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Preparation of *N*-nitrohydroxylamines by substitutive nitration

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Interaction of Na- or K-salts of *N*-acetyl-*N*-methylhydroxylamines with acyl or aryl halides results in corresponding *O*-substituted *N*-acetyl-*N*-methylhydroxylamines. Nitration of these compounds by nitronium salts or dinitrogen pentoxide results in *O*-substituted *N*-methyl-*N*-nitrohydroxylamines.

Key words: *N*-acetylhydroxylamines, substitutive nitration; *N*-nitrohydroxylamines; nitronium salts, dinitrogen pentoxide.

Earlier, it has been shown that *N*-nitrohydroxylamines (NHA) of the general formula $R^1N(NO_2)OR^2$ (where R^1 is alkyl, R^2 is benzoyl or nitroaryl) can be obtained by direct nitration of the corresponding *N,O*-disubstituted hydroxylamines (HA) by nitronium salts or by a mixture of nitric acid and acetic anhydride.[1,2] This procedure is of limited application since it is known that certain NHA are unstable under the action of acids.[1] Moreover, the preparation of *N,O*-disubstituted HA involves the introduction of protective groups. Here we describe the synthesis of NHA by substitutive nitration of *N*-acetyl-*N,O*-disubstituted HA, which occurs at a minimum acidity. The starting compounds, *i.e.*, *N*-acetyl-HA, are obtained without formation of intermediate *N,O*-disubstituted HA.

N-Acetyl-*N*-methyl-*O*-substituted HA **1a—d** have been used as the substrates of nitration. Compound **1a** can be easily obtained from *N*-methyl-HA hydrochloride and acetic anhydride.[3] Hydroxylamines **1b—d** were synthesized by the reaction of the corresponding halides with the potassium or sodium salt of *N*-acetyl-*N*-methyl-HA. (These salts are formed on treatment of compound **1a** with sodium alkoxides or KOH.) With different nitrating agents, the corresponding NHAs **2a—d** were obtained in all cases.

$$\underset{\textbf{1a—d}}{\mathrm{MeN(COMe)OR}} \xrightarrow{NO_2^+} \underset{\textbf{2a—d}}{\mathrm{MeN(NO_2)OR}}$$

R = Ac (**a**), MeOCO (**b**), $C_6H_4(NO_2)_2$ (**c**), $C_6H_3(NO_2)_3$ (**d**)

NO_2BF_4, a complex of NO_2BF_4 with 3,5-lutidine, $(NO_2)_2SiF_6$, and N_2O_5 were used to nitrate compounds **1a** and **1c**. The reaction with NO_2BF_4 in acetonitrile at −5 °C resulted in rather rapid disappearance of the starting HA from the mixture and the formation of new compounds (according to TLC). Following aqueous workup and extraction with chloroform, nitration products **2a** and **2c** were isolated. Compound **2c** proved to be identical with a product of independent synthesis.[2] As to compound **2a**, its spectral characteristics were in agreement with the expected structure, but it was rather unstable and decomposed completely at 20 °C in 1—2 h. Supposing that the decomposition of this compound is caused by traces of acid, we treated the reaction mixture with an aqueous solution of $NaHCO_3$; in this manner we succeeded in isolating quite a stable product. The acid that destroys NHA **2a** is BF_3, which seems to be generated upon decomposition of acetyl

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tetrafluoroborate, the latter being formed in the course of the reaction of substitutive nitration

$$[\mathrm{MeCO}]^+\mathrm{BF_4}^- \longrightarrow \mathrm{MeCOF} + \mathrm{BF_3}.$$

We confirmed experimentally that BF_3 destroyed NHA **2a**, so that this process proceeded rather slowly at −10 °C and practically complete decomposition of compound **2a** took place at 20 °C in 30 min. As it should be expected, compound **2c,** which is resistant even against nitric acid,[2] is absolutely inert to the action of BF_3.

To bind BF_3 released during the nitration, we studied the nitration of HA **1a** and **1c** by a complex of NO_2BF_4 with 3,5-lutidine. However, since this reagent possessed a weaker nitrating activity, longer reaction time required. In this case, compound **2a** was isolated in only 10 % yield, and compound **2c** was isolated in ~60 % yield. $(NO_2)_2SiF_6$ manifested itself a perfect nitrating agent, whose application resulted in more than 90 % yields of NHA **2a** and **2c**, the workup of the reaction mixture with sodium hydrogen carbonate was not necessary in the case of preparation of compound **2a**. Obviously, this is asssociated with the fact that either Lewis acid SiF_4 formed in the reaction is evaporated from the mixture at the reaction temperature or product **2a** is inert to this acid.

The reaction of compound **1a** with N_2O_5 results in NHA **2a** in a high yield, and workup with sodium hydrogen carbonate was not necessary as well. However, compound **1c** is absolutely inert to the action of N_2O_5. The nitration of HA **1b** and **1d** proceeds successfully under the action of NO_2BF_4, whereas compound **1d** does not react with N_2O_5.

