

Dedicated to Full Member of the Russian Academy of Sciences
V.A. Tartakovskii on the 70th Anniversary of His Birth

Chemistry of Urea Nitro Derivatives: IV.* Reaction of *N,N'*-Dinitrourea with Formaldehyde

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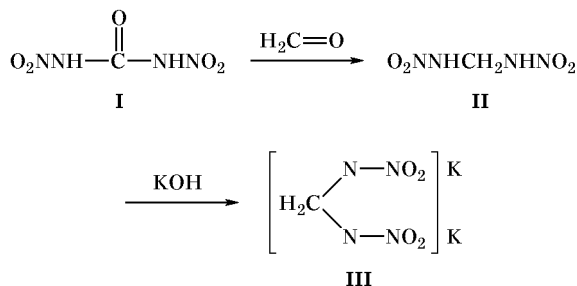
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Abstract—Reaction of *N,N'*-dinitrourea with formaldehyde, depending on the conditions, leads to formation of various hydroxymethyl derivatives of *N*-nitroamines and products of their further transformations.

We previously reported on the synthesis of symmetric dinitrourea and its transformations into nitramide and various *N*-nitro amines and *N*-nitro amides [1–3]. Nitroamino groups in the molecule of dinitrourea can be classed with primary ones, for which the reaction with formaldehyde is typical [4].

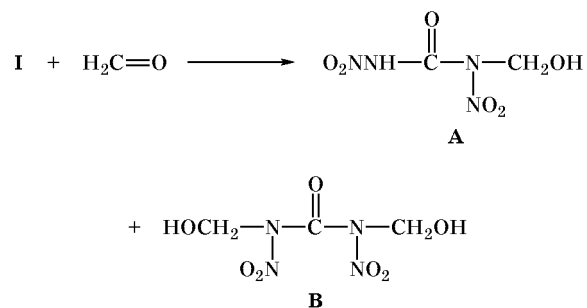
The condensation of *N,N'*-dinitrourea (**I**) with formaldehyde at a molar ratio of 1:1 in aqueous medium in the presence of sulfuric acid at 20–80°C gives an oily substance whose IR spectrum suggests the presence of CH₂, OH, NH, and NNO₂ groups. Its UV spectrum contains an absorption band with λ_{max} 226–228 nm, which is characteristic of the expected product, *N,N'*-dinitromethylenediamine (λ_{max} 226 nm [5]). Treatment of this product with KOH yields dipotassium salt **III**. Spectrophotometric monitoring of the reaction course showed that the yield of *N,N'*-dinitromethylenediamine (**II**) ranges from 4 to 89%, depending on the temperature and reaction time. The yield of salt **III** is 45%.



The condensation is accompanied by heat evolution, and the mixture spontaneously warms up from 20 to 80°C; under uncontrolled conditions, the mixture may warm up to 110–120°C, resulting in decomposition.

Salt **III** is converted into *N,N'*-dinitromethylenediamine (**II**) in high yield by the action of gaseous hydrogen chloride in diethyl ether.

The reaction of *N,N'*-dinitrourea (**I**) with 2 equiv of formaldehyde gives different products, depending on the conditions. When the reaction was carried out at 0°C, extraction from the aqueous phase afforded a transparent oily substance with $n_{\text{D}}^{20} = 1.4980$. Its IR spectrum contained no carbonyl absorption band, but those belonging to nitroamino, hydroxymethyl, and NH groups were present (3310, 1580 cm⁻¹). Presumably, this product is a mixture of hydroxymethyl derivatives of nitramide, which are formed as a result of hydrolysis of primary condensation products, *N*-hydroxymethyl- and *N,N'*-bis(hydroxymethyl)-*N,N'*-dinitroureas **A** and **B**. We failed to isolate compounds **A** and **B** in the pure state. They decompose



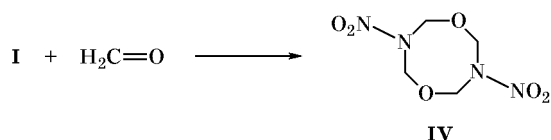
* For communication III, see [1].

