Synthesis and properties of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine

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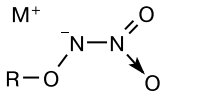
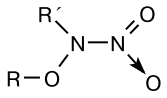
Salts of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine were synthesized by a new method of oxidative nitration, involving the reaction of *O*-(4-nitrophenyl)hydroxylamine with KNO_2 or $NaNO_2$ in the presence of $PhI(OAc)_2$ or PhIO as oxidants. When using $Na^{15}NO_2$, the samples containing the nitro group labeled with the ^{15}N isotope were obtained. Acidification of the appropriate salt gave *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine. It is the first *N*-nitrohydroxylamine isolated in the H-form. Its thermal stability was investigated and the probable mechanism of decomposition was suggested. From a comparison of the ^{14}N and ^{15}N NMR spectra of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine with those of its *O*- and *N*-methylated derivatives, its equilibrium with the *aci*-form (N=NOOH) was inferred.

Key words: hydroxylamines, nitrohydroxylamines, oxidative nitration, oxodiazonium ion, thermal stability, ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra.

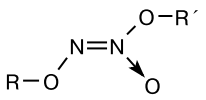
A method for the synthesis of salts of *O*-alkyl-*N*-nitrohydroxylamines **A** (R = Alk) was developed in the 1990s. It includes nitration of *N*-acetyl-*O*-alkylhydroxylamines followed by the treatment of the produced *N*-acetyl-*N*-nitro compounds with potassium methoxide.[1] Salts **A** are thermally stable. The *N*- and *O*-alkylated derivatives of nitrohydroxylamines **B** and **C** (R,R′ = Alk) are also relatively stable.[1] At the same time, the H-form of nitrohydroxylamines **D** is substantially less stable and has not been isolated in pure state. It was synthesized *in situ* as exemplified by nitrohydroxylamine with R = 2,4-$(NO_2)_2C_6H_3$ by nitration of the *N*-Me_3Si derivative of *O*-(2,4-dinitrophenyl)hydroxylamine (reagents and conditions: $(NO_2)_2SiF_6$, CH_2Cl_2, −10 °C) and converted into the *O*-methyl derivative **C** (R = 2,4-$(NO_2)_2C_6H_3$, R′ = Me) in a yield of 31% by the reaction with diazomethane at 0 °C (see Ref. 2).



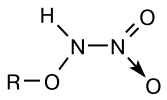
A



B



C



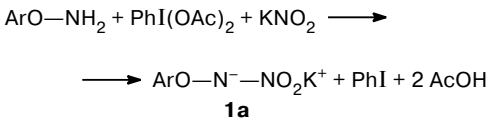
D

Earlier, we have synthesized the H-forms of nitrohydrazines.[3] In the present work, our aim was to prepare the H-form of nitrohydroxylamines **D** and to study its stability. *N*-Nitro-*O*-(4-nitrophenyl)hydroxylamine was chosen as the model compound.

Results and Discussion

Synthesis. Potassium *N*-nitro-*O*-(4-nitrophenyl)hydroxylaminide **1a** was prepared by oxidative nitration of *O*-(4-nitrophenyl)hydroxylamine. This method of N-nitration developed recently in our laboratory[4] makes it possible to avoid the strongly acidic medium in performing the reaction (Scheme 1). The nitrating agent is KNO_2 in the presence of $PhI(OAc)_2$ as an oxidant. The reaction was performed at 0 °C in methanol, the solvent was removed *in vacuo* and the product was chromatographically separated from the by-product, *viz.*, *p*-nitrophenol. Salt **1a** prepared according to this procedure in a yield of 38% contains potassium acetate as the admixture (^1H NMR control).

Scheme 1



1a

Ar = 4-$NO_2C_6H_4$

For the preparation of an analytically pure sample of salt **1a**, we used a solution of PhIO in methanol as the

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oxidant instead of $PhI(OAc)_2$. In this case, the yield of salt **1a** was 41%.

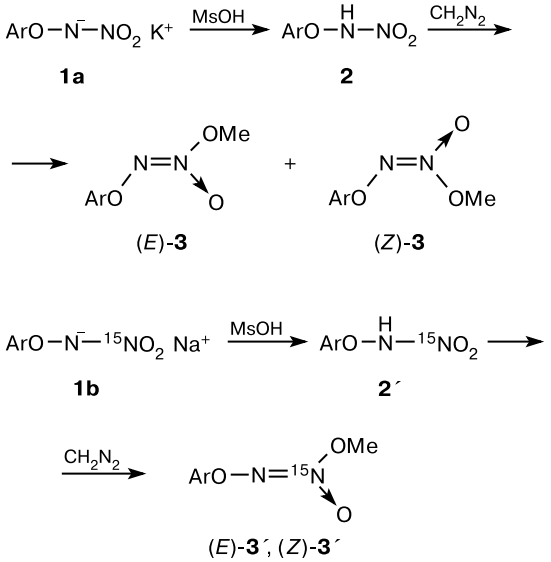
For the preparation of the compound with the ^{15}N labeled nitro group, *O*-(4-nitrophenyl)hydroxylamine was nitrated with the system $Na^{15}NO_2$—$PhI(OAc)_2$ using the commercially available sodium nitrite with 92% enrichment by the ^{15}N isotope. Sodium salt **1b** was synthesized in a yield of 40%.

The salts prepared by these methods contain no nitrite impurities, which was established by the negative color reaction with the Griess reagent.

Potassium salt **1a** is yellow powder melting with decomposition at 145—155 °C. The structure of the salt was confirmed by the data from IR, ^1H, ^{13}C, and ^{14}N NMR spectroscopy and elemental analysis. Sodium salt **1b** was spectroscopically characterized, particularly by ^{15}N NMR spectroscopy, and was not isolated in analytically pure state.

A suspension of potassium salt **1a** in diethyl ether was carefully acidified with an etheral solution of methanesulfonic acid at 0 °C for the preparation of the H-form of nitrohydroxylamine (NHA) **2**. Nitrohydroxylamine **2´** with the ^{15}N-labeled nitro group (Scheme 2) was synthesized analogously from sodium salt **1b**. Acidification is best performed with the preparations of salts **1** that contain a small amount of KOAc or NaOAc (see Experimental). Pure samples of NHA **2** and **2´** are white crystals. Upon acidification, the excess of methanesulfonic acid should be avoided, otherwise, the NHA samples obtained after concentration of the ether solution are light yellow in color and contaminated with 4-nitrophenol and 2,4-dinitrophenol.

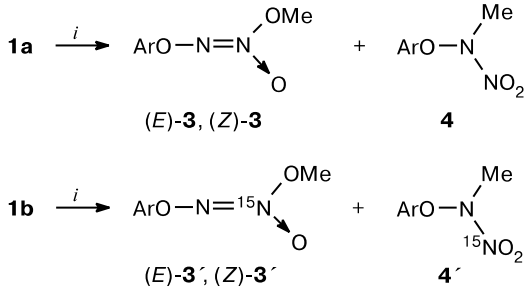
Scheme 2



Nitrohydroxylamines **2** and **2´** melt with decomposition at 69—70 °C. These compounds were characterized by ^1H, ^{13}C, ^{14}N, ^{15}N NMR spectroscopy. Their elemental analysis could not be performed because of their tendency to spontaneously decompose at room temperature. At the same time, the structures of NHA **2** and **2´** were unambiguously confirmed by methylation. The reactions of these compounds with diazomethane in ether afford *O*-methyl derivatives **3** and **3´**, respectively (see Scheme 2), which, according to the ^1H and ^{13}C NMR spectral data, are mixtures of the *E*- and *Z*-stereoisomers in a ratio of 2.2 : 1 (*cf.* Ref. 2). By analogy with the *O*-methylated nitramines,[5] we can ascribe the *E*-configuration to the major isomer.

