Brief Communications

Preparation of *N*-nitrohydroxylamines by direct nitration

*E. N. Khodot, I. M. Petrova, O. V. Anikin, and I. E. Chlenov**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The possibilities for stabilization of compounds with the A—B—NO_2 fragment, where A is an atom containing a lone electron pair, were examined. It was shown that *N*-methyl-*O*-2,4-dinitro- and 2,4,6-trinitrophenylhydroxylamines undergo nitration with nitronium tetrafluoroborate or with a mixture of nitric acid and acetic anhydride to give the corresponding *N*-nitrohydroxylamines in high yields. *N*-Nitro-2,4-dinitrohydroxylamine that contains no methyl group at the nitrogen atom is unstable and forms a product of *O*-alkylation upon reaction with diazomethane.

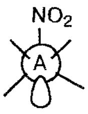
Key words: *N*-nitrohydroxylamines, nitration.

Compounds with the A—B—NO_2 fragment (**1**), where A is an atom containing a lone electron pair, are poorly known. Apparently, this is because of their instability resulting from conversions according to the following scheme:

$$\underset{\mathbf{1}}{A{-}B{-}NO_2} \rightleftharpoons \underset{\mathbf{2}}{[A{-}B]^+} + NO_2^- \rightleftharpoons$$

$$\rightleftharpoons \underset{\mathbf{3}}{A{-}B{-}ONO} \longrightarrow \text{decomposition}$$

Because the nitrite anion is ambident, its reaction with cation **2** may occur at the nitrogen atom to give an initial nitro compound **1** as well as at the oxygen atom to give nitrite **3**. Apparently, compound **3** is thermally unstable, and as a result of its decomposition, the equilibrium shifts to the right. In principle, stabilization of **1** may occur in two ways. One of these ways results from the fact that conformation (**C**), in which the splitting out of a nitrite anion with an antiperiplanar arrangement of the nitro group and a lone electron pair of atom A should occur, is hindered or impossible for **2**.



C

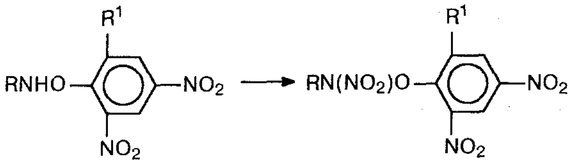
This stabilization was found in the case of compounds with N—C—NO_2 (see Ref. 1) and N—N—NO_2 fragments.[2] The second way of stabilization of **1** may occur through the attachment of electronegative substituents to atom A (probably, to atom B as well), which should hinder formation of cation **2**. We examined this hypothesis using *N*-nitrohydroxylamines as an example.

The performance of this program requires the development of methods for obtaining *N*-nitrohydroxylamines with a rather wide range of substituents at the N and O atoms. Data on these compounds are scarce in the literature. *N*-Nitrohydroxylamines in the series of oxadiazolidine[3] and *N*-alkyl-*O*-benzoyl-*N*-nitrohydroxylamines, which were synthesized by nitration of the corresponding *N,O*-disubstituted hydroxylamines with nitronium salts,[4] were described in the literature.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2276—2278, November, 1995.

1066-5285/95/4411-2183$12.50

In principle, both *O*-mono- and *N,O*-disubstituted *N*-nitrohydroxylamines are suitable as model compounds. It is possible to use nitration for obtaining both types of *N*-nitrohydroxylamines; alkylation of salts of *O*-substituted *N*-nitrohydroxylamines is possible to use for preparing compounds of the second type.[5] In this work, we found that nitration of hydroxylamines **4a,b** with nitronium tetrafluoroborate gives the corresponding *N*-nitrohydroxylamines (**5a,b**) in almost quantitative yields. The same products but in slightly lower yields were obtained when nitric acid and acetic anhydride were used as a nitrating mixture:



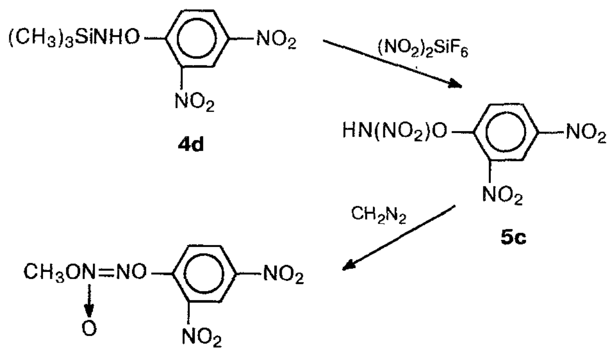
4a,b **5a,b**

R = Me; R¹ = H (**a**), R¹ = NO_2 (**b**)

It should be particularly noted that high yields of compounds **5** are indicative of the stability of these compounds in acidic media, whereas *N*-alkyl-*O*-benzoyl-*N*-nitrohydroxylamines are very unstable in acidic media.[4] Therefore, instability to acids is not an intrinsic property of the —O—N(NO_2)— system but depends on the nature of the substituent at the O atom.

