Dinitramide and its salts

10.* Synthesis of dinitramide salts from *N,N*-dinitro derivatives of organic amides

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N,N-Dinitro derivatives of alkylurethanes, benzamide, and *p*-toluenesulfamide were synthesized for the first time. Their reactions with ammonia afforded the ammonium salt of dinitramide in 44—85 % yields.

Key words: dinitramide salts, *N,N*-dinitrourethanes, *N,N*-dinitrobenzamide, *N,N*-dinitro-*p*-toluenesulfamide, *N*-nitramides.

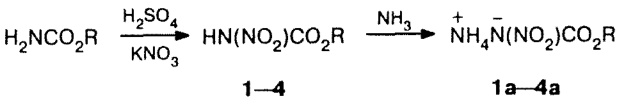
Dinitramide (DNA) salts[1] are of interest primarily as effective components of solid rocket fuels. This leads to the necessity of finding efficient methods for their synthesis. One method is the transformation of hitherto unknown *N,N*-dinitramides of organic acids under the action of bases similarly to the preparation of *N*-nitramide salts from *N*-nitroimides.[2]

In the present work, the possibility of synthesis of *N,N*-dinitramides of organic and inorganic acids by nitration of *N*-nitramides or their salts and the transformation of dinitramides into DNA salts have been studied.

In this respect, we studied the most extensively ammonium salt (**1a**) of *N*-nitrourethane (**1**). The regularities found for this compound are also valid for ammonium salts (**2a**, **3a**) of *N*-nitrourethylane (**2**) propyl *N*-nitrocarbamate (**3**), and potassium salt (**4b**) of butyl *N*-nitrocarbamate (**4**).

The initial salts **1a**—**4a** were obtained[3] by nitration of the corresponding urethanes with a mixture of H_2SO_4 with KNO_3 followed by the treatment with ammonia in ether (Scheme 1).

Scheme 1



$$H_2NCO_2R \xrightarrow[KNO_3]{H_2SO_4} HN(NO_2)CO_2R \xrightarrow{NH_3} \overset{+}{N}H_4\overset{-}{N}(NO_2)CO_2R$$

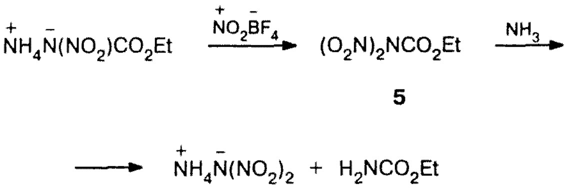
1—4 **1a—4a**

R = Et (**1**); Me (**2**); Pr (**3**); Bu (**4**)

Unlike salts **1a**—**3a**, ammonium salt **4a** is unstable (decomposes at ~50 °C); therefore, we used potassium salt **4b**, which was obtained by the treatment of compound **4** with K_2CO_3 in EtOH.

We showed that salt **1a** can be nitrated with nitronium tetrafluoroborate (NTFB) to afford *N,N*-dinitrourethane (**5**), and the latter can be transformed into ammonium dinitramide (ADNA) under the action of NH_3 (Scheme 2).

Scheme 2



$$\overset{+}{N}H_4\overset{-}{N}(NO_2)CO_2Et \xrightarrow{\overset{+}{N}O_2\overset{-}{B}F_4} (O_2N)_2NCO_2Et \xrightarrow{NH_3}$$

5

$$\longrightarrow \overset{+}{N}H_4\overset{-}{N}(NO_2)_2 + H_2NCO_2Et$$

It was found that the yield of ADNA depends critically on the reaction conditions for both steps. This is not surprising if one takes into account that the nitrourethane anion has three centers for electrophilic attack (amide nitrogen atom and oxygen atoms of the nitro group), and compound **5** has three centers for nucleophilic attack (carbonyl group and nitro groups). Thus, DNA salts can be formed only if the nitrogen atom is nitrated at the first step and the alkoxycarbonyl group is subjected to nucleophilic attack at the second step. It should be noted that the product of the first step, compound **5**, is very unstable and decomposes at a temperature higher than 0 °C, which precludes its isolation in the individual state. However, the formation of the product **5** was confirmed not only by its transformation into DNA salts, but also by studies of the IR spectra of solutions that contained the absorption bands of the alkoxycarbonyl group at 1800 cm^{-1} and the nitro group at 1670 cm^{-1}. The yield of the product **5** was deter-

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* For Part 9, see *Izv. Akad. Nauk, Ser. Khim.*, 1996, 451 [*Russ. Chem. Bull.*, 1996, **45**, 433 (Engl. Transl.)].

