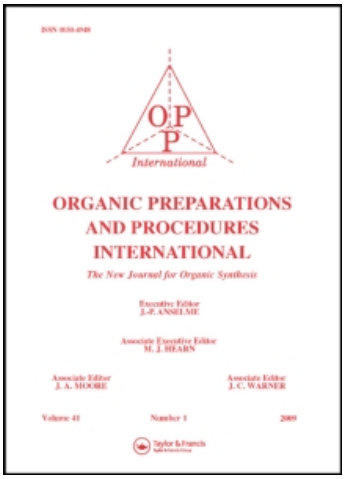

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CONVENIENT SYNTHESIS OF 4-NITROBENZOYL CHLORIDE

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A CONVENIENT SYNTHESIS OF 4-NITROBENZOYL CHLORIDE

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Although carboxylic acids can be conveniently converted to acid chlorides with thionyl chloride, this method is not generally used in the case of aromatic acids that contain a negative substituent in the position para to the carboxyl group (eg. p-nitrobenzoic acid, p-chlorobenzoic acid, etc.). In such cases, conversion to acid chloride is usually effected by phosphorus pentachloride.

The preparation of p-nitrobenzoyl chloride, by the action of phosphorus pentachloride on p-nitrobenzoic acid, has been reported in Organic Syntheses[1]. The yield of the acid chloride, however, depends to a great extent upon the quality of the reagents used. Commercial pure phosphorus pentachloride has been found unsatisfactory.

We now report that p-nitrobenzoyl chloride can be prepared conveniently, by refluxing one equivalent of p-nitrobenzoic acid with two equivalents of thionyl chloride. A near quantitative yield of the

$$p\text{-}O_2N\cdot C_6H_4\cdot COOH + SOCl_2 \rightarrow p\text{-}O_2N\cdot C_6H_4\cdot COCl + SO_2 + HCl$$

product obtained and it does not depend critically on the quality of the reagents employed. The method may also be used for the preparation of benzoyl chlorides bearing negative substituents with lower sigma values.

EXPERIMENTAL

A mixture of p-nitrobenzoic acid (Eastman White Label) (16.7 g., 0.10 mole) and $SOCl_2$ (Eastman White Label) (16 ml., 0.22 mole) in a 500 ml. round-bottomed flask fitted with condenser and $CaCl_2$ drying tube is heated under gentle reflux for 20 hrs. As the reaction progresses, HCl gas is evolved and the solid reaction mixture liquefies gradually. At the end of the reaction, there is no further evolution of HCl gas and a clear yellow homogeneous liquid is formed. The reaction flask is then placed in a boiling water bath and the excess $SOCl_2$ removed under reduced pressure. The residual liquid solidifies to a mass of pale yellow, long, slender needles. The yield of p-nitrobenzoyl chloride is 18-18.2 g. (97-98%), mp. 72-73°, lit[1]. 73°.

With pure p-nitrobenzoic acid and practical grade $SOCl_2$, the yield and mp. of product are not affected. However, with technical grade acid and pure $SOCl_2$, the product obtained is green yellow and the yield is 17.6 g. (95%), mp. 71-72°. However, the product can be purified by dissolution in anhydrous diethyl ether, filtration from the insoluble dark green impurities and removal of the ether under reduced pressure.

A sample of the green yellow product when refluxed with two equivalents of aniline in benzene solution, gives p-nitrobenzanilide in almost quantitative yield, mp. 214-217°, lit[2]. mp. 216°.

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