2,3-DIMETHOXYPERHYDRO-1,4,2,3-DIOXADIAZINE: SYNTHESIS, CONFORMATION, AND CONVERSION TO 1-(2-HYDROXYETHOXY)-2-METHOXYDIAZENE-1-OXIDE. CRYSTAL STRUCTURE OF 1-[2-(*para*-NITROBENZOYLOXY)-ETHOXY]-2-METHOXYDIAZENE-1-OXIDE

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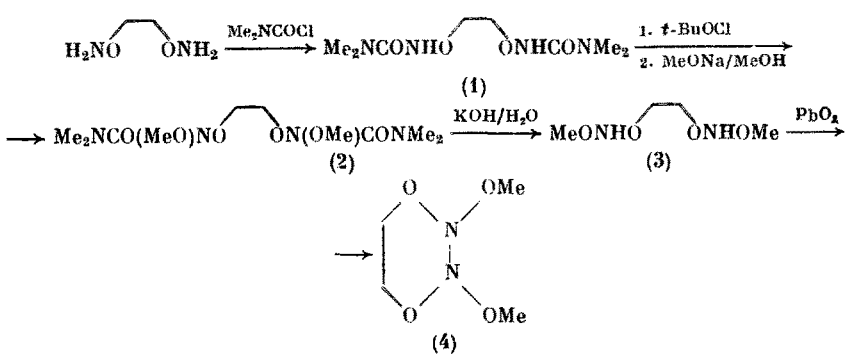
The oxidation of 1,2-bis(methoxyaminooxy)ethane (3) with PbO_2 afforded 2,3-dimethoxyperhydro-1,4,2,3-dioxadiazine (4) in the form of the 55:45 mixture of the trans-*4ee- and* cis-*4 isomers. The barrier of the ring conversion ($\Delta G_{238}^{\neq}$ = 11.3 kcal/mole) of the* cis-*4 isomer was determined by the method of ^{13}C NMR. The regio- and stereospecific stereoelectronically controlled reaction of (4) with* para-*nitrobenzoic acid gives the equimolar mixture of methyl* para-*nitrobenzoate and the 1,2-dialkoxydiazene oxide (5), the structure of which, and the (E)-configuration, were shown by the x-ray structural data of its acylation product — the diazene oxide (6).*

Keywords: *dialkoxyaminyl biradicals, 2,3-dimethoxyperhydro-1,4,2,3-dioxadiazine, dialkoxydiazene oxides, conformation, inversion, x-ray structure analysis, stereoelectronic control.*

Oxidation of dialkoxyamines leads to the formation of stable dialkoxyaminyl radicals, existing in solution in equilibrium with their diagmagnetic dimers — the tetraalkoxyhydrazines, which were isolated in the pure form [1, 2]. The only previously described aminyl biradicals ArṄSArSṄAr give macrocyclic polyhydrazines by recombination [3]. Therefore, both intra- and intermolecular recombination are expected for biradicals such as, for example, RO$\dot{N}$O(CH$_2$)$_n$O$\dot{N}$OR. The "entropy preferableness" of the intramolecular cyclization was thereby proposed for the biradicals with n = 2. Such a cyclization is "advantageous" from the viewpoint of the empirical rules of Baldwin [4]. In order to test this proposition, the synthesis of 1,2-bis(methoxyaminooxy)ethane (3) was accomplished by a general scheme for the isolation of dialkoxyamines [5].



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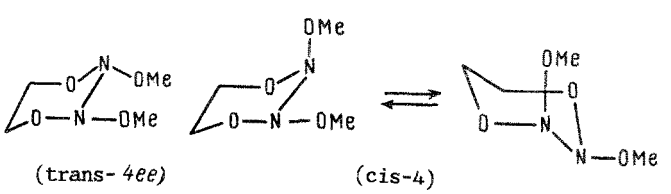
As was expected, the oxidation of (3) by PbO_2 gave an almost quantitative yield of the six-membered heterocycle (4) — the first example of cyclic tetraalkoxyhydrazines. In the series of the perhydro-1,4,2,3-dioxadiazines, only the 2,3-dialkoxycarbonyl derivatives were previously described [6]. An attempt to isolate their 2,3-dialkyl derivatives was unsuccessful [7]. The synthesis and properties of the acyclic mono- and dialkoxyhydrazines are considered in [8].