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Table 1. Effect of conditions of nitration of nitrourethane salts with an equimolar amount of nitronium tetrafluoroborate (NTFB) on the yield of ADNA

Nitrourethane salt	Amount of MeCN /mL per g of salt	Reaction temperature /°C	Reaction time /min	Yield of ADNA (%)*
$NH_4N(NO_2)CO_2Et$ (**1a**)	7.5	−40	20	56
	7.5	−40	25	74
	7.5	−40	40	57
	35	−35	30	56
	35	−35	35	59
	35	−35	40	63
	35	−35	60	51
	15	−20	35	53
	10	−5	10	40
	10	−5	12.5	65
	10	−5	15	58
	10	−5	17.5	40
	10	−5	20	38
	20	−5	25	10
$NH_4N(NO_2)CO_2Me$ (**2a**)	10	−40	25	66
$NH_4N(NO_2)CO_2Pr$ (**3a**)	10	−40	25	68
$KN(NO_2)CO_2Bu$ (**4b**)	10	−40	25	63

* Reaction mass was diluted with four volumes (for **1a**) or three volumes (for **2a**, **3a**, and **4b**) of ether before NH_3 was added.

Table 2. Effect of solvent on the yield of ADNA in the nitration of **1a** with NTFB

Solvent	Amount of solvent /mL per g of **1a**	Reaction temperature /°C	Reaction time /min	Yield of ADNA (%)
EtOAc	25	0	25	30
EtOAc	20	−25	60	31
EtOAc/MeCN (2.5 : 1.5)	25	−43	40	53
EtOAc/MeCN (4 : 15)	25	−45	60	53
EtOAc/MeCN (4 : 15)	25	−45	90	50
MeCN	30	−40	40	64

mined from the amount of ADNA formed from **5** upon treatment with liquid NH_3 in ether or toluene at −40 °C. The content of ADNA in the reaction mixture was measured by UV spectroscopy. In this way we have studied the dependence of the yield of the product **5** on temperature, reaction time, type of solvent used for nitration, method of mixing the reagents, reagent ratio, and the character and quality of nitronium salt. Some of these results are given in Tables 1 and 2.

Temperature and reaction time have a rather strong effect on the yield of ADNA, each temperature corresponding to its own optimal time (see Table 1). The maximum yields can be obtained if the nitration is carried out at −35 to −45 °C, but a sufficiently high yield (> 60 %) can also be achieved at −5 °C. MeCN and AcOEt, which have been successfully used previously for the nitration of alkylnitramines, were used as solvents. MeCN is more preferable (see Table 2).

The nitration of salt **1a** under the action of NTFB proceeds rather vigorously, but the order of mixing the reagents has practically no effect on the yield of ADNA. With the use of a small excess of NTFB (~10 %) it was possible to increase somewhat the yield of ADNA, which may be accounted for by the partial hydrolysis of NTFB used. In fact, preliminary heating of NTFB *in vacuo* for 4—5 h at 80 °C results in an increase in the yield of ADNA by 10—15 %. The decrease in the yield of ADNA, caused by the presence of the products of hydrolysis (inorganic acids) in NTFB, may be explained by the fact that the action of the acids on salt **1a** leads to the liberation of free *N*-nitrourethane **1**. Even under optimal conditions (2—5 min at 40 °C), compound **1** can be transformed into ADNA under the action of NTFB at most in ~24—26 % yield (Scheme 3).

Scheme 3

$$\mathbf{1} \xrightarrow{\overset{+}{N}O_2\overset{-}{B}F_4} \mathbf{5} \xrightarrow{NH_3} \overset{+}{N}H_4\overset{-}{N}(NO_2)_2$$

For this reason, the yield of ADNA does not exceed 10 % on the direct nitration of urethane with two moles of NTFB followed by the treatment with NH_3 (Scheme 4).

