β,β-Dinitro derivatives of *N*-alkyl-*N'*-alkoxydiazene-*N*-oxides

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Methods of synthesis of *N*-alkyl-*N'*-alkoxydiazene-*N*-oxides containing a carbonyl group in the β-position of alkyl or alkoxy radicals were developed. β,β-Dinitro derivatives of *N*-alkyl-*N'*-alkoxydiazene-*N*-oxides were synthesized for the first time *via* nitration of oximes obtained from the ketones.

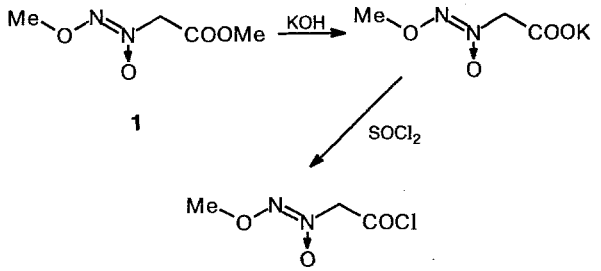
Key words: *N*-alkyl-*N'*-alkoxydiazene-*N*-oxides, ketones, oximes, *gem*-dinitro derivatives, β,β-dinitro derivatives.

β-Polynitro derivatives of *N*-nitramines (PNNA) represent one of the best studied classes of energy-rich substances.[1] The isomeric β-polynitro derivatives of *N*-alkyl-*N'*-alkoxydiazene-*N*-oxides (AADO) have a similar structure from the thermodynamic point of view. Therefore, we can expect high energy efficiency of AADO β,β-dinitro derivatives. However, these derivatives have not been described yet.

In this work, we developed methods for synthesis of AADO β,β-dinitro derivatives containing nitro groups in *N*-alkyl or *N'*-alkoxyl radicals for the primary estimation of their properties.

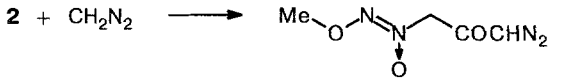
Considering AADO stability to electrophilic reagents, we based the synthesis on the well studied reaction of ketoxime nitration, which in most cases results in the dinitro derivatives in question. Therefore, our problem was reduced essentially to the search for efficient methods of obtaining the unknown AADO β-carbonyl derivatives.

In two stages methyl ester (**1**) afforded acid chloride (**2**) in a quantitative yield; some of its transformations into *N*-β-oxoalkyl-*N'*-alkoxodiazene-*N*-oxides were studied.



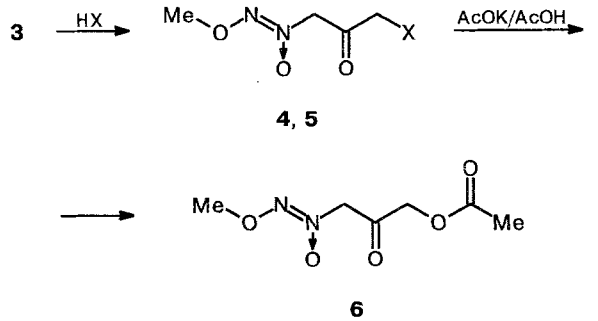
1 **2**

The attempts to replace the chlorine atom in acid chloride **2** for an aryl radical *via* Friedel—Crafts reaction (with benzene or anisole) or *via* interaction with diphenylcadmium failed. In the former case, a complex mixture of products was obtained, and biphenyl was obtained in the latter case instead of the product in question. Chloride **2** with diazomethane affords diazoketone (**3**) in 60 % yield.



3

Unlike the unsubstituted aliphatic diazoketones, **3** does not react with AcOH and is decomposed by CF_3CO_2H and diluted H_2SO_4 and HNO_3; however, when treated with HCl and HBr gases, it affords halocarbonyl derivatives (**4** and **5**). The latter are readily transformed into acetoxy derivative (**6**) upon heating with AcOK in AcOH.