Methylation with methyl iodide of the silver salts of NHA prepared by the reactions of salts **1a** and **1b** with $AgNO_3$ gives a mixture of *O*- and *N*-methyl isomers **3**, **4** and **3´**, **4´**, respectively (Scheme 3), in a ratio of 1 : 1 (*cf.* Ref. 6). The *O*-methylated compounds are a mixture of the *E*- and *Z*-stereoisomers in a ratio of 4.4 : 1. The *N*-methyl isomers **4** and **4´** were not isolated in the individual state. Their structures were confirmed by spectral studies (^1H, ^{13}C, ^{14}N, and ^{15}N NMR), including ^{15}N INEPT NMR and two-dimensional ^1H—^{15}N-correlation spectrosopy (^1H—^{15}N COSY). The latter experiments allowed us to unambiguously determine the position of the signal for the N-nitro group, which coincides with the signal for the nitro group of the phenyl ring in the ^{14}N NMR spectra.

Scheme 3



i. 1) $AgNO_3$, 2) MeI.

The signals for the methyl groups of compounds **3** and **4** in the ^1H and ^{13}C NMR spectra are close to the corresponding signals for the previously[2] prepared *O*- and *N*-methyl derivatives of *O*-(2,4-dinitrophenyl)-*N*-nitrohydroxylamine.

In the ^{14}N and ^{15}N NMR spectra, the position of the signal for the *N*-nitro group of both salt **1a** and the H-form **2** significantly depends on the solvent. The maximum difference between the chemical shifts, equal to 12 ppm (see Table 1), is observed for the H-form **2**. The positions of the signal for the C-nitro group of the phenyl ring, the signal for the *N*-nitro group of compound **4** and the signal for $N(O)OCH_3$ of compound **3** depend little on the solvent.

Table 1. ^{14}N NMR spectra data for compounds **1a**, **2**, **3**, **4** and ^{15}N NMR spectral data for compounds **1b**, **2'**, **3'**, **4'** in different solvents

Compound	Fragment	$\delta(^{14}N)$, ($\Delta\nu_{1/2}$/Hz), [$\delta(^{15}N)$, J/Hz]			
		$CDCl_3$	CD_3OD	Acetone-d_6	D_2O
1a	N—$\underline{N}O_2$	—	−21 (40)	−18 (40)	−28 (60)*
	C—NO_2	—	−8 (200)	−11 (240)	−9 (720)
1b	N—$^{15}NO_2$	—	—	—	[−28.5]
2	N—$\underline{N}O_2$	−41 (220)**	−40 (80)	−30 (180)	−29 (40)
	C—NO_2	−12 (380)**	−11 (340)	−12 (150)	−11 (460)
2´	N—$^{15}NO_2$	—	[−40.1]	—	[−28.5]
3	N(→O)OMe	−58 (200)	−56 (120)	−56 (110)	—
	C—NO_2	−12 (270)	−12 (200)	−12 (180)	—
3´	^{15}N(→O)OMe	[−58.6, ^3J(H—^{15}N) = 3.9]	—	—	—
4	N—$\underline{N}O_2$	−17 (100)	−14 (60)	−14 (30)	—
	C—NO_2	−14 (250)	−12 (200)	−12 (180)	—
4´	N—$^{15}NO_2$	[−16.3, ^3J(H—^{15}N) = 3.4]	—	—	—

* Addition of KOH (2 equiv.) does not change the chemical shift. ** The temperature of spectral registration is −20 °C.

In the case of salts **1**, the considerable dependence of the position of the signal for the nitramine group on the solvent can be explained by different structures of the solvated ion pairs. In the case of the H-form **2**, one of the reasons for such dependence may be different degree of dissociation in different solvents, however, this is obviously not the only factor (see Table 1).

Formally, the primary *N*-nitroamines (—$NHNO_2$) would exist in the isonitramine form (—N=N(O)OH), however, it is not generally observed, which is confirmed by the comparison of the positions of the ^{14}N or ^{15}N signals for the primary *N*-nitroamines and their *N*- and *O*-methylated or trimethylsilylated derivatives.[7] As is seen from Table 2, the difference between the chemical shifts of nitramines and isonitramines is ~30 ppm and the signals for the primary and secondary nitramines differ only slightly.

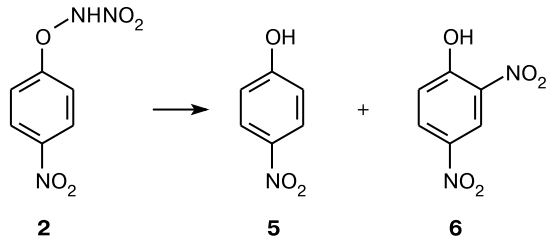
From the comparison of the ^{14}N and ^{15}N signals for NHA **2** ($\delta(N) = -29$—-41) with the signals for *O*-methyl compound **3** ($\delta(N) = -56$—-58) and *N*-methyl compound **4** ($\delta(N) = -14$—-17), it can be seen that the signals for the H-form **2** are nearly in the middle between the signals for compounds **3** and **4** (see Table 1). This can be explained by the fact that, for the H-form **2**, the nitramine and isonitramine forms are in a rapid equilibrium on the NMR time scale.

Table 2. ^{15}N NMR spectral data (from $Na^{15}NO_3$, CH_2Cl_2) for nitramines and the *O*-substituted isonitramines[7]

Compound	$\delta(^{15}N)$
$MeNH—^{15}NO_2$	−20.9
$Me_2N—^{15}NO_2$	−22.0
$Me(SiMe_3)N—^{15}NO_2$	−16.4
$MeN=^{15}N(→O)OMe$-(*E*)	−49.1
$MeN=^{15}N(→O)OSiMe_3$-(*E*)	−51.8

Thermal decomposition. The major organic products of thermal decomposition of NHA **2** are 4-nitrophenol (**5**) and 2,4-dinitrophenol (**6**) (Scheme 4). The ratio of these products ranges from 10 : 1 to 4 : 1 depending on the decomposition conditions (Table 3).

Scheme 4



2 **5** **6**

The thermal stability of NHA **2** in the solid phase depends significantly on the purity of the sample. The pure sample (m.p. 69—70 °C with decomp.) weighing 3—5 mg is completely decomposed at 20 °C in 20 min (see Table 3). Upon decomposition of larger amounts (~100 mg), brown vapor of nitric oxides is observed in the flask. If the gases produced are continuously evacuated (the residual pressure in the reaction flask is 1 Torr), the stability of NHA **2** is considerably increased. Only 6% of the compound is decomposed within 3 h at 20 °C (see Table 3). Apparently,

Table 3. Thermal decomposition of NHA **2** in the solid state and in solution[a]

Solvent	T/°C[b]	t/h[c]	Conversion of NHA **2** (%)	Yield (%)	
				5	**6**
—[d]	20	0.3	100	76	14
—[d]	0	24	100	73	16
—[e]	20	3	6	83	15
$CHCl_3$	20	5	100	71	20
CH_2Cl_2	20	5	100	70	19
PhH	20	6	100	72	19
H_2O	40	14	53	74	11

[a] The conversion and the yields of the products were determined according to the ^{1}H NMR spectra. [b] The reaction temperature. [c] The reaction time. [d] Decomposition in the solid state. [e] Decomposition in the solid state under evacuation (the residual pressure is 1 Torr).

the nitric oxides evolved upon decomposition of NHA considerably accelerate decomposition.

The reduction of the temperature to 0 °C increases the time of total decomposition of NHA **2** up to 24 h (see Table 3). NHA **2** can be stored at –20 °C without any change for more than two months.