Scheme 4

$$H_2NCO_2Et \xrightarrow[2.\ NH_3]{1.\ NO_2BF_4} \overset{+}{N}H_4\overset{-}{N}(NO_2)_2$$

We failed to carry out nitration of compound **1** with nitronium salts that are more accessible than NTFB, *e.g.*, acid nitronium pyrosulfate (ANP) or neutral nitronium pyrosulfate (NNP). However, NNP and ANP are suitable for the nitration of salt **1a**, but in this case the yield of ADNA is substantially lower than in the case of NTFB (Scheme 5).

Scheme 5

$$\mathbf{1a} \xrightarrow[2.\ NH_3]{1.\ (NO_2)_2S_2O_7/(NO_2)S_2O_7H} \overset{+}{N}H_4\overset{-}{N}(NO_2)_2$$

The studies of dealkoxycarbonylation of *N,N*-dinitrourethane **5** under the action of different nucleophiles (NH_3, H_2O, EtOH, KI, as well as 5 % solutions of KOH in H_2O and CsOH in EtOH) showed that the highest yields of ADNA (75—85 % with respect to the starting urethane **1**) are achieved in the case of NH_3.

KI gives a satisfactory yield (~50 %) (Scheme 6).

Scheme 6

$$\mathbf{5} \xrightarrow{KI} KN(NO_2)_2$$

When solutions of KOH in H_2O and CsOH in EtOH are used, the corresponding yields of DNA salts are 2 and 4 times lower than in the case of NH_3. The only process that occurs upon the action of H_2O and EtOH is the denitration of dinitrourethane **5** into urethane **1**.

The direction of the transformation of dinitrourethane **5** under the action of NH_3 depends significantly on the type of solvent (Table 3). The worse results are obtained when the reaction is carried out directly in MeCN, which has been used for the nitration. The best results are obtained when the reaction mixtures are diluted with two or four volumes of ether, toluene, or ethyl acetate. In this case, the yield of ADNA is increased 2.5—3-fold.

The rate of NH_3 addition, its aggregation state, and the amount are also of great importance (Table 4). The optimal conditions are the rapid addition of ~3.5 moles of liquid NH_3 per mole of salt **1a** in one portion at low temperature.

When the same amount of gaseous NH_3 is added over a prolonged period, the yield of ADNA is decreased several times. When dinitrourethane **5** reacts with NH_3 according to the Scheme 2, urethane is formed along with ADNA in the same yield, and salt **1a** is formed in ~15 % yield. The latter is not the product of the denitration of dinitrourethane **5** with NH_3. This is proved by studying the nitration of nitrourethane **1a**-^{15}N followed by the decomposition of dinitrourethane **5**-^{15}N formed under the action of NH_3. According to the mass-spectral data, the percentage of ^{15}N in the salt **1** formed in this case is equal to that in the original nitrourethane salt. Thus, the nucleophilic attack of NH_3

Table 3. Effect of a co-solvent on the yield of ADNA in the reaction of **5** with NH_3

Amount of MeCN /mL per g of **1a**	Reaction time /min	Co-solvent	Content of ADNA in a crude product (%)	Yield of ADNA (%)
7.5	25	Et_2O	71	75.3
7.5	25	PhMe	77.4	73.8
7.5	25	EtOAc	60.3	71.5
15	40	Hexane	37	60
15	40	CH_2Cl_2	65.5	52.3
15	40	EtOAc	60	64.4
15	40	MeCN	30	26
10	25	PhMe	84	76.5
10	25	EtOAc	49	81.5

Table 4. Effect of amount and method of addition of NH_3 on the yield of ADNA in the ammonolysis of **5**

Amount of MeCN /mL per g of **1a**	Reaction temperature/°C	Reaction time /min	Amount of liquid NH_3 /mL per g of **1a**	Method of addition NH_3	Yield of ADNA (%)
15	−35	40	1	l*	63
15	−20	40	1.5	g**	15
15	−20	40	1.5	l	43
10	−40	25	0.6	l	76.5

* In liquid form. ** In gaseous form.

occurs only at the C atom of alkoxycarbonyl group, and a small amount of salt **1a** is formed probably from dinitrourethane **5** as a result of its hydrolysis by the atmosphere moisture and/or simply from nitrourethane formed on the acidification of salt **1a** with the products of NTFB hydrolysis.

