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BRIEF COMMUNICATIONS

Synthesis of Condensed Nitrofuroxanes Using Hydroxylamine

O. R. Klyuchnikov, V. I. Starovoitov, F. G. Khairutdinov, and V. V. Golovin

Kazan State Technological University, Kazan, Tatarstan, Russia

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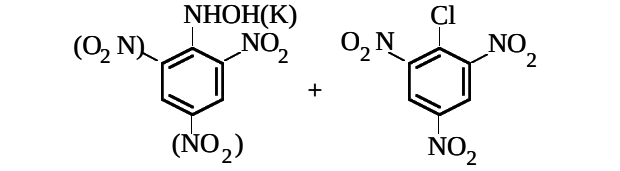
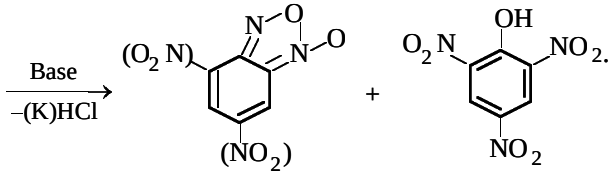
Abstract—The possibility of preparing condensed nitrofuroxanes using hydroxylamine was examined.

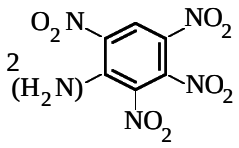
Benzofuroxanes exhibit biological activity and are intermediates in synthesis of a number of effective antimicrobial agents; 4,6-dinitrobenzofuroxane in the form of salts is used in priming charges [1]. In this connection, it is interesting to develop relatively safe methods for preparing nitrofuroxanes without using azides.

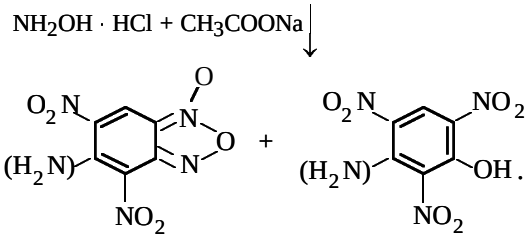
Previous studies concerning formation of the furoxane ring in synthesis of 4,6-dinitrobenzofuroxane by reaction of picryl chloride, hydroxylamine hydrochloride, and sodium acetate showed that the intermediate in this procedure is picrylhydroxylamine [2]. This finding allowed preparation of 3-nitro[4,5-*c*]pyridofuroxane by the reaction of 4-hydroxylamino-3,5-dinitropyridine with picryl chloride [3]. Similarly, the reaction of 2,4- or 2,6-dinitrophenylhydroxylamine or its potassium salt with picryl chloride also yielded, respectively, 4- or 6-nitrobenzofuroxane and picric acid:





From compounds containing a labile nitro group, 4,6-dinitrobenzofuroxane derivatives are formed also:





EXPERIMENTAL

4- and 6-Nitrobenzofuroxanes were prepared by adding 2.48 g (0.01 mol) of picryl chloride to a suspension of 2.37 g (0.01 mol) of potassium salt of, respectively, 2,6- and 2,4-dinitrophenylhydroxylamine in 30 ml of MeOH at room temperature with stirring. The mixture was left for 0.5 h and poured into 60 ml of water. The precipitate of 4- or 6-nitrobenzofuroxane was filtered off, washed with water, and dried. Yield of 4-nitrobenzofuroxane 1.67 g (92%), mp 112°C (from EtOH); yield of 6-nitrobenzofuroxane 1.59 g (88%), mp 74–76°C (from EtOH).

4,6-Dinitrobenzofuroxane was prepared by gradual addition of 5.16 g (0.02 mol) of 1,2,3,5-tetranitrobenzene to a suspension of 1.39 g (0.02 mol) of hydroxylamine hydrochloride and 3.28 g (0.04 mol) of sodium acetate in 50 ml of MeOH at 45–50°C with stirring. The mixture was stirred at this temperature for an additional 1 h, after which it was cooled and diluted with water; the precipitate was filtered off, washed with water, and dried. Yield 2.1 g (93%), mp 172°C (from MeOH).

5-Amino-4,6-dinitrobenzofuroxane was prepared similarly by adding 5.46 g (0.02 mol) of 2,3,4,6-tetranitroaniline to a suspension of 1.39 g (0.02 mol) of hydroxylamine hydrochloride and 3.28 g (0.04 mol) of sodium acetate in 50 ml of MeOH at 45–50°C. The reaction mixture was kept at this temperature for an additional 2 h, after which it was cooled, and the pre-

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cipitate was filtered off, washed with water, and dried. Yield 2.0 g (83%), mp 265–266°C (from AcOH).

The physicochemical constants of the compounds prepared coincide with those of the authentic samples prepared by the azide method [4–6].

CONCLUSION

A procedure for preparing condensed nitrofuroxanes in good yields using hydroxylamine was suggested to replace the less safe azide method.

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