The stability of NHA **2** in solutions strongly depends on the solvents, which can be divided into several groups. The first group includes the nonpolar solvents (CH_2Cl_2, $CHCl_3$, benzene), wherein NHA is unstable. In these solvents, decomposition at 20 °C starts almost immediately after dissolution and is completed in 5—6 h. NHA is somewhat more stable in these solutions at low temperatures (Table 4). The second group includes the polar aprotic solvents (EtOAc, MeCN, acetone). The first traces of the decomposition products of NHA in these solvents at 20 °C, *viz.*, compounds **5** and **6**, appear after 25—40 min. The strongest stabilizing effect was shown by the aprotic basic solvents (THF, dioxane, Et_2O) and polar protic solvents (H_2O, H_2O : MeOH = 1 : 1, MeOH, EtOH), wherein the first traces of the decomposition products of NHA appear after 1—10 days (see Table 4).

Putative decomposition pathways. Since the *O*- and *N*-alkyl derivatives of NHA are comparatively stable compounds[1,2] and decomposition of NHA **2** starts even at room temperature, one can assume that the first step of decomposition is autoprotolysis (Schemes 5 and 6). A series of structures can be produced upon protonation of NHA, but only two of them, *viz.*, **E** and **F**, can dissociate, at least formally, to form the stabilized cations, *viz.*, nitronium cation and oxodiazonium cation **G**, respectively (Scheme 5), which, in turn, can be involved in further reactions.

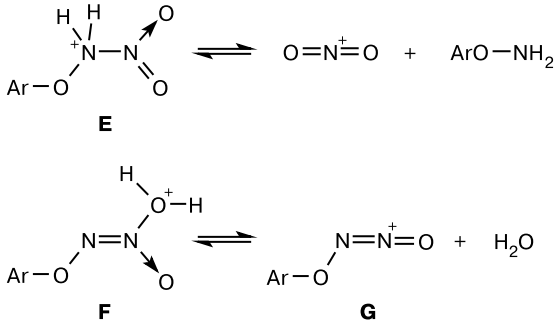
Probably, cations **E** and **F**, being the members of ion pairs **E** + **H** and **F** + **H**, can react with anion **H** without

Table 4. Solvent-dependence of the decomposition rate of NHA

Solvent	T/°C[a]	t_1[b]	t_2[c]
CH_2Cl_2	0	0[d]	1 day
CH_2Cl_2	20	0[d]	5 h
Benzene	20	0[d]	5 h
$CHCl_3$	–20	2—3 days[e]	—
$CHCl_3$	4	75 min	1 day
$CHCl_3$	20	5 min	6 h
MeCN	20	25 min	1 day
Acetone	20	30 min	3 days
EtOAc	20	40 min	3 days
Et_2O	20	1 day	—
Dioxane	20	1 day	—
MeOH	20	1—2 days	—
EtOH	20	2 days	—
THF	20	2 days	—
H_2O	20	6 days	—
H_2O/MeOH (1 : 1)	20	10 days	—

[a] The temperature at which the decomposition was carried out. [b] The time period from the point of mixing of NHA with the solvent to the point of appearance of the first traces of **5** and **6** (TLC).
[c] The time of complete decomposition of NHA **2** (TLC). [d] The decomposition products appear immediately after mixing of NHA with the solvent.
[e] During the reaction, a portion of NHA **2** is precipitated as colorless crystals.

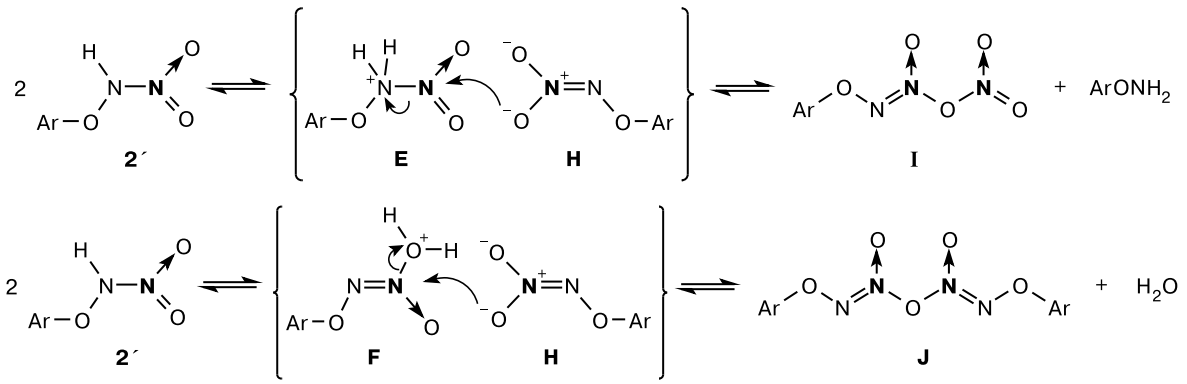
Scheme 5



dissociation to yield compounds **I** and **J**, respectively (Scheme 6).

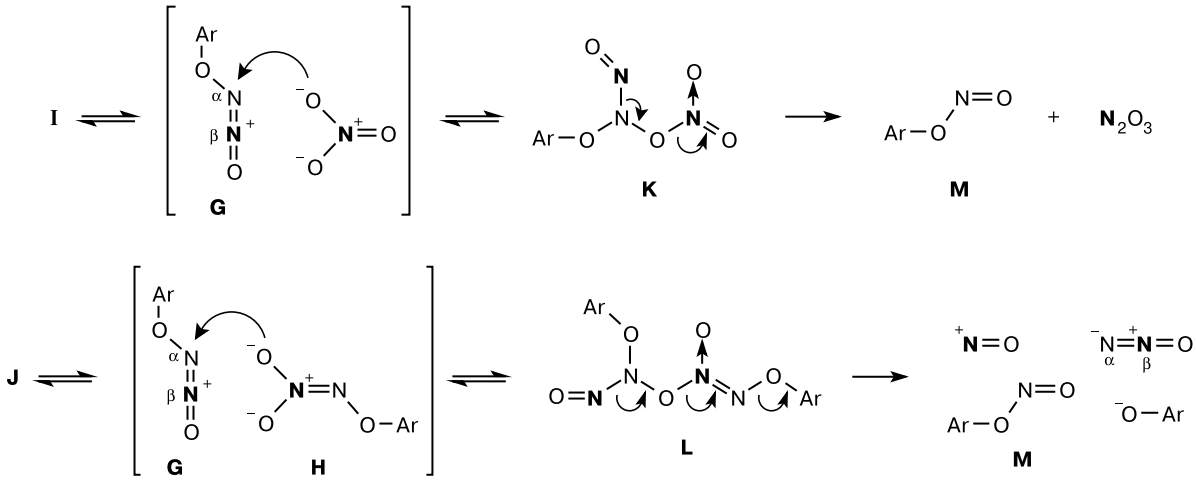
In turn, compounds **I** and **J** can dissociate to form cation **G** and the corresponding anions (Scheme 7), which can reattack the ambident cation **G** at the α-nitrogen atom to produce compounds **K** and **L**, respectively. These compounds can be irreversibly decomposed: compound **K** is decomposed to form *O*-nitrosophenol **M** and N_2O_3 and compound **L** is decomposed according to the concerted mechanism of fragmentation to form *O*-nitrosophenol **M**, N_2O, the nitrosonium cation, and the 4-nitrophenolate anion. In such case, the key step of decomposition of

Scheme 6



Note. Hereinafter, displayed in bold type are ^{15}N labeled atoms.

Scheme 7



compounds **I** and **J** is migration of the anionic groups from the β-nitrogen atom to the α-nitrogen atom to form a new N—O bond.