The PMR spectrum of the hydrazine (4) at ~20°C lacks the paramagnetic broadening of the signals; this indicates the complete, or virtually complete shift of the biradical ⇄ (4) equilibrium to the right. The 55:45 signals of the two isomers (4a) and (4b) are thereby observed. The spectrum of the isomer (4a) contains the singlet of protons of the MeO groups and the highly associated AA′BB′ system of the ring protons, the parameters of which were obtained from the spectral analysis using the LAOCN3 iterational program [9]. The broad singlet of protons of the MeO groups and the unresolved signals of the ring protons are observed in the spectrum of the isomer (4b) at ~20°C. The PMR spectrum of the isomer (4a) is unchanged at −50°C and, in the case of (4b), it is transformed into the well-resolved signals of the two MeO groups and the ABCD system of the ring protons. Signals of two isomers are also observed in the ^{13}C NMR spectra of the hydrazine (4) at ~20°C: the two signals for (4a) correspond to the C atoms of the MeO groups and the ring and, for (4b), there is the signal of the C atoms of the MeO groups and two broad signals of the ring C atoms. The spectrum of the isomer (4a) is unchanged at −50°C, and the nonequivalence of the C atoms both of the MeO groups and of the ring appears clearly in the spectrum of (4b). Using the merging of the signals of the first under the conditions of the uncoupling from the protons, the following parameters were found for the observed dynamic process in the case of the isomer (4b): T_c = 238 K, $\Delta\nu$ = 85 Hz, k = 188.7 sec^{-1}, and $\Delta G^{\neq}$ = 11.3 kcal/mole.

Utilizing the vicinal SSCCs of the ring protons of the isomers (4a) and (4b), the Lambert parameter $R = J_{trans}/J_{cis}$ was calculated [10]; its value [1.8 for (4a), and 2.1 for (4b)] indicates the "chair" conformation of these isomers. For comparison, R = 2.2 for cyclohexane [11], and $R \simeq 1$ for six-membered rings in the "bath" form [10, 11]. The values of the torsion angles, calculated from the equation in [11], OCCO of 56° for the isomer (4a) and 58° for (4b) are also in good agreement with the chair form of these heterocycles [11].

In the hydrazine (4), the N atoms are connected with electronegative substituents and, consequently, should be characterized by high configurational stability. Thus, the estimated value of the barrier to inversion of the N atom in the closest analogs of (4) — 2-alkylperhydro-1,3,2-dioxazines — comprises >27 kcal/mole [12]. Therefore, the picture of the inversion processes in (4), observed from the NMR spectra, is simplified considerably by comparison with the usual six-membered hydrazines — hexahydropyridazines [13], due to the exclusion of the inversion of the N atoms. In principle, *trans* and *cis* isomers are possible for the hydrazine (4), and conformational equilibrium due to ring conversion is possible for each of them. The equilibrium in the case of the *trans* isomer may thereby be displaced to one side or the other due to the energy nonequivalence of the conformers.

For 1,2-dimethylhexahydropyridazine, the methods of ^{13}C NMR [14] and photoelectronic spectroscopy [15] established the presence of only the *ee* and *ae* isomers with the predominance of the first (the ring conversion barrier of the *ae* isomer equals 11.6 kcal/mole [16]). It was shown that the *ee* isomer is preferred to the *ae* isomer by 0.4 kcal/mole in solution [14], and by 1.2 kcal/mole in the gas phase [15]. The estimated value of the energy disadvantage of the *aa* isomer by comparison with the *ae* isomer comprises ~3 kcal/mole [15]. According to our calculations by the method of molecular mechanics [17], the *trans* isomer (4*ee*) is preferred to the *cis* isomer by 1.2 kcal/mole, and is preferred to the *trans* isomer (4*aa*) by 2 kcal/mole. It was shown by the x-ray structural method that the acyclic analog (4) — tetramethoxyhydrazine — exists in the crystal with the conformation having the antiperiplanar disposition of the unshared electron pairs (UEPs) of the N atoms [2]; this corresponds with the isomer *trans*-(4*ee*). Starting from these data and the analysis of the NMR spectra of (4), it can be concluded that this compound exists in the form of two diastereomers in solution. The diastereomer (4a), which was mentioned previously, is the *trans*-(4*ee*) isomer, and the diastereomer (4b) is the *cis* isomer (4), which occurs in the equilibrium (4*ae*) ⇄ (4*ea*) with the ring inversion barrier of 11.3 kcal/mole. The preferableness of the (4*ee*) isomer by comparison with the other isomers of (4) is probably determined by the same electronic and steric factors as apply in the case of hexahydropyridazines [13] and acyclic tetraalkoxyhydrazines [2].



