of the amino compounds because of the difficulty of preparing the amino anhydrides from the corresponding acids and also because of the general difficulty of using unprotected amines in the Friedel and Crafts' reaction.

Preparation of Nitro-phthalic Acids .- Several methods of preparing nitrophthalic acids have been described. Beilstein and Kurbatowi nitrated haphthalene and oxidized the product, Miller' nitrated phthalic acid and May,³ Edinger,⁴ and Poupold⁵ obtained nitrophthalic acids by nitration of phthalic anhydride. Bogert and Boroschek,⁶ using the latter method, increased the yield of 3-nitro-phthalic acid from 25% to 38% by renitration. In the method described below larger quantities of the mixed acids are used and renitration is unnecessary. A mixture of 125 g. of nitric acid (sp. gr. 1.5) and 125 g. of sulfuric acid (sp. gr. 1.834) was cooled and put in a 2-liter flask containing 50 g. of phthalic anhydride. The flask was heated gently on a water-bath until the temperature reached 75°, and then removed. Vigorous nitration began at about 80° and the flask was kept at about 100° for 3 hours, then allowed to cool, and the contents was poured into an equal volume of water. After standing overnight the precipitated acids were collected on a filter and the 3-nitrophthalic acid was obtained by recrystallization of the product from hot water. The mother liquor was concentrated and 4-nitro-phthalic acid extracted with ether. The 4-nitro-phthalic acid may be purified by dissolving it in 95% alcohol and gradually adding benzene to the solution; but the method described by Bogert and Boroschek was found to give a purer product. This preparation gave a yield of 42% of the 3-nitrophthalic acid and 47% of the 4-nitro-phthalic acid.

Preparation of 3-Nitro-phthalic Anhydride.—Bogert and Boroschek heated 3-nitro-phthalic acid for from 6 to 8 hours at $235-240^{\circ}$ and obtained the anhydride in good condition. Kahn⁷ gave 218° as the maximum temperature to be used. but later⁸ used 230° . Bogert's experiment, repeated, gave considerable tarry material, and the product melted at $162-4^{\circ}$. The method finally adopted was to put the acid into a small flask and heat it in an air-oven at $215-7^{\circ}$ (thermometer bulb in the melt) from 3 to 4 hours. When recrystallized from glacial acetic acid, the anhydride had a very pale yellow-brown color and melted sharply at 164° . Yield, about 89%. Quantitative determinations showed that at 215° the anhydride was slowly volatilized.

- ¹ Beilstein and Kurbatow, Ann., 202, 217 (1880).
- * Miller, ibid., 208, 223 (1881).
- ¹ May, Inaug. Dissertation, Frieburg, 1880.
- ⁴ Edinger, J. prakt. Chem., [2] 53, 382 (1895).
- ¹ Poupold, Inaug. Dissertation, Basle, 1897.
- Bogert and Boroschek, THIS JOURNAL, 23, 743 (1902).
- 7 Kahn, Ber., 35, 472 (1902).
- * Ibid., 35, 3859 (1902).

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