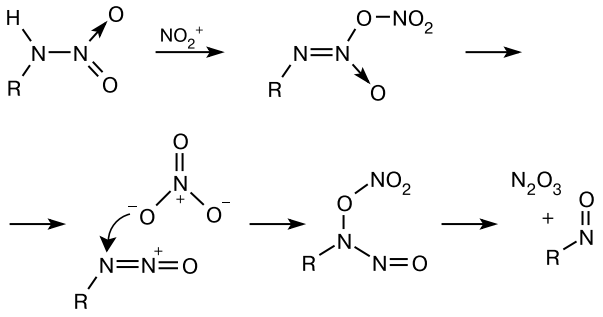
This migration is analogous to the processes occured in the furazan and tetrazole series upon transformation of the nitramine group into the nitroso group under the action of nitrating agents (Scheme 8).[8]

The nitrosation species formed according to Scheme 7, including N_2O_3, would, in turn, react with the starting NHA **2**. Nitrosation most likely occurs at the N atom to afford N_2O and nitroether **O** (Scheme 9). The latter can be a precursor of HNO_3, which, upon the reaction with N_2O_3, can result in the formation of N_2O_4.

The nitrating agents (nitro ester **O** or HNO_3) can also react with the starting NHA **2** according to a scheme analogous to Scheme 8 (Scheme 10). Nitroso ester **M** and N_2O_3 may be the products of this reaction.

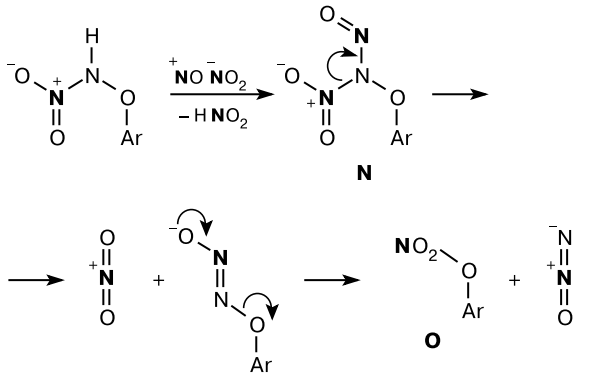
In order to verify the proposed mechanisms, we estimated the approximate rates of decomposition of NHA **2**

Scheme 8

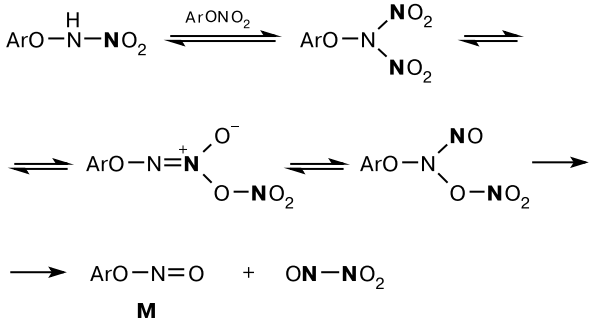


($CHCl_3$, 0 °C) in the presence of HNO_3, as well as in the presence of N_2O_4 (see Scheme 4 and Table 5). When neither of these reagents was added, the decomposition reaction proceeds with the induction period. The reaction starts only after 75 min that is easy to control by the appearance of the yellow coloration of the solution caused by com-

Scheme 9



Scheme 10



pounds **5** and **6** and by observing the first traces of these products using TLC. The reaction rate is then sharply increased (the degree of conversion is ~50% in 50 min according to the data from the ^{1}H NMR spectrum), however, NHA completely disappears only after ~24 h. The addition of 0.1 equiv. of HNO_3 does not virtually influence the induction period, the total reaction time, and the ratio of the reaction products **5** and **6** (see Scheme 4 and Table 5). The considerable amount of HNO_3 (2 equiv.) decreases the induction period, however, this does not eliminate this period completely. At the same time, upon addition of 0.1 equiv. of N_2O_4, the reaction proceeds without the induction period. Although the addition of 1 equiv. of N_2O_4 does not influence the total conversion time of NHA, it causes the considerable increase in the fraction of **6** among the reaction products and, upon addition of 2 equiv. of N_2O_4, the total conversion time of NHA is reduced to 2 min.

The data of Table 5 (see Scheme 4) suggest that N_2O_4 reacts with NHA **2** considerably faster than HNO_3 and it is nitrosating rather than nitrating species that are responsible for the formation of **6**. This fact was confirmed by the independent experiments. It was shown that compound **5** was not nitrated by HNO_3 in $CHCl_3$ for 1 day at 0 °C, while the reaction with N_2O_4 was completed in 4 h (Scheme 11, Table 6). Note that the reaction of N_2O_4

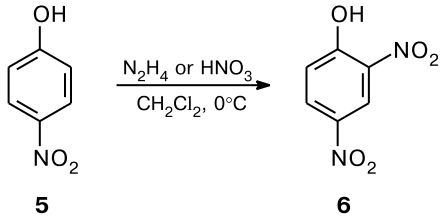
Table 5. Decomposition[a] of NHA **2** in $CHCl_3$ in the presence of HNO_3 and N_2O_4

Reagent	**2** : Reagent (mol/mol)	t_1/min[b]	t_2[c]	Yield (%)	
				5	**6**
—[d]	—[d]	75	24 h	73	16
HNO_3	1 : 0.1	65	24 h	71	16
HNO_3	1 : 1	60	24 h	68	17
HNO_3	1 : 2	10	24 h	67	21
N_2O_4	1 : 0.1	0	24 h	70	19
N_2O_4	1 : 1	0	24 h	23	75
N_2O_4	1 : 2	0	2 min	18	77

[a] The reaction temperature is 0 °C and the concentration of NHA **2** is 0.05 mol L^{-1}; the product yields were determined according to the ^{1}H NMR spectra.
[b] The time period from the point of mixing of NHA with the reagent to the point of appearance of the first traces of **5** and **6** (TLC).
[c] The time of complete transformation of NHA **2**.
[d] Decomposition of NHA **2** without addition of the reagents.

with NHA **2** is faster than the reaction with compound **5**: the conversion of **5** at the two-fold excess of N_2O_4 was only 16% in 10 min (Table 6), whereas the reaction with NHA **2** was completed already in 2 min (see Table 5).

Scheme 11



The data presented confirm the following scheme of decomposition of NHA **2**. At first, the reaction of two molecules proceeds according to one of the mechanisms

Table 6. Reaction of **5** with the nitrating and nitrosation agents in $CHCl_3$[a]

Reagent	t[b]	**5** : Reagent (mol/mol)	Conversion of **5** (%)	Yield **6** (%)
HNO_3	1 day	1 : 1	0	0
HNO_3	1 day	1 : 2	2	50
N_2O_4	4 h	1 : 1	96	98
N_2O_4	10 min	1 : 2	16	88

[a] The reaction temperature is 0 °C, the concentration of **5** is 0.07 mol L^{-1}; the conversion and the yields of the products were determined according to the ^{1}H NMR spectra.
[b] The reaction time.

shown in Schemes 6 and 7. These reactions are slow (the initiation step). As a result of these reactions, the nitrosating species are produced, which rapidly react with NHA to form N_2O and the nitrating species. To explain the sharp acceleration of the reaction, one should suppose that the nitration step proceeds at the rate comparable with that of nitrosation. It is obvious that, in this case, the nitrating agent is not HNO_3, but more reactive species, for example, nitronitroso derivative **N** or 4-nitrophenyl nitrate **O**. Upon its reaction with NHA **2**, some new nitrosation species are produced (see Scheme 10) and the decomposition process is accelerated.

