Dinitramide and its salts*
1. Synthesis of dinitramide salts by decyanoethylation of *N,N*-dinitro-β-aminopropionitrile

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A strategy of organic synthesis has been developed for a new class of inorganic compounds, *viz.*, dinitramide and its metal, ammonium, and substituted ammonium salts. The basic concepts have been tested in model reactions of β-substituted derivatives of *N*-alkyl-*N*-nitrotoluenesulfonamides with bases and have been confirmed by the decyanoethylation of *N,N*-dinitro-β-aminopropionitrile taken as an example.

Key words: dinitramide, dinitramide salts, nitrosulfamides, decyanoethylation, retro-Michael reaction, methylation.

The synthesis of novel oxidizers for composite solid missile fuels and explosive compositions which are superior to the known compositions in efficiency and have an acceptable combination of properties is likely to be one of the more complex problems in the synthesis of large energy compounds. Since the 50's, investigators have searched intensely for organic oxidizers mainly among polynitro derivatives usually containing several nitro groups at the carbon atoms. However, despite impressive achievements in the synthesis of various polynitro compounds, it has not been possible to obtain structures possessing the desired combination of properties, primarily, satisfactory thermal and chemical stability.

It may be assumed that there are two main sources of instability of the majority of compounds having several nitro groups at one central atom: first, the easy abstraction of the nitronium cation, which is favored by the low energy of the anion formed; second, the possibility of nucleophilic attack at the central atom with replacement of one of the nitro groups.

We analyzed the possible variants for the creation of novel oxidizers and reached the conclusion that the above sources of instability of *gem*-polynitro moieties should not manifest themselves if these moieties are included in an anion system. In fact, the attack of a nucleophile at an anion is rather unlikely, and the abstraction of the nitronium cation is unlikely at all since it would result in the respective dianion which is extremely energetically unfavorable.

Among systems of this type, the $^{-}C(NO_2)_3$ and $^{-}N(NO_2)_2$ anions are of the most interest. Trinitromethane salts are well known, but, unfortunately, they are insufficiently stable even at room temperature. As for the salts based on dinitramide (DNA), no approaches to obtaining this anion had been reported in the literature by 1971, *i.e.*, when we elaborated the method for their synthesis. To our knowledge, even the cardinal question of the possibility of their existence had not been discussed (naturally, the same holds for DNA itself).

There existed strong reasons to consider that DNA, like primary nitramines and many primary nitramides, would be unstable in strongly acid media. DNA itself had to be one of the strongest acids, which implied that DNA would also be unstable in the individual form. This made it suitable to form the DNA anion in an alkaline medium. Therefore, the first approach to synthesizing DNA salts was based on the reaction of *N,N*-dinitramines with bases.

It was reasonable to expect that if an anionic center is created in the part of the molecule containing the $(NO_2)_2N—R$ moiety, then one of the probable means of stabilizing such a molecule would involve the abstraction of a DNA anion characterized by low energy of formation due to charge delocalization. Among other objects selected for this study, we chose compounds of the $(NO_2)_2NCH_2CH_2X$ type (**1**), where X are electron-withdrawing groups activating the α-hydrogen atoms to nucleophilic attack and thus facilitating the creation of an anionic center in the β-position to the dinitramine moiety. However, there existed some reasons to assume that the type **1** have at least one more center for nucleophilic attack, *viz.*, the N atom of one of the nitro

* In the communications of this series, we are going to report the results of work on dinitramide carried out in 1970—1980 that could not be published previously. The synthesis of dinitramide salts was first published in the patent literature in 1992.[1,2]

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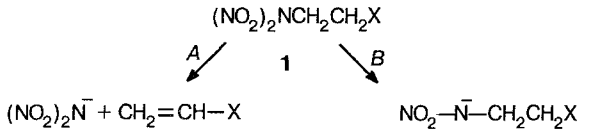
groups, since, as was shown previously,[3] *N*-alkyl-*N*,*N*-dinitramines abstract one nitro group when treated with nucleophilic compounds.

Thus, the reaction of the type **1** compounds with bases could result either in DNA (pathway *A*) or in primary nitramines (pathway *B*) (Scheme 1).