Thus, it is established that NO_2BF_4, $(NO_2)_2SiF_6$, and N_2O_5 can be used to nitrate *N*-acyl-HA. The choice among them is determined in each case by the combination of at least two factors: the nitrating ability of the reagent and the resistance of the nitration products to acids. There may be certain correlation between ease of nitration of *N*-acyl-HA and the resistance of the corresponding NHA to the action of acids: the easier *N*-acyl-HA is nitrated, the less stable to acids is the corresponding NHA.

Experimental

IR spectra were recorded in KBr pellets.

***N*-Acetyl-*N*-methyl-*O*-methoxycarbonylhydroxylamine (1b).** HA **1a** (2.77 g, 21.12 mmol) in 3 mL of anhydrous MeOH was added to a solution of sodium methoxide (from 0.5 g of Na in 20 mL of anhydrous MeOH) with cooling with ice water. The mixture was kept at 20 °C for 30 min. Methanol was removed, anhydrous MeCN (50 mL) and then methyl chloroformate (2.4 g, 25.4 mmol) were added to the sodium salt obtained (slight heating was observed), and the reaction mixture was stirred at 20 °C for 3 h and left for 12 h. A precipitate was filtered off, and the filtrate was concentrated and distilled to give 2.1 g (67.5 %) of HA **1b**, b.p. 56—57 °C (1 Torr), n_D^{20} 1.4322. Found (%): C, 40.68; H, 6.25; N, 9.37. $C_5H_9NO_4$. Calculated (%): C, 40.82; H, 6.17; N, 9.52. IR, ν/cm^{-1}: 1690 (C(O)N); 1800 (C(O)O). ^{1}H NMR ($CHCl_3$), δ: 2.03 (s, 3 H, MeCO); 3.29 (s, 3 H, NMe); 3.92 (s, 3 H, MeO).

***N*-Acetyl-*N*-methyl-*O*-2,4-dinitrophenylhydroxylamine (1c).** HA **1a** (0.8 g, 6.1 mmol) in 3 mL of ethanol was added to a solution of KOH (0.4 g, 14.89 mmol) in 8 mL of ethanol with cooling with water. The reaction mixture was stirred at 20 °C for 15 min, and the solution obtained was added dropwise to 1-chloro-2,4-dinitrobenzene (1.23 g, 6.1 mmol) in 20 mL of ethanol at 5—7 °C. Cooling was discontinued after 30 min, and the reaction mixture was stirred at 20 °C for 1.5 h and poured into 100 mL of water. The precipitate that sedimented was filtered off and washed with water, and 1 g (64.5 %) of HA **1c** was obtained, m.p. 100—109 °C (from CH_2Cl_2). Ref. 4: m.p. 102—103 °C.

Analogously, 1.41 g (85 %) of ***N*-acetyl-*N*-methyl-*O*-picrylhydroxylamine (1d)** were obtained from KOH (0.31 g, 5.53 mmol), HA **1a** (0.75 g, 5.53 mmol), and picryl chloride (1.37 g, 5.3 mmol), m.p. 134—135 °C (from CH_2Cl_2). Found (%): C, 36.05; H, 2.97; N, 18.43. $C_9H_8N_4O_8$. Calculated (%): C, 36.01; H, 2.69; N, 18.66. IR, ν/cm^{-1}: 1360, 1550 (NO_2); 1620 (C=C); 1720 (C=O). ^{1}H NMR (acetone-d_6), δ: 2.06 (s, 3 H, CMe); 3.37 (s, 3 H, NMe); 9.01 (s, 2 H, NCH_2); 9.01 (s, 2 H, H arom.).

***N*-Methyl-*N*-nitro-*O*-dinitrophenylhydroxylamine (2c).** *A.* NO_2BF_4 (0.21 g, 1.6 mmol) was added to a solution of HA **1c** (0.4 g, 1.57 mmol) in 5 mL of anhydrous MeCN at −25 °C, the temperature was raised to 20 °C, and the reaction mixture was stirred for 2 h, then poured into H_2O, and neutralized with $NaHCO_3$. The precipitate that sedimented was filtered off and washed with water, and 0.38 g (96 %) of NHA **2c** was obtained, m.p. 95—96 °C. Ref. 2: m.p. 95—96 °C.

B. HA **1c** (0.21 g, 8.2 mmol) was added at 0 °C to a complex obtained from NO_2BF_4 (0.13 g, 9.8 mmol) and 3,5-lutidine (0.1 g, 9.3 mmol) in 3 mL of anhydrous MeCN. The reaction mixture was stirred at 20 °C for 12 h. The solvent was removed, and after passing the residue through a column with SiO_2 100/160 (CH_2Cl_2 as the eluent), 0.12 g (57 %) of NHA **2c** were obtained, m.p. 95—96 °C.