Table 1. Yields of 1,3,5-trinitrohexahydro-1,3,5-triazin-2-one (**VIII**) in the nitration of hexamethylenetetraminium *N,N'*-dinitrourea nitrate (**VII**) (reaction time 30 min)

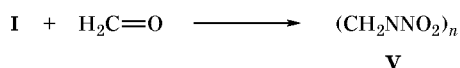
Nitrating system	[HNO ₃], %	Nitration number	Temp., °C	Yield, %
HNO ₃	98	1.3	6	27
HNO ₃	98	3	20	90
HNO ₃ -H ₂ SO ₄	70	3	20	93
HNO ₃ -H ₂ SO ₄	50	3	20	90

very rapidly during extraction with an organic solvent, and we succeeded only in detecting displacement of the UV absorption maximum from λ 272 nm (typical of compound **I**) to 221 nm.

The condensation of *N,N'*-dinitrourea (**I**) with formaldehyde at a molar ratio of 1:2 at 10–80°C, apart from hydroxymethyl nitramide derivatives, gave a crystalline product which was insoluble in water. Its melting point and IR spectrum coincided with the corresponding data for 3,7-dinitro-1,5-dioxo-3,7-diazacyclooctane (**IV**); however, the yield of **IV** was insignificant.



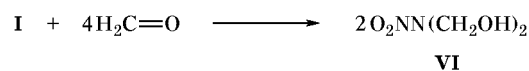
When the reaction mixture was allowed to warm up to 90–105°C, a solid separated from the solution. The product is insoluble in water and organic solvents, and it melts with decomposition at 205–215°C. Its elemental composition corresponds to *N*-nitromethylenimine $\text{CH}_2=\text{NNO}_2$. A similar compound was reported in [6, 7] as poly(methylenenitroamine) (**V**):



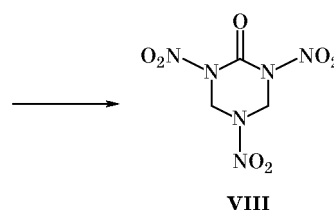
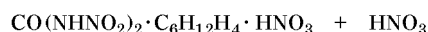
Compound **V** slowly dissolves in aqueous alkali at room temperature to form *N,N'*-dinitromethylenediamine salt; similar observations for an analogous polymer were reported in [8].

In the presence of a large excess of formaldehyde (more than 4 equiv), dinitrourea decomposes with formation of bis(hydroxymethyl)nitroamine (**VI**). Compound **VI** was also obtained by dilution with water of the reaction mixture in the nitration of urea [1], followed by hydrolysis of dinitrourea **I** in the

presence of formaldehyde at 0–60°C. The yield of the oily product was 56–60% (calculated for 2 mol of diol **VI** per mole of dinitrourea). Compound **VI** reacts with formaldehyde to give cyclic product **IV**.

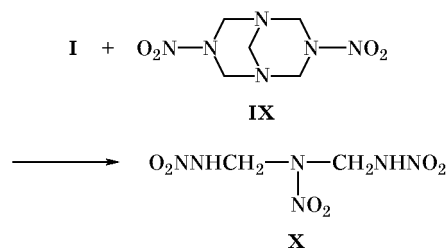


N,N'-Dinitrourea reacts with urotropin nitrolysis products in nitric acid or its mixture with sulfuric acid, yielding 1,3,5-trinitrohexahydro-1,3,5-triazin-2-one (**VIII**) [1]. In the nitration of hexamethylenetetraminium *N,N'*-dinitrourea nitrate (**VII**) at 0–20°C, the yield of compound **VIII** is 93% (Table 1).



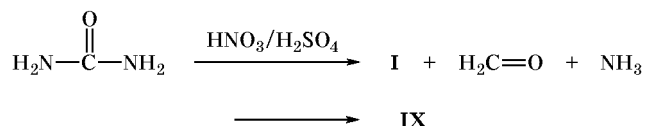
Compound **VIII** is stable under standard conditions, but it decomposes on exposure to moisture or by the action of amines, bases, alkalis, metals, and other compounds [9]. For instance, a solid product precipitates from a solution of **VIII** in DMF at 80°C, and the process is accompanied by gas evolution. The product was identified as poly(methylenenitroamine) (**V**) according to the IR data.

The reaction of dinitrourea with nitrolysis products of dinitropentamethylenetetramine (**IX**) in mixtures of sulfuric and nitric acids yields 1,3,5-trinitro-1,3,5-triazapentane (**X**).



