[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COMMERCIAL SOLVENTS CORPORATION]

THE PREPARATION OF 3-NITROPHTHALIC ACID

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The preparation of 3-nitrophthalic acid, as recorded in the literature, is a somewhat long and tedious process. There are two general methods available for the preparation of this acid from common raw materials. According to the first method naphthalene may be nitrated and the nitronaphthalene oxidized to nitrophthalic acid. The second and simpler method consists of nitrating phthalic anhydride. Miller[1] nitrated phthalic acid with fuming nitric acid in the presence of sulfuric acid, at 100°. Kenner and Mathews[2] followed the same procedure as Miller with the exception that they used phthalic anhydride instead of phthalic acid. More recently, Bogert and Boroschek[3] continued the studies on 3-nitrophthalic acid and its derivatives, but they also used the method of Miller for the preparation of their acid.

The method of Miller has several disadvantages. Probably the two most important ones are the amount of work involved and the poor yields. Among the disadvantages of less importance are the decomposition occurring through the use of fuming nitric acid, the formation of higher nitration products and the difficulty of isolation of the finished product.

This paper has for its purpose the presentation of a simplified method for the production of 3-nitrophthalic acid.

Experimental Part

In a 3-liter flask are placed 175 cc. of nitric acid (d., 1.42) and 185 g. of phthalic anhydride. After the mass has been thoroughly mixed, 175 cc. of sulfuric acid (d., 1.84) is slowly added during constant shaking. After the addition of the acid, the flask and its contents are heated on a steam-bath for two and a half to three hours. As the reaction nears completion the contents of the flask become thick and sometimes harden completely. Occasionally, after the heating has proceeded for 10–15 minutes, a false solidification occurs. This, however, disappears on further heating. When the reaction is complete, the flask is cooled and the contents are poured into 500 cc. of water, with constant agitation. Should the agitation be omitted, lumping will take place and it will be found very difficult to remove the adhering water and nitric acid. The precipitate of 3-nitrophthalic acid is filtered off with the help of suction and washed with 200–300 cc. of water. The suction is continued until no more liquid is

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[1] Miller, *Ann.*, **208**, 223 (1881).

[2] Kenner and Mathews, *J. Chem. Soc.*, **105**, 2476 (1914).

[3] Bogert and Boroschek, THIS JOURNAL, **23**, 740 (1901).

removed by this method. The combined filtrates may be concentrated and a small additional amount of the acid recovered on cooling.

The crude acid as thus obtained is transferred to a 3-liter distilling flask and mixed with 600 cc. of benzene. The benzene is then distilled until 300 cc. of distillate has been obtained or until the distillate is no longer turbid. More benzene may be added if necessary. By this procedure the small quantities of water in the crude acid are removed and any free nitric acid is converted into nitrobenzene. After cooling, the contents of the flask are filtered and the product allowed to air-dry for 12–24 hours. This method results in yields of 85–90% of a product melting at 198° (open tube) and having a neutral equivalent of 209. If the material is not dried thoroughly the melting point may drop as low as 150°. Pure 3-nitrophthalic acid may be obtained by one crystallization of the above-described product from glacial acetic acid. When recrystallizing the crude product it is well to allow the cooled mixture to stand for at least 48 hours, as crystal formation is rather slow. The material obtained by this method melts at 206° (open tube) and has a neutral equivalent of 210.

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THE SUBSTITUTED THIO-UREAS. V. THE SYNTHESIS OF THIO-UREAS FROM AMINO-ETHANOLS AND OF THIAZOLIDINE DERIVATIVES

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This investigation is a continuation of a general study[1] of the action of alkylene bromides upon the disubstituted thio-ureas, RNHCSNHR′, where the groups R and R′ are different, with the purpose of ascertaining the effects of various groups upon the constitution of the resulting thiazolidines.

The most satisfactory method for the identification of the bases thus obtained was found to be their comparison with thiazolidines of known structure. This necessitated, therefore, the synthesis of a number of these thiazoles from the ethanol thio-ureas, whose reactions were studied somewhat in detail, as well as the preparation of a number of intermediates whose properties are recorded briefly.

Experimental Part

Preparation of Intermediates

Aryl-(alkyl)-amino-ethanols. ***p*-Xylyl-amino-ethanol,** 2,4-$(CH_3)_2C_6H_3NHCH_2CH_2OH$.—Ethylene chlorohydrin and *p*-xylidine (2 molecular equivalents) were heated

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[1] Dains, Brewster, Blair and Thompson, THIS JOURNAL, **44**, 2637 (1922).