The Synthesis of Nitriles From Aldehydes

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Recently, the ammoxidation reaction in a liquid phase has attracted interest because it may be carried out under mild conditions. While studying some aspects of liquid-phase ammoxidation reactions, we have discovered a one-step method of synthesizing nitriles from aldehydes and ammonia in the presence of iodine.

Previously-reported methods for the production of nitriles from the corresponding aldehydes involve the application of a thoria catalyst at about 440°C to a mixture of aldehyde and ammonia,[1] the reaction of phenyl-imidophosgene with benzaldoxime,[2] or other methods using such selective reagents as *O*, *N*-bis-(trifluoroacetyl)-hydroxylamine,[3] hydroxylamine and sodium formate,[4] hydroxylamine and sodium acetate,[5] or nitropropane and ammonium dibasic phosphate.[6] Brackman and Smit[7] obtained nitriles by stirring a methanolic solution of aldehydes, ammonia, a complexed copper salt, and a strong base under oxygen. Parameswaran and Friedman[8] found a method using lead tetraacetate as an oxidizing agent.

It was found in the present study that iodine is a more convenient oxidizing agent than oxygen and a copper complex or lead tetraacetate. By this method, benzonitrile (reaction time: 1.5 hr.; yield: 50%), heptanenitrile (0.15 hr.; 26%), cinnamonitrile (1.5 hr.; 10%) anisonitrile (2 hr., 50%), and *p*-chlorobenzonitrile (1.5 hr., 68%) can be prepared from the corresponding aldehydes at room temperature.

A typical procedure is the preparation of benzonitrile.

Benzonitrile.—Thirty-two grams (0.3 mol.) of benzaldehyde and 16 g. (0.3 mol.) of sodium methoxide were added to 400 ml. of methanol saturated with ammonia. After the sodium methoxide had been dissolved 76 g. (0.3 mol.) of iodine (in 100 ml. of methanol) was added to the solution. Ammonia gas was continuously bubbled into the mixture during the reaction at room temperature. When the color of the solution became a light yellow (in 1.5 hr.), the bubbling in of ammonia gas was stopped. After the volatile reactants had then been removed from the reaction solution in vacuo, the residual oil was extracted with ether. The ethereal solution was treated with an aqueous solution of sodium bisulfite and distilled. Benzonitrile was thus obtained in a yield of 50% (16 g.); b. p. 83°C/20 mmHg; n_D^{20} 1.526.

When hydrobenzamide was used as the starting material in place of benzaldehyde, benzonitrile was again obtained, though in a small yield. This fact supports the theory that benzilideneimine is a possible intermediate.

The simplicity, rapidity, and mildness of this method make it apparent that it can be a convenient method for the preparation of nitriles,[9] especially aromatic nitriles.

Detailed results and a discussion of the possible mechanism will be published in the near future.

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