Depending on the duration of nitrolysis of **IX**, the yield of **X** changes from 60% to 0. Treatment of **IX** with a mixture of sulfuric and nitric acids in the absence of dinitrourea does not lead to formation of compound **X**.

The formation of bis(hydroxymethyl)nitroamine (**VI**) from dinitrourea prompted us to consider the possibility for synthesizing dinitropentamethylenetetramine (**IX**) directly from urea without isolation of crystalline dinitrourea. Some antecedents indicating that compound **IX** is formed through intermediate **VI** from nitramide [10, 11] and nitrourea [12] have been reported.



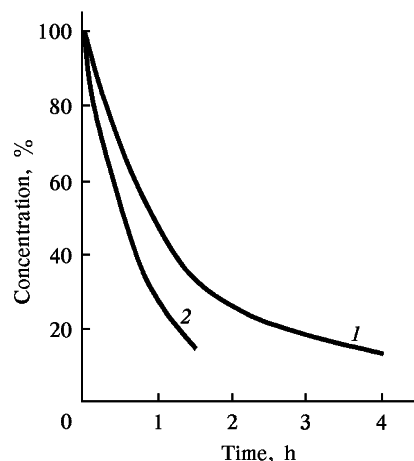
It should be noted that our study was aimed at obtaining compound **IX** through a series of hydroxymethyl derivatives of dinitrourea **I** and nitramide, taking into account that *N*-nitro amines in acid media are stabilized via conversion into hydroxymethylnitroamines [13]. Moreover, in preliminary experiments involving complete hydrolysis of dinitrourea in waste acids to nitramide with subsequent addition of formaldehyde and ammonia the yield of **IX** did not exceed 20%. This is explained by instability of nitramide in acid medium [14, 15].

However, the hydrolysis of dinitrourea in the presence of formaldehyde or urotropin was faster (see figure, curve 2) than in the absence of these compounds (curve 1). Clearly, the hydrolysis occurs through formation of stable hydroxymethyl nitramide derivatives since the subsequent neutralization with ammonia gives compound **IX** in 50% yield. The yield of **IX** (Table 2) increases when anhydrous nitrating mixture with greater concentration of sulfuric acid is used at the stage of urea nitration; maintaining the temperature within a narrow range during the condensation of the nitration products with formaldehyde, as well as some special techniques in the isolation of the target product, are also advisable.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer in KBr. The UV spectra were measured on Specord UV-Vis and Specord M-40 instruments from solutions in water. Compounds **I** and **VII** were synthesized by the procedures reported in [2] and [1], respectively. Hydrolysis of dinitrourea was studied by the procedure described in [3].

***N,N'*-Dinitromethylenediamine.** A suspension of 2.2 g (9 mmol) of salt **III** (preliminarily dried in a vacuum desiccator over P₂O₅ for 24 h, mp 95–98°C) in 200 ml of anhydrous diethyl ether was saturated



Kinetic curves for the hydrolysis of *N,N'*-dinitrourea (**I**) at 30°C (1) in water and (2) in a solution of urotropin.

with gaseous hydrogen chloride at 0–5°C (2 h). The mixture was stirred for 1 h, the precipitate was filtered off, and the filtrate was evaporated to dryness under reduced pressure. Yield 1.22 g (87%), mp 104–105°C; published data: mp 94–98°C [9], 101°C [16]). The IR spectrum of the product was identical to that reported in [5]. Found, %: C 8.8; H 3.00; N 40.0. CH₄N₄O₄. Calculated, %: C 8.8; H 2.94; N 41.18.

***N,N'*-Dinitromethylenediamine dipotassium salt (**III**).** *a.* A 5.7-g portion of dinitrourea containing 4.5 g (0.03 mol) of the main substance and 1.2 g (0.0122 mol) of H₂SO₄ was added with stirring at 20–25°C to 2.81 g (0.03 mol) of a 32% formaldehyde solution. The mixture was stirred for 20 min at 65–70°C, a sample was withdrawn, and the concentration

Table 2. Yields of dinitropentamethylenetetramine (**IX**) in the condensation of urea with formaldehyde in a mixture of nitric and sulfuric acids

