dried over $MgSO_4$. After ether evaporation the product was purified by thin-layer chromatography (Silperl, eluent — benzene/hexane, 1 : 1).

The following DO were obtained:

1-(2-Bromopropyl)-2-*tert*-butyldiazene-1-oxide (2a), yield 35 %, NMR spectrum (δ_H): 1.23 (s, 9 H, CMe_3); 2.12 (s, 6 H, MeCBr) (*cf.* Ref. 1). **1-(1-Bromocyclohexyl)-2-*tert*-butyldiazene-1-oxide (2b)**, yield 52 %, NMR spectrum (δ_H): 1.26 (s, 9 H, CMe_3); 2.35 (m, 4 H, 2 CH_2CBr). IR spectrum (ν/cm^{-1}): 1450 (NO); 1500 (N=N). Found (%): C, 45.44; H, 7.50; Br, 30.49; N, 10.75. $C_{10}H_{19}BrN_2O$. Calculated (%): C, 45.62; H, 7.22; Br, 30.41; N, 10.64. **1-(1-Bromoadamantyl)-2-*tert*-butyldiazene-1-oxide (2c)**, yield 60.5 %, m.p. 35—37 °C, NMR spectrum (δ_H): 1.26 (s, 9 H, CMe_3); 2.87 (m, 2 H, 2 CHCBr). IR spectrum (ν/cm^{-1}): 1455 (NO); 1500 (N=N). Found (%): C, 53.13; H, 7.48; Br, 25.30; N, 8.90. $C_{14}H_{23}BrN_2O$. Calculated (%): C, 53.33; H, 7.30; Br, 25.39; N, 8.88.

Preparation of compound 3. A solution of benzophenone oxime (0.4 g in 10 mL anhydrous CH_2Cl_2) was added dropwise, with stirring, to a solution of *N,N*-dibromo-*tert*-butylamine (0.47 g in 10 mL anhydrous CH_2Cl_2) at −5 °C under an Ar atmosphere, stirred for 2 h at −5÷0 °C, and the precipitate was filtered off. After evaporation of the filtrate, hexane (2 mL) was added to the remaining oil-like residue, the precipitated crystals were filtered off, and 0.33 g (87.5 %) of compound **3**, m.p. 170—171 °C (hexane—benzene, 10 : 1) was obtained.

References

1. V. Nelson, A. Serianz, and P. Covacic, *J. Org. Chem.*, 1976, **41**, 1751.
2. E. Kerby, *Anomernyi effekt kislorodsoderzhaschikh soedinenii [Anomeric effect of oxygen-containing compounds]*, Mir, Moscow, 1985, 195 (Russ. Transl.).
3. M. Frojmovic and G. Just, *Can. J. Chem.*, 1968, **46**, 3719.
4. B. A. Frenz, *Enraf-Nonius Structure Determination Package*, College Station, Texas, USA and Enraf-Nonius, Delift, Holland, 1982.

Received October 22, 1993

Synthesis of potassium salts of *O*-substituted *N*-nitrohydroxylamines

E. N. Khodot, I. E. Chlenov,* and V. A. Tartakovskii

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5085

Potassium salts of *O*-substituted *N*-nitrohydroxylamines were synthesized by nitration of *O*-substituted *N*-acetylhydroxylamines followed by treatment of the reaction products with potassium methoxide.

Key words: *N*-nitrohydroxylamines; *O*-substituted *N*-hydroxylamines; potassium salts; nitration.

Disubstituted salts of *N*-nitrohydroxylamine, Angeli salts,[1] are known, whereas no salts of *O*-substituted *N*-nitrohydroxylamines (NHA) have been reported to date. The present communication is devoted to the preparation of compounds of this class.

Hydroxylamines (HA) **1a—d** were studied as model compounds.

