# Organic Chemistry

## Synthesis of ammonium salts of *O*-substituted *N*-nitrohydroxylamines

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Ammonium salts of *O*-substituted *N*-nitrohydroxylamines were synthesized by nitration of *O*-substituted *N*-benzoyl- or *p*-nitrobenzoylhydroxylamines followed by treatment of the reaction products with an alcohol solution of ammonia.

**Key words**: *N*-nitrohydroxylamines, benzoylation, nitration; ammonium salts.

Synthesis of potassium salts of *O*-substituted *N*-nitrohydroxylamines (NHA) *via* nitration of *N*-acetylhydroxylamines (HA) by nitrogen pentoxide or nitronium tetrafluoborate followed by treatment of the *N*-acetyl-NHA formed with potassium alkoxide has been described in the preceding report.[1] A disadvantage of this procedure is the fact that the salts of NHA are obtained as a mixture with inorganic nitrates or tetrafluoborates, which makes it difficult to isolate the target products. Ammonium salts of NHA appear to be universal compounds to synthesize salts of NHA with other cations. The treatment of the former with the alkoxide of a corresponding metal has led to the substitution of $NH_4^+$ for a chosen cation. Nevertheless, it turned out that *N*-acetyl-NHA obtained by the described procedure[1] formed ammonium salts of NHA with an alcohol solution of ammonia. Only with considerable losses can these salts be separated from ammonium nitrate or tetrafluoroborate present in the reaction mixture. Apparently, preliminary isolation of *N*-acyl-NHA from the mixture is necessary to overcome this, but it is unlikely because of their thermal instability. It could be supposed that the stability of NHA derivatives depends on the nature of the substituent at the nitrogen atom. That is why we studied nitration of compound **2a—d**, the *N*-benzoyl derivatives of HA **1a—d**.

RONHR′
**1a—d**
**2a—d**

R′ = H(**1**), PhCO (**2**)
R = Me (**a**), $CH_2N(NO_2)Me$ (**b**), $CH_2CH_2ONHR'$ (**c**), $CH_2ONHR'$ (**d**)

After the nitration of HA **1a—d** (under the action of $N_2O_5$ or nitronium tetrafluoborate in MeCN at −30 to −20 °C) was completed, the reaction mixture was treated with an equimolar (with respect to nitrating agent) amount of sodium acetate in ethanol to remove acids formed. Solid products (**3b**,**d**) were obtained from compounds **2b**,**d**, and liquid products (**3a**,**c**) were obtained from compounds **2a**,**c**. Using spectral methods it was established that compounds **3b**,**d** were *N*-nitro derivatives. They are rather stable in the solid state (decomp. >70 °C), but in a solution their stability decreases. On

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treatment of NHA **3b**,**d** with an alcohol solution of ammonia pure ammonium salts **4b**,**d** are isolated in high yields.

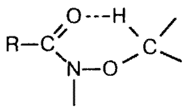
$PhC(O)N(NO_2)OCH_2N(NO_2)Me$ **3b**

$(PhC(O)N(NO_2)O)_2CH_2$ **3d**

$NH_4^+[N(NO_2)OCH_2N(NO_2)Me]^-$ **4b**

$NH_4^+[N(NO_2)OCH_2ON(NO_2)]^{2-}NH_4^+$ **4d**

According to spectral data, liquid nitration products do not contain nitro groups. Probably, they are decomposition products of corresponding NHA. Difference in thermal stability of compounds **3b**,**d** and **3a**,**c** seems to be related with the peculiarities of their structures. It is logical to suppose that decomposition of *N*-acyl-NHA proceeds through cyclic intermediate state of the type **A** postulated[2] for the decomposition of *N*-acyl-HA.



**A**

In the case of compounds **3b**,**d** this process must be hampered because it involves the appearance of negative charge on the C atom, in α-position to which an atom with free electron pair (N in compound **3b** or O in compound **3d**) is localized. Therefore, these products are relatively stable. One can expect that stability of the compounds will increase if proton transfer to carbonyl O atom becomes more difficult. To check this assumption, we studied nitration of compounds **5a**,**c**, the *p*-nitrobenzoyl derivatives of compounds **1a**,**c**, and isolated corresponding solid NHA **3a**,**c** which, on treatment with an alcohol solution of ammonia, result in ammonium salts **4a**,**c** in high yields.

