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SHORT COMMUNICATIONS

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

Nitration of *N*-Alkyl-*N′*-nitroureas

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The development of a convenient procedure for the synthesis of mononitro alkylureas from *N*,*N′*-dinitrourea [1] made it possible to perform extensive studies of the nitration of these compounds with the goal of obtaining *N*-alkyl-*N*,*N′*-dinitroureas.

During the nitration of *N*-methyl-*N′*-nitrourea with a mixture of anhydrous sulfuric and nitric acids the target product precipitates from the reaction mixture, and it can be separated by filtration like *N*,*N′*-dinitrourea [2]. Moreover, the nitration product can readily be separated by pouring the acid mixture onto ice. The product is unstable: it decompose over a period of 2 h in the cold under reduced pressure and ignites on storage in a desiccator over P_2O_5, as well as in air. The melting point of a moist sample is 47–50°C (with decomposition). *N*-Methyl-*N*,*N′*-dinitrourea undergoes fast hydrolysis in water at room temperature, which is accompanied by fast displacement of the UV absorption maximum from λ 270 to 230 nm. By extraction of the aqueous solution with diethyl ether we isolated methyl-*N*-nitroamine; mp 38°C [3]; UV spectrum (water): λ_{max} 230 nm, ε 6800 $\mathrm{l\,mol^{-1}\,cm^{-1}}$. Methylnitroamine was also detected among decomposition products of the crystalline product stored in a vial with a ground-glass cap. Addition of potassium hydroxide to the aqueous solution induces vigorous gas evolution which indirectly indicates the presence of nitramide. Nitration of the hydrolysis products in a concentrated aqueous solution with a mixture of sulfuric and nitric acids at –30°C yields dinitramide [4]. We failed to determine the elemental composition of the product, for it ignited on weighing.

Taking into account the above data and IR spectra of the product, we presumed that it has the structure of *N*-methyl-*N*,*N′*-dinitrourea. Its yield depends on the nitration number (the weight ratio of the nitration mixture and the substrate) and attains 58% when the nitration number is equal to 4. The same product was obtained by nitration of *N*-methyl-*N′*-nitrourea. The nitration of *N*-butyl-*N′*-nitrourea follows an analogous pattern.

$$\mathrm{M[O_2NNCONHAlk]} \xrightarrow{\mathrm{HNO_3/H_2SO_4}} \mathrm{O_2NNHCON(NO_2)Alk}$$

Alk = Me, Bu; M = H, K.

***N*-Methyl-*N′*-nitrourea potassium salt.** Water, 20 ml, was added to a solution of 18.8 g (0.1 mol) of *N*,*N′*-dinitrourea potassium salt, 22.3 ml (0.2 mol) of a 30% aqueous solution of methylamine was then added, the mixture was stirred for 40 min at 30°C, and the solvent was distilled off under reduced pressure at 40°C. Yield 14.3 g (91%), mp 159–161°C (decomp.); published data [1]: mp 156°C (decom.).

***N*-Butyl-*N′*-nitrourea potassium salt** was synthesized in a similar way using butylamine instead of 30% aqueous methylamine. Yield 90%, decomposes at 190–191°C [1].

***N*-Methyl-*N′*-nitrourea.** A solution of 6.28 g of *N*-methyl-*N′*-nitrourea potassium salt in 5 ml of water was added with stirring to 10 ml of 64% nitric acid at such a rate that the temperature did not exceed 40°C. The precipitate was filtered off, washed with a minimal amount of ice water, and dried at 60°C. Yield 4.28 g (90%), mp 146–148°C; published data [1]: decomposition point 162°C.

Nitration of *N*-methyl-*N′*-nitrourea potassium salt. A 5-g (0.0318-mol) portion of *N*-methyl-*N′*-nitrourea potassium salt was added at 0–5°C to a mixture of 10 g of nitric acid (d = 1.51 $\mathrm{g/cm^3}$) and 10 g of oleum (24% of SO_3). The mixture was stirred for 85 min at 0–5°C and poured onto 20 g of crushed ice,

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and the precipitate was filtered off. Yield 3.0 g (58%, calculated on the *N*-methyl-*N'*-nitrourea). UV spectrum (H_2O), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 203 (8700), 270 (8430). IR spectrum, ν, cm^{-1}: 3280 (NH); 2960, 2920, 1385 (CH_3); 1755 (C=O); 1630, 1625, 1580, 1555, 1305 (NNO_2); 1440, 1410, 1220, 1180, 1125, 1060, 980, 910,760, 735, 715, 670, 660, 595.

Nitration of *N*-methyl-*N'*-nitrourea. *N*-Methyl-*N'*-nitrourea, 4.76 g (0.04 mol), was added at 0–5°C to a mixture of 10 g of nitric acid (d = 1.51 g/cm^3) and 10 g of oleum (24% of SO_3). The mixture was stirred for 1 h at 0–5°C and cooled to –12°C, and the precipitate was filtered off through a glass filter with suction. Yield 1.7 g (26%). The filtrate was diluted with 20 g of ice water, and the precipitate was filtered off to obtain an additional portion of the product, 2.0 g (30%). Overall yield 3.7 g (56%).

Nitration of *N*-butyl-*N'*-nitrourea potassium salt. A 5-g (0.0251-mol) portion of *N*-butyl-*N'*-nitrourea potassium salt was added at 0–5°C to a mixture of 10 g of nitric acid (d = 1.51 g/cm^3) and 10 g of oleum (24% of SO_3). The subsequent procedure was the same as in the nitration of *N*-methyl-*N'*-nitrourea potassium salt. Yield 2.6 g (50%), mp 47–50°C (decomp.). UV spectrum (H_2O), λ_{max}, nm (ε, l mol^{-1} × cm^{-1}): 203 (8700), 270 (8500). IR spectrum, ν, cm^{-1}: 3280 (NH); 3050 (CH_2); 2950, 2880 (CH_3, CH_2); 1750 (C=O); 1580, 1555, 1305 (NNO_2).

The IR spectra were recorded on a Specord M-80 spectrometer in KBr. The UV spectra were measured in water on Specord UV-Vis and Specord M-40 spectrophotometers.

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REFERENCES

1. Il’yasov, S.G., Lobanova, A.A., Popov, N.I., and Sataev, R.R., *Russ. J. Org. Chem.*, 2002, vol. 38, no. 12, pp. 1739–1743.
2. Lobanova, A.A., Sataev, R.R., Popov, N.I., and Il’yasov, S.G., *Russ. J. Org. Chem.*, 2000, vol. 36, no. 2, pp. 164–167.
3. Franchimont, A. and Klobbie, E., *Recl. Trav. Chim. Pays–Bas,* 1888, vol. 7, p. 343.
4. Luk’yanov, O.A., Shvedova, S.N., Shepelev, E.V., Varfolomeeva, O.N., Milkina, N.N., and Tartakovskii, V.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, no. 6, pp. 1569–1570.