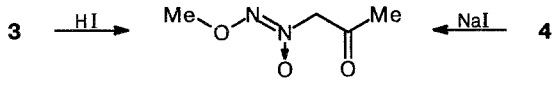


X = Cl (**4**), Br (**5**)

Reduction of diazoketone **3** with HI *via* the standard procedure[2] affords the AADO ketone in question (**7**) in extremely low yield. Reduction of chloride **4** with NaI is

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1534—1538, August, 1995.

more selective, but even in this case the yield of **7** does not exceed 16 %.

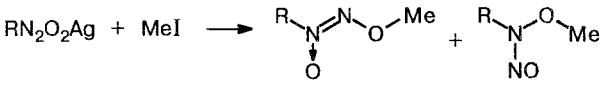


7

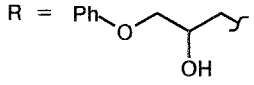
When treated with $NH_2OH \cdot HCl$ in methanol, these ketones are readily transformed into oximes (according to ^1H NMR spectroscopy, the ratio of *syn*- and *anti*-isomers is 1 : 1): $MeON{=}N(O)CH_2C(NOH)R$, R = CH_2Cl (**8**), CH_2Br (**9**), and Me (**10**).

Nitration of these oximes with N_2O_5 in $CHCl_3$ afforded the first representatives of AADO containing nitro groups in the β-position of the alkyl radical; they are quite stable low-melting compounds: $MeON{=}N(O)CH_2C(NO_2)_2R$, R = CH_2Cl (**11**), CH_2Br (**12**), and Me (**13**).

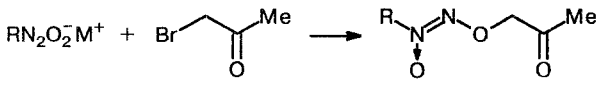
AADO containing a carbonyl group in the β-position of the alkoxyl radical were obtained by alkylation of salts of *N*-(2-hydroxy-3-phenoxypropyl)-*N*-nitrosohydroxylamine (**14**), which is available and has moderate stability, with bromacetone (**15**) and its oxime (**16**). It is known that alkylation of salts of *N*-alkyl-*N*-nitrosohydroxylamines (ANHA) often affords the mixture of AADO and *N,O*-dialkyl-*N*-nitrosohydroxylamines (DANH). We showed that the ratio of methylation products **17** and **18** in the reaction between silver salt **14** (**14a**) and MeI is 4 : 1.



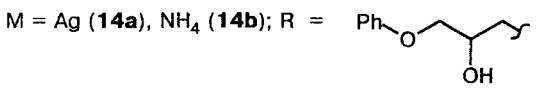
14a **17** **18**



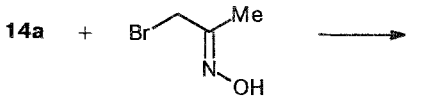
On the contrary, only AADO (**19**) can be isolated from the products of the reaction between **15** and **14a** or ammonium salt of **14** (**14b**) independently of the reaction conditions; the maximum yield is 65 % for **14a** and 25 % for **14b**.



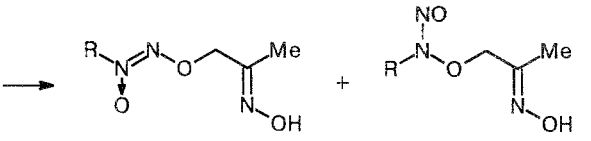
14a,b **15** **19**



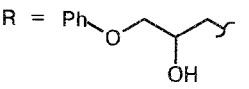
At the same time, the interaction between **14a** and **16** affords both possible alkylation products (**20** and **21**) with the yields of 43 and 23 %, respectively.