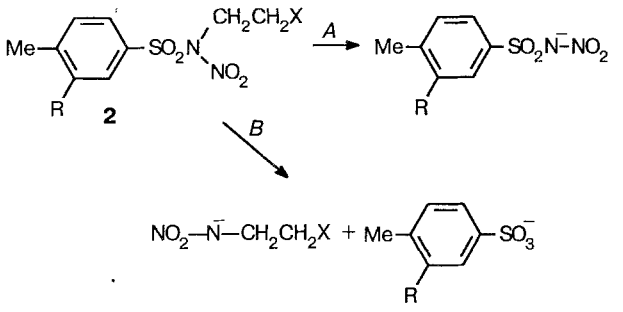
Scheme 1



Evidently, the direction of this reaction can be controlled by selecting the substituent X. It follows from general considerations that the substituents facilitating pathway *A* should form the series: NO_2 > CHO, COR > COOR > CN.

Since the type **1** compounds were not described in the literature and could be expected to be dangerous in handling, we decided first to test the validity of the above considerations in a model reaction involving the more available type **2** compounds (Scheme 2).

Scheme 2



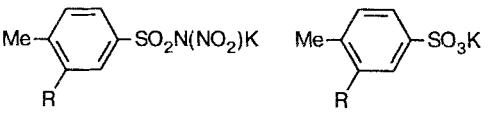
Obviously, nitrosulfamides **2** can also react with bases by pathways *A* or *B*. Since the electronic effects of the nitro group and the sulfonyl group are rather similar, it can be considered as the first approximation that the electrophilicity of the protons in compounds **1** is equal to that in **2**.

Hence, to compare the reactions of compounds **1** and **2** with bases, the difference in the electrophilicity of the nitrogen atom in compounds **1** and that of the sulfur atom in **2** had to be taken into account first of all. Therefore, competitive reactions with KOH in methanol were studied in order to determine the relative activity of analogs of compounds **1** and **2**, *viz.*, methyldinitramine and *N*-methyl-*N*-nitro-*p*-toluenesulfamide. It was shown that the latter compound is much more electrophilic than the former.

The results of the reaction of compound **2*** with bases are presented in Table 1.

* Compound **2a** (R = NO_2, X = CN) was synthesized by tosylation of β-aminopropionitrile followed by nitration. The preparation of compounds **2** (X = CHO, $COCH_3$, or CN) will be described in a subsequent communication.

Table 1. Reactions of *N*-nitro-*N*-(β-X-ethyl)-3-R-*p*-toluenesulfonamides with KOH in methanol



L **M**

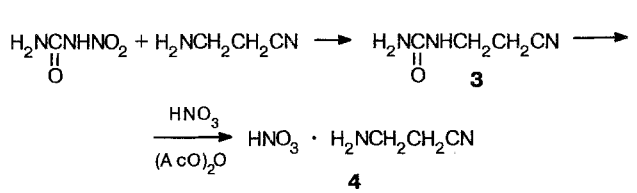
Run	X	R	Yield (%)	
			L	**M**
1	COMe	H	93	—
2	COMe	NO_2	73	—
3	CHO	NO_2	43	32
4	CN	NO_2	6	82

As is evident from Table 1, the nature of the substituent X very strongly affects the direction of the reaction of nitrosulfamides **2** with bases. For example, the reaction with X = $COCH_3$ occurs almost completely by route *A*, but the opposite picture is observed with X = CN: the yield of the compound formed by route *A* is as low as 6 %. However, the electrophilicity of the nitrogen atom of the nitro group in compound **1** is much lower than that of the sulfur atom in compound **2**, and the DNA anion should be a more efficient leaving group than the nitrosulfamide anion. Hence, there was every reason to assume that compounds **1** even with X = CN would mainly react by route *A* to give the target dinitramide salts. Thus, the results obtained showed that treatment of compounds **1** with bases should result in DNA salts.