Temperature, °C	Time, min	Yield, %
30	40	51
35	40	56
40	10	57
40	20	60
40	25	59
40	40	58
40	40	62 ^a
45	40	55
50	40	46
60	40	33

^a The reaction mixture was diluted with the filtrate obtained in the preceding experiment.

of compound **II** was determined by spectrophotometry (λ 226 nm, ϵ 12530 l mol⁻¹ cm⁻¹). Yield 3.63 g (89%). The mixture was cooled to 20°C and extracted with ether (4 × 25 ml). The extract was dried over MgSO₄ and evaporated under reduced pressure. To the oily residue (2 g), 16 ml of 10% aqueous potassium hydroxide and a mixture of 10 ml of ethanol and 10 ml of methanol were added. The precipitate was filtered off, washed with alcohol and ether, and dried for 24 h at room temperature. Yield 3.11 g (45%), K₂[O₂NNCH₂NNO₂]·H₂O, mp 90°C (in a capillary). IR spectrum, ν , cm⁻¹: 3450 br (H₂O); 2950, 2850 (CH₂); 1640 w (H₂O); 1460, 1430, 1355, 1335 (NNO₂). Found, %: K⁺ 34.63. CH₂K₂N₄O₄·H₂O. Calculated, %: K⁺ 33.91.

b. The procedure was the same as above with the difference that, after stirring for 20 min at 65–70°C, the mixture was cooled to 20°C and 10% aqueous potassium hydroxide was added to pH 7–8. A mixture of 2.5 ml of ethanol and 2.5 ml of methanol was added, the precipitate of K₂SO₄ was filtered off, and a mixture of 10 ml of ethanol and 10 ml of methanol was added to the filtrate. The precipitate was filtered off, washed with alcohol and ether, and dried for 24 h at room temperature. The yield of salt **III** was the same as in *a*.

3,7-Dinitro-1,5-dioxo-3,7-diazacyclooctane (IV). A 5.7-g portion of *N,N'*-dinitrourea (**I**) containing 4.5 g (0.03 mol) of the main substance and 1.2 g (12.2 mmol) of H₂SO₄ was added with stirring at 20–25°C to 5.63 g (0.06 mol) of a 32% formaldehyde solution. The mixture was stirred for 20 min at 65–70°C, 20 ml of water was added, the mixture was cooled to 10°C, and the precipitate was filtered off, washed with cold water, alcohol, and ether, and dried at room temperature. Yield 0.1 g (1.6%), mp 260°C; published data [10]: mp 263–264°C.

Poly(methylenenitroamine) (V). *a.* A 4.5-g (0.03-mol) portion of *N,N'*-dinitrourea containing no sulfuric acid (see method *a* in [2]) was added under stirring at 20–25°C to 2.81 g (0.03 mol) of a 32% formaldehyde solution. The cooling bath was removed, and the mixture spontaneously warmed up to 105°C. It was cooled to 10°C, and the precipitate was filtered off, washed with cold water, alcohol, and ether, and dried at room temperature. Yield 1.11 g (50%), mp 205–215°C. IR spectrum, ν , cm⁻¹: 3040, 2985 (CH₂); 1570, 1270 (NNO₂); 1440, 1210, 930. Found, %: C 16.0; H 2.75; N 36.2. CH₂N₂O₂. Calculated, %: C 16.22; H 2.70; N 37.84.

b. A 4.72-g (0.02-mol) portion of compound **VIII** was added under stirring to 100 ml of DMF. The mixture was stirred for 60 min at 80–85°C, and the

precipitate was filtered off, washed with alcohol and ether, and dried at room temperature. Yield 2.9 g (98%), mp 200°C. IR spectrum, ν , cm⁻¹: 3040, 2985 (CH₂); 1570, 1270 (NNO₂); 1440, 1210, 930. Found, %: C 16.2; H 2.70; N 37.2. CH₂N₂O₂. Calculated, %: C 16.22; H 2.70; N 37.84.

