SYNTHESIS OF 3,5-DICYANOPYRIDINE BY OXIDATIVE AMMONOLYSIS OF 3,5-LUTIDINE*

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UDC 547.821.412.826.07:542.943.7

Pyridine-3,5-dicarboxylic acid was synthesized by oxidative ammonolysis of 3,5-lutidine and hydrolysis of the resulting 3,5-dicyanopyridine.

Pyridine-3,5-dicarboxylic acid (I) is obtained either by oxidation of 3,5-substituted pyridine derivatives with selenium derivatives [2] or by condensation of formaldehyde with β-aminovinyl methyl ketone in the presence of ammonium acetate [3]. We have established that oxidative ammonolysis may serve as a convenient method for the conversion of 3,5-lutidine (II) to 3,5-dicyanopyridine (III), from which such interesting (from a practical point of view) monomers as acid I and 3,5-bis(aminomethyl)pyridine can in turn be obtained by hydrolysis or hydrogenation.

The oxidative ammonolysis of I was carried out with a flow-action apparatus [4] in the presence of a fused vanadium—titanium oxide catalyst. The chief reaction products were dinitrile III and 3-cyano-5-methylpyridine (IV) at feed rates of 15-30 g of lutidine II,† 480-640 liters of oxygen (in the form of air), and 45-80 g of ammonia per liter of catalyst per hour, a contact time of 0.3-0.7 sec, and 300-370°C.

The most favorable conditions for the formation of III were a II to O_2 to NH_3 molar ratio of 1:9:17, a contact time of 0.5 sec, and a temperature of ~350°. The yield of dinitrile III in this case exceeded 40% based on the amount of lutidine II used. Under milder conditions (a reduced contact time and a temperature of 300-340°) the chief reaction product was nitrile IV, while profound oxidation processes dominated under more severe conditions.

3,5-Dicyanopyridine (III) was isolated from the catalyzate by filtration. After sublimation at 80-90° (10 mm) and subsequent recrystallization from dilute ethanol, it melted at 112-113° and had an IR spectrum corresponding to that described in the literature [6]. Refluxing of dinitrile III (4.7 g) in 150 ml of 1 N potassium hydroxide solution for 2 h and appropriate workup of the hydrolyzate gave 5.7 g (95%) of acid I with mp 321-323° (dec.) [7] and a neutralization equivalent of 83.4.

3-Cyano-5-methylpyridine (IV) was isolated from the filtrate (after separation of III) by extraction with diethyl ether. Two recrystallizations from ethanol gave a product with mp 75-76° (mp 76° [8]).

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*Communication XCIV from the series "Oxidation of Organic Compounds"; see [1] for communication XCIII.

†The 3,5-lutidine was prepared by V. N. Gudz' by the method in [5].

Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 819-820, June, 1973. Original article submitted August 17, 1971.

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