For the refinement of the reaction mechanism, decomposition of the labeled NHA **2´** was studied. Decomposition was performed in a sealed NMR tube in $CDCl_3$ at 20 °C for 5 h. The reaction products were identified by ^{14}N and ^{15}N NMR spectroscopy. In the spectra, besides the signals for the nitro groups of compounds **5** and **6**, the signals for HNO_3 were observed. The ^{14}N NMR spectra also contained the signals for the unlabeled nitrous oxide NNO corresponding to the central and terminal N atoms (cf. Ref.[9]) and the signals for the labeled nitrous oxide $N^{15}NO$ corresponding to the terminal N atom. The ^{15}N NMR spectra displayed the signal for the labeled nitrous oxide $N^{15}NO$ corresponding to the central N atom (cf. Ref. 10). Nitrous oxide labeled in the terminal N atom is not formed. No molecular nitrogen, neither labeled nor unlabeled, is also produced upon decomposition. According to the ^{14}N NMR spectra, the ratio of the labeled and unlabeled nitrous oxides in view of the degree of enrichment is 2 : 1. The intergration of the signals in the ^{14}N spectra was performed by taking into account the ratio of the signal intensities in the spectra of certain samples of N_2O in the corresponding solvent, which were determined in the same mode of signal accumulation.

After recording the spectra, compound **5** and compound **6** were isolated from the reaction mixture in yields of 70% and 19%, respectively (Scheme 4). The mass spectral data allow us to determine that, in view of the degree of enrichment, the molar ratio of compounds **6** with the unlabeled nitro groups, one labeled nitro group and two labeled nitro groups is 1 : 2.0 : 0.2.

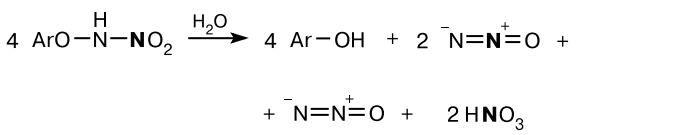
Since the nitrosation species account for the formation of **6**, the ratio of compounds **6** with the labeled and unlabeled nitro groups, equal to ~2 : 1, evidences that the labeled and unlabeled nitrosation species were in the same ratio.

The formation of a small amount of the double-labeled **6** upon nitration of **5** with labeled nitric acid in the presence of nitric oxides was also observed by other authors.[11,12] It was assumed that this process involves the radical species.

The formation of labeled nitrous oxide upon nitrosation of labeled NHA **2´** with the labeled nitrosation species conforms with Scheme 9. The unlabeled nitrous oxide can be formed according to the analogous scheme upon the reaction of the labeled NHA **2´** with the unlabeled nitrosation species. The ~2 : 1 ratio of the labeled and unlabeled nitrous oxides indicates that the labeled and unlabeled nitrosation species are also in the ratio 2 : 1. This is in agreement with Scheme 10 where the molecule of N_2O_3 corresponds to two nitrosation species.

Summing the presented equations describing decomposition of the labeled compound **2´** and adding the water molecule to the left side of an equation, one can derive the chemical equation (Scheme 12), which demonstrates the ratio of the labeled and unlabeled nitrous oxides.

Scheme 12



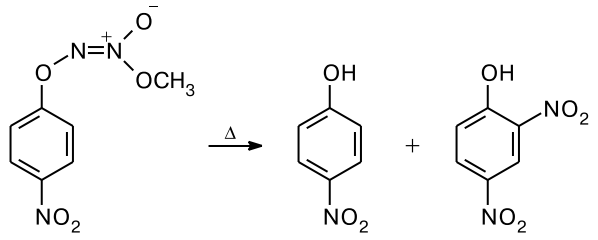
The suggested mechanism of decomposition conforms with the experimental data, however, the real mechanism is probably more complex. For example, some steps can proceed involving the radical species.

In view of the data obtained for the decomposition reactions, we can explain some features of the solvent effect on the stability of **2**. In the non-polar solvents (CH_2Cl_2, $CHCl_3$), the molecules of NHA **2** can be associated into dimers (*cf.* data in Ref. 13 for the primary nitramines), which increases the rate of autoprotolysis. The increase in stability in the polar solvents is caused by the fact that the concentration of the dimers in these solvents is significantly lower due to solvation. The ion pairs formed as a result of autoprotolysis are in solvate-divided state, which retards their interaction with each other. One of the factors influencing the increase in the stability of the NHA **2** in H_2O is, apparently, dissociation to form the stable anion. The considerable degree of dissociation is evidenced by the chemical shift of the *N*-nitro group of NHA **2** in the ^{14}N NMR spectrum at δ −29, which is close to the chemical shift of potassium salt of NHA **1a** at δ(^{14}N) −28 (see Table 1).

O-Methyl derivative of nitrohydroxylamine **3** is considerably more stable than the H-form **2**. When heated in $CHCl_3$ at 61 °C for 1.3 h, its conversion is merely 8%. The decomposition products are compounds **5** (the yield based on the converted substance is 75%) and **6** (13%). Heating in octane at 70 °C for 14 h leads to 57% conversion, the yields of **5** and **6** are 89% and 7%, respectively (Scheme 13).

Thus, decomposition of the H-form of nitrohydroxylamine **2** is a multistep process. Within the present work, we are intrested not so much in the features of the total decomposition reaction of NHA, as in the possibility to establish the first reaction step, which eventually determines the stability of the compound. As it follows from

Scheme 13



3 **5** **6**

the foregoing, the reason for the low stability of the H-form **2** in the non-polar solvents (benzene, CH_2Cl_2, $CHCl_3$) and in solid state is relatively fast formation of the nitrosation species to be involved in subsequent reactions. The key step responsible for the formation of the nitrosation species is the reaction of the nucleophiles with oxodiazonium ion **G** at the α-nitrogen atom (see Scheme 7). Formally, oxodiazonium ion **G** can be also formed due to the initial denitration reaction of NHA (see Scheme 5) or the equivalent reaction (see Scheme 6, reaction (1)) and due to the initial elimination of the water molecule from NHA (Scheme 5) or the equivalent reaction (see Scheme 6, reaction (2)). The same reactions would also occur upon decomposition of the primary nitramines, however, they are more stable in actual practice than NHA **2**. The denitration processes of the primary nitramines and NHA most likely proceeds at the comparable rates and the process of water elimination would proceed faster in the case of NHA **2**, since this compound apparently exists as an equilibrium mixture of the nitramine and isonitramine forms. It is possible that this feature is the reason for the lower thermal stability of NHA. Hereafter, we are planning to study the formation of the oxodiazonium ion from NHA **2** in the strongly acidic medium.

Experimental

^1H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer with working frequencies 300.13, 75.5, and 21.5 MHz, respectively. The ^{15}N NMR spectra were recorded on a Bruker DRX-500 (50.70 MHz) spectrometer. The chemical shifts are given relative to $SiMe_4$ (^1H, ^{13}C) or $MeNO_2$ (^{14}N, ^{15}N, external standard, the upfield chemical shifts are negative). IR spectra were recorded on a Specord M-80 spectrometer. Mass spectra were obtained on a Kratos MS-300 (EI, 70 eV) instrument. The course of the reaction was monitored by TLC using Silufol UV-254 and Merck 60 F_{254} plates. Silica gel was used for column chromatography. *O*-(4-Nitrophenyl)hydroxylamine[14] and an etheral solution of diazomethane[15] were prepared according to known procedures. Quantitation of the products using ^1H NMR spectroscopy was carried out with tetrachloroethane as the internal standard.