We showed that, similarly to nitrourethane salts, *N,N*-dinitro derivatives can also be synthesized from ammonium salt (**6a**) of *N*-nitrobenzamide (**6**) under the action of NTFB (Scheme 7). Dinitramide **7** is even less stable than dinitrourethane **5**, and this is probably the reason why ADNA can be obtained in satisfactory yield (44 %), according to the Scheme 7, only at temperatures not higher than −65 °C.

Scheme 7

$$\underset{\textbf{6a}}{\text{PhCO}\overset{-}{\text{N}}(\text{NO}_2)\overset{+}{\text{N}}\text{H}_4} \xrightarrow{\text{NO}_2\text{BF}_4} \underset{\textbf{7}}{\text{PhCON(NO}_2)_2} \xrightarrow{\text{NH}_3}$$

$$\longrightarrow \overset{+}{\text{N}}\text{H}_4\overset{-}{\text{N}}(\text{NO}_2)_2$$

At higher temperatures, the main product (the yield is 68 %) is benzamide (Scheme 8).

Scheme 8

$$\textbf{6a} \xrightarrow{\text{NO}_2\text{BF}_4} \textbf{7} \xrightarrow[-\text{N}_2\text{O}]{} \text{PhCOONO}_2 \xrightarrow{\text{NH}_3}$$

$$\longrightarrow \text{PhCONH}_2$$

Positive results are also obtained in the nitration of ammonium salt (**8a**) of *N*-nitro-*p*-toluenesulfamide (**8**) with the formation of dinitro derivative (**9**) followed by ammonolysis to give ADNA (the yield is 55 %) (Scheme 9).

Scheme 9

$$\underset{\textbf{8a}}{\overset{+}{\text{N}}\text{H}_4\overset{-}{\text{N}}(\text{NO}_2)\text{Ts}} \xrightarrow{\text{NO}_2\text{BF}_4} \underset{\textbf{9}}{(\text{O}_2\text{N})_2\text{NTs}} \xrightarrow{\text{NH}_3}$$

$$\longrightarrow \overset{+}{\text{N}}\text{H}_4\overset{-}{\text{N}}(\text{NO}_2)_2$$

In this case, the nitration and ammonolysis should be carried out at even lower temperatures (< −75 °C).

Our attempts to carry out similar transformations with potassium salts of *N*-nitrocyanamide, *N*-nitrourea, and dipotassium salt of *N*-nitrocarbamine acids were unsuccessful.

Experimental

^{1}H NMR spectra were recorded on a Perkin Elmer R-12 instrument (60 MHz), IR spectra were obtained on a UR-10 spectrometer, and UV spectra were obtained on a Unicam SP-800 spectrophotometer.

Ammonium salt of ethyl *N*-nitrocarbamate (1a). Powdered KNO_3 (8.55 g) and ethyl carbamate (5 g) were gradually added to 98 % H_2SO_4 (15 mL) at a temperature below 25 °C with stirring. The mixture was kept at 25 °C for 15 min, poured onto crushed ice (60 g), and then extracted with CH_2Cl_2 (7×225 mL). The extracts were dried with $MgSO_4$. Then dry NH_3 was passed through the solution under cooling. The precipitate formed was filtered off to give product **1a** in 89—92 % yield, m.p. 164—165 °C.

Ammonium salt of methyl *N*-nitrocarbamate (2a). Methyl carbamate (4.22 g) was gradually added at 25 °C to a mixture of 98 % H_2SO_4 (15 mL) and KNO_3 (8.55 g). The mixture was stirred for 15 min, poured onto crushed ice (60 g), and extracted with ether (7×25 mL). The extract was dried with $MgSO_4$ and ether was distilled off to afford 5.4 g (86 %) of nitrourethane **2**, m.p. 85—87 °C. NH_3 was passed through a solution of **2** (5 g) in ether (100 mL). The precipitate formed was filtered off to give 5.7 g of product **2a**, m.p. 129—131 °C. Found (%): N, 30.34. $C_2H_7N_3O_4$. Calculated (%): N, 30.32.

