



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

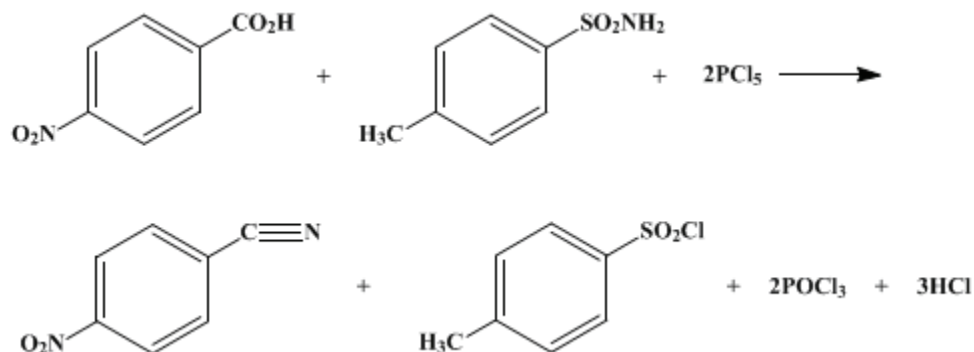
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## *p*-NITROBENZONITRILE

[Benzonitrile, *p*-nitro-]



Submitted by Charles S. Miller

Checked by Arthur C. Cope and James J. Ryan.

### 1. Procedure

In a 1-l. round-bottomed flask with a ground-glass joint are mixed 100.3 g. (0.6 mole) of *p*-nitrobenzoic acid and 109.9 g. (0.64 mole) of *p*-toluenesulfonamide (Note 1). To this mixture is added 262.2 g. (1.26 moles, 5% excess) of phosphorus pentachloride, which is manually stirred into the mixture while the flask is rotated to facilitate mixing (Note 2). The flask is then attached to a short column fitted with a thermometer and side arm for distillation. The thermometer is adjusted so that the bulb is immersed in the reaction mixture, and the mixture is then warmed gently in a hot-air bath to initiate the reaction (Note 3). In some cases this initial reaction must be controlled by a cold-water bath which temporarily replaces the hot-air bath. After the first reaction has subsided and the contents of the flask have become almost liquid, the temperature is gradually raised to 205° and maintained at 200–205° until no more material distills (Note 4). The cooled reaction mixture is treated with 240 ml. of pyridine and warmed gently with manual stirring until solution is complete. To this solution is added cautiously 1.1 l. of water with manual stirring (Note 5), and the cooled suspension is filtered. The solid is washed with water and suspended in 400 ml. of 5% sodium hydroxide solution. After this mixture has been stirred for 30 minutes, the solid is removed, washed thoroughly with water, and dried. The yield of the light-tan product is 74.5–80 g. (85–90%); m.p. 146–147° (cor.) (Note 6) and (Note 7). This product may be further purified with 91% recovery by recrystallization from 50% acetic acid (6.5 ml. per gram). The recrystallized material melts at 147–148° (cor.).

### 2. Notes

1. Benzenesulfonamide and *p*-nitrobenzenesulfonamide have also been used in place of *p*-toluenesulfonamide.
2. This preparation is carried out in a hood.
3. The air bath consists of a hemispherical metal pan about 5 in. in diameter fitted to the bottom of the flask so as to leave an air space of 1/8 in. to 1/4 in. between the metal and the flask. The bath is heated with a small flame.
4. This operation requires about 30 minutes, and the phosphorus halides that distil over weigh 145–155 g.
5. The water should be added about 1 ml. at a time at the beginning. Since this decomposition is very vigorous, the solution is stirred until the reaction subsides before the next addition is made. Later in the addition the water may be poured in slowly.
6. Alternatively, according to the submitter, the cooled reaction mixture may be treated with crushed ice to decompose the remaining phosphorus halides, after which the oily solid is separated from the water by filtration and washed thoroughly with water. The oily solid is added to a mixture of 350 ml. of 14%