16



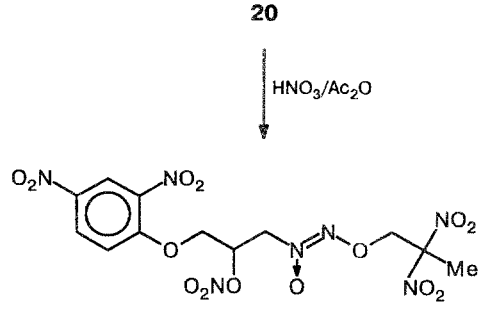
20 **21**



The structure of alkylation products **17**—**21** was confirmed by elemental analysis, NMR (^{13}C and ^{14}N) and IR spectroscopy, qualitative reactions, and some chemical transformations. Thus, products **18** and **21**, unlike **17** and **20**, give the qualitative reaction for the N—NO group with the Ph_2NH—H_2SO_4 mixture (blue color). Ketone **19** is transformed into oxime **20** by $NH_2OH \cdot HCl$.

^{14}N NMR spectroscopy is an effective method for structure determination of ANHA alkylation products, because rather narrow signal of *N*-oxide nitrogen in the range −65 to −70 ppm is observed for AADO, not for DANH. If the mixture of AADO and DANH is formed in the alkylation reaction, the inspection of ^{13}C NMR spectrum is enough for identification since the signal of carbon at the *N*-oxide nitrogen is shifted by ~10 ppm downfield with respect to the carbon at nitrogen in DANH (Table 1).

Heating of oxime **20** with the mixture of concentrated HNO_3 and Ac_2O in CCl_4 results in nitration at *ortho* and *para* positions of aromatic ring and at the hydroxyl group together with the transformation of oxime fragment into dinitromethylene group.



22

Product **22** (quite stable oil) is the first representative of AADO containing a β,β-dinitroalkoxyl radical.

Experimental

IR spectra were registered using a Specord spectrometer; ^{1}H NMR spectra were recorded using a Tesla BS-467 spectrometer (60 MHz, TMS or HMDS as internal standard); ^{13}C and ^{14}N NMR spectra were obtained using a Bruker AM-300 spectrometer (^{13}C: 75.5 MHz, acetone-d_6 (30.0 ppm), DMSO-d_6 (39.5 ppm), or chloroform-d (77.0 ppm) solvent; ^{14}N: 21.7 MHz, $MeNO_2$ external standard). Mass spectra were obtained using a Varian MAT CH-6 device (direct inlet of sample into the source, ionizing electron energy 70 eV, emission current 10 μA, accelerating voltage 1.75 kV, source temperature 180 °C).

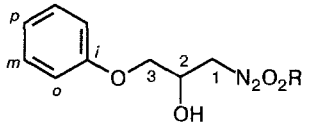
***N*-(Methoxycarbonylmethyl)-*N'*-methoxydiazene-*N*-oxide (1)** was prepared using a modified procedure.[3] 60 g (0.46 mol) of $MeCOCH_2CO_2Et$ was added to a EtONa solution in EtOH (23 g of Na (1 mol) and 680 mL of EtOH). NO was passed steadily for 4 h through the solution obtained. The precipitate formed was filtered off, washed with EtOH (2×50 mL), and dissolved in 100 mL of H_2O, then 100 mL of 10 % NaOH was added, and the solution was carefully warmed until termination of gas evolution. Water was removed *in vacuo*, the residue was treated with 500 mL of EtOH, and the precipitate formed was filtered off and washed with EtOH and Et_2O. 65.8 g (89 %) of $NaO_2N_2CH_2CO_2Na$ was obtained.

A mixture prepared from 10 g (0.061 mol) of this salt, 100 g of acetone, 30 mL of water, and 17 g (0.183 mol) of Me_2SO_4 was heated with stirring for 1.5 h at 55 °C, and then was cooled, and aqueous NH_3 was added to a pH of 8; the solution was filtered, the solvents were evaporated, and the residue was extracted with $CHCl_3$ (3×50 mL). The extracts were combined, dried over $MgSO_4$, and evaporated. The residue was distilled at 92—93 °C (3 Torr). 3.27 g (36 %) of **1** was obtained in the form of an oil, which upon storage crystallized into plate-like crystals with a m.p. of 36 °C. Found (%): C, 32.43; H, 5.42; N, 19.60. $C_4H_8N_4O_2$. Calculated (%): C, 32.43; H, 5.44; N, 18.91. IR spectrum (ν/cm^{-1}): 1760 (C=O); 1510, 1330 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 3.36 (s, 3 H, MeOC); 4.5 (s, 3 H, MeON); 4.7 (s, 2 H, CH_2).