(trans-4*ee*) (cis-4)

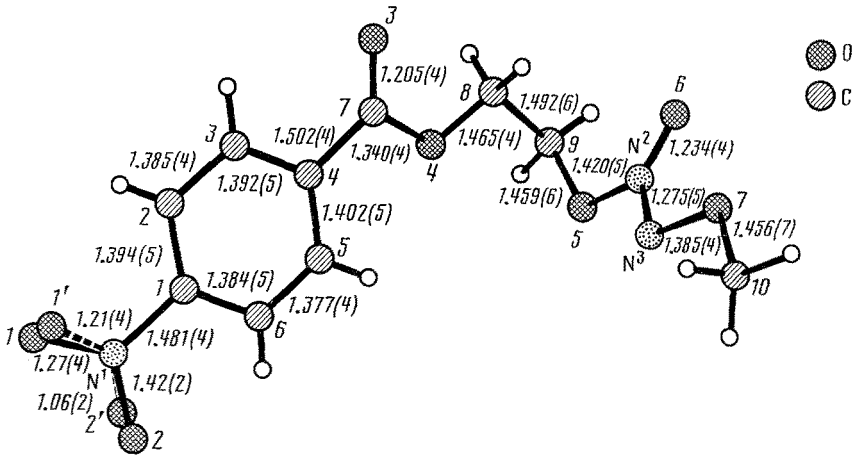
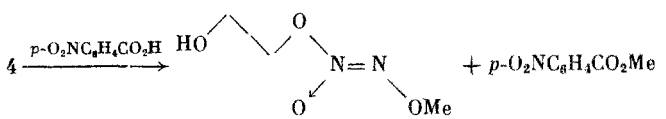


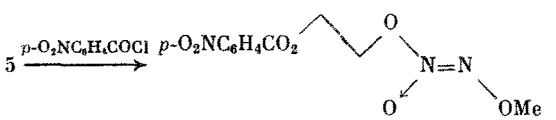
Fig. 1. General view of the molecule of (**6**) with the designation of the atoms and the bond lengths (Å).

The hydrazine (**4**) is thermally and chemically unstable: It decomposes when it is heated briefly in toluene, on the solution in MeOH, and on chromatography using neutral Al_2O_3 and silica gel. It is converted quantitatively by *para*-nitrobenzoic acid to the equimolar mixture (according to the PMR spectrum of the reaction mixture) of methyl *para*-nitrobenzoate and the dialkoxydiazene oxide (**5**) — the first example of this class of compounds.



(5)

The 1,2-dialkyl- and 1-alkyl-2-alkoxydiazene-1-oxides (AADOs) [18, 19] have been well studied. Compound (**5**) is a diester of the hypothetical hyponitric (oxyhyponitrous) acid, $H_2N_2O_3$, the salts of which — the hyponitrates (the Na salt is the salt of Angeli [20]) — have been known for a long time [21]. The product (**5**) is thermally and chemically stable: it is distilled *in vacuo* (bp ~70°C at 1 mm of Hg stem), is unchanged when chromatographed on neutral Al_2O_3, and by the action of *para*-nitrobenzoic acid and an aqueous solution of Na_2CO_3. Its structure was established on the basis of the data of the PMR, UV, and mass spectra. The PMR spectrum of (**5**) contains the signals of one of the possible isomers. The electronic spectrum is characterized by the sole band of the $\pi-\pi^*$ transition in the region characteristic of the AADO: 234-239 nm (ε_{max} = 5800-8200) [22]. In the mass spectrum of chemical ionization, the dominating peaks are those of the ions $[M + H]^+$ and $[MeON=N=O]^+$, which is probably formed by the elimination of ethylene glycol from the first ion. A similar fragmentation under electron impact — the cleavage of RON_2O from the molecular ion — is known for the AADOs R'N(O)=NOR [22, 23]. The structure of (**5**) was shown unambiguously by the x-ray structural investigation of the product of its acylation (**6**).



(6)

The general view of the molecule (**6**), the designation of the atoms, and the bond lengths are presented in Fig. 1. The coordinates of the atoms are presented in Table 1. The bond angles are presented in Table 2, and the torsion angles are presented in Table 3. The molecule of (**6**) has the (*E*)-configuration with the orientation of the N^2-O^6 and N^3-O^7 bonds on one side of the N=N bond as in the case of the (*Z*)-isomers which are formed preferentially in the isolation of the AADOs [24]. One of the possible factors stabilizing such a geometry for (**6**) is the hyperconjugation $n_{N^3}-\sigma^*_{N^2-O^6}$. The oxydiazene oxide fragment in (**6**) is practically planar as in the AADOs [24] and the salt of Angeli [25]: the $O^5N^2N^3O^7$ and $O^6N^2N^3O^7$ torsion angles are equal to 174.6° and −1.9° correspondingly. This is determined by the presence of $p-\pi$-conjugation in (**6**) — the interaction

