

Oxidative nitration of the amino group: synthesis of dinitramide and cyanonitramide salts*

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A convenient preparative method for the synthesis of potassium dinitramide and cyanonitramide salts was developed. The method involves reactions of nitramide or cyanamide with KNO_2 and $\text{PhI}(\text{OAc})_2$ or PhIO in methanol.

Key words: dinitramide salts, cyanonitramide salts, nitrites, iodosobenzene, iodosobenzene diacetate, oxidative nitration.

Dinitramide (DNA) salts are currently rated among the most promising components of solid propellants, liquid monopropellants, and smokeless gunpowders as well as meet the modern requirements of "green chemistry".¹ The nearest structural analog of DNA is cyanonitramide; its salts are also of interest as components of energetic formulations. However, in contrast to DNA salts, they remain poorly studied so far.²

Recently,^{3,4} we have developed a method for oxidative nitration of the amino group with nitrites in combination with the phenyliodine(III) derivatives $\text{PhI}(\text{OAc})_2$ (**1**) or PhIO (**2**). Under these conditions, secondary amines can be transformed into mixtures of *N*-nitro and *N*-nitroso compounds in different proportions,³ while *O*-(4-nitrophenyl)hydroxylamine yields a potassium salt of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine.⁴

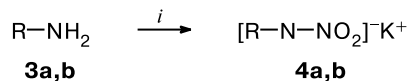
The next step in this direction was a study of oxidative nitration of compounds in which a primary amino group is bound to an electron-withdrawing substituent.

We used nitramide (**3a**) and cyanamide (**3b**) as substrates of oxidative nitration. Nitramide **3a**, which is an immediate precursor of DNA salts, was first obtained more than 100 years ago. At present, this compound is much more accessible through its recent synthesis^{5,6} from urea. Several schemes of nitration of compound **3a** are available; the best results⁷ have been achieved with nitronium tetrafluoroborate or fluorosulfonate in MeCN at -20°C . Cyanonitramide salts have been obtained earlier² by nitration of a 90% aqueous solution of **3b** with a mixture of H_2SO_4 and HNO_3 .

We found that amides **3a,b** react with phenyliodine(III) derivatives **1** and **2** in the presence of KNO_2 in MeOH at 0 – 5°C to give potassium salts **4a,b** (Scheme 1). The yields

of salt **4a** were higher with compound **1** as an oxidant. For salt **4b**, oxidant **2** proved to be preferred since the use of diacetate **1** leads to the formation of acetic acid, which hinders isolation and purification of the target product. Direct contact of amides **3a,b** with oxidants **1** and **2** results in unwanted side processes; that is why we did not add the oxidant to the reaction mixture until compounds **3a,b** were mixed with KNO_2 . Because the rates of both the desired and side processes are high, we mixed the reagents for 3–5 min while vigorously stirring the reaction mixtures. In both cases, the reaction time did not exceed 30 min (monitoring by TLC).

Scheme 1



3,4: R = NO_2 (**a**), CN (**b**)

i. KNO_2 , $\text{PhI}(\text{OAc})_2$ (for **3a**) or PhIO (for **3b**), MeOH, 0 – 5°C , 30 min.

After the solvent was removed *in vacuo*, products **4a,b** were isolated by crystallization from EtOH. The melting point and UV spectrum of potassium salt **4a** are identical with those of an authentic sample of potassium dinitramide.⁷ Potassium salt **4b** has a melting point in agreement with the literature data;² its ^{13}C NMR spectrum is similar to the published one.⁸ The signal for the nitro group in the ^{14}N NMR spectrum of salt **4b** ($\delta = -4$) is close to an analogous signal for structurally related potassium dinitramide ($\delta = -9.4$).⁹

Since this synthesis is easy to perform and the starting reagents are accessible, this reaction can be proposed as a preparative route to potassium salts **4a** and **4b**.

* Dedicated to Prof. A. M. Churakov on the occasion of his 60th birthday.

Experimental

^{13}C and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (75.5 and 21.5 MHz, respectively). Chemical shifts are referenced to SiMe_4 (^{13}C) or MeNO_2 (^{14}N , external standard; high-field chemical shifts are negative). The course of the reactions was monitored by TLC on Silufol UV-254 and Merck 60 F₂₅₄ plates. The electronic absorption spectrum of salt **4a** was recorded on a Specord UV-VIS instrument (Carl Zeiss, Jena).

Nitramide (**3a**) was prepared and purified by recrystallization from dichloroethane–propan-2-ol (9 : 1) as described earlier.⁵ Iodosobenzene (**2**)¹⁰ and cyanamide (**3b**)¹¹ were prepared according to known procedures.

Potassium dinitramide (4a). Finely divided KNO_2 (0.90 g, 11 mmol) was added in one portion to a cooled (with ice water) and stirred solution of compound **3a** (0.37 g, 6 mmol) in MeOH (10 mL). Then a solution of $\text{PhI}(\text{OAc})_2$ (1.61 g, 5.0 mmol) in MeOH (15 mL) was added dropwise for 5 min. The reaction mixture was stirred at 0–5 °C for 30 min and concentrated *in vacuo*. The solid residue was washed with CH_2Cl_2 (2×20 mL) and dried *in vacuo*. The product was extracted with boiling acetone (30 mL), the extract was concentrated *in vacuo*, and the residue was recrystallized from EtOH. The yield of potassium salt **4a** was 0.36 g (42%), m.p. 125–128 °C (*cf.* Ref. 1: m.p. 127–131 °C (from EtOH)).

Potassium cyanonitramide (4b). A solution of PhIO (1.10 g, 5 mmol) in MeOH (20 mL) was added dropwise for 5 min to a cooled (with ice water) and stirred mixture of KNO_2 (0.45 g, 5.3 mmol) and compound **3b** (0.31 g, 7.4 mmol) in MeOH (10 mL). The reaction mixture was stirred at 0–5 °C for 30 min and concentrated *in vacuo*. The residue was washed with hexane (2×10 mL), dried *in vacuo*, and recrystallized from EtOH. The yield of potassium salt **4b** was 0.34 g (37%), m.p. 132–136 °C (*cf.* Ref. 2: m.p. 135–136 °C (from EtOH)). ^{13}C NMR (D_2O),

δ : 117.0 (CN) (*cf.* Ref. 8 (D_2O), δ : 116.4). ^{14}N NMR (D_2O), δ : –4 (NO_2 , $\Delta\nu_{1/2} = 10$ Hz).

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Received December 21, 2011;
in revised form April 18, 2012