Potassium *N*-nitro-*O*-(4-nitrophenyl)hydroxylaminide (1a). Procedure *A*. Synthesis with the use of PhI(OAc)$_2$. To a solution of *O*-(4-nitrophenyl)hydroxylamine (2.17 g, 14.1 mmol) in MeOH (100 mL) at 0 °C, finely ground KNO_2 (1.2 g, 14.1 mmol) was carefully added at once and the mixture was stirred until the solid completely dissolved. A solution of $PhI(OAc)_2$ (4.54 g, 14.1 mmol) in MeOH (50 mL) was then added dropwise with stirring to the resulting mixture over 15 min. The reaction mixture was kept for 5 min at 0 °C and the solvent was removed *in vacuo*. The solid residue was carefully ground in a mortar and washed with CH_2Cl_2 (2×50 mL) with vigorous mixing for 30 min. Upon washing, PhI and the major part of *p*-nitrophenol passed into the CH_2Cl_2 solution. The residue was dissolved in MeOH (80 mL), silica gel (5 g) was added to the solution, the solvent was removed *in vacuo* and the residue was transfered onto a column with silica gel (d = 50 mm, h = 20 mm) and eluted with a 4 : 1 mixture of $CHCl_3$ and AcOEt (200 mL). The eluate contained the last portion of *p*-nitrophenol; the total yield of *p*-nitrophenol according to the ^1H NMR spectral data was 50%. AcOEt (200 mL) and a 1 : 1 mixture of MeOH and AcOEt (200 mL) were then used as eluents. The combined eluates were concentrated. A yellowish powder (1.5 g) was obtained, which contained according to the ^1H NMR spectral data (Et_4NBr as the quantitative internal standard) potassium salt **1a** (1.28 g, 38%) and AcOK (220 mg). This preparation containing 15% (w/w) AcOK was then used for the preparation of the H-form of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine.

Procedure *B*. Synthesis with the use of PhIO. To a solution of *O*-(4-nitrophenyl)hydroxylamine (1.08 g, 7.01 mmmol) in MeOH (50 mL) at 0 °C, finely ground KNO_2 (0.6 g, 7.05 mmol) was added at once and the mixture was stirred until the solid completely dissolved. A solution of PhIO (1.54 g, 7.01 mmol) in MeOH (50 mL) was then added dropwise with stirring over 5 min. The reaction mixture was kept for 5 min at 0 °C, silica gel (3 g) was added and the mixture was concentrated to dryness. The solid residue was transfered onto a column filled with silica gel (d = 50 mm, h = 20 mm). The elution was performed first with a 4 : 1 mixture $CHCl_3$ — AcOEt (200 mL) and then with AcOEt (150 ml) to afford a mixture (910 mg) of *p*-nitrophenol (500 mg, 52%) and PhI. Subsequent elution with a 1 : 1 mixture MeOH—AcOEt (100 mL) gave potassium salt **1a** (685 mg, 41%) as a yellow powder, m.p. 145—155 °C (decomp.). Found (%): C, 30.31; H, 1.66; N, 17.83; K, 16.59. $C_6H_4KN_3O_5$. Calculated (%): C, 30.38; H, 1.68; N, 17.61; K, 16.48. IR (KBr), ν/cm^{-1} (region of 1200—1550 cm^{-1}): 1260, 1308, 1340, 1348, 1384, 1456, 1508. ^1H NMR (D_2O), δ: 7.10 (d, 2 H, H(2), H(6), J = 9.3 Hz); 8.10 (d, 2 H, H(3), H(5), J = 9.3 Hz). ^{13}C NMR (D_2O), δ: 113.7 (C(2), C(6)); 125.5 (C(3), C(5)); 141.6 (C(4)); 160.9 (C(1)).

Sodium *N*-[nitro-^{15}N]-*O*-(4-nitrophenyl)hydroxylaminide (1b). Sodium salt **1b** was synthesized from *O*-(4-nitrophenyl)-hydroxylamine (330 mg, 2.14 mmol), $Na^{15}NO_2$ (150 mg, 2.14 mmol, the degree of enrichment is 92%), and $PhI(OAc)_2$ (690 mg, 2.14 mmol) according to the procedure analogous to the procedure *A* for the preparation of **1a**. According to the ^1H NMR spectral data, the specimen obtained contained sodium salt **1b** (191 mg, 40%) and AcONa (29 mg). This mixture containing 13% (w/w) AcONa was then used for the preparation of the H-form **2′**. ^1H NMR (D_2O), δ: 7.27 (d, 2 H, H(2), H(6), J = = 9.3 Hz); 8.27 (d, 2 H, H(3), H(5), J = 9.3 Hz). ^{14}N NMR (D_2O), δ: −10 (CNO_2, $\Delta\nu_{1/2}$ = 380 Hz); −29 ($N\underline{N}O_2$, $\Delta\nu_{1/2}$ = 40 Hz).

N*-Nitro-*O*-(4-nitrophenyl)hydroxylamine (2).** ***Warning! Compound **2** can spontaneously decompose at room temperature. It is recommended to store it at −20 °C in solid state or as an etheral solution (10 mg mL^{-1}).

Procedure *A*. To a suspension of a sample of K salt **1a** (238 mg, 1.0 mmol) and AcOK (42 mg, 0.43 mmol), which was prepared according to procedure *A*, in Et_2O (7 mL), a solution of MsOH (0.083 mL, 1.29 mmol) in Et_2O (1 mL) was added dropwise at 0 °C over 1 min with vigorous stirring. The reaction mixture was vigorously stirred for 1 h at 0 °C. The precipitate that formed was filtered off, washed with Et_2O (5×5 mL) and the solvent was removed *in vacuo*. The residue was dried *in vacuo* (1 Torr) for 15 min at 0 °C to obtain NHA **2** (180 mg, 90%) as white crystals, m.p. 69—70 °C (decomp.).

Procedure *B*. Potassium salt **1a** (100 mg, 0.42 mmol) prepared according to procedure *B* was dissolved in MeOH (15 mL). A freshly calcined AcOK (30 mg, 0.31 mmol) was added to the solution and the mixture was stirred until the solids completely dissolved. The solvent was evaporated *in vacuo*. The solid residue was vigorously ground in a mortar, suspended in Et_2O (10 mL) and cooled to 0 °C. A solution of MsOH (0.042 mL, 0.66 mmol) in Et_2O (1 mL) was added dropwise to the suspension over 1 min with vigorous stirring. The reaction mixture was vigorously stirred for 1 h at 0 °C. The work-up of the reaction mass was performed as described in the previous experiment, NHA **2** (60 mg, 72%) was obtained as white crystals, m.p. 63—65 °C (decomp.). The attempts to prepare NHA **2** without use of AcOK resulted in the yellowish preparations containing the impurity of *p*-nitrophenol. IR (KBr), ν/cm^{-1} (region of 1300—1600 cm^{-1}): 1336, 1488, 1504, 1588. ^1H NMR (dioxane-d_8), δ: 7.36 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.30 (d, 2 H, H(3), H(5), J = 9.2 Hz). ^1H NMR (CD_3OD), δ: 7.44 (d, 2 H, H(2), H(6), J = 9.3 Hz); 8.37 (d, 2 H, H(3), H(5), J = 9.3 Hz). ^{13}C NMR (dioxane-d_8), δ: 114.7 (C(2), C(6)); 125.5 (C(3), C(5)); 144.6 (C(4)); 162.2 (C(1)). ^{14}N NMR (dioxane-d_8), δ: −14 (C—NO_2, $\Delta\nu_{1/2}$ = 610 Hz); −37 (N—$\underline{N}O_2$, $\Delta\nu_{1/2}$ = 670 Hz). ^{14}N NMR (CD_3COOD), δ: −9 (C—NO_2, $\Delta\nu_{1/2}$ = 380 Hz); −30 (N—NO_2, $\Delta\nu_{1/2}$ = 120 Hz).