***N*-Chlorocarbonylmethyl-*N'*-methoxydiazene-*N*-oxide (2).** 1.5 g (0.022 mol) of KOH in 10 mL of MeOH was added to the solution of 3 g (0.02 mol) of **1** in 20 mL of MeOH, the precipitate formed was filtered off, washed with a small amount of MeOH and ether. After drying, 3.3 g (95 %) of potassium *N'*-methoxydiazene-*N*-oxidoacetate was obtained. Then 1 g (5.8 mmol) of this salt was gradually added to 10 mL of distilled $SOCl_2$, the solution obtained was exposed at 60 °C for 40 min, the excess of $SOCl_2$ was removed, the residue was treated with dry ether, the ether extract was evaporated, and 0.88 g (100 %) of **2** was obtained in the form of a light thick oil. IR spectrum (ν/cm^{-1}): 1760 (C=O); 1510, 1320 (N_2O_2). ^{1}H NMR spectrum (benzene, HMDS, δ): 3.68 (s, 3 H, OMe); 4.94 (s, 2 H, CH_2).

***N*-(3-Diazo-2-oxopropyl)-*N'*-methoxydiazene-*N*-oxide (3).** An ethereal solution of 0.88 g (0.005 mol) of **2** was added to an ethereal solution of 0.63 g (0.015 mol) of CH_2N_2 at −60 °C in an atmosphere of dry nitrogen, the mixture was

Table 1. ^{13}C and ^{14}N NMR spectra of compounds **17—22**[a]



Compound	δ ^{13}C								δ ^{14}N
	C(1)	C(2)	C(3)	*i*-C	*o*-C	*m*-C	*p*-C	R	
17[b]	66.99	67.49	70.62	159.81	115.60	130.46	121.93	61.14 (Me)	−68.1
18[b]	56.57	67.28	70.80	159.82	115.57	130.42	121.88	62.85 (Me)	—
19[c]	68.57	66.85	76.87	157.95	114.39	129.43	121.33	65.81 (CH_2); 203.4 (C=O); 26.15 (Me)	−68.5
20[d]	66.11 66.15	65.41 65.50	74.41	158.28	114.56	129.51	120.84	69.44, 69.46 (CH_2); 151.42, 151.47 (C=N); 11.47 (Me)	−69
21[b]	57.20	67.27	70.71	152.51	115.60	130.44	121.91	77.13 (CH_2); 159.82 (C=N); 12.22 (Me)	—
22[b]	62.62	77.19	69.41	156.54	116.87; 139.87	122.59; 130.36	141.94	73.84 (CH_2); 117.37 $C(NO_2)_2$; 20.46 (Me)	−68.7 (NO); −49.2 (ONO_2); −15.9 (NO_2); −10.3 (NO_2)

[a] The authors are grateful to Yu. A. Strelenko for recording and interpreting the spectra. [b] In acetone-d_6. [c] In chloroform-d. [d] In DMSO-d_6.

kept at this temperature for 15 min, then the temperature was increased to −25 °C, and 60 mL of dry $CHCl_3$ was added. The solution was evaporated, 0.52 g (60 %) of **3** was isolated in the form of thick oil from the residue by means of TLC (silica gel, ether, R_f = 0.1). IR spectrum (ν/cm^{-1}): 2120 (N_2); 1650 (C=O); 1510, 1320 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 4.06 (s, 3 H, OMe); 4.75 (s, 2 H, CH_2); 5.7 (s, H, CH).

