

portion. The filtrate contained the 2 possible benzoyl-nitrobenzoic acids as sodium salts, from which the free acids were obtained by the addition of 5% hydrochloric acid. The hydrochloric acid was added very slowly and at intervals of several hours; otherwise the precipitate was a gummy mass which made subsequent operations difficult. The 2 constituents of this precipitate have different solubilities in cold 95% alcohol, but the separation by acetic acid was found better than fractional crystallization from alcohol.

Hot 80% acetic acid dissolved one of these constituents and only a trace of the other. The acetic acid solution was filtered while hot, water was added until a faint cloudiness appeared, and after the solution had stood overnight, the precipitate was filtered off and dried. It softens at 140° and melts, with decomposition, at 158–61°. The portion insoluble in acetic acid melts with decomposition at 217–21°.

Identification of the Portion Insoluble in Acetic Acid.—*Hydrolysis.*—The finely divided substance was added to molten potassium hydroxide contained in a nickel dish and the temperature was kept a few degrees above the fusion point for from one to two hours. Then the mass was dissolved in water, acidified with hydrochloric acid, washed, and kept in a vacuum-oven at 100° until the residue had a constant melting-point, 146–8°—that of *o*-nitrobenzoic acid. The sublimate was benzoic acid.

Synthesis.—(A convenient method of preparation.) Ten g. of 2-carboethoxy-3-nitrobenzoic acid was dissolved in 15 cc. of thionyl chloride and kept at 60–70° until hydrogen chloride and sulfur dioxide were no longer given off. The excess thionyl chloride was then removed by distillation under reduced pressure. The resulting acid chloride is a light brown crystalline substance, is soluble in benzene and in ether, melts at 76–7°. To a solution of 8.4 g. of the acid chloride in 50 cc. of benzene, 9 g. of powdered aluminum chloride was added slowly. When the initial reaction had ceased, the flask was heated on the water-bath until the evolution of hydrogen chloride ceased. After acidification, the benzene was distilled with steam and the precipitate saponified with alcoholic potassium hydroxide. Water and hydrochloric acid were added which caused the precipitation of a light brown crystalline substance that melted with decomposition at 220–1° and was identical with the substance described above as insoluble in acetic acid. Yield, 45%, calculated on the acid chloride used.¹

This method of synthesis and the products of hydrolysis leave no doubt that the acid is 6-benzoyl-2-nitrobenzoic acid.

Calc. for $C_{16}H_9O_4N$: N, 5.16. Found: 5.10.

¹ Mr. M. E. Smith is working on the use of ester acid chlorides in Friedel and Crafts' reaction, in this laboratory.