

*m*- and *p*-Nitrobenzazide

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**M**-Nitrobenzazide is recommended<sup>1-5</sup> as an excellent reagent for the characterization and estimation of aliphatic and aromatic hydroxyl compounds, as it forms well crystallizing *m*-nitrophenylcarbamic esters<sup>3-6</sup> in which the nitro group may be titrated with titanous chloride. Recently<sup>7,8</sup> it has been employed as a reagent also for amines, with which it reacts to form substituted *m*-nitrophenylureas.

The preparation previously given<sup>3,5</sup>, involves the treatment of methyl *m*-nitrobenzoate with hydrazine hydrate and the subsequent treatment of *m*-nitrobenzohydrazide with nitrous acid. As hydrazine hydrate is expensive and frequently unavailable, it was considered desirable to develop a method of preparation from cheaper starting materials. The method of treating the acid chloride with sodium azide, as mentioned by Naegeli and Tyabji<sup>9</sup> has proved to be successful in this case. Sodium azide is commercially available and comparatively cheap and the method described below is somewhat simpler than that previously described and gives as good a yield.

*m*-Nitrobenzoyl chloride, b. p. 153–154° at 12 mm (m. p. 33°) is obtained from *m*-nitrobenzoic acid<sup>10</sup> and excess of thionyl chloride in about 90 % yield.

*m*-Nitrobenzazide. As small amounts of the toxic hydrazoic acid may be liberated, the reaction should be carried out in a hood. A solution of 78 g (1.2 moles) of sodium azide in 500 ml of water, kept at room temperature (20–25°) by means of a water-bath, is efficiently stirred, and a solution of 185.5 g (1 mole) of *m*-nitrobenzoyl chloride in 300 ml of acetone is added from a dropping funnel during

one hour. The *m*-nitrobenzazide separates at once as a white precipitate. The reaction mixture is stirred for  $\frac{1}{2}$  hour, 500 ml of water added and stirring continued for  $\frac{1}{2}$  hour. The azide is filtered, washed with water and dried in the air. The yield is almost quantitative. The product melts at 68° as reported in the literature<sup>5</sup> and is, in general, sufficiently pure as a reagent. It may, however, be recrystallized with about 15 % loss from a mixture of equal parts of benzene and ligroin (b. p. 100–140°), the maximum temperature used for the dissolution being below 50°. *m*-Nitrobenzazide is then obtained as almost colorless crystals, m. p. 68° (the melted substance decomposes with liberation of nitrogen).

Similarly *p*-nitrobenzazide was prepared. In this case the crude product, obtained in 90 % yield, was slightly discolored. It was, therefore, dissolved in a small amount of benzene, decolorizing charcoal added and the solution filtered. An equal volume of ligroin was added to the resultant reddish yellow solution. On seeding, *p*-nitrobenzazide crystallized in yellow crystals, m. p. 71–72° (reported 69°), yield 70 %.

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Received November 13, 1951.