SYNTHESIS OF N′-METHOXYDIAZENE N-OXIDES FROM METHOXYAMINE AND NITROSO COMPOUNDS

O. A. Luk'yanov, G. A. Smirnov, and A. M. Vasil'ev

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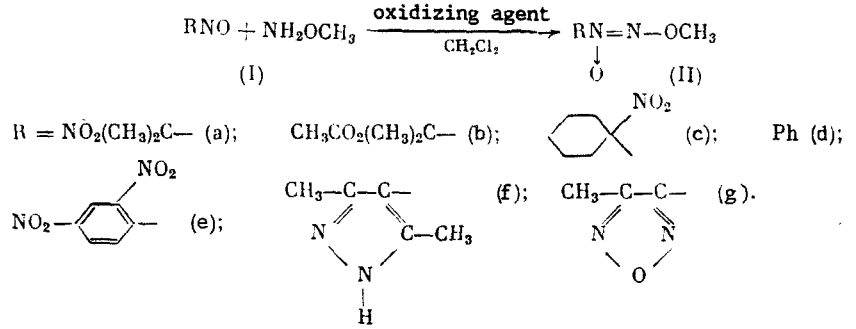
The reaction of methoxyamine with nitroso compounds in the presence of oxidizing agents is rather general in nature and may serve as a convenient method for the synthesis of aliphatic, aromatic, and heterocyclic N′-alkoxydiazene N-oxides.

Most of the N′-alkoxydiazene N-oxides (ADO) described in the literature have been synthesized by the alkylation of nitrosohydroxylamines or their salts. Such reactions proceed in good yield, while the unstable N-nitroso-N,O-dialkylhydroxylamines, formed as side products, hinder the isolation of the ADO. Ioffe et al. [1,2] have recently reported the formation of ADO upon the reaction of alkoxyamines with nitroso derivatives of tertiary alkanes in the presence of lead tetraacetate (LTA).

In order to determine the scope of the reaction of alkoxyamines with nitroso compounds in the presence of oxidizing agents, we studied the reaction of methoxyamine (MA) with a series of aliphatic, aromatic, and heterocyclic nitroso compounds. Derivatives of linear and cyclic alkanes were studied as aliphatic nitroso compounds. α-Nitro and α-acetoxy derivatives were studied for a more precise determination of the effect of the substituents in the nitroso component. For this reason, 2,4-dinitronitrosobenzene was studied along with nitrosobenzene among nitrosoaromatic compounds. Heterocyclic nitroso compounds were represented by azoles with two and three heteroatoms, including derivatives containing a labile N-H group proton.

The reaction of (Ia) with LTA under the conditions proposed by Ioffe et al. [1,2] proceeds with 12-16% yield. This led us to search for a more efficient oxidizing agent.



Dibromoisocyanuric acid (DBI), phenyl iodosodiacetate (PIDA), and bromine were used as the oxidizing agent. These results are given in Table 1, which shows that the reaction of MA with nitroso compounds is rather general in nature and may serve as a convenient method for the synthesis of aliphatic, aromatic, and heterocyclic N′-methoxydiazene N-oxides and their derivatives. Even strong electron-withdrawing substituents in the starting nitroso derivatives do not hinder the reaction in the desired direction. Thus, DBI, PIDA, and even bromine may be used as oxidizing agents along with LTA.

All the ADO obtained are colorless, crystalline compounds, which are entirely stable. Their structure was determined by elemental analysis, IR and PMR spectroscopy, and, in some cases, by mass spectrometry.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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TABLE 1. Conditions for the Preparation and Indices of the Products of the Reaction of Methoxyamine with Nitroso Compounds in the Presence of Oxidizing Agents

Starting nitroso compound	Oxidizing agent	Reaction temp., °C	Time, h	Reaction product	Yield, %	Bp, °C	Found/Calculated, %			Chemical formula	IR spectrum ($\nu \cdot cm^{-1}$)	PMR spectrum, δ, ppm (J, Hz)	Mass spectrum,* m/z
							C	H	N				
(Ia)	DBI LTA NBS	20	1,5	(IIa)	50 16 12	49,5–50,5	29,45 30,12	5,56 5,87	25,76 25,06	$C_4H_9N_3O_4$	3020, 2970 1570, 1380 1350, 1050	2,08 s (6H, $2CH_3C$) 4,12 s (3H, CH_3O)	163 [M+], 118 [M−$NOCH_3$]+, 117 [M−NO_2]+, 72[M−NO_2NOCH_3]+
(Ib) **	PIDA	35	4	(IIb)	17	42	41,24 40,9	6,7 6,86	16,86 15,90	$C_6H_{12}N_2O_4$	3400, 3000 2950, 1770 1500, 1450 1380, 1200 1170, 1130 1030, 100	1,78 s (6H, $2CH_3C$) 1,98 s (3H, $CH_3C{=}O$) 3,91 s (3H, CH_3O)	176 [M+], 117 [M−$OCOCH_3$]+, 101 [M−$N_2O_2CH_3$]+
(Ic)	PIDA DBI LTA Br_2	35	1,5	(IIc)	53 11 8 5	141–142	41,02 41,38	6,41 6,45	20,68 20,68	$C_7H_{13}N_3O_4$	3000, 1570 1460, 1380 1320, 1080	1,57 m (10H $(CH_2)_5$) 4,08 s (3H, CH_3O)	203 [M+], 157 [M−NO_2]+, 113 [M−NO_2NOCH_3]+
(Id)	PIDA	35	4	(IId)	35	39,5–40,5 (lit. 40) [3]	–	–	–		–	–	–
(Ie)	Br_2	20	43	(IIe)	20	150–151	34,65 34,17	2,48 2,32	23,13 23,98	$C_7H_6N_4O_6$	3120, 2940 1620, 1610, 1550, 1460 1420, 1360 1040	4,13 s (3H, CH_3O) 8,18 d (1H, H^6, $J_{5,6}$=9), 8,61 d.d (1H, H^5, $J_{5,6}$=9, $J_{3,5}$=2,5), 8,79 d (1H, H^3, $J_{3,5}$=2,5)	242 [M+], 227 [M−CH_3]+, 212 [M−NO]+, 197 [M−$NOCH_3$]+
(If)	DBI	20	24	(IIf)	44	193–195	42,35 41,13	5,92 6,02	32,93 31,91	$C_6H_{10}N_4O_2$	3220, 1590 1450, 1300 1050	2,42 s (6H, $2CH_3$ | C=N), 4,15 s (3H, CH_3O), 9,88 s (1H, HN)	
(Ig)	DBI PIDA	20	4	(IIg)	68 26	42–42,5	30,77 30,38	3,89 3,82	35,39 35,44	$C_4H_6N_4O_3$	3010, 2940 1580, 1410 1380, 1350 1280, 1200 1050	| 2,53 s (3H, $CH_3C{=}N$), 4,25 s (3H, CH_3O)	158 M+, 143 [M−CH_3]+, 113 [M−OCH_3]+