***N*-[Nitro-^{15}N]-*O*-(4-nitrophenyl)hydroxylamine (2´).** To a suspension of the preparation containing sodium salt **1b** (87 mg, 0.39 mmol) and AcONa (13 mg, 0.16 mmol) in Et_2O (7 mL), a solution of MsOH (0.033 mL, 0.5 mmol) in Et_2O (1 mL) was added dropwise at 0 °C over 1 min with vigorous stirring. The reaction mixture was vigorously stirred for 1 h at 0 °C. The work-up of the reaction mixture as described in the previous experiment (procedure *A*) afforded NHA **2´** (65 mg, 84%) as white crystals, m.p. 69—70 °C (decomp.). Product **2´** was dissolved in Et_2O (13 mL) and the solution was stored at −20 °C. ^1H NMR (dioxane-d_8), δ: 7.35 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.31 (d, 2 H, H(3), H(5), J = 9.2 Hz). ^{15}N NMR (dioxane-d_8), δ: −36.2 (N—NO_2).

1-Methoxy-2-(4-nitrophenyl)diazene 1-oxide (3). Procedure *A*. To a suspension of a sample containing potassium salt **1a** (238 mg, 1.0 mmol) and AcOK (42 mg, 0.43 mmol) in Et_2O (5 mL), a solution of MsOH (0.083 mL, 1.29 mmol) in Et_2O (1 mL) was added dropwise at 0 °C over 1 min with vigorous stirring. The reaction mixture was vigorously stirred for 1 h at 0 °C and an excess of a solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (0.2 g) in Et_2O (5 mL) was added dropwise. The residue was filtered off and washed with Et_2O (5×5 mL). The solvent was removed *in vacuo*. Product **3** (170 mg, 80%) was obtained as white crystals, m.p. 93—96 °C.

Procedure *B*. To a solution of NHA **2** (100 mg, 0.5 mmol) in Et_2O (10 mL), an excess of a solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (0.2 g) in Et_2O (5 mL) was added dropwise at 0 °C. The solvent was removed *in vacuo*. Product **3** (107 mg, 99%) was obtained as white crystals, m.p. 93—96 °C (a mixture of the *E*/*Z*-isomers in a ratio of 2.2 : 1). After recrystallization from MeOH, the ratio of the *E*/*Z*-isomers was 9 : 1, m.p. 102—106 °C (decomp.). Found (%): C, 39.57; H, 3.34; N, 19.63. $C_7H_7N_3O_5$. Calculated (%): C, 39.44; H, 3.31; N, 19.71. MS, *m*/*z*: 213 $[M]^+$, 183 $[M - CH_2O]^+$. IR (KBr), ν/cm^{-1}: 1344, 1492, 1520, 1540, 1568.

Major isomer (*E*). ^1H NMR ($CDCl_3$), δ: 4.11 (s, 3 H, Me); 7.34 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.27 (d, 2 H, H(3), H(5), J = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 57.5 (Me); 115.1 (C(2), C(6)); 125.8 (C(3), C(5)); 144.0 (C(4)); 160.3 (C(1)).

Minor isomer (*Z*). ^1H NMR ($CDCl_3$), δ: 4.13 (s, 3 H, Me); 7.34 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.27 (d, 2 H, H(3), H(5), J = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 57.1 (Me); 114.8 (C(2), C(6)); 125.9 (C(3), C(5)); 144.0 (C(4)); 160.3 (C(1)).

1-Methoxy-2-(4-nitrophenyl)diazene[1-^{15}N] 1-oxide (3´). To a solution of NHA **2'** (30 mg, 0.15 mmol) in Et_2O (2 mL), an excess of a solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (0.1 g) in Et_2O (5 mL) was added dropwise at 0 °C. The solvent was removed *in vacuo*. Product **3´** (32 mg, 99%) was obtained as white crystals, m.p. 93—96 °C. The product is a mixture of the *E*/*Z*-isomers in a ratio of 2.2 : 1.

Major isomer (*E*). ^1H NMR ($CDCl_3$), δ: 4.10 (d, 3 H, Me, $J(^1H—^{15}N)$ = 4.0 Hz); 7.33 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.26 (d, 2 H, H(3), H(5), J = 9.2 Hz).

Minor isomer (*Z*). ^1H NMR ($CDCl_3$), δ: 4.12 (d, 3 H, Me, $J(^1H—^{15}N)$ = 4.0 Hz); 7.34 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.27 (d, 2 H, H(3), H(5), J = 9.2 Hz).

***N*-Methyl-*N*-nitro-*O*-(4-nitrophenyl)hydroxylamine (4) and *E*(*Z*)-1-methoxy-2-(4-nitrophenyl)diazene 1-oxide (3).** A solution of $AgNO_3$ (0.36 g, 2.1 mmol) in distilled water (1 mL) was added dropwise to a solution of K salt **1a** (0.5 g, 2.1 mmol) in distilled water (6 mL). The voluminous beige-colored precipitate was filtered off, washed with EtOH (5 mL) and dried in a vacuum desiccator over P_2O_5 for 12 h. The Ag salt (615 mg, 95%) was obtained as white crystals, m.p. 162—168 °C (decomp.). The Ag salt obtained was then used in the synthesis without additional purification. To a suspension of the Ag salt (165 mg, 0.54 mmol), MeI (0.05 mL, 0.8 mmol) in dry MeCN (5 mL) was added at once at 20 °C in an argon atmosphere. The reaction mixture was stirred for 12 h at 20 °C. The precipitate that formed was filtered off and washed with CH_2Cl_2 (5 mL). The filtrates were combined and the solvent was removed *in vacuo*. A mixture of compounds **3** and **4** (100 mg, 87%) was obtained in a ratio of 1 : 1 according to the ^1H NMR spectral data. Compound **3** is a mixture of the *E*/*Z*-isomers in a ratio of 4.4 : 1; according to the ^1H NMR spectral data, it is identical to the compound **3** prepared above.

Compound 4. ^1H NMR ($CDCl_3$), δ: 3.68 (s, 3 H, Me); 7.22 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.27 (d, 2 H, H(3), H(5), J = 9.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 45.5 (Me); 114.0 (C(2), C(6)); 125.9 (C(3), C(5)); 143.9 (C(4)); 162.5 (C(1)).

***N*-Methyl-*N*-[nitro-^{15}N]-*O*-(4-nitrophenyl)hydroxylamine (4´) and *E*(*Z*)-1-methoxy-2-(4-nitrophenyl)diazene[1-^{15}N] 1-oxide (3´).** A mixture of compounds **3´** and **4´** (in a ratio of 1 : 1) was prepared from sodium salt **1b** according to the procedure analogous to that for the preparation of the unlabeled products **3** and **4**. ^1H NMR ($CDCl_3$), δ: 3.68 (d, 3 H, Me, $J(^1H—^{15}N)$ = = 3.4 Hz); 7.22 (d, 2 H, H(2), H(6), J = 9.2 Hz); 8.27 (d, 2 H, H(3), H(5), J = 9.2 Hz).

Decomposition of NHA 2 in the solid state. For the preparation of the solid sample of NHA **2**, we used a standard procedure

that included vacuum concentration (1 Torr) to dryness of a solution of NHA **2** (10 mg, 0.05 mmol) in Et_2O (1 mL) in a one-necked flask at 0 °C in 5 min. The subsequent operations were performed in the same flask. Air was let in the flask, the sample was heated to 20 °C and kept for 20 min. The reaction products were dissolved in CD_3OD (0.55 mL). The product yields were determined by ^1H NMR spectroscopy (see Table 3).

Decomposition of NHA 2 in the solid state under evacuation. A sample of NHA **2** prepared according to the standard procedure as described in the previous experiment was heated to 20 °C and kept for 2 h at the residual pressure of 1 Torr. The flask was then cooled to 0 °C, air was let in and the reaction products were immediately dissolved in CD_3OD (0.55 mL). The yields of the products were determined by ^1H NMR spectroscopy (see Table 3).

