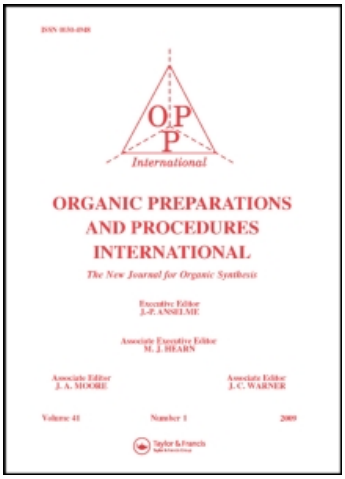

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AN IMPROVED SYNTHESIS OF 2-ISOCYANATOBENZONITRLE

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AN IMPROVED SYNTHESIS OF 2-ISOCYANATOBENZONITRILE

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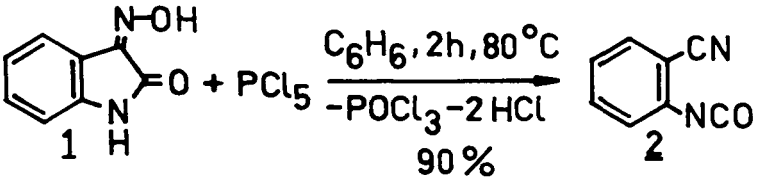
2-Isocyanatobenzonitrile, a useful reagent for the synthesis of ureas[1] and heterocycles,[2] can be prepared by dehydration and rearrangement[3] of isatin oxime. However, all literature procedures have serious disadvantages. In our hands, the use of diethyl ether in the method of Borsche et al.[4] was quite unsuitable as reaction medium because both isatin oxime and phosphorus pentachloride are nearly insoluble in it; as a result, the reaction is slow and a number of distillations of the crude product are necessary. An attempt to overcome these difficulties by



the use of excess phosphorus oxychloride led to another hazardous and inconvenient work-up procedure involving numerous distillations.[5] We now describe a convenient procedure for a modified synthesis of 2-isocyanatobenzonitrile.

The use of a solution of phosphorus pentachloride in dry benzene or toluene insured a clean and rapid reaction, especially since isatin oxime is sufficiently soluble as well. After the reaction ceases, simple extraction without distillation afforded 2-isocyanatobenzonitrile (2) in high yield.[6]

EXPERIMENTAL SECTION

The mp. was determined on a Boetius micro hotstage and is uncorrected. The micro analysis was made on an elemental analyzer Heraeus CHN-O-RAPID. Isatin oxime was prepared according to the literature.[4b]

2-Isocyanatobenzonitrile (2).- To a stirred suspension of isatin oxime (1) (16.2 g, 0.10 mol) in warm dry benzene (200 ml) was rapidly (5 min) added a solution of phosphorus pentachloride (20.9 g, 0.10 mol) in warm dry benzene (250 ml). After refluxing for 2 hrs, the mixture became nearly clear. The solution was filtered and the filtrate was evaporated and the oily pale orange residue extracted with boiling ligroin (bp 50-80°) (2 x 125 ml). On cooling the extract, 13.7 g of crude product separated and, after recrystallisation from ligroin, 13.0 g (90%) of 2-isocyanatobenzonitrile was obtained as colorless needles, mp. 61-62°, lit.[4b] mp. 61°.

Anal. Calcd. for $C_8H_4N_2O$: C, 66.64; H, 2.80; N, 19.45. Found: C, 66.41; H, 2.86; N, 19.45

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A CONVENIENT "HYDROGEN TRANSFER" HYDROGENATION OF TESTOSTERONE

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17β-hydroxy-5α-androstane-3-one (2) and 17β-hydroxy-5β-androstane-3-one (3) are the prominent metabolites of testosterone (1) and are under active pharmacological investigation.[1] Thus, any easy access to these compounds would be of interest. The catalytic hydrogenation of 3-oxo-4-ene steriods, like that of testosterone, usually requires large excesses of Pd catalyst and gives mainly the 5β-epimer.[2] Recently, it has been reported that sodium hypophosphite and 10%