$p\text{-}O_2NC_6H_4C(O)NROMe$ **3a, 5a**

$[p\text{-}O_2NC_6H_4C(O)NRO]_2C_2H_4$ **3c, 5c**

$R = NO_2$ (**3**), H (**5**)

$NH_4^+[N(NO_2)OMe]^-$ **4a**

$NH_4^+[N(NO_2)OCH_2CH_2ON(NO_2)]^{2-}NH_4^+$ **4c**

Compounds **3a**,**c** are less stable than **3b**,**d**. They decompose upon melting (>60 °C), and their spontaneous decomposition was also observed in certain cases in the course of drying. Therefore, they should be entered into the reaction immediately after filtration.

As it was expected, treatment of compounds **4a—d** with alkoxides of alkaline or alkaline-earth metals allows one to substitute easily ammonium cation for other ones. These salts can be obtained directly from compounds **3a—d** as well, by their treatment with alkoxides of corresponding metals.

## Experimental

Synthesis of compounds **1a—d** was described earlier.[1,3]

**Synthesis of compounds 2a—d.** Benzoylation of HA **1a—d** was carried out with benzoyl chloride in water in the presence of equimolar amounts of sodium acetate. Benzoyl derivatives **2a—d** were obtained, respectively. Compound **2a**: yield 80 %, m.p. 62 °C (from hexane—ether) (cf. Ref. 4). Compound **2b**: yield 80 %, m.p. 100—101 °C (from $CHCl_3$—$CCl_4$, 4 : 1). Found (%): C, 48.11; H, 4.87; N, 18.53. $C_9H_{11}N_3O_4$. Calculated (%): C, 48.00; H, 4.92; N, 18.66. Compound **2c**: yield 77 %, m.p. 147—149 °C (from 50 % EtOH) (*cf.* Ref. 5). Compound **2d**: yield 80 %, m.p. 121—122 °C (from 50 % EtOH). Found (%): C, 62.84; H, 4.89; N, 9.75. $C_{15}H_{14}N_2O_4$. Calculated (%): C, 62.93; H, 4.93; N, 9.79.

**Synthesis of compound 5a.** MeCOONa (11.1 g, 135 mmol) and *p*-nitrobenzoyl chloride (10 g, 57 mmol) in 50 mL of $CH_2Cl_2$ were added with stirring to $MeONH_2 \cdot HCl$ (4.8 g, 57 mmol) in 80 mL of water. The reaxtion mixture was stirred for 30 min, the precipitate was filtered off and washed with water to give 10.5 g (94 %) of compound **5a**, m.p. 185 °C (from EtOH). Found (%): C, 48.95; H, 4.03; N, 14.17. $C_8H_8N_2O_4$. Calculated (%): C, 48.98; H, 4.11; N, 14.28.

Analogously, compound **5c** was obtained from HA **1c**. Yield 90 %, m.p. 228—229 °C. Found (%): C, 49.03; H, 3.42; N, 14.15. $C_{16}H_{19}N_4O_2$. Calculated (%): C, 49.24; H, 3.62; N, 14.35.

**Synthesis of compound 4a.** Compound **5a** (2.14 g, 109 mmol) was added with stirring to $N_2O_5$ (1.18 g, 109 mmol) in 5 mL of anhydrous MeCN at −25 to −20 °C. After precipitate was formed, a solution of MeCOONa (0.9 g, 109 mmol) in 5 mL of EtOH was added dropwise at the same temperature. The temperature was then raised up to −10 to −5 °C, and the reaction mixture was diluted with water. The precipitate of compound **3a** was filtered off, washed with water, and added with stirring to 50 mL of a cooled alcohol solution of ammonia. After 30 min the solution was concentrated at 30—35 °C, and 20 mL of ethyl acetate was added to the residue. The precipitate was filtered off, dissolved in EtOH at 40—50 °C, and reprecipitated with ethyl acetate. 1.08 g (90.9 %) of compound **4a** were obtained. M.p. (decomp.) 118—119 °C (from EtOH). Found (%): C, 11.20; H, 6.31; N, 38.54. $CH_7N_3O_3$. Calculated (%): C, 11.01; H, 6.47; N, 38.52. IR, $\nu$/cm$^{-1}$: 1290, 1420 ($NNO_2^-$). UV ($H_2O$), $\lambda_{max}$/nm: 246 (ε 7270).