As for nitration of hydroxylamine **4c** (R = R¹ = H), the use of nitronium tetrafluoroborate or a mixture of nitric acid and acetic anhydride in this reaction results in isolation of only 2,4-dinitrophenol from the reaction mixture. Because compound **4c** is stable to acids (this compound is prepaired in the presence of $HClO_4$), the fact of obtaining of phenol may be an evidence of formation of the corresponding unstable *N*-nitrohydroxylamine. To exclude the effect of an acidic medium, attempts were made to nitrate compounds **4c** with acetone cyanohydrin nitrate, but this compound appears to be inert to this reagent. However, the reaction of compound **4d** (trimethylsilyl derivative of **4c**) with nitronium hexafluorosilicate in dichloromethane, which was carried out according to the procedure described previously,[7] results in quantitative isolation of $(CH_3)_3SiF$ (determined from the ^1H NMR spectrum) and in formation of product (**5c**), which is unstable and decomposes to 2,4-dinitrophenol at 5 °C. When **5c** was treated with an ether solution of diazomethane, stable compound **6** was obtained; according to the data of elemental analysis and ^1H and ^{13}C NMR spectra, this compound is a product of *O*-alkylation of *N*-nitrohydroxylamine **5c**.

Based on NMR spectra, diazene oxide **6** is formed as a mixture of two isomers. In the ^1H NMR spectrum, Me protons give signals at δ 4.06 (predominant isomer) and δ 4.09 (minor isomer); in the ^{13}C NMR spectrum,



4d **5c** **6**

signals at δ 58.9 (predominant isomer) and 58.4 (minor isomer) correspond to the methyl group. These data unambiguously established the structure of **6** (*cf.* values of chemical shifts of the Me group of compound **5a**: δ 3.83 and 45.8).

Therefore, it may be concluded that the —ON(NO_2)H system is not stable, and, hence, the study of the effect of substituents on the stability of *N*-nitrohydroxylamines should be carried out using *N,O*-disubstituted products as an example.

Experimental

Starting hydroxylamines **4a—c** were obtained according to the procedures described previously.[6,8]

***N*-Methyl-*O*-2,4-dinitro-*N*-nitrohydroxylamine (5a). a.** NO_2BF_4 (0.2 g, 20 mmol) was added to a solution of **4a** (0.4 g, 18.8 mmol) in 5 mL of anhydrous CH_2Cl_2 at −25 °C, the temperature of the mixture was raised to 20 °C, and then the mixture was poured into water and neutralized with $NaHCO_3$. The crystals formed were filtered off and washed with water, and compound **5a** was obtained in 96 % yield (0.47 g), m.p. 95—96 °C (from the 1 : 1 CH_2Cl_2—hexane mixture).

Found (%): C, 32.68; H, 2.12; N, 21.46. $C_7H_6N_4O_7$. Calculated (%): C, 32.54; H, 2.32; N, 21.69. ^1H NMR (acetone-d_6, δ, *J*/Hz): 3.83 (s, 3 H, MeN); 7.9 (d, 1 H, H-6, $J_{6,5}$ = 7.5); 8.58 (q, 1 H, H-5, $J_{5,6}$ = 7.5, $J_{5,3}$ = 3); 8.82 (d, 1 H, H-3, $J_{3,5}$ = 3). ^{13}C NMR (DMSO-d_6, δ): 45.8 (Me); 118.8, 123.0; 131.1; 138.2; 144.2; 156.4 (C arom.).

b. Compound **4a** (0.3 g, 14.1 mmol) was added portionwise to the nitrating mixture prepared from Ac_2O (0.6 g) and HNO_3 (*d* = 1.5, 0.3 g) at 0 °C; the mixture was stirred for 1 h at 5 °C and was poured into ice water. When the mixture was neutralized, the formed oil crystallized out. Compound **5a** was obtained in 83 % yield (0.3 g).

***N*-Methyl-*N*-nitro-*O*-picrylhydroxylamine (5b). a.** NO_2BF_4 (0.34 g, 25 mmol) was added to a suspension of **4b** (0.6 g, 23.2 mmol) in 4 mL of anhydrous MeCN at −10 °C, the temperature was raised to ~20 °C, and then the mixture was poured into water and neutralized with $NaHCO_3$. The crystals formed were filtered off and washed with water; compound **5b** was obtained in 95 % yield (0.67 g), m.p. 103—105 °C with decomposition (1.5:1 CH_2Cl_2—hexane). Found (%): C, 27.91; H, 1.90; N, 23.01. $C_7H_5N_5O_5$. Calculated (%): C, 27.71; H, 1.65; N, 23.09. ^1H NMR (acetone-d_6, δ): 3.75 (s, 3 H, Me); 9.08 (s, 1 H, H arom.).

b. Compound **4b** (0.3 g, 11.6 mmol) was added portionwise to the nitrating mixture prepared from HNO_3 (d = 1.5, 0.3 g) and Ac_2O (0.6 g) at 0 °C; the mixture was stirred at 5 °C for 1 h and poured into ice water. When the mixture was neutralized, the formed oil crystallized out. Compound **5b** was obtained in 80 % yield (0.4 g).