Bis(hydroxymethyl)nitroamine (VI). Dinitrourea, 3 g (0.02 mol), was added under stirring at –5 to 0°C to 6.0 g (0.08 mol) of a 40% formaldehyde solution. The mixture was stirred for 3 h at 20–30°C and extracted with ether (5 × 10 ml). The extract was dried over MgSO₄, and the solvent was distilled off under reduced pressure to obtain a yellowish oily substance. Yield 2.92 g (60%). IR spectrum, ν , cm⁻¹: 3500–3400 br (OH); 2970, 2920, 2840 (CH₂); 1560, 1295 (NNO₂). Found, %: C 19.7; H 5.0; N 22.0. C₂H₆N₂O₄. Calculated, %: C 19.67; H 4.92; N 22.95.

1,3,5-Trinitrohexahydro-1,3,5-triazin-2-one (VIII). Salt **VII** [1], 14.12 g (0.04 mol), was added under stirring at –5 to 0°C to 24 ml of a mixture of equal amounts (by weight) of H₂SO₄ and HNO₃ (d = 1.756 g/cm³). The mixture was stirred for 30 min at 20°C and poured into 40 g of an ice–water mixture. The precipitate was filtered off, washed with cold water, alcohol, and ether, and dried at room temperature. Yield 8.4 g (89%), mp 170–180°C, 200–201°C (from nitromethane, with decomposition). IR spectrum, ν , cm⁻¹: 3040, 2980, 2910, 2840 (CH₂); 1750 (C=O); 1600, 1300, 1280 (NNO₂); 1450, 1220, 1150, 1080, 1040, 920, 900, 880, 820, 790, 730, 705, 615, 560, 485, 460. Found, %: C 15.4; H 1.4; N 34.9. C₃H₄N₆O₇. Calculated, %: C 15.25; H 1.69; N 35.59.

Dinitropentamethylenetetramine (IX). Urea, 5 g (0.0833 mol), was added under stirring at –5 to 0°C to a mixture of 10 ml of 98% of nitric acid and 10 ml of technical-grade oleum (20% SO₃). The mixture was stirred for 30 min at 0–5°C and poured into 30 g of an ice–water mixture, and 30 ml of a 37% formaldehyde solution was added at a temperature not exceeding 20°C. The mixture was heated to 40°C, stirred for 20 min, cooled, and neutralized to pH 6 with 25% aqueous ammonia at 20–25°C. It was then stirred for 45 min at 20°C, and the precipitate was filtered off, washed with water, and dried at room temperature until constant weight. Yield 11 g (60%), mp 186–190°C; published data [11]: mp 202–205°C. IR spectrum, ν , cm⁻¹: 3000, 2925 (CH₂); 1530, 1270, 1250 (NNO₂); 1500, 1440, 1400, 1335, 1205, 1190, 1080. Found, %: C 27.5; H 4.6; N 37.5. C₅H₁₀N₆O₄. Calculated, %: C 27.5; H 4.6; N 38.5.

1,3,5-Trinitro-1,3,5-triazapentane (X). Urea, 5 g (0.0833 mol), was added under stirring at –5 to 0°C to 28.5 ml of a mixture of equal amounts (by weight)

of H_2SO_4 and HNO_3 ($d = 1.756 \text{ g/cm}^3$). The mixture was stirred for 5–7 min, and 8.3 g (0.0395 mol) of compound **IX** was added at 0–4°C. The mixture was stirred for 5 min and poured into 60 g of an ice–water mixture. The resulting mixture was filtered from unreacted compound **IX**, and the filtrate was heated for 20 min at 40°C and cooled to 2–3°C. The precipitate was filtered off, washed with ice water, and dried for 24 h at room temperature. Yield 3.8 g (48%), mp 107–110°C (decomp.). The filtrate was kept for 24 h at 2–4°C, and the precipitate was filtered off, washed with water, and dried for 24 h at room temperature. An additional 1 g of product **X** was thus isolated. Overall yield 4.8 g (60%; calculated on the assumption that 1 mol of **X** is formed from 1 mol of **IX**). After repeated treatment with ice-cold diethyl ether, the melting point of the product rose to 153–154°C; published data [3]: mp 130–135°C. IR spectrum, ν , cm^{-1} : 3360 (NH); 3040, 2920 (CH_2); 1600, 1550, 1275 (NNO_2); 1420, 1390, 1220, 1085, 1025, 915. Found, %: C 10.8; H 3.0; N 39.8. $\text{C}_2\text{H}_6\text{N}_6\text{O}_6$. Calculated, %: C 11.4; H 2.9; N 40.0.

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