*-oxide (3).** A solution of salt K-**1a** (15.64 g, 0.137 mol) and dichloroethane (110 mL, 1.37 mol) in 200 mL of MeOH was refluxed for 2 days and concentrated *in vacuo*. $CHCl_3$ (50 mL) was added, and the precipitate was filtered off. Unreacted compound **1a** was isolated from the precipitate as its salt Cu-**1a** (1.79 g, 12%). From the filtrate, the solvent was evaporated, and the residue was distilled *in vacuo*. The yield of **3** was 11.39 g (60% or 68% based on the reacted salt K-**1a**), b.p. 113—114 °C (3.5 Torr), n_D^{20} 1.4881. After repeated distillation, boiling point was 83.5—84.5 °C (0.1 Torr); n_D^{20} 1.4882. IR, ν/cm^{-1}: 3015, 2950, 2875, 2820, 1515 (N_2O_2), 1425 (N_2O_2), 1395 (N_2O_2), 1320 (N_2O_2), 1300, 1195, 1100, 1070, 1030, 1015, 995, 955, 840, 760, 670, 640, 625. UV (H_2O), λ_{max}/nm: 232 (ε 9820). ^{1}H NMR (10% in DMSO-d_6), δ: 3.87 (t, overlap, 2 H, CH_2Cl); 3.89 (s, 3 H, Me); 4.45 (t, 2 H, CH_2O, J = 5.2 Hz).

***N*-Methyl-*N'*-(2-bromoethoxy)diazene *N*-oxide (4).** *A*. A solution of NEt_4-**1a** (58 g, 0.171 mol)[3] in MeCN was gradually added with stirring over a period of 2 h to a solution of 1,2-dibromoethane (65 g, 0.346 mol) in dry MeCN. The temperature was maintained in the range of 25—30 °C. The mixture was allowed to stand for 2 days, Et_2O (100 mL) was added, and the precipitate of Et_4NBr (31.5 g, 87%) was filtered off. The filtrate was concentrated *in vacuo*, and the residue (37 g) was distilled *in vacuo*. The yield of **4** was 14.95 g (48%), b.p. 108—110 °C (1 Torr), n_D^{20} 1.5150. ^{1}H NMR (without a solvent), δ: 3.73 (t, 2 H, CH_2Br); 3.93 (s, 3 H, Me); 4.56 (t, 2 H, CH_2O). MS (EI, 70 eV), m/z (I_{rel}(%)): 184 $[M]^+$ (1), 182 $[M]^+$ (1), 154 $[M-NO]^+$ (3), 152 $[M-NO]^+$ (3), 109 $[M-MeN_2O_2]^+$ (38), 107 $[M-MeN_2O_2]^+$ (38), 95 $[M-MeN_2O_2CH_2]^+$ (3), 93 $[M-MeN_2O_2CH_2]^+$ (3), 75 $[M-CH_2CH_2Br]^+$ (5), 59 (2), 57

(6), 45 (27), 44 (5), 43 (8), 42 (4), 41 (7), 30 (32), 29 (12), 28 (34), 27 (100), 26 (7).

2,3,8,9-Tetraaza-4,7-dioxadeca-2,8-diene 2,9-dioxide (5). A solution of salt NEt_4-**1a** in $MeNO_2$ (26.86 g, 0.0706 mol) was added to a solution of dibromoethane (13.27 g, 0.0707 mol) in 15 mL of $MeNO_2$. The reaction mixture spontaneously warmed to 50 °C; it was stirred for 2 h, Et_2O (50 mL) was added, the precipitate of Et_4NBr was filtered, and the filtrate was concentrated *in vacuo*. The residue (14.85 g) was separated by FC. The yield of **4** was 3.49 g (27%), that of **5** was 6.28 g (36%); m.p. 78—88 °C; after recrystallization from a THF—Et_2O mixture, the melting point was 91—92.5 °C, d_4^{20} = 1.40 (flotation). Found (%): N, 31.39. $C_4H_{10}N_4O_4$. Calculated (%): N, 31.45. IR (paste with CCl_4), ν/cm^{-1}: 2995, 2970, 2890, 1520 (N_2O_2), 1430 (N_2O_2), 1325 (N_2O_2), 1285, 1110, 1085, 1025, 880. UV (H_2O), λ_{max}/nm: 232 (ε 17300). ^1H NMR (20% in MeCN), δ: 3.84 (s, 6 H, Me); 4.47 (s, 4 H, CH_2). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 178 $[M]^+$ (9), 120 (3), 104 (5), 103 $[M-MeN_2O_2]^+$ (100), 75 $[M-MeN_2O_2CH_2CH_2]^+$ (12), 72 (2), 60 (2), 59 $[M-MeN_2O_2CH_2CH_2O]^+$ (39), 46 (4), 45 $[MeNO]^+$ (36), 44 (9), 43 (34), 42 (3), 32 (2), 31 (2), 28 (12).

