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### AN IMPROVED SYNTHESIS OF 2-ISOCYANATOBENZONITRILE

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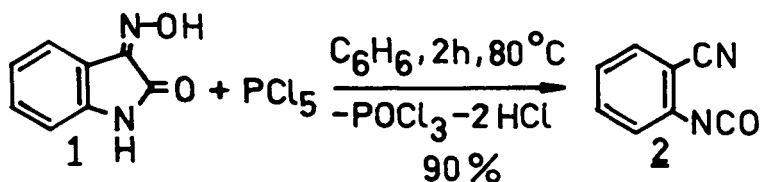
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## AN IMPROVED SYNTHESIS OF 2-ISOCYANATOBENZONITRILE

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(11/15/88)

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2-Isocyanatobenzonitrile, a useful reagent for the synthesis of ureas<sup>1</sup> and heterocycles,<sup>2</sup> can be prepared by dehydration and rearrangement<sup>3</sup> 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.*<sup>4</sup> 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.<sup>5</sup> 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.<sup>6</sup>

## 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.<sup>4b</sup>

**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.<sup>4b</sup> mp. 61°.

**Anal.** Calcd. for C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O: 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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17 $\beta$ -hydroxy-5 $\alpha$ -androstane-3-one (2) and 17 $\beta$ -hydroxy-5 $\beta$ -androstane-3-one (3) are the prominent metabolites of testosterone (1) and are under active pharmacological investigation.<sup>1</sup> Thus, any easy access to these compounds would be of interest. The catalytic hydrogenation of 3-oxo-4-ene steroids, like that of testosterone, usually requires large excesses of Pd catalyst and gives mainly the 5 $\beta$ -epimer.<sup>2</sup> Recently, it has been reported that sodium hypophosphite and 10%