***N*-(2-Oxo-3-chloropropyl)-*N'*-methoxydiazene-*N*-oxide (4).** An ethereal solution of 0.88 g (0.005 mol) of **2** was added to an ethereal solution of 0.63 g (0.015 mol) of CH_2N_2 at −60 °C in an atmosphere of dry nitrogen, the mixture was kept at this temperature for 15 min, 60 mL of dry $CHCl_3$ was added, and at this temperature a flow of dry HCl was passed for a distinctly acidic reaction. The solvents were evaporated, and the residue was recrystallized from acetone. 0.72 g (75 %) of product **4** was obtained in the form of light yellow crystals, m.p. 126 °C. IR spectrum (ν/cm^{-1}): 1750 (C=O); 1500, 1320 (N_2O_2). ^{1}H NMR spectrum ($(CD_3)_2CO$, HMDS, δ): 3.91 (s, 3 H, OMe); 4.53 (s, 2 H, CH_2Cl); 5.17 (s, 2 H, CH_2CO). Mass spectrum, *m/z*: 166 $[M]^+$, 135 $[M^+-OMe]$, 121 $[M^+-NOMe]$, 117 $[M^+-CH_2Cl]$, 91 $[M^+-MeO_2N_2]$. Found (%): C, 29.05; H, 4.27; N, 18.0; Cl, 21.27. $C_4H_7ClN_2O_3$. Calculated (%): C, 28.83; H, 4.23; N, 16.8; Cl, 21.30.

***N*-(3-Bromo-2-oxopropyl)-*N'*-methoxydiazene-*N*-oxide (5).** HBr gas was passed at −10 °C through a solution of 0.34 g (2.2 mmol) of **3** in 20 mL of dry $CHCl_3$ for an acidic reaction. The solvent was evaporated, and the residue was recrystallized. 0.21 g (46 %) of **5** was obtained in the form of colorless crystals with m.p. of 102 to 102.5 °C. IR spectrum (ν/cm^{-1}): 1750 (C=O); 1500, 1320 (N_2O_2). ^{1}H NMR spectrum ($(CD_3)_2CO$, HMDS, δ): 3.96 (s, 3 H, OMe); 4.33 (s, 2 H, CH_2Br); 5.26 (s, 2 H, CH_2CO). Mass spectrum, *m/z*: 210, 212 $[M]^+$, 179, 181 $[M^+-OMe]$, 165, 167 $[M^+-NOMe]$, 135, 137 $[M^+-MeO_2N_2]$, 131 $[M^+-Br]$.

***N*-(3-Acetoxy-2-oxopropyl)-*N'*-methoxydiazene-*N*-oxide (6).** A mixture of 0.12 g (0.72 mmol) of **4**, 0.08 g (0.8 mmol) of $MeCO_2K$, and 10 mL of $MeCO_2H$ was boiled for 4 h; then the acid was removed *in vacuo*. 0.06 g (56 %) of **6** in the form of thick oil was isolated from the residue by means of TLC (silica gel, ethyl acetate, R_f = 0.48). ^{1}H NMR spectrum ($(CD_3)_2CO$, HMDS, δ): 2.11 (s, 3 H, Me); 4.09 (s, 3 H, OMe), 4.82 (s, 2 H, CH_2O); 5.00 (s, 2 H, CH_2CO).

***N*-(2-Oxopropyl)-*N'*-methoxydiazene-*N*-oxide (7).** A solution of 1.95 g (13 mmol) of NaI in 10 mL of acetone was added to a solution of 0.72 g (4.6 mmol) of **4** in 10 mL of acetone, and the mixture was stirred for 40 min. The precipitate was filtered off, the solution was evaporated, extracted with $CHCl_3$, washed with sodium thiosulfate, and the solvent was removed. 0.08 g (15.5 %) of **7** in the form of light thick oil was isolated from the residue by means of TLC (silica gel, ethyl acetate, R_f = 0.34). IR spectrum (ν/cm^{-1}): 1750 (C=O); 1500, 1320 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 2.24 (s, 3 H, Me); 4.07 (s, 3 H, OMe), 4.76 (s, 2 H, CH_2).