Decomposition of NHA 2 in solutions. To a sample of NHA **2** prepared according to the standard procedure, the solvent ($CHCl_3$, CH_2Cl_2, or benzene) (1 mL) was added. The decomposition conditions (reaction temperature and time) are given in Table 3. After completion of the reaction, the solvent was removed *in vacuo*. The product yields were determined by ^1H NMR spectroscopy (see Table 3).

Decomposition of NHA 2 in H_2O. To a sample of NHA **2** prepared according to the standard procedure, H_2O was added. The reaction mixture was heated at 40 °C for 14 h, then cooled to 20 °C and extracted with AcOEt (4×1 mL). Et_2O (2 mL) was added to the extract in order to stabilize the unconsumed NHA **2**. The combined organic layer was washed with a brine (0.5 mL), dried with $MgSO_4$ and concentrated *in vacuo* at 0 °C. The reaction products were immediately dissolved in CD_3OD (0.55 mL). The product yields were determined by ^1H NMR spectroscopy (see Table 3).

Solvent-dependence of the decomposition rate of NHA 2. To a sample of NHA **2** prepared according to the standard procedure, the solvent (0.5 mL) was added at the temperature indicated in Table 4. The time period from the point of mixing of NHA **2** with the solvent to the time of appearance of the first traces of compounds **5** and **6** was determined by TLC ($CHCl_3$—AcOEt, 4 : 1). The total decomposition time of NHA **2** was determined in the same manner.

Reaction of NHA 2 with HNO_3 in $CHCl_3$. To a sample of NHA **2** prepared according to the standard procedure, $CHCl_3$ (1 mL) precooled to 0 °C was added and the mixture was stirred at 0 °C until dissolution of **2**. A solution of HNO_3 (the amount is given in Table 5) in $CHCl_3$ (0.02 mL) was added at the same time. The time period from the point of mixing of NHA **2** with the reagent to the point of appearance of the first traces of **5** and **6** was determined by TLC. After completion of the reaction (TLC), the solvent was removed *in vacuo*. The product yields were determined by ^1H NMR spectroscopy (see Table 5).

Reaction of NHA 2 with N_2O_4 in $CHCl_3$. To the sample of NHA **2** prepared according to the standard procedure, $CHCl_3$ (0.8 mL) precooled to 0 °C was added and the mixture was stirred at 0 °C until dissolution of **2**. A solution of N_2O_4 (the amount is given in Table 5) in $CHCl_3$ (0.2 mL) was added at the same time, the solution immediately becoming yellow. The reaction mixture was kept at 0 °C for the period indicated in Table 5. After completion of the reaction (TLC), the solvent was removed *in vacuo*. The product yields were determined by ^1H NMR spectroscopy (see Table 5).

Reaction of 4-nitrophenol with HNO_3 in $CHCl_3$. To a solution of 4-nitrophenol (10 mg, 0.07 mmol) in $CHCl_3$ (1 mL), a precooled to 0 °C solution of HNO_3 (the amount is given in Table 6) in $CHCl_3$ (0.02 mL) was added with stirring at 0 °C at once. The reaction mixture was kept for 1 day at 0 °C. After completion of the reaction (TLC), the solvent was removed *in vacuo*. The conversion of 4-nitrophenol and the yield of 2,4-dinitrophenol were determined by ^1H NMR spectroscopy (see Table 6).

Reaction of 4-nitrophenol with N_2O_4 in $CHCl_3$. To a solution of 4-nitrophenol (10 mg, 0.07 mmol) in $CHCl_3$ (0.8 mL), a precooled to 0 °C solution of N_2O_4 (the amount is given in Table 6) in $CHCl_3$ (0.2 mL) was added with stirring at 0 °C at once. The reaction mixture was kept with vigorous stirring at 0 °C for the period indicated in Table 6. After completion of the reaction (TLC), the solvent was removed *in vacuo*. The conversion of 4-nitrophenol and the yield of 2,4-dinitrophenol were determined by ^1H NMR spectroscopy (see Table 6).

Decomposition of NHA 2′ in $CDCl_3$. NHA **2′** (20 mg, 0.10 mmol) ground at 0 °C was placed under argon into an NMR tube cooled to −30 °C. $CDCl_3$ (0.6 mL) precooled to −20 °C was then added at once. The cooled tube was sealed, then heated to 20 °C and kept for 5 h. The ^1H, ^{14}N, and ^{15}N NMR spectra were recorded. In the ^1H NMR spectrum, the signals for 4-nitrophenol and 2,4-dinitrophenol coinciding with those for the authentic samples were observed. ^{14}N NMR ($CDCl_3$), δ: −13 (NO_2 groups of **5** and **6**, $\Delta\nu_{1/2}$ = 240 Hz), −47 (HNO_3, $\Delta\nu_{1/2}$ = 30 Hz; the signal coincided with that for the knowing sample of HNO_3 in $CDCl_3$), −148 (br.s, the central N atom in NNO, $\Delta\nu_{1/2}$ = = 15 Hz, $^1J(^{14}N—^{14}N)$ = 4.2 Hz, cf. Ref. 9), −231 (the terminal N atom in NNO and $N^{15}NO$, $\Delta\nu_{1/2}$ = 20 Hz). The molar ratio NNO : $N^{15}NO$, equal to 0.3 : 0.7, was determined from the ratio of the signal intensities for the central and terminal N atoms taking into account the integral intensities of the corresponding signals in the solution of the authentic sample of N_2O in $CDCl_3$. ^{15}N NMR ($CDCl_3$), δ: −14.04 (dd, 2-$^{15}NO_2$ group of the 2,4-dinitrophenyl fragment, $^3J(^1H—^{15}N)$ = 2.5 Hz, $^4J(^1H—^{15}N)$ = = 1.0 Hz), −46.8 ($H^{15}NO_3$), −147.2 (t, the central N atom in $N^{15}NO$, $^1J(^{14}N—^{15}N)$ = 6.2 Hz, cf. Ref. 10).

After recording of the spectra, the NMR tube was opened and the reaction mixture was concentrated *in vacuo*. The reaction products were separated by preparative TLC on silica gel ($CHCl_3$) to obtain 2,4-dinitrophenol (3 mg) and 4-nitrophenol (9 mg). 2,4-Dinitrophenol obtained was analyzed by mass spectrometry. MS, *m/z* (ratio of the signal intensities): 287, 288, 289 $[M]^+$ (1 : 1.9 : 0.19). In veiw of the degree of enrichment, the molar ratio of **6** with the unlabeled nitro groups, **6** with one and two labeled nitro groups is 1 : 2.0 : 0.2.

Thermal decomposition of 1-methoxy-2-(4-nitrophenyl)-diazene 1-oxide (3) in $CHCl_3$. A solution of compound **3** (10 mg, 0.047 mmol) in $CHCl_3$ (7.5 mL) was refluxed (61 °C) for 1.3 h, then cooled and the solvent was removed *in vacuo*. According to the ^1H NMR spectral data, the conversion of compound **3** is 8%, the yields of **5** and **6** based on the consumed material are 75% and 13%, respectively.

Thermal decomposition of 1-methoxy-2-(4-nitrophenyl)-diazene 1-oxide (3) in octane. A solution of compound **3** (10 mg, 0.047 mmol) in octane (1 mL) was kept at 70 °C for 14 h, then cooled and the solvent was removed *in vacuo*. According to the ^1H NMR spectral data, the conversion of compound **3** is 57%, the yields of **5** and **6** based on the consumed material are 89% and 7%, respectively.

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