2,3,17,18-Tetraaza-4,7,10,13,16-pentaoxanonadeca-2,17-diene 2,18-dioxide (6). K_2CO_3 (0.14 g, 1 mmol) was added to a solution of K-**1a** (2.6 g, 0.023 mol) and $(ClCH_2CH_2OCH_2CH_2)_2O$ (2.31 g, 0.01 mol) in MeOH (5 mL), the mixture was refluxed with stirring for a week, concentrated *in vacuo*, mixed with $CHCl_3$ (50 mL), passed through a layer of Al_2O_3 (20 g) on a filter, washed with $CHCl_3$ (100 mL), and concentrated *in vacuo*. The residue was recrystallized from PhMe (7 mL) to give 1.86 g of **6** (yield 60%), m.p. 50—51 °C. Recrystallization from a $CHCl_3$—Et_2O mixture gave 1.56 g of **6**, m.p. 50.5—52 °C. ^1H NMR (10% in DMSO-d_6), δ: 3.54 (s, 8 H, $CO\underline{H}_2C\underline{H}_2OC$); 3.67 (t, 4 H, $NOCH_2C\underline{H}_2$, J = 4.5 Hz); 3.87 (s, 6 H, Me); 4.30 (t, 4 H, $NOC\underline{H}_2CH_2$).

1,8-Diphenyl-1,2,7,8-diaza-3,6-dioxaocta-1,7-diene 1,8-dioxide (7). Et_4NBr (2.1 g, 0.01 mol) and 1,2-dibromoethane (18 mL, 0.208 mol) were added to a suspension of K-**1e** (86 g, 0.493 mol) in DMSO (190 mL). The mixture was stirred at 25 °C for 21 h and at 100—105 °C for 8 h. The mixture was diluted with water (800 mL) and extracted with $CHCl_3$ (5× 100 mL). The extract was washed with water (100 mL), 5% NaOH (100 mL), 10% H_2SO_4 (100 mL), and again with water (100 mL), dried with $CaCl_2$, and concentrated *in vacuo*. By FC of the residue (39.5 g), a fraction containing **7** (R_f 0.15) (6.88 g) was obtained. This fraction was recrystallized from MeOH (40 mL) to give 6.62 g of **7** (yield 10.5%), m.p. 108—110 °C; after three additional recrystallizations from MeOH, CCl_4, and EtOH, the melting point was 111—112 °C. IR (KBr), ν/cm^{-1}: 3075, 3020, 2985, 2900, 2840, 1485 (N_2O_2), 1480 (N_2O_2), 1455, 1435, 1370, 1320, 1315, 1295, 1240, 1120, 1090, 1070, 1030, 1020, 1015, 970, 940, 840, 770, 690, 680, 655. UV, λ_{max}/nm: 256 (ε 16000), λ_{min}/nm: 230 (ε 7940). ^1H NMR (10% in CD_3CN), δ: 4.78 (s, 4 H, CH_2); 7.53 (m, 6 H, 3,4,5-$\underline{H}_3C_6H_2$); 7.94 (d, 4 H, 2,6-$\underline{H}_2C_6H_3$, J = 7.7 Hz).