***N*-(2-Oxyimino-3-chloropropyl)-*N'*-methoxydiazene-*N*-oxide (8).** A solution of 0.3 g (1.8 mmol) of **4** and 0.15 g (2.1 mmol) of $NH_2OH \cdot HCl$ in 10 mL of anhydrous MeOH was boiled for 30 min and evaporated; the residue was extracted with $CHCl_3$. After drying and removal of solvent, 0.3 g (94 %) of **8** was obtained in the form of thick oil. IR spectrum (ν/cm^{-1}): 3300 (OH); 1660 (C=N); 1510, 1300 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 4.06 (s, 3 H, OMe); 4.26 (s, 2 H, CH_2Cl); 4.33 (s, 2 H, CH_2Cl); 4.88 (s, 2 H, CH_2N); 4.95 (s, 2 H, CH_2N).

***N*-(3-Bromo-2-oxyiminopropyl)-*N'*-methoxydiazene-*N*-oxide (9)** was prepared similarly to **8**; the yield was 98 %, oil. IR spectrum (ν/cm^{-1}): 3300 (OH); 1650 (C=N); 1510, 1300 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 4.08 (s, 3 H, OMe); 4.13 (s, 2 H, CH_2Br); 4.17 (s, 2 H, CH_2Br); 4.93 (s, 2 H, CH_2N); 5.17 (s, 2 H, CH_2N).

***N*-(2-Oxyiminopropyl)-*N'*-methoxydiazene-*N*-oxide (10)** was prepared similarly to **8**; the yield was 98 %, oil. IR spectrum (ν/cm^{-1}): 3300 (OH); 1660 (C=N); 1510, 1300 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 1.91 (s, 3 H, Me); 4.00 (s, 3 H, OMe); 4.62 (s, 2 H, CH_2N); 4.93 (s, 2 H, CH_2N).

***N*-(2,2-Dinitro-3-chloropropyl)-*N'*-methoxydiazene-*N*-oxide (11).** 0.3 g (1.85 mmol) of **8** in 10 mL of $CHCl_3$ was added to the solution of 0.43 g (3 mmol) of N_2O_5 in 10 mL of dry $CHCl_3$ at 55 °C. The mixture was kept at this temperature for 1 h, cooled, washed with 5 % Na_2CO_3 solution and water, dried over $MgSO_4$; the solvent was removed, and the residue was recrystallized. 0.05 g (15 %) of **11** was obtained in the form of crystals with m.p. 60—61 °C (hexane). Found (%): C, 20.66; H, 3.11; N, 22.60; Cl, 14.80. $C_4H_7ClN_4O_6$. Calculated (%): C, 19.80; H, 2.91; N, 23.10; Cl, 14.62. IR spectrum (ν/cm^{-1}): 1590, 1320 ($C(NO_2)_2$); 1500, 1360 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 4.11 (s, 3 H, OMe); 4.55 (s, 2 H, CH_2Cl); 5.31 (s, 2 H, $CH_2C(NO_2)_2$). Mass spectrum, *m/z*: 242 $[M]^+$, 227 $[M^+-Me]$, 196 $[M^+-NO_2]$, 180 $[M^+-NO_2-O]$, 150 $[M^+-2NO_2]$, 131 $[M^+-MeO_2N_2-HCl]$.

***N,N*-(3-Bromo-2,2-dinitropropyl)-*N'*-methoxydiazene-*N*-oxide (12)** was prepared similarly to **11** with a yield of 12 % in the form of colorless crystals, m.p. 57—58 °C (hexane). IR spectrum (ν/cm^{-1}): 1590, 1320 ($C(NO_2)_2$); 1500, 1360 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 4.11 (s, 3 H, OMe); 4.55 (s, 2 H, CH_2Br); 5.33 (s, 2 H, $CH_2C(NO_2)_2$). Mass spectrum, *m/z*: 286, 288 $[M]^+$, 271, 273 $[M^+-Me]$, 240, 242 $[M^+-NO_2]$, 224, 226 $[M^+-NO_2-O]$, 207 $[M^+-Br]$, 194, 196 $[M^+-2NO_2]$.