The ammonium salt of propyl *N*-nitrocarbamate (3a) was obtained from propyl carbamate similarly to compound **2a**. $CHCl_3$ was used for the extraction of urethane **3**. The yield of product **3a** was 89 %, m.p. 113—114 °C. Found (%): N, 25.09. $C_4H_{11}N_3O_4$. Calculated (%): N, 25.22.

Potassium salt of butyl *N*-nitrocarbamate (4b). Nitrourethane **4** in 85 % yield was obtained by nitration of butyl carbamate similarly to compound **3**. K_2CO_3 (2.8 g) was added with stirring to a solution of compound **4** (7 g) in EtOH (70 mL). After the salt was dissolved, the mixture was concentrated to a small volume. The residue was filtered off and crystallized to give 7.1 g of product **4b**, m.p. 132—134 °C. Found (%): N, 14.43. $C_5H_9N_2O_4K$. Calculated (%): N, 14.00.

Synthesis of ammonium dinitramide (ADNA). ***A.*** NTFB (2 g) was added to a suspension of salt **1a** (2 g) in abs. MeCN (20 mL) with vigorous stirring at −40 to −45 °C. The mixture was stirred for 40 min at this temperature, then abs. toluene (60 mL) and liquid anhydrous NH_3 (1.2 mL) were added. The temperature of the mixture was raised to ~20 °C, the precipitate was filtered off and washed with EtOAc (5×10 mL), and the filtrates were evaporated. The crystalline mass obtained was washed with ether (5×10 mL) to afford 1.5 g of the product containing 84.2 % of ADNA (the yield of ADNA was 76.5 %). When the same amount of abs. ether was added instead of toluene, 2.02 g of the product containing 68.5 % of ADNA was obtained (the yield of ADNA was 84.2 %).

B. NNP (0.9 g) was added to a suspension of salt **1a** (1 g) in abs. MeCN (15 mL) at −35 °C with stirring. The mixture was stirred at −30 to −35 °C for 40 min, then liquid anhydrous NH_3 (1.5 mL) was added. The mixture was treated as described above to give 0.39 g of the product containing 77 % of ADNA (the yield of ADNA was 36.6 %).

C. Nitration of salt **1a** (1.71 g) in abs. MeCN (40 mL) at −30 °C under the action of ANP (2.54 g) for 40 min afforded 0.46 g of an oily product containing 43 % of ADNA (the yield of ADNA was 13.8 %).

Reaction of dinitrourethane 5 with KI. Salt **1a** (1 g) was nitrated with NTFB for 40 min at −40 °C as described above.

The precipitate was filtered off and abs. acetone (20 mL) and ground KI (1.1 g) were added to the filtrate. The mixture was stirred for 20 min at −40 °C and 1 h at 0 °C. The precipitate was separated. The filtrate was concentrated, EtOH (10 mL) was added to the residue, and the undissolved residue was filtered off. From the filtrate, 0.63 g of the product was obtained containing 74 % of potassium ADNA (the yield of potassium ADNA was 48.5 %).

Synthesis of ADNA by nitration of salt 6a. NFTB (0.37 g) was added to a suspension of compound **6a** (0.5 g) in abs. MeCN (10 mL) and abs. EtOAc (10 mL) at −65 °C with stirring. The mixture was stirred for 1 h at −65 °C, the residue containing 0.1 g of **6a** was separated, and liquid NH_3 (0.3 mL) was added to the filtrate. The precipitate formed was separated again, and the filtrate was evaporated to afford 0.2 g of the product containing 61 % of ADNA (the yield of ADNA was 44 %).

Synthesis of ADNA by nitration of salt 8a. NFTB (0.56 g) was added to a suspension of compound **8a** (1 g) in abs. MeCN (15 mL) and abs. EtOAc (15 mL) at −65 °C with stirring. The mixture was stirred for 4.5 h at −70 to −75 °C. The residue was separated (0.6 g of compound **8a** was isolated from the residue by TLC on Silufol in acetone). Liquid NH_3 (0.5 mL) was added to the filtrate at −75 °C, the residue was filtered off, and the filtrate was evaporated to give 0.12 g of the product containing 97.5 % of ADNA (the yield of ADNA was 55 %).

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