Taking into account that strong electrophilic and nucleophilic reagents were to be used in the schemes chosen by us for the synthesis of DNA, we decided it would be appropriate to start the work with compound **1** having X = CN (**1a**) as an example since, among the aforementioned groups, the nitrile group is the most inert to the above reagents.

Initially, we intended to synthesize compound **1a** by nitration of β-cyanoethylurea **3** prepared by treatment of β-aminopropionitrile with nitrourea. However, the reaction resulted in a nitric acid salt of β-aminopropionitrile (**4**) (Scheme 3).

Scheme 3



Therefore, a different method for synthesizing compound **1a** was elaborated.* Dinitramine **1a** is a yellow oil. It was not additionally purified due to insufficient stability, but its structure was confirmed by IR and ^{1}H NMR spectral data. The IR spectrum contains bands of the dinitramine moiety (ν 1645, 1610, 1245, and 850 cm^{-1}) and the nitrile group (ν 2260 cm^{-1}), and the ^{1}H NMR spectrum contains two triplets of the methylene groups at δ 4.55 and 2.95.

Treatment of compound **1a** with potassium hydroxide in ethanol results in DNA potassium salt (K-DNA):

$$(O_2N)_2NCH_2CH_2CN + KOH \rightarrow KN(NO_2)_2 + CH_2{=}CH{-}CN,$$

K-DNA is a white, non-hygroscopic, quite stable powder, m.p. 129—131 °C. The salt is easily soluble in water, satisfactorily soluble in the lowest alcohols, poorly soluble in polar solvents containing no hydroxyls, and insoluble in nonpolar solvents, such as ether, benzene, hexane, halohydrocarbons, *etc.* In the pure form, K-DNA is not sensitive to impact or friction.

The structure of K-DNA was confirmed by the following transformations:

$$KN(NO_2)_2 \xrightarrow[-KNO_3]{AgNO_3} AgN(NO_2)_2 \xrightarrow{MeI} \underset{\mathbf{5}}{MeN(NO_2)_2}$$

Methylnitramine **5** obtained in this way proved to be identical with an authentic sample.[4]

The cesium or rubidium salts of DNA are obtained similarly to K-DNA from dinitramine **1a** and cesium or rubidium hydroxides. Their melting points are 85—88 °C and 102—106 °C, respectively. Like K-DNA, they are not sensitive to impact.

Salts of DNA with nitrogen-containing bases can also be obtained in a similar way. For example, the ammonium salt of DNA (ADNA), which is of practical importance, was synthesized by treatment of compound **1a** with ammonia:

$$\mathbf{1a} \xrightarrow{NH_3} NH_4N(NO_2)_2 .$$

ADNA is a crystalline, somewhat hygroscopic compound sensitive to mechanical effects, m.p. 93—98 °C.

Thus, the treatment of *N,N*-dinitro-β-aminopropionitrile with bases is the general method for obtaining DNA salts. DNA forms quite stable salts not only with inorganic but also with organic bases. In particular, the guanidine (m.p. 135—139 °C (dec.)) and double ethylenediamine salts of DNA can be obtained by reactions of the free bases with DNA solutions. To prepare the latter, suspensions of DNA salts in inert solvents (absolute ether, benzene, or methylene dichloride) were treated with a great excess of dry HCl, the precipitate was isolated, and the solvent together with the excess HCl were distilled off *in vacuo* at −5÷+10 °C:

$$MN(NO_2)_2 + HCl \rightarrow HN(NO_2)_2 + MCl.$$

In all cases, DNA appeared as a colorless or slightly yellowish mobile liquid, which decomposed with spontaneous heating after several minutes to give initially colorless and then brown nitrogen oxides. Sometimes, the decomposition led to an explosion. On the other hand, if DNA obtained by the above procedure was immediately dissolved, *e.g.*, in water or in ether, fairly stable DNA solutions formed.

Experimental

^{1}H NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer (60 MHz). IR spectra were obtained on a UR-10 spectrophotometer (without a solvent in the case of liquid compounds, or in KBr pellets for solid compounds).