***N*-(2-Dinitropropyl)-*N'*-methoxydiazene-*N*-oxide (13)** was prepared similarly to **11** with the yield of 12 % in the form of colorless crystals, m.p. 51 °C (hexane). Found (%): C, 23.77; H, 4.09; N, 27.73. $C_4H_8N_4O_6$. Calculated (%): C, 23.08; H, 3.87; N, 26.92. IR spectrum (ν/cm^{-1}): 1590, 1320 ($C(NO_2)_2$); 1510, 1360 (N_2O_2). ^{1}H NMR spectrum ($CDCl_3$, HMDS, δ): 2.2 (s, 3 H, Me); 4.02 (s, 3 H, OMe); 5.09 (s, 2 H, $CH_2C(NO_2)_2$).

Ammonium salt of *N*-(2-hydroxy-3-phenoxypropyl)-*N*-nitrosohydroxylamine (14b).* A solution of 0.38 g (5.5 mmol) of $NaNO_2$ in 5 mL of H_2O was added with stirring to a solution of 1 g (5.5 mmol) of *N*-(2-hydroxy-3-phenoxypropyl)-hydroxylamine[4] in 20 mL of 1 % HCl cooled to −3 °C. The mixture was kept at this temperature for 5 min, the precipitate was filtered off, washed with cold water, and dissolved in 100 mL of ethyl acetate, and NH_3 was passed. The precipitate formed was filtered off, washed with ethyl acetate and ether, and dried. 1.15 g (89 %) of **14b** was obtained, m.p. 116—120 °C (with decomposition, MeOH). IR spectrum (ν/cm^{-1}): 3200—2800, 1590, 1580, 1500, 1480, 1440, 1395, 1260, 1220, 1050, 960, 920, 750, 680. Found (%): C, 47.10; H, 6.59; N, 18.39. $C_9H_{15}N_3O_4$. Calculated (%): C, 47.16; H, 6.55; N, 18.34.

Silver salt of *N*-(2-hydroxy-3-phenoxypropyl)-*N*-nitrosohydroxylamine (14a).* 0.74 g (4.4 mmol) of $AgNO_3$ in 5 mL of H_2O was added upon stirring to the solution of 1 g

* This procedure was developed with the assistance of A. Z. Lisitsin.

(4.4 mmol) of **14b** in 20 mL of H_2O, the precipitate was filtered off, washed with water, and dried. 1.39 g (100 %) of **14a** was obtained, m.p. 147—148 °C (decomp.). IR spectrum (ν/cm^{-1}): 3300, 2940, 2880, 1610, 1590, 1400, 1240, 1160, 1050, 950, 750, 700.

***N*-(2-Hydroxy-3-phenoxypropyl)-*N'*-methoxydiazene-*N*-oxide (17) and *N*-(2-hydroxy-3-phenoxypropyl)-*O*-methyl-*N*-nitrosohydroxylamine (18).** A mixture of 0.7 g (2.3 mmol) of **14a** and 0.3 g (2.3 mmol) of MeI in 20 mL of anhydrous methanol was stirred for 1 h at ~20 °C, and the mixture was filtered. The filtrate was evaporated. TLC of the residue (silica gel—ether) afforded 0.37 g (84 %) of **17** (R_f = 0.44, m.p. 112—114 °C from benzene) and 0.07 g (15 %) of **18** (R_f = 0.78, thick oil). IR spectrum of **17** (ν/cm^{-1}): 3500 (OH); 1590 (Ph); 1480, 1320 (N_2O_2); 1050 (OMe). IR spectrum of **18** (ν/cm^{-1}): 3400, 1490, 1450, 1400, 1230, 1030, 800, 750.