TABLE 1. Coordinates of the Atoms ($\times 10^4$ and $\times 10^3$ for H)*

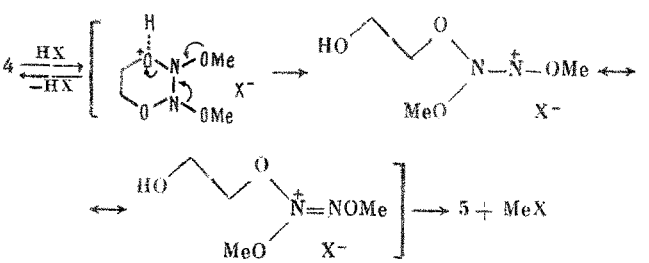
Atom	X	Y	Z	Atom	X	Y	Z
O^1	−2705(63)	6293(50)	−2486(23)	C^8	3953(7)	8737(6)	3060(2)
O^2	−5168(24)	5419(38)	−1500(17)	C^9	2783(8)	8190(7)	3840(3)
O^3	4773(4)	9568(4)	1398(2)	C^{10}	−2422(10)	14410(8)	3867(4)
O^4	2472(4)	8134(3)	2229(1)	$O^{1'}$	−2553(69)	6786(51)	−2360(24)
O^5	698(5)	9025(4)	3860(2)	$O^{2'}$	−4555(25)	5421(33)	−1576(17)
O^6	2670(5)	11563(4)	4612(2)	H^2	88(5)	780(4)	−153(2)
O^7	−474(5)	13504(4)	4194(2)	H^3	342(5)	877(4)	−28(2)
N^1	−3133(6)	6248(4)	−1664(2)	H^5	−111(5)	714(4)	133(2)
N^2	980(6)	10935(5)	4133(2)	H^6	−349(5)	627(4)	3(2)
N^3	−751(6)	11689(5)	3839(2)	H^{81}	527(7)	807(5)	302(3)
C^1	−1541(5)	6907(4)	−860(2)	H^{82}	419(6)	1014(5)	311(2)
C^2	509(6)	7675(4)	−990(2)	H^{91}	229(7)	682(6)	377(3)
C^3	1993(6)	8240(4)	−229(2)	H^{92}	366(7)	857(5)	440(3)
C^4	1418(5)	8028(4)	645(2)	H^{101}	−378(11)	1369(9)	391(5)
C^5	−666(5)	7274(4)	754(2)	H^{102}	−231(8)	1452(6)	327(3)
C^6	−2159(6)	6711(4)	3(2)	H^{103}	−218(9)	1567(8)	415(4)
C^7	3091(6)	8677(4)	1444(2)				

*The equivalent anisotropic (isotropic for the H atoms) temperature factors can be obtained from the authors.

of the UEPs of the π-type of the O^5, O^6, and O^7 oxygen atoms with the π^*-orbital of the N=N bond. A consequence of this is the relative shortening of the N−O bonds (1.385 Å for N^3-O^7, and 1.420 Å for N^2-O^5) by comparison, for example, with Me_2NOMe (1.513 Å [26]) and the lengthening of the N=N bond (1.275 Å) in relation, for example, to MeN=NMe (1.254 Å) [27] and ArN(O)=NAr (1.218 Å) [28].

Attention should be paid to the fact that the N^2-O^5 bond in the molecule of (**6**) is lengthened (1.420 Å) by comparison with the N^3-O^7 bond (1.285 Å), and the N^2-O^6 bond is shortened (1.234 Å) by comparison with the AADOs (1.261 Å) [24] and diaryldiazene oxides (1.279 Å) [28]. This is probably a consequence of the $n_{O^6}-\sigma^*_{N-O^5}$ hyperconjugation which is specific for (**6**).

Therefore, the structure of the diazene oxide (**6**) was shown unambiguously, and, consequently, also the structure of its precursor (**5**). This allows a return to the question of the mechanism of the reaction of the hydrazine (**4**) with *para*-nitrobenzoic acid. Here, there are two possible alternatives. The first includes the protonation of the endocyclic O atom in (**4**) and the subsequent stereoelectronically controlled [29] cleavage of the N−O cyclic bond with the formation of the resonance-stabilized nitrenium ion.



HX = p-$O_2NC_6H_4CO_2H$.

