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SYNTHESIS OF 2-CYANO-5-NITROFURAN

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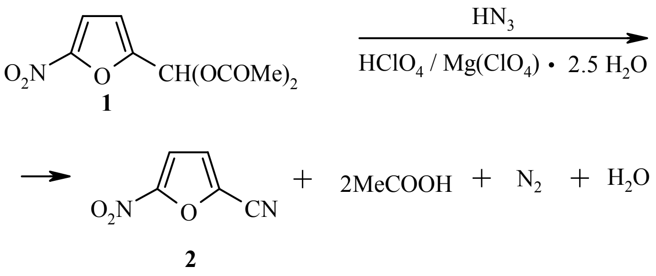
A new method has been developed for the preparation of 2-cyano-5-nitrofuran from 5-nitrofurfural diacetate using the Schmidt reaction.

The synthesis of 5-nitrofurfural is carried out in three steps: 1) conversion of furfural to diacetate, 2) nitration of diacetate, and 3) hydrolysis of the resultant 5-nitrofurfural diacetate (**1**). Nitration of furfural cannot be carried out without prior protection of the aldehyde group by acylation and removal of the protective group is carried out by treatment of acetate **1** using concentrated aqueous solutions of sulfuric acid at high temperature with subsequent repeated washing to remove sulfuric acid [1].

Comparison of the conditions for deacylation of diacetate **1** with our conditions for the Schmidt reaction in the synthesis of various furan nitriles from the corresponding aldehydes allows to suggest that 2-cyano-5-nitrofuran (**2**) may be obtained directly from nitrodiacetate **1** [2, 3] taking into account the high reactivity of 5-nitrofurfural.



Our variant involving the removal of the protective group and simultaneous introduction of the nitrile group proved highly efficient for the preparative synthesis of 2-cyano-5-nitrofuran **2**. This permits elimination of the laborious step involving the sulfuric acid hydrolysis of diacetate **1** and washing out the sulfuric acid. The yield of nitrile **2** relative to the starting furfural is improved.

A small amount of 72% $HClO_4$ (3-5 drops) was added with stirring to mixture of nitrodiacetate **1** (24.4 g, 0.1 mol), hydrazoic acid (0.11 mol) solution in chloroform, and $Mg(ClO_4)_2\cdot 2.5H_2O$ ("anhydrone") (25.0 g, 0.1 mol) at about 20°C. Nitrogen begins to evolve after 3-5 min. Then, 72% $HClO_4$ (1.4 ml, 0.01 mol) was slowly added maintaining the temperature of the reaction mixture not higher than 30-35°C using an ice bath. At the end of nitrogen evolution after 40-45 min, the reaction mixture was treated with water and filtered.

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The chloroform layer was separated and washed thrice with water. The solution was decolorized with activated charcoal and filtered. Chloroform was removed at reduced pressure to give 13.5 g (98%) of 2-cyano-5-nitrofuran **2**; mp 65°C.

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