***O*-Acetyl-*N*-methyl-*N*-nitrohydroxylamine (2a).** *A.* NO_2BF_4 (1.99 g, 13 mmol) was added to a solution of HA **1a** (1.95 g, 14.9 mmol) in 2.5 mL of anhydrous MeCN at −20 °C. The reaction mixture was stirred at −5 °C for 2 h. $NaHCO_3$ (1.5 g) in 10 mL of H_2O was added, the solution obtained was extracted with chloroform, and the extract was dried with $MgSO_4$. Following removal of the solvent, the residue was passed through a column with SiO_2 100/160 (ether as the eluent), and 1.72 g (86 %) of NHA **2a** was obtained as an almost colorless liquid. Found (%): C, 26.98; H, 4.64; N, 20.91. $C_3H_6N_2O_4$. Calculated (%): C, 26.87; H, 4.57; N, 20.89. IR, ν/cm^{-1}: 1300, 1600 (N—NO_2); 1806 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.16 (s, 3 H, Ac); 3.45 (s, 3 H, NMe).

B. $(NO_2)_2SiF_6$ (0.12 g, 5.1 mmol) was added to a solution of HA **1a** (0.93 g, 9.9 mmol) in 2 mL of anhydrous MeCN at −20 °C, and the reaction mixture was stirred at this temperature for 45 min. The solvent was removed, and 0.12 g (92 %) of NHA **2a** was obtained (purification as in the above experiment).

C. N_2O_5 (0.21 g, 21 mmol) was added to a solution of HA **1a** (0.26 g, 19.8 mmol) in 2 mL of anhydrous MeCN at −20 °C, and the reaction mixture was stirred at this temperature for 30 min. The solvent was removed, and 0.22 g (84 %) of NHA **2a** was obtained (purification as in the above experiments).

***N*-Methyl-*O*-methoxycarbonyl-*N*-nitrohydroxylamine (2b).** NO_2BF_4 (0.65 g, 48.94 mmol) was added to a solution of HA **2b** (1 g, 48.34 mmol) in 3 mL of anhydrous MeCN at −25 °C. The reaction mixture was stirred at −10 °C for 3 h. $NaHCO_3$ (0.94 g) in 10 mL of H_2O was added. The solution obtained was extracted with dichloromethane. After CH_2Cl_2 was removed, the residue was passed through a column with SiO_2 100/160 (CH_2Cl_2 as the eluent), and 0.66 g (91.6 %) of NHA **2b** was obtained as a colorless liquid. Found (%): C, 24.23; H, 3.38; N, 18.36. $C_3H_6N_2O_5$. Calculated (%): C, 24.01; H, 4.03; N, 18.68. IR, ν/cm^{-1}: 1360—1600 (NNO_2); 1805 (C=O). ^1H NMR ($CDCl_3$), δ: 3.55 (C, 3 H, NMe); 3.97 (s, 3 H, OMe).

***N*-Methyl-*N*-nitro-*O*-picrylhydroxylamine (2d).** NO_2BF_4 (0.34 g, 25.6 mmol) was added to a suspension of HA **1d** (0.6 g, 20.1 mmol) in 4 mL of anhydrous MeCN at −10 °C. The temperature was raised to 20 °C, and the reaction mixture was stirred for 2 h and then poured into water. The precipitate that sedimented was filtered off and washed with water, and 0.58 g (95 %) of NHA **2a** was obtained, m.p. 103—105 °C (decomp.). Ref. 2: m.p. 103—105 °C (decomp.).

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Formation of diamond from carbyne

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Highly disperse diamond (HDD) was obtained by heating amorphous carbyne in the presence of small amounts of HDD.

Key words: carbon, allotropic modifications, carbyne, diamond.

Consideration of carbon as a polymeric system consisting of C atoms allows one to distinguish three types of polymers: (1) spatial polymer (diamond); (2) "parquet" polymer (graphite); and (3) linear polymer (carbyne).

Polyynic carbon polymer, carbyne, has been obtained from acetylene used as the initial material (monomer).[1] Other allotropic forms of carbon can also be synthesized using benzene and adamantane as initial monomers. The first attempt to synthesize diamond from adamantane at normal pressures and temperatures was performed in 1976.[2] The authors of this work[2] have synthesized polyadamantane by bromination of adamantane followed by dehydrobromination. The data of X-ray diffraction analysis, electron diffraction, and IR spectroscopy made it possible to establish that the product of dehydropolycondensation of adamantane is a spatial carbon polymer in the form of adamantane cores "linked" by saturated C—C bonds.

A low-energy method for preparation of diamond from carbyne at a pressure of 5 GPa or lower without preliminary heating has been published recently.[3] The author of Ref. 3 believes that the use of carbyne as the initial material for the preparation of diamond allows one to decrease the high activation energy necessary for rearrangement of parquet layers of graphite into a spatial polymer.

It is likely that the mechanism of diamond formation is associated with the interaction of carbon chains (retained in the initial carbyne due to weak van der Waals bonds), which are transformed with explosion into diamond-like carbon. It was not merely accidental that

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