

factor; at about 22° , no tin salt was obtained, but when the reducing solution was allowed to become hot (sometimes 75° was reached) the double salt was found.

Twenty g. of the dry hydrochloride was dissolved in 80 cc. of acetic anhydride and boiled for 5 minutes. The acetyl-amino-phthalic anhydride crystallized when the solution was cooled, and was recrystallized from alcohol. M. p. $185-6^{\circ}$. Yield, 55%, calculated from the nitro compound.

Preparation of 4-Acetyl-amino-phthalic Anhydride.—The direct reduction of 4-nitro-phthalic acid with stannous chloride gives a double tin salt. When tin is precipitated by hydrogen sulfide this compound is converted into aminobenzoic acid with loss of carbon dioxide. Several indirect methods of preparing the amino acid have been proposed,¹ the one used below is that given by Bogert and Renshaw.²

The acid ammonium salt of 4-nitro-phthalic acid was converted into the imide and the nitro-imide reduced with stannous chloride. The amino-phthalimide, when boiled with ammonia, gave the ammonium salt of amino-phthalic acid from which the free acid was liberated by addition of hydrochloric acid. The 4-amino-phthalic acid was dissolved in acetic anhydride, boiled for a few minutes, allowed to cool and the acetyl-amino-phthalic anhydride filtered off. The product, recrystallized from ethyl acetate and acetyl chloride, did not have a sharp melting-point ($203-6^{\circ}$). The yield was less than 10%, calculated on the acid ammonium salt.

3-Nitrophthalic Anhydride with Benzene and Aluminum Chloride.

Because of the slight solubility of the anhydride in benzene, a larger excess of this reagent was used. A mixture of 100 cc. of benzene and 6.5 g. of 3-nitro-phthalic anhydride (finely powdered) was put in a 300-cc. flask attached to a reflux condenser and boiled for a few minutes on the water-bath. After cooling the product, 9.0 g. of powdered aluminum chloride was added slowly while the flask was shaken at intervals. The mixture darkened rapidly and soon assumed a deep brown color. Then it was heated on the water-bath until hydrogen chloride ceased to escape, which usually required about 4 or 5 hours. When the mixture became cold, 80 cc. of 10% hydrochloric acid was added and the excess of benzene was distilled with steam. The solution was cooled to 15° and filtered to remove the black gummy mass. The filtrate, evaporated to half its volume and extracted twice with ether, gave 3-nitro-phthalic acid equivalent to 55-60% of the anhydride used.

The black residue from the reaction was thoroughly agitated with a warm 5% solution of sodium hydroxide and filtered from the insoluble

¹ *Ber.*, 34, 4352 (1901); *J. Chem. Soc.*, 87, 1269 (1905).

² Bogert and Renshaw, *This Journal*, 30, 1137 (1908).

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