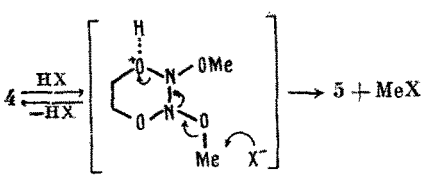
The charge in this ion should be localized to a large extent on the dialkoxyamine atom of N (due to its higher electron-donor capacity by comparison with the O atom) and, consequently, on the neighboring O atoms as well. Therefore, the dealkylation of this cation by the action of the anion occurring in the reaction should proceed with the formation of the diazene oxide. The ionic mechanism of this reaction is in agreement with the data on the acid-catalyzed reactions of the carbon analogs of (**4**) — *ortho*-ethers [29]. The possibility of the formation of alkoxynitrenium ions as a kinetically independent species was shown experimentally [30]. The 1,1-dialkyl-2-alkoxydiazenium salts are known [31]. However, this scheme does not explain the observed regio- and spectrospecificity of the reaction. Therefore, the synchronous mechanism is probably preferred.

TABLE 2. Bond Angles (deg) of the Diazene Oxide (6)

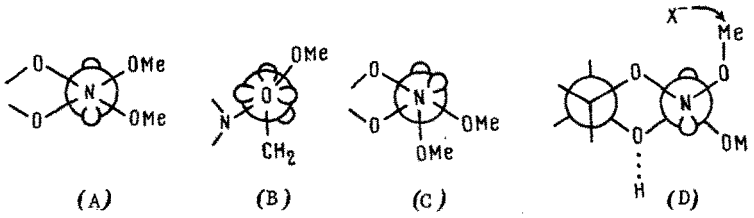
Angle	ω	Angle	ω
$N^1-O^1-O^{1'}$	71.8(75)	$O^7-N^3-N^2$	106.2(3)
$N^1-O^2-O^{2'}$	25.1(44)	$N^1-C^1-C^2$	119.8(3)
$C^7-O^4-C^8$	115.7(3)	$N^1-C^1-C^6$	117.8(3)
$N^2-O^5-C^9$	112.0(3)	$C^2-C^1-C^6$	122.4(3)
$N^3-O^7-C^{10}$	107.7(3)	$C^1-C^2-C^3$	118.9(3)
$O^1-N^1-O^2$	118.9(19)	$C^2-C^3-C^4$	119.7(3)
$O^1-N^1-C^1$	123.0(17)	$C^3-C^4-C^5$	120.1(3)
$O^2-N^1-C^1$	118.0(10)	$C^3-C^4-C^7$	117.2(3)
$O^1-N^1-O^{1'}$	18.1(23)	$C^5-C^4-C^7$	122.7(3)
$O^2-N^1-O^{1'}$	130.2(21)	$C^4-C^5-C^6$	120.8(3)
$C^1-N^1-O^{1'}$	110.8(18)	$C^1-C^6-C^5$	118.1(3)
$O^1-N^1-O^{2'}$	115.3(21)	$O^3-C^7-O^4$	123.7(3)
$O^2-N^1-O^{2'}$	9.3(16)	$O^3-C^7-C^4$	125.4(3)
$C^1-N^1-O^{2'}$	120.1(13)	$O^4-C^7-C^4$	110.9(3)
$O^{1'}-N^1-O^{2'}$	129.1(22)	$O^5-C^8-C^9$	105.6(3)
$O^5-N^2-O^6$	119.8(3)	$O^5-C^9-C^8$	112.8(4)
$O^5-N^2-N^3$	108.5(3)	$O^1-O^{1'}-N^1$	90.2(80)
$O^6-N^2-N^3$	131.6(3)	$O^2-O^{2'}-N^1$	145.6(60)

TABLE 3. Torsion Angles (deg) of the Diazene Oxide (6)

Angle	φ	Angle	φ
$O^2N^1O^1O^{1'}$	133.5	$C^7C^4C^3C^2$	−179.6
$C^1N^1O^1O^{1'}$	−51.0	$C^3C^4C^5C^6$	0.9
$O^1{}'N^1O^1O^{1'}$	0.0	$C^7C^4C^5C^6$	179.4
$O^2{}'N^1O^1O^{1'}$	143.2	$C^5C^6C^1N^1$	178.3
$O^1N^1O^2O^{2'}$	70.0	$C^5C^6C^1C^2$	−1.0
$C^1N^1O^2O^{2'}$	−105.8	$C^4C^5C^6C^1$	0.1
$O^1{}'N^1O^2O^{2'}$	87.2	$C^8O^4C^7O^3$	1.7
$O^2{}'N^1O^2O^{2'}$	0.0	$C^8O^4C^7C^4$	−178.2
$O^6N^2O^5C^9$	−25.3	$O^3C^7C^4C^3$	9.9
$N^3N^2O^5C^9$	157.7	$O^3C^7C^4C^5$	−168.7
$C^{10}O^7N^3N^2$	179.7	$O^4C^7C^4C^3$	−170.2
$O^5N^2N^3O^7$	174.6	$O^4C^7C^4C^5$	11.2
$O^6N^2N^3O^7$	−1.9	$C^9C^8O^4C^7$	172.6
$C^2C^1N^1O^1$	2.2	$C^8C^9O^5N^2$	−72.0
$C^2C^1N^1O^2$	177.8	$O^5C^9C^8O^4$	−59.4
$C^2C^1N^1O^{1'}$	−12.7	$N^1O^1{}'O^1N^1$	0.0
$C^2C^1N^1O^{2'}$	167.4	$O^1N^1N^1{}'O^1$	0.0
$C^6C^1N^1O^1$	−177.1	$O^2N^1O^1{}'O^1$	−56.4
$C^6C^1N^1O^2$	−1.5	$C^1N^1O^1{}'O^1$	135.9
$C^6C^1N^1O^{1'}$	168.0	$O^2{}'N^1O^1{}'O^1$	−44.3
$C^6C^1N^1O^{2'}$	−11.9	$N^1O^2{}'O^2N^1$	0.0
$C^3C^2C^1N^1$	−178.4	$O^1N^1O^2{}'O^2$	−114.4
$C^3C^2C^1C^6$	0.9	$O^2N^1O^2{}'O^2$	0.0
$C^4C^3C^2C^1$	0.1	$C^1N^1O^2{}'O^2$	79.3
$C^5C^4C^3C^2$	−1.0	$O^1{}'N^1O^2{}'O^2$	−100.6