$RONH_2$

1a—d

R = C_4H_9 (**a**), CH_3(**b**), $CH_3N(NO_2)CH_2$(**c**), $NH_2OCH_2CH_2$(**d**)

It was found that the method used for synthesizing Angeli salts[1] and nitramine salts,[2] consisting of treatment of the respective substrates with alcohol nitrates in the presence of alkaline metal ethoxides, is not suitable for obtaining NHA salts since the HA studied do not undergo this reaction. However, nitration of compound **1a** with ethyl nitrate in the presence of potassium *tert*-butoxide in THF affords the respective potassium salt of NHA (**2a**) in a yield of up to 40 %. This is not a general procedure. For example, it is not applicable to compound **1c**, which is rapidly decomposed by potassium *tert*-butoxide under the reaction conditions.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 178—179, January, 1994.

1066-5285/94/4301-0174 $12.50

The most general method for obtaining nitramine salts is nitration of *N*-acylamines followed by removal of the acyl protection under alkaline conditions.[3]

Therefore, we synthesized acyl derivatives (**3a—d**) from HA **1a—d** and studied the nitration of the former with various reagents.

When compounds **3a—d** are treated with HNO_3 in acetic anhydride at −10÷−15 °C, the respective NHA cannot be isolated. Apparently, this is due to the instability of the latter in acid media. Treatment of compounds **3a—c** with nitrogen pentoxide or nitronium fluoroborate in CH_2Cl_2 or MeCN results in rapid dissolution of the nitrating reagent at −30÷−20 °C, while an increase in the temperature to −10 °C leads to decomposition with evolution of gaseous products. However, signals attributable to the respective NHA (δ: 4.08 (MeO); 2.7 (MeCO)) could be detected in the ^1H NMR spectra of the reaction mixture produced from compound **3b**. The products of nitration of compounds **3a,b** proved to be unstable in neutral media as well. For example, the addition of an equimolar amount of EtONa to the reaction mixture at 0 °C gave rise to intense gas evolution. Thus, the preparation of NHA salts by the action of bases on the intermediate *N*-acetyl-NHA should be performed without isolation of the latter.

In fact, nitration of compounds **3a—d** with N_2O_5 or NO_2BF_4 followed by rapid treatment of the reaction mixture with potassium methoxide proved to be an efficient method for obtaining K-salts of NHA, **2a—d**.

$[RON(NO_2)]K$ $K[N(NO_2)OCH_2CH_2ON(NO_2)]K$

2a—c **2d**

It should be noted that this procedure results in the formation of potassium nitrate or fluoroborate along with salts **2a—d**. It is sometimes difficult to separate the former from the target products due to their similar solubility. Therefore, an appropriate nitrating agent should be selected in each case. For example, compounds **2a,b** should be obtained using nitrogen pentoxide, while compounds **2c,d** should be produced using nitronium fluoroborate. If, for example, compound **2b** is obtained by treatment with nitronium fluoroborate, the product cannot be purified by recrystallization.

Experimental

Compounds **1a,b,d** were prepared by the known procedures.[4,5,6]

***O*-(Methylnitraminomethyl)hydroxylamine 1c.** A mixture of sodium *N*-hydroxyphthalimide (16.1 g, 87 mmol) and 1-chloro-2-nitroazapropane (10.82 g, 87 mmol) in dry DMF (80 mL) was heated with stirring for 3 h at 50—60 °C and poured into water. The precipitate was filtered off, washed with aqueous sodium bicarbonate and water, and dried in the air to give 20.3 g (93 %) of *N*-(2-nitroazapropyloxy)phthalimide, m.p. 192—193 °C (C_6H_6). The product obtained and hydrazine hydrate (8.1 mL) in MeOH (500 mL) were stirred for 24 h at 20 °C. The precipitate was filtered off and washed with C_6H_6. The mother liquor was concentrated, and the residue was extracted with C_6H_6. The solvent was distilled off, and the residue was redistilled to give 8.05 g (82.5 %) of compound **1c**, b.p. 98—100 °C (3 Torr), n_D^{20} 1.4912. Found (%): C, 19.71; H, 5.65; N, 34.62. $C_2H_7N_3O_3$. Calculated (%): C, 19.83; H, 5.78; N, 34.71. ^1H NMR ($CDCl_3$), δ: 3.43 (s, 3 H, CH_3); 5.19 (s, 2 H, CH_2); 5.57 (br.s, NH_2).