*The authors thank N. F. Karpenko for taking and interpreting the spectra.
**Obtained in situ from acetone oxime.

EXPERIMENTAL

The IR spectra were taken neat or in KBr pellets on a UR-20 or Specord spectrometer. The PMR spectra were taken in $CDCl_3$ on a Tesla 60 spectrometer relative to HMDS. The mass spectra were taken on a Varian CH-6 mass spectrometer at 70 eV. The chromatography was carried out on Silpearl UV-254 silica gel manufactured in Czechoslovakia.

N-(1-Methyl-1-nitroethyl)-N′-methoxydiazene N-oxide (IIa). A solution of 0.28 g (0.06 mole) MA in 10 ml CH_2Cl_2 was added dropwise with stirring to a mixture of 0.35 g (0.003 mole) (Ia) and 3.4 g (0.019 mole) DBI in 15 ml CH_2Cl_2 at 0°C. The reaction mass was heated to 20°C and stirred for an additional 1.5 h. The precipitate was separated. The filtrate was evaporated and the residue was subjected to thin-layer chromatography on silica gel (R_f 0.47, chloroform) to give 0.24 g (IIa).

N-(1-Acetoxy-1-methyl)-N′-methoxydiazene N-oxide (IIb). A sample of 0.5 g (0.007 mole) $(CH_3)_2C{=}NOH$ was added with stirring to a mixture of 4.4 g (0.0137 mole) PIDA and 10 ml CH_2Cl_2 at 20°C and maintained for 30 min. A sample of 0.32 g (0.007 mole) MA in 10 ml CH_2Cl_2 was then added at 35°C. The reaction mixture was maintained at 35°C for an additional 4 h and filtered. The filtrated was washed with two 10-ml portions of cold water and dried over $MgSO_4$. Magnesium sulfate was filtered off and the solvent was evaporated. The residue was subjected to thin-layer chromatography on silica gel (R_f 0.54, ether) to give 0.2 g (IIb).

N-(1-Nitrocyclohexyl)-N′-methoxydiazene N-oxide (IIc) was obtained by analogy to (IIb) from 0.41 g (0.087 mole) MA, 0.035 g (0.0022 mole) (Ic), and 3.1 g (0.0096 mole) PIDA. The residue was subjected to thin-layer chromatography on silica gel (R_f 0.56, methylene chloride) to give 0.24 g (IIc).

N-Phenyl-N′-methoxydiazene N-oxide (IId) was obtained by analogy to (IIb) from 0.5 g (0.00747 mole) (Id), 1.5 g (0.0047 mole) PIDA, and 0.22 g (0.0047 mole) MA. The residue was subjected to thin-layer chromatography on silica gel (R_f 0.3, chloroform) to give 0.25 g (IId).

N-(2,4-Dinitrophenyl)-N′-methoxydiazene N-oxide (IIe). A sample of 0.15 g (0.0032 mole) MA was added to a mixture of 0.2 g (0.001 mole) (Ie) and 0.1 g (0.001 mole) Br_2 in 10 ml CH_2Cl_2 at 0°C. The precipitate formed was filtered off and the filtrate was evaporated. The residue was subjected to thin-layer chromatography on silica gel (R_f 0.55, 25:1 chloroform–methanol) to give 0.05 g (IIe).

N-(3,5-Dimethyl-1H-pyrazol-4-yl)-N′-methoxydiazene N-oxide (IIf) was obtained by analogy to (IIa) from 0.25 g (0.002 mole) (If), 0.75 g (0.0026 mole) DBI, and 0.1 g (0.002 mole) MA. The residue was subjected to thin-layer chromatography on silica gel (R_f 0.18, 1:23 methanol-chloroform) to give 0.15 g (IIf).

N-(3-Methylfurazan-4-yl)-N′-methoxydiazene N-oxide (IIg) was obtained by analogy to (IIa) from 0.3 g (0.00265 mole) (Ig), 3 g (0.01 mole) DBI, and 0.25 g (0.005 mole) MA. The residue was subjected to thin-layer chromatography on silica gel (R_f 0.3, chloroform) to give 0.24 g (IIg).

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