The selective opening of the N−O bond in the ring of (4) is a consequence of the stereoelectronic control of the reaction [29]. Thus, the orientation of the UEPs of the N atoms in the *trans* isomer (4) favors the opening of both the endo- and the exocyclic N−O bonds to the same degree [see (A) — the Newman projection along the N−N bond].



(A) (B) (C) (D)

At the same time, the orientation of the UEPs of the ring O atoms is not favorable for the $n_O-\sigma^*_{N-OMe}$ overlap [see (B) — the Newman projection along the CH_2O-N bond], and the conformation with the antiperiplanar orientation of the UEP of the O atom of the π-type in relation to the neighboring N–O bond is obtained readily for the MeO group. That is also the cause of the selective cleavage of this bond in the *trans* isomer. In the *cis* isomer, the stereoelectronic situation for the endo- and exocyclic O atoms remains as previously, but the orientation of the UEP of the N atom connected to the axial MeO group thereby becomes antiperiplanar to the vicinal cyclic N–O bond [see (C) — the Newman projection along the N–N bond of the *cis* isomer]. Together with the stereoelectronic effect of the O atom of the MeO group, this also determines the opening of the N–O endocyclic bond.

The close to coplanar disposition of all the bonds being broken and the nonbonding orbitals participating in the reaction is necessary for the consistent course of the reaction of (**4**) with *para*-nitrobenzoic acid. In the given case, this is the endocyclic N–O bond, the orbital of the UEP of the neighboring N atom, and the Me–O or CH_2O bonds. It is understood that there is a high possibility of the required orientation for the MeO group [see, e.g., (D) — the double Newman projection along the N–N and C–C bonds for the *cis* isomer] by comparison with the endocyclic CH_2–O bond. That is probably also the determining factor, guaranteeing the selectivity of the cleavage of the Me–O bond.

EXPERIMENTAL

The NMR spectra were measured on the Bruker WM-400 spectrometer (^1H, 400.13 MHz; ^{13}C, 100.62 MHz from TMS). The mass spectra were measured on the Hitachi M-80-A chromato-mass spectrometer. The IR and UV spectra were measured on the UR-20 and Specord UV-VIS spectrophotometers correspondingly.

The 1,2-bis(aminooxy)ethane was obtained according to [32]; the yield was 69%, and the bp was 64°C (1.5 mm of Hg stem).

1,2-Bis(dimethylcarbamoylaminooxy)ethane (1). The solution of 8.14 g (88.5 mmoles) of 1,2-bis(aminooxy)ethane, 17.91 g (177 mmoles) of Et_3N, and 19.02 g (177 mmoles) of Me_2NCOCl in 70 ml of abs. MeCN was maintained for 5 days at 20°C and then boiled for 3.5 h. The solvent was removed *in vacuo*, and the residue was treated with an aqueous solution (70 ml) of 18.76 g (177 mmoles) of Na_2CO_3. The solution obtained was evaporated, and the residue was extracted twice with $CHCl_3$. The extracts were concentrated *in vacuo*. The yield of 19.72 g (95%) of (**1**) was obtained as an oil. The PMR spectrum (C_6D_6, δ, ppm) was as follows: 2.63 s (12H, Me_2N), 4.10 s (4H, CH_2), and 9.77 s (2H, NH). The product was utilized further without additional purification.