***N*-Nitro-*N*-(β-cyanoethyl)-*m*-nitro-*p*-toluenesulfonamide (2a).** *p*-Toluenesulfonyl chloride (16.47 g) was added at 20—40 °C to a solution of β-aminopropionitrile (5.5 g) and pyridine (6.85 g) in benzene (25 mL). The reaction mixture was refluxed for 1 h and cooled. Benzene (25 mL) was added. The mixture was poured into water, and the organic layer was washed with water, 5 % HCl, and once more with water to give 10.1 g (57.3 %) of *N*-(β-cyanoethyl)-*p*-toluenesulfonamide, m.p. 80—83 °C. Evaporation of benzene gave an additional amount (2.73 g) of the compound, overall yield 73.8 %. Found (%): S, 14.27. $C_{10}H_{12}N_2O_2S$. Calculated (%): S, 14.30.

N-(β-Cyanethyl)-*p*-toluenesulfonamide (2 g) was added in small portions at 0 °C to conc. HNO_3 (30 mL). The mixture was stirred for 10 min at 0 °C and for 1 h at 20 °C and then poured onto ice to give 2.52 g (90 %) of compound **2a** , m.p. 108—110 °C (from benzene). Found (%): C, 38.32; H, 3.50; S, 10.18. $C_{10}H_{10}N_4O_6S$. Calculated (%): C, 38.20; H, 3.21; S, 10.20.

Reaction of nitrosulfamides 2 with KOH. a. KOH (0.4 g) was added at 25 °C to a suspension of *N*-nitro-*N*-(3-oxobutyl)-*m*-nitro-*p*-toluenesulfamide (1 g) in methanol (20 mL). The mixture was stirred for 5 h, and 0.66 g (65 %) of the K salt of *N*-nitro-*m*-nitro-*p*-toluenesulfamide was isolated by filtration, m.p. 220—225 °C (from water). An additional amount (0.08 g, 8 %) of the salt was isolated from the mother liquor. The compound was identified by comparing it with an authentic sample.

b. KOH (0.22 g) was added to a suspension of *N*-nitro-*N*-(3-oxopropyl)-*m*-nitro-*p*-toluenesulfamide (0.54 g) in methanol (11 mL). The mixture was stirred for 7 h, the alcohol was evaporated, and the residue was washed with ether to give 0.38 g of a mixture of the potassium salts of *N*-nitro-*m*-nitro-*p*-toluenesulfamide and *m*-nitro-*p*-toluenesulfonic acid (identified on the basis of IR and ^{1}H NMR spectra). The suspension of the salts obtained in ether was saturated with dry HCl, the precipitate (0.15 g) was separated, and the ether was removed to give 0.19 g of *N*-nitro-*m*-nitro-*p*-toluenesulfamide, m.p. 115—116 °C (dec.). The yield of nitrosulfamide potassium salt was 43 %, and that of potassium sulfonate was 32 %.

* The method for synthesizing compound **1a** will be described later.

c. KOH (2.2 g) was added to a suspension of compound **2a** (5.88 g) in methanol (120 mL). The mixture was stirred for 3 h, and 3.89 g (81.52 %) of potassium *m*-nitro-*p*-toluenesulfonate was filtered off, m.p. 343 °C (dec.). The filtrate was concentrated, and the residue was dissolved in a minimum amount of water, acidified, and extracted with ether. The ether was dried and distilled off, and the residue was dissolved in methanol (5 mL) and treated with KOH (0.68 g) to give 0.35 g (5.7 %) of the potassium salt of *N*-nitro-*m*-nitro-*p*-toluenesulfamide.

Reaction of KOH with a mixture of methyldinitramine and *N*-methyl-*N*-nitro-*m*-nitro-*p*-toluenesulfamide. KOH (0.35 g, 0.007 mol) in methanol (3 mL) was added at 20 °C to a solution of methyldinitramine (0.63 g, 0.005 mol) and *N*-methyl-*N*-nitro-*m*-nitro-*p*-toluenesulfamide (0.95 g, 0.00345 mol). The mixture was stirred for 4 h, and 0.75 g (85 %) of potassium *m*-nitro-*p*-toluenesulfonate was isolated by filtration, m.p. 344 °C (dec.).