**Synthesis of compound 4b.** Compound **2b** (2.6 g, 11 mmol) was added with stirring to $N_2O_5$ (1.25 g, 11 mmol) in 10 mL of anhydrous MeCN at −25 to −20 °C. After 10 min a solution of MeCOONa (0.95 g, 11 mmol) in EtOH was added dropwise at the same temperature. The reaction mixture was diluted with water. The precipitate of compound **3b** was filtered off, washed with water, and added portionwise to 50 mL of a cooled alcohol solution of ammonia. After stirring during 1h, the mixture was concentrated to one quarter volume remains, and 30 mL of ethyl acetate was added. The precipitate was filtered off to give 1.7 g (84 %) of compound **4b**, m.p. (decomp.) 140 °C. Found (%): C, 13.03; H, 4.90; N, 38.17. $C_2H_9N_5O_5$. Calculated (%): C, 13.12; H, 4.95; N, 38.25. IR, $\nu$/cm$^{-1}$: 1260—1330, 1410—1530 ($NNO_2^-$, $NNO_2$). UV ($H_2O$), $\lambda_{max}$/nm: 242 (ε 13150).

**Synthesis of compound 4c.** Compound **5c** (1.44 g, 37 mmol) was added portionwise to $N_2O_5$ (0.8 g, 74 mmol) in 5 mL of anhydrous MeCN at −25 to −20 °C, and the reaction mixture was stirred at the same temperature for 15 min. A solution of MeCOONa (0.61 g, 74 mmol) in EtOH was then added dropwise, and the mixture obtained was diluted with water. The precipitate of compound **3c** was filtered off, washed with water, and added portionwise with stirring to 50 mL of a cooled alcohol solution of ammonia. After 30 min the precipitate was filtered off, washed with EtOH, and compound **4c** (0.66 g, 82 %) was obtained. M.p. (decomp.) 165—166 °C (from 80 % EtOH). Found (%): C, 11.28; H, 5.47; N, 38.59. $C_2H_{12}N_6O_6$. Calculated (%): C, 11.11; H, 5.60; N, 38.89. IR, $\nu$/cm$^{-1}$: 1270—1300, 1420—1490 ($NNO_2^-$). UV ($H_2O$), $\lambda_{max}$/nm: 247 ($\varepsilon$ 14860).

**Synthesis of compound 4d.** *A*. Compound **2d** (2.15 g, 7.5 mmol) was added to $NO_2BF_4$ (2g, 15 mmol) in 20 mL of anhydrous MeCN at −30 to −25 °C, and the reaction mixture was stirred for 10 min. A solution of MeCOONa (1.23 g, 15 mmol) in EtOH was then added at −20 to −15 °C. The precipitate of compound **3d** was filtered off, washed with water, and added portionwise to 50 mL of a cooled alcohol solution of ammonia. After 30 min the precipitate was filtered off, and 1.3 g (85 %) of compound **4d** was obtained. Decomp. at 120 °C (from 70 % EtOH). Found (%): C, 6.08; H, 5.09; N, 41.41. $CH_{10}N_6O_6$. Calculated (%): C, 5.94; H, 4.99; N, 41.58. IR, $\nu$/cm$^{-1}$: 1280—1330, 1400—1435 ($NNO_2^-$). UV ($H_2O$), $\lambda_{max}$/nm: 242 ($\varepsilon$ 14290).

***B***. Compound **2d** (2.58 g, 9 mmol) was added portionwise to $N_2O_5$ (1.95 g, 18 mmol) in 20 mL of anhydrous MeCN at −30 to −25 °C, and the reaction mixture was stirred for 10 min, followed by addition of MeCOONa (1.53 g, 18 mmol) in ethanol. The reaction mixture was diluted with water, and the precipitate of compound **3d** was filtered off, washed with water, and added portionwise to 50 mL of a cooled alcohol solution of ammonia. After 30 min the precipitate was filtered off and washed with EtOH, and 1.6 g (88 %) of compound **4d** was obtained.

**Synthesis of alkaline and alkaline-earth salts of NHA from ammonium salts (general procedure).** Equimolar amounts of metal (Li, Na, K, Mg) alkoxide and an ammonium salt of NHA in MeOH were stirred at 20—30 °C for 1—2 h and concentrated, then ether was added, and the precipitate formed was filtered off. The product yields were close to quantitative.

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## References

1. E. N. Khodot, I. N. Chlenov, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 178 [*Russ. Chem. Bull.*, 1994, **43**, 174 (Engl. Transl.)].
2. F. Brown and G. Mechan, *Aust. J. Chem.*, 1968, **21**, 1581.
3. C. McDowell and C. Merrill, USA Pat. 3,714,199, 1972.
4. J. Cooley, W. Billy, and J. Throckmorton, *J. Org. Chem.*, 1960, **25**, 1734.
5. L. Bauer and K. Surlsh, *J. Org. Chem.*, 1963, **28**, 1064.

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