ammonium hydroxide and 350 ml. of acetone and stirred for 15–30 minutes to ensure complete reaction between the *p*-toluenesulfonyl chloride and ammonia. The acetone is evaporated on a steam bath, and, after cooling, the solid is filtered and ground in a mortar with a pestle. The finely divided solid is then stirred with 300 ml. of 10% sodium hydroxide until all the *p*-toluenesulfonamide is dissolved (0.5 to 1 hour). The solid *p*-nitrobenzotrile is filtered, washed with water, and dried. The alkaline filtrate is treated with charcoal, filtered and acidified with dilute hydrochloric acid to yield about 75% of the *p*-toluenesulfonamide that was used as a reactant.

7. The submitter states that a number of aromatic mono- and dinitriles have been prepared by this procedure with slight or no modification in the temperature. The reaction mixtures were usually worked up by the acetone-ammonia method described in Note 6. Among the compounds prepared by this method are *o*-nitrobenzotrile, *o*-bromobenzotrile, *m*-methoxybenzotrile, 4,4'-dicyanodiphenylsulfone, 4,4'-dicyanostilbene,  $\alpha,\gamma$ -di-(4-cyanophenoxy) propane. With the last, a temperature of 185–190° for 20 minutes gave the best results. The yields before purification ranged between 75% and 95% and after purification between 63% and 79%. Aliphatic acids give low yields of the corresponding nitriles and, in some cases, chlorinated by-products.

### 3. Discussion

*p*-Nitrobenzotrile has been prepared by the action of phosphorus pentoxide on *p*-nitrobenzamide,<sup>1,2</sup> by the Sandmeyer reaction on *p*-nitroaniline,<sup>3,4</sup> by thermal decomposition of *p*-nitrophenylglyoxylic acid oxime,<sup>5</sup> by the thermal decomposition of *o*-benzoyl-*p*-nitrobenzaldoxime,<sup>6</sup> by the action of acetic anhydride and phosphorus pentoxide on *p*-nitrobenzaldoxime,<sup>7</sup> by the action of fused sodium chloride-aluminum chloride on *p*-nitrobenzamide,<sup>8</sup> by the action of tertiary amines on *syn-p*-nitrobenzaldoxime benzoate,<sup>9,10</sup> by heating *p*-nitrobenzoic acid or *p*-nitrobenzoic anhydride with benzenesulfonamide or *p*-toluenesulfonamide,<sup>11</sup> and by heating *p*-nitrobenzamide with sulfamic acid.<sup>12</sup>

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### References and Notes

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### Appendix

#### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sodium chloride-aluminum chloride

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

acetic anhydride (108-24-7)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

acetone (67-64-1)

charcoal (7782-42-5)

pyridine (110-86-1)

ammonium hydroxide (1336-21-6)

acetone-ammonia (298-08-8)

Benzenesulfonamide (98-10-2)

4,4'-dicyanodiphenylsulfone

4,4'-dicyanostilbene

sulfamic acid (5329-14-6)

p-Toluenesulfonyl chloride (98-59-9)

p-NITROBENZOIC ACID (62-23-7)

phosphorus pentoxide (1314-56-3)

p-toluenesulfonamide (70-55-3)

p-nitroaniline (100-01-6)

p-NITROBENZONITRILE,  
Benzonitrile, p-nitro- (619-72-7)

p-nitrobenzoic anhydride

p-nitrobenzenesulfonamide (6325-93-5)

o-nitrobenzonitrile (612-24-8)

o-bromobenzonitrile (2042-37-7)

m-methoxybenzonitrile (1527-89-5)

p-nitrobenzamide (619-80-7)

p-nitrophenylglyoxylic acid oxime

o-benzoyl-p-nitrobenzaldoxime

p-nitrobenzaldoxime

syn-p-nitrobenzaldoxime benzoate

$\alpha,\gamma$ -di-(4-cyanophenoxy) propane