***N*-Trimethylsilyl-*O*-2,4-dinitrophenylhydroxylamine (4d).** All reactions with silyl-substituted compounds were carried out under argon in anhydrous CH_2Cl_2.

A solution of *N*-trimethylsilyl-*N,N'*-diphenylurea (0.84 g, 33.8 mmol) in 2 mL of CH_2Cl_2 was added to a suspension of **4c** (0.59 g, 29.6 mmol) in 1 mL of CH_2Cl_2 at 20 °C; the mixture was stirred for 20 min, the precipitate was filtered off and washed with CH_2Cl_2, then the solution was evaporated at 20 °C (10 Torr), and compound **4d** was obtained in 100 % yield (0.8 g). ^1H NMR (CH_2Cl_2, δ): 1.09 (s, MeSi). When **4d** was treated with methanol, compound **4c** was obtained in a quantitative yield.

1-Methoxy-2-(2,4-dinitrophenoxy)diazene 1-oxide (6). A solution of **4d** (2.17 g, 80 mmol) in 6 mL of CH_2Cl_2 was added to a suspension of $(NO_2)_2SiF_6$ (1 g, 40.3 mmol) in 2 mL of CH_2Cl_2 at −20 °C, and the mixture was stirred for 1 h at −15 to −10 °C. In the ^1H NMR spectrum of the reaction mixture, a doublet at δ 0.15 was observed (Me_3SiF). When volatile compounds were distilled off at −15 to −10 °C (8 Torr), an ether solution of diazomethane (170 mmol) was added dropwise to the residue, the mixture was stirred at −10 to −5 °C for 20 min, then ether was distilled off at 20 °C, and compound **6** (0.64 g, 31 %), m.p. 95—96 °C (EtOH), was obtained by preparative TLC of the residue (silica gel 5/40, a 6 : 1 benzene—chloroform mixture was used as the eluent), R_f = 0.6. Found (%): C, 32.61; H, 2.31; N, 21.34. $C_7H_6N_4O_7$. Calculated (%): C, 32.54; H, 2.31; N, 21.69. ^1H NMR ($CDCl_3$, δ): 4.06 (predominant isomer); 4.09 (minor isomer) (s, 3 H, Me). ^{13}C NMR (DMSO-d_6): predominant isomer: 58.9 (Me), 118.8, 122.5, 130.7, 137.6, 143.3, 153.0 (C arom.); minor isomer: 58.4 (Me), 118.5, 122.5, 130.7, 137.4, 143.1, 153.8 (C arom.).

The work was supported by the International Science Foundation (Grant NGN 000).

References

1. I. E. Chlenov, N. S. Morozova, and V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1889 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1713 (Engl. Transl.)].
2. V. A. Tartakovsky, S. L. Ioffe, A. V. Kalinin, E. T. Apasov, and Y. N. Strelenko, *Mendeleev Commun.*, 1991, 95.
3. J. Burdon and A. Ramirez, *Tetrahedron*, 1973, **29**, 4195.
4. E. H. White, J. Reefer, R. H. Ericksen, and P. M. Dzadzic, *J. Org. Chem.*, 1984, 4872.
5. E. N. Khodot, I. E. Chlenov, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 178 [*Russ. Chem. Bull.*, 1994, **43**, 174 (Engl. Transl.)].
6. Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis*, 1977, 1.
7. M. S. Pevzner, T. N. Kulibabina, S. L. Ioffe, I. A. Maslina, B. V. Gidaspov, and V. A. Tartakovsky, *Khim. Geterotsikl. Soedin.*, 1979, **4**, 550 [*Chem. Heterocycl. Compd.*, 1979, **4** (Engl. Transl.)].
8. T. Sheradsky, G. Salemnick, and Z. Nik, *Tetrahedron*, 1972, **28**, 3833.

Received February 21, 1995;
in revised form April 28, 1995

Complexes of lanthanum with radical anions of 2,2-bipyridyl and 3,6-di-*tert*-butyl-*o*-benzoquinone

*I. L. Fedushkin, V. I. Nevodchikov, and M. N. Bochkarev**

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhny Novgorod, Russian Federation.
Fax: +7 (831) 235 6480

Complexes of a rare-earth element containing only one radical-anion ligand have been synthesized and isolated in pure states for the first time. The $LaI_2(bpy)(THF)_3$ complex has been prepared from $[LaI_2(THF)_3]_2(C_{10}H_8)$ and 2,2-bipyridyl in DME. The semiquinone complex $LaI_2(SQ)(THF)_3$ has been obtained by reaction of lanthanum iodide with 3,6-di-*tert*-butyl-*o*-benzoquinone in THF in the presence of lanthanum powder. ESR spectra of the complexes have been studied.

Key word: lanthanum, radical-anion ligands, ESR spectra.

Various complexes of most transition and non-transition metals with radical-anion ligands have been synthesized and studied by ESR spectroscopy. Nevertheless, only a few complexes of such kind are known in

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2278—2280, November, 1995.