Nitration of compound 1a with ethyl nitrate. A mixture of sublimed potassium *tert*-butoxide (1 g), compound **1a** (0.53 g), and ethyl nitrate (0.8 g) in abs. THF (6 mL) was stirred for 20 h at 20 °C and concentrated at 25 °C (12 Torr) to give 0.4 g (39 %) of compound **2a**, decomp. >200 °C. Found (%): K, 22.48. $C_4H_9N_2O_3K$. Calculated (%): K, 22.65. IR, ν/cm^{-1}: 1305, 1430.

***O*-Substituted *N*-acetylhydroxylamines 3a—d.** Compounds **1a—d** were acetylated by refluxing with acetic anhydride in C_6H_6 for 1—2 h. Product **3a** was obtained in 88 % yield, n_D^{20} 1.4395. Found (%): N, 10.63. $C_6H_{13}NO_2$. Calculated (%): N, 10.68. The yield of compound **3b** was 72 %, b.p. 88—90 °C (6 Torr). Found (%): N, 15.67. $C_3H_7NO_2$. Calculated (%): N, 15.73. The yield of compound **3c** was 75 %, m.p. 85—86 °C ($CHCl_3$—CCl_4, 4:1). Found (%): N, 15.77. $C_6H_{12}N_2O_4$. Calculated (%): N, 15.90. The yield of compound **3d** was 87 %, m.p. 83—84 °C ($CHCl_3$—CCl_4, 4:1). Found (%): N, 15.77. $C_6H_{12}N_2O_4$. Calculated (%): N, 15.90.

Potassium salts of *O*-substituted *N*-nitrohydroxylamines 2a,b. Compound **3a** or **3b** (10 mmol) in abs. MeCN (2 mL) was added at −30÷−25 °C to a stirred solution of N_2O_5 (10 mmol) in abs. MeCN (4 mL). After the N_2O_5 dissolved, MeOK (obtained from 20 mmol of K in 5 mL of abs. MeCN) was added dropwise at −20÷−25 °C, then the temperature was increased to 20 °C. The resulting precipitate was filtered off, washed with EtOH, and recrystallized from EtOH. The yield of salt **2a** was 79 %, decomp. >250 °C. The yield of salt **2b** was 92 %, m.p. 66—67 °C, decomp. >250 °C. Found (%): K, 29.76. $CH_3N_2O_3K$. Calculated (%): K, 29.99. IR, ν/cm^{-1}: 1310, 1430.

Potassium salts of NHA 2c,d. To a stirred suspension of nitronium borofluoride (1 g) in abs. MeCN (8 mL), an equimolar amount of compound **3c** or **3d** was added at −30÷−25 °C. After the precipitate dissolved, a twofold molar amount of MeOK in abs. MeOH was added dropwise at −20÷−25 °C. The precipitate was filtered off and recrystallized from 70 % aqueous EtOH. The yield of salt **2c** was 82 %, decomp. >200 °C. Found (%): K, 19.27. $C_2H_5N_4O_5K$. Calculated (%): K, 19.11. IR, ν/cm^{-1}: 1305, 1410, 1505—1520. The yield of salt **2d** was 80 %, decomp. >200 °C. Found (%): K, 30.35. $C_2H_4N_4O_6K$. Calculated (%): K, 30.23. IR, ν/cm^{-1}: 1300—1330, 1390—1430.

References

1. A. Angeli, *Gazz. Chim. Ital.*, 1896, **26**, II, 12.
2. D. Banthorpe, E. Hughes, and D. Williams, *J. Chem. Soc.*, 1964, 5349.
3. S. S. Novikov, G. A. Shvekhgeimer, V. V. Sevast'yanova, and V. A. Shlyapochnikov, *Khimiya alifaticheskikh i alitsiklicheskikh nitrosoedinenii* (*Chemistry of Aliphatic and Alicyclic Nitro Compounds*), Mir, Moscow, 1974, 415 (in Russian).
4. H. Hjedes, *Acta Chem. Scand.*, 1965, **19**, 1764.
5. L. Bauer and K.Suresh, *J. Org. Chem.*, 1963, **28**, 1604.
6. O. Scherer, G. Hörlein, and K. Härtel, *Ang. Chev.*, 1963, **75**, 851.

Received October 22, 1993