***N*-β-Cyanoethylurea (3).** A solution of β-aminopropionitrile (1 g) and nitrourea (1.28 g) in ethanol (100 mL) was refluxed for 6 h, and then the ethanol was distilled off to give 1.38 g (85 %) of compound **3**, m.p. 107—110 °C (from ethanol). Found (%): C, 42.47; H, 6.15; N, 36.55. $C_4H_7N_3O$. Calculated (%): C, 42.47; H, 6.24; N, 37.15.

Nitrate of β-aminopropionitrile (4). Ac_2O (25.8 mL) was added dropwise at 0—5 °C to conc. HNO_3 free from nitrogen oxides (22.3 g). The mixture was stirred for 15 min and cooled to −5 °C. Then compound **3** (8.2 g) was added in small portions (intense evolution of gaseous products). The mixture was stirred for 30 min at −5÷0 °C, and compound **4** (4.83 g, 50.5 %) was isolated by filtration, m.p. 119—121 °C. Found (%): N, 31.64. $C_3H_6N_2 \cdot HNO_3$. Calculated (%): N, 31.57.

Potassium salt of DNA (K-DNA). KOH (7.45 g) was added at 0÷5 °C to a vigorously stirred solution of compound **1a** (17.28 g) in ethanol (100 mL). The mixture was stirred for 30 min at 20 °C and cooled to ~0 °C. K-DNA (11.72 g, 74.8 %) was isolated by filtration, m.p. 124—126 °C. Recrystallization from ethanol gave 9.46 g of the salt, m.p. 127—131 °C. Found (%): K, 26.59; N, 28.58. KN_3O_4. Calculated (%): K, 26.94; N, 28.90.

Cesium salt of DNA. Cesium hydroxide (0.75 g) in a minimum amount of ethanol was added dropwise at 0 °C to a solution of compound **1a** (0.8 g) in ethanol (25 mL). The mixture was stirred for 1 h at 0 °C, and then 0.97 g (82.3 %) of the salt was isolated by filtration, m.p. 70—76 °C (after recrystallization from ethanol, m.p. 85—88 °C). Found (%): N, 17.57. CsN_3O_4. Calculated (%): N, 17.57.

Rubidium salt of DNA was obtained similarly to the cesium salt from compound **1a** and rubidium hydroxide. The yield of Rb-DNA was 67 %, m.p. 101—106 °C. After recrystallization from methanol, m.p. 102—106 °C. Found (%): N, 21.88. RbN_3O_4. Calculated (%): N, 21.90.

Ammonium salt of DNA (ADNA).* Dry NH_3 was passed for 30 min at 8—10 °C through a solution of compound **1a** (12.22 g) in abs. dioxane (50 mL). Then the system was purged with dry nitrogen until NH_3 was completely removed. The resulting precipitate of ADNA was isolated by filtration and washed with an abs. dioxane — ethyl acetate mixture (10 : 1) and ether to give 6.11 g (65 %) of ADNA, m.p. 86—92 °C (after recrystallization from a dioxane — ethyl acetate mixture (5 : 1), m.p. 89—94 °C). Found (%): H, 3.54; N, 45.28. $H_4N_4O_4$. Calculated (%): H, 3.25; N, 45.16.

Ethylenediammonium salt of DNA was obtained by treatment of an ethereal solution of DNA with a solution of ethylenediamine, m.p. 123—126 °C (from ethanol). Found (%): N, 40.81. $C_2H_8N_2 \cdot 2HN_3O_4$. Calculated (%): N, 40.80.

Transformation of K-DNA to methyldinitramine. Equimolar amounts of saturated solutions of silver nitrate and K-DNA in CH_3CN were mixed. The resulting precipitate was removed, the filtrate was concentrated to ~1/3 of the original volume, and KNO_3 was removed once more. The filtrate was diluted with a small amount of CH_3CN, and CH_3I was added. Distillation afforded methyldinitramine, yield 50 %, b.p. 39 °C (16 Torr), n_D^{20} 1.4471).[4]

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* A. A. Onishchenko and O. S. Reshetova (Institute of Organic Chemistry of the RAS) took part in the development of the procedure.

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