1,9-Diphenyl-1,2,8,9-tetraaza-3,7-dioxanona-1,8-diene 1,9-dioxide (8). A solution of cupferron (7.75 g, 0.05 mol) in a 20% solution of Me_4NOH (23.2 g, 0.0535 mol) was concentrated *in vacuo*, PhMe (50 mL) was added, and the mixture was concentrated to dryness. A solution of 1,3-dichloropropane (2.48 g, 0.022 mol) in dry MeCN (70 mL) was added to the residue, the mixture was refluxed for 5 h, concentrated *in vacuo*, diluted with water (50 mL), and extracted with $CHCl_3$ (5×30 mL), and the extract was concentrated *in vacuo*. FC of the residue (5.7 g) gave 0.36 g of **8** (R_f 0.17) (yield 7%), m.p. 82—83 °C (EtOH). ^1H NMR (10% in DMSO-d_6), δ: 2.33 (quintet, 2 H, CCH_2C); 4.58 (t, 4 H, CH_2O, J = 6.2 Hz); 7.57—7.68 (m, 6 H, 3,4,5-$\underline{H}_3C_6H_2$); 7.96 (d, 4 H, 2,6-$\underline{H}_2C_6H_3$, J = 7.4 Hz).

Table 6. Coordinates of atoms (×10^4) in molecule Cu-**1b**

Atom	*x*	*y*	*z*
Cu(1)	0(0)	0(0)	0(0)
O(1)	−1599(5)	150(3)	−1711(3)
O(2)	2099(4)	−1151(2)	−1058(3)
N(1)	1314(6)	−1192(3)	−2332(3)
N(2)	−551(6)	−544(4)	−2690(4)
C(1)	2716(7)	−2064(4)	−3314(5)
C(2)	3070(9)	−3299(4)	−2674(5)
C(3)	1565(10)	−2018(6)	−4696(6)
C(4)	4869(9)	−1717(5)	−3471(6)
H(1)	4558(61)	−850(33)	−3839(45)
H(2)	3858(64)	−3783(33)	−3232(41)
H(3)	5652(58)	−2162(33)	−4085(45)
H(4)	1835(66)	−3434(34)	−2625(43)
H(5)	2394(78)	−2666(42)	−5135(46)
H(6)	3416(69)	−3262(37)	−1850(49)
H(7)	1430(71)	−1291(39)	−5113(42)
H(8)	−13(74)	−2327(41)	−4562(54)
H(9)	5377(53)	−1580(28)	−2954(38)

X-ray diffraction study of compounds **2a**, **2e**, and Cu-**1b**. Crystals of $C_3H_8N_4O_4$ (**2a**, mol. weight 164.12) are monoclinic, a = 9.980(1), b = 8.365(1), c = 8.584(1) Å, γ = 90.65(2)°, V = 716.56 Å^3, d_{calc} = 1.520(2) g cm^{-3}, λ = 1.5418 Å; space group $P2_1/b$, Z = 4. Crystals of $C_{13}H_{12}N_4O_4$ (**2e**, mol. weight 288.27) are triclinic, a = 15.161(10), b = 11.154(9), c = 4.098(4) Å, α = 100.46(8), β = 97.46(8), γ = 88.85(6)°, V = 675.73 Å^3, d_{calc} = 1.416(3) g cm^{-3}, λ = 0.7107 Å; space group $P\bar{1}$, Z = 2. Crystals of $CuC_8H_{18}N_4O_4$ (Cu-**1b**, mol. weight 297.76) are monoclinic, a = 6.278(5), b = 11.500(2), c = 9.603(2) Å, γ = 75.66(2)°, V = 671.69 Å^3, d_{calc} = 1.471 g cm^{-3}, λ = 1.5418 Å; space group $P2_1/b$, Z = 2. The intensities of 1071 (**2a**) and 1025 (Cu-**1b**) observed independent reflections were measured on a DAR-UM diffractometer in the $0.07 < \sin\theta/\lambda < 0.6$ range, those of 1584 (**2e**) reflections were measured in the $0.002 < \sin\theta/\lambda < 0.5$ range on a four-circle diffractometer by $\omega/2\theta$-scanning. The structures of **2a** and Cu-**1b** were solved by the direct method on a personal computer using the AREN program package, and the structure of **2e** was solved by the direct method using the SHELX-86 program package. The coordinates of atoms in **2a**, **2e**, and Cu-**1b** (Tables 4—6) were refined in a full-matrix approximation to R equal to 0.045, 0.029, and 0.061, respectively; the thermal parameters were refined in the anisotropic approximation for nonhydrogen atoms and in the isotropic approximation for hydrogen atoms. The coordinates of hydrogen atoms were determined by a differential synthesis of electron density.

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