1,2-Bis(N-dimethylcarbamoyl-N-methoxyaminooxy)ethane (2). To the solution of 3.23 g (13.8 mmoles) of (**1**) in 50 ml of abs. CH_2Cl_2 were added, at −78°C and with stirring, 3.37 g (31.1 mmoles) of *t*-BuOCl. The mixture was concentrated *in vacuo*. To the residue was added the solution of MeONa (from 0.64 g of Na) in 30 ml of abs. MeOH at −78°C. The mixture was maintained at 1 h at −8°C and for 20 min at 20°C prior to the saturation with CO_2. The solvent was removed *in vacuo*, and the residue was extracted with Et_2O (50 ml). The extract was evaporated. The yield of 3.05 g (75%) of (**2**) was obtained as an oil. The PMR spectrum (C_6D_6, δ, ppm) was as follows: 2.55 s (12H, Me_2N), 3.50 s (6H, MeO), and 4.04 s (4H, CH_2). The product decomposes on distillation *in vacuo* and on column chromatography (neutral Al_2O_3, Et_2O), and was therefore utilized without additional purification.

1,2-Bis(methoxyaminooxy)ethane (3). The suspension of 2.64 g (8.9 mmoles) of (**2**) in 10 ml of an aqueous solution of 1.01 g (17.9 mmoles) of KOH and 0.2 g of $[Et_3NCH_2Ph]^+Cl^-$ was stirred for 2 days at 20°C. The mixture was saturated with NaCl and extracted with Et_2O. The extract was dried over $MgSO_4$ (1 h) and concentrated *in vacuo*. The yield of 0.76 g (56%) of (**3**) was obtained; it had the bp 80-81°C (1.5 mm of Hg stem). Found, %: C 31.50; H 7.59; N 18.09. $C_4H_{12}N_2O_4$. Calculated, %: C 31.58; H 7.95; N 18.41. The PMR spectrum (C_5D_6, δ, ppm) was as follows: 3.41 s (6H, MeO), 3.86 m (2H, CH_2), 3.92 m (2H, CH_2), and 7.74 d (2H, NH, $\Delta\nu$ = 3.4 Hz). The mass spectrum (CI, *i*-C_4H_{10}, 70 eV), given as *m/z* (I_{rel}), was as follows: 210 $[M + C_4H_{10}]^+$ (71), 153 $[M + H]^+$ (23), 152 $[M]^+$ (2), and 103 (100).

2,3-Dimethoxyperhydro-1,4,2,3-dioxadiazine (4). The suspension of 2.39 g (10 mmoles) of PbO_2 in 5 ml of an ether solution of 0.15 g (1 mmole) of (**3**) was stirred for 3 h at 20°C. The residue was separated and the filtrate was concentrated *in vacuo*. The yield of 0.14 g (95%) of the oil (**4**) was obtained. Found, %: C 31.56; H 6.73; N 19.02. $C_4H_{10}N_2O_4$. Calculated, %: C 32.00; H 6.71; N 18.66. The PMR spectrum (toluene-d_8, 27°C, δ, ppm, *J*, Hz) of the *trans* isomer was as follows: 3.49 s (6H, MeO), 2.94 m (2H, H_e, $^3J_{ee}$ = 2.1), and 4.39 m (2H, H_a, ^2J = −11.8, $^3J_{aa}$ = 10.5, $^3J_{ae}$ = 3.5). The PMR spectrum (toluene-d_8, 27°C) of the *cis* isomer was as follows: 3.56 s (6H, MeO), 3.41 m (2H, H_e), and 3.80 m (2H, H_a). The PMR

spectrum (toluene-d_8, −50°C) of the *cis* isomer was as follows: 3.49 s (3H, MeO), 3.64 s (3H, MeO), 2.75 m and 3.48 m (2H, H_e, $^2J = -11.1$, $^3J_{ae} = 3.1$, $^3J_{ee} = 0.8$), and 4.24 m and 4.32 m (2H, H_a, $^3J_{aa} = 11.9$). The ^{13}C NMR spectrum (toluene-d_8, 27°C) of the *trans* isomer was as follows: 58.81 (MeO, $^1J = 144.3$), and 56.39 (CH_2, $^1J = 148.4$). The ^{13}C NMR spectrum (toluene-d_8, 27°C) of the *cis* isomer was as follows: 60.03 (MeO, $^1J = 144.9$), 57.2 br.s and 68.9 br.s (CH_2). The ^{13}C NMR spectrum (toluene-d_8, −50°C) of the *cis* isomer was as follows: 59.61 and 60.22 (MeO, $^1J = 145$), 56.22 (CH_2, $^1J = 148.1$), and 68.64 (CH_2, $^1J = 146.3$). The mass spectrum (CI, *i*-C_4H_{10}, 70 eV), given as the *m/z* (I_{rel}), was as follows: 208 $[M + C_4H_{10}]^+$ (1), 150 $[M]^+$ (1), and 45 (100).