***N*-(2-Hydroxy-3-phenoxypropyl)-*N'*-2-oxopropoxydiazene-*N*-oxide (19).** A mixture of 1.6 g (5 mmol) of **14b** and 0.7 g (5 mmol) of bromoacetone in 30 mL of anhydrous acetonitrile was stirred at 20 °C for 18 h, and the precipitate was filtered off, the filtrate was evaporated, and TLC of the residue (silica gel—ether, R_f = 0.27) afforded 0.86 g (64 %) of **19** in the form of a thick oil. IR spectrum (ν/cm^{-1}): 3400 (OH); 1720 (C=O); 1600 (Ph); 1490, 1300 (N_2O_2). ^1H NMR spectrum ($CDCl_3$, HMDS, δ): 2.06 (s, 3 H, Me); 4.28 (m, 6 H, $CH_2CH(OH)CH_2$); 4.71 (s, 2 H, CH_2); 7.01 (s, 5 H, Ph).

N*-(2-Hydroxy-3-phenoxypropyl)-*N'*-(2-oxyiminopropoxy)-diazene-*N*-oxide (20) and *N*-(2-hydroxy-3-phenoxypropyl)-*O*-(2-oxyiminopropyl)-*N'*-nitrosohydroxylamine (21).** ***A. A solution of 1.6 g (5 mmol) of **14a** and 0.8 g (5 mmol) of bromoacetone oxime in 25 mL of anhydrous acetonitrile was stirred at 20 °C for 8 h and filtered, and the filtrate was evaporated. TLC of the residue (silica gel—ether) afforded 0.61 g (43 %) of **20** (R_f = 0.27, m.p. 136—138 °C from acetone—hexane, 1 : 1) and 0.33 g (23 %) of **21** (R_f = 0.56, m.p. 78—81 °C from hexane). **20**. Found (%): C, 50.21; H, 5.97; N, 15.75. $C_{12}H_{16}N_3O_9$. Calculated (%): C, 50.88; H, 6.05; N, 14.83. IR spectrum (ν/cm^{-1}): 3300, 1590, 1490, 1300, 1240, 1100, 1020, 950, 750. IR spectrum of **21** (ν/cm^{-1}): 3400, 3300, 1610, 1480, 1440, 1210, 1050, 910, 750.

B. A solution of 0.21 g of $NH_2OH \cdot HCl$ in 5 mL of H_2O neutralized with sodium carbonate was added to a solution of 0.9 g (3.4 mmol) of **19** in 10 mL of MeOH. In a day, 0.65 g (68 %) of **20** was filtered off, m.p. 138 °C; the product was identical to **20** obtained from **14a**.

***N*-[2-Nitroxy-3-(2,4-dinitrophenoxy)propyl]-*N'*-(2,2-dinitropropoxy)diazene-*N*-oxide (22).** 2.2 mL of freshly distilled acetic anhydride was added upon stirring to a solution of 2 mL of HNO_3 (d = 1.5 g cm^{-3}) in 12 mL of dry CCl_4 at 0 °C. The nitrating mixture obtained was heated to 45 °C, 0.13 g (5 mmol) of **20** was added simultaneously, the mixture was stirred for 15 min and poured into water, and the product of nitration was extracted with $CHCl_3$ (4×20 mL). The combined extract was washed with water to a neutral reaction and was dried over $MgSO_4$, the solvent was evaporated, and TLC (silica gel, MeOH—$CHCl_3$, 1 : 30, R_f = 0.11) afforded 0.19 g (38 %) of **22** in the form of an oil. IR spectrum (ν/cm^{-1}): 1650 (ONO_2); 1600 (arom. NO_2); 1550 [$C(NO_2)_2$]; 1500, 1320 (N_2O_2). ^1H NMR spectrum ($(CD_3)_2CO$, HMDS, δ, J/Hz): 2.31 (s, 3 H, Me); 4.8 (m, 2 H, CH_2N); 4.95 (m, 2 H, OCH_2); 5.3 (s, 2 H, $OCH_2C(NO_2)_2$); 6.23 (m, H, CH); 7.6 (d, H, H_aC, J_{ab} = 9.3); 8.565 (dd, H, H_bC, J_{bc} = 2.8); 8.78 (d, H, H_cC, J_{bc} = 2.8).

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Received February 20, 1995