1-(2-Hydroxyethoxy)-2-methoxydiazene-1-oxide (5). The solution of 0.24 g (1.6 mmoles) of (**4**) and 0.27 g (1.6 mmoles) of *para*-nitrobenzoic acid in 72 ml of abs. Et_2O was maintained for 2 days at 20°C. After evaporation, the residue was chromatographed on a column (neutral Al_2O_3, eluent Et_2O). Methyl *para*-nitrobenzoate was obtained with the yield of 0.13 g (45%) (identified with a known sample according to the mp and PMR spectrum) together with 0.09 g (40%) of (**5**) as an oil. Found, %: C 26.89; H 5.94; N 20.20. $C_3H_8N_2O_4$. Calculated, %: C 26.47, H 5.93; N 20.58. The IR spectrum (thin layer, ν, cm^{-1}) was as follows: 3400, 1580, 1480, 1225, 1075, 1030, and 940. The UV spectrum taken in *n*-heptane was characterized at the λ_{max} 232 nm ($\varepsilon = 2760$). The UV spectrum taken in MeOH was characterized at the λ_{max} 233 nm ($\varepsilon = 8400$). The mass spectrum (CI, *i*-C_4H_{10}, 70 eV), given as the *m/z* (I_{rel}), was as follows: 137 $[M + H]^+$ (99.5), 136 $[M]^+$ (2), 119 $[M - HO]^+$ (6), 107 (30), 92 (10), 90 (11), 77 (26), and 75 (100). The PMR spectrum (CD_3CN) was as follows: 3.12 t (1H, HO, $^3J = 5.5$), 3.71 m (2H, $\underline{CH_2}OH$), 3.95 s (3H, MeO), and 4.36 m (2H, CH_2).

1-[2-(*para*-Nitrobenzoyloxy)ethoxyl]-2-methoxydiazene-1-oxide (6). The solution of 0.05 g (0.36 mmole) of (**5**), 0.07 g (0.36 mmole) of *para*-nitrobenzoyl chloride, and 0.04 g (0.36 mmole) of Et_3N in 6 ml of abs. C_6H_6 was maintained for 3 days at 20°C. The mixture was washed with an aqueous solution of Na_2CO_3 and water, dried over $MgSO_4$, and evaporated *in vacuo*. The yield of 0.09 g (93%) of (**6**), with the mp 84-85°C (from Et_2O), was obtained. Found, %: C 42.37; H 3.55; N 14.46. $C_{10}H_{11}N_3O_7$. Calculated, %: C 42.11; H 3.89; N 14.73. The PMR spectrum (CD_3CN, δ, ppm, *J*, Hz) was as follows: 3.92 s (3H, MeO), 4.59 m (2H, CH_2), 4.71 m (2H, CH_2), 8.17 and 8.30 (4H, C_6H_4, $^2J = 9.3$). The mass spectrum (CI, *i*-C_4H_{10}, 70 eV), given as the *m/z* (I_{rel}), was as follows: 286 $[M + H]^+$ (5), 256 (4), 226 (21), 194 (100), 150 (38), and 104 (18).

The main crystallographic data of (**6**) are as follows. $C_{10}H_{11}N_3O_7$. $M = 285$, $d_{calc} = 1.44$ g/cm^3, $a = 6.177(6)$ Å, $b = 7.308(7)$ Å, $c = 14.733(11)$ Å, $\alpha = 94.03(7)°$, $\beta = 96.75(8)°$, $\gamma = 93.74(8)°$, $V = 657.3(5)$ Å^3, $Z = 2$. The space group was $P\bar{1}$, and the intensities of the 3273 independent reflections $I \geq 2\sigma(I)$ were measured at 20°C on the Siemens R3/PC automatic four-circle diffractometer (λMoK_α) with a graphite monochromator, $\theta/2\theta$-scanning, and the $2\theta_{max} = 55°$. The intensities of the standard reflections fell by 50% from the original values when the experiment was carried out; this was taken into account in the treatment of the experimental data. The structure was interpreted by the direct method and specified in the isotropic, and then the anisotropic, approximation for all nonhydrogen atoms. The O atoms of the disordered nitro groups were specified with equal weight. All the H atoms were developed from the difference synthesis and specified using the isotropic approximation. At the final stage, the specification was performed from the 1678 reflections with the $F \geq 8\sigma$. The final value of $R = 0.062$, and $R_w = 0.07$. All calculations were performed using the Shelxtl program.

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