



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.

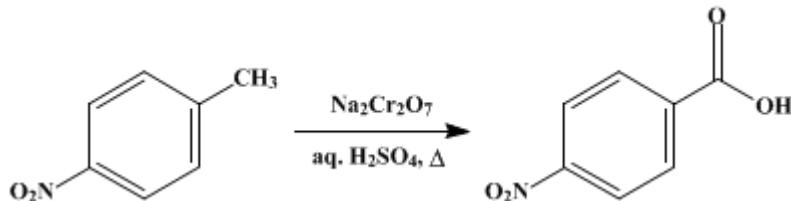
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.392 (1941); Vol. 2, p.53 (1922).*

## **p-NITROBENZOIC ACID**

### [Benzoic acid, *p*-nitro-]



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### 1. Procedure

In a 5-l. round-bottomed flask, fitted with a mechanical stirrer, are placed 680 g. (2.3 moles) of sodium dichromate, 1500 cc. of water, and 230 g. (1.7 moles) of *p*-nitrotoluene. Stirring is started, and 1700 g. of concentrated sulfuric acid is allowed to flow in during about thirty minutes (Note 1). The heat of dilution of the sulfuric acid will cause the nitrotoluene to melt, and rapid oxidation will soon take place. The last half of the sulfuric acid must be added gradually, in order to prevent too violent a reaction. Since a small amount of nitrotoluene is volatilized, it is advisable to carry on this work under a hood.

After the sulfuric acid has been added and the spontaneous heating of the reaction mixture has subsided, the mixture is heated to gentle boiling for about one-half hour (Note 2). When the reaction mixture has cooled, 2 l. of water is added, the cooled solution is filtered through a cloth filter, and the product washed with about 1 l. of water. In order to remove the chromium salts as completely as possible, the crude *p*-nitrobenzoic acid is warmed on the water bath and agitated with 1 l. of dilute (5 per cent) sulfuric acid solution (Note 3). After cooling, the product is again filtered. It is then dissolved in 5 per cent sodium hydroxide solution, filtered from any chromium hydroxide remaining, and also from unchanged nitrotoluene. The filtrate, which should be light yellow or greenish in color, is acidified with dilute sulfuric acid, with stirring. It is usually preferable to run the alkaline solution into the dilute sulfuric acid, rather than to use the reverse procedure, for the precipitation of the nitro acid (Note 4). The precipitated product is filtered with suction, washed thoroughly, and dried. The product should have only a light lemon color. The yield is 230–240 g. (82–86 per cent of the theoretical amount).

For a product of special purity, crystallization from benzene is advisable. For most purposes, however, the nitrobenzoic acid may be used without crystallization, since its melting point is found to be within 2° of the correct value of 238°.

### 2. Notes

1. The above procedure differs from that recorded in the literature, mainly in the use of a fairly large excess of sulfuric acid. This shortens the reaction time from forty hours to about one hour, which is especially convenient in the preparation of the acid on a laboratory scale. Because of the use of this large excess of sulfuric acid, the reaction is apt to be rather violent if the directions given are not carefully followed. The oxidation should be carried out under a hood. Small amounts of nitrotoluene are lost by volatilization, but this loss is not serious, as can be seen from the yield of product obtained.
2. Ten or 20 g. of unchanged nitrotoluene can be recovered from the reaction mixture by steam distillation, but the value of the by-product would not pay for the time spent in recovery.
3. The washing of the crude reaction product with dilute sulfuric acid is advisable, if good material is to be obtained. If an efficient centrifuge is available for use at this stage of the operation, this separate washing may prove to be less essential.
4. When a sparingly soluble organic acid is precipitated from fairly concentrated solution, the

precipitate is liable to carry down with it some of the salt of the organic acid. Addition of the salt solution to the mineral acid, with stirring, avoids this difficulty.

### 3. Discussion

*p*-Nitrobenzoic acid can be prepared by the oxidation of *p*-nitrotoluene with nitric acid,<sup>1</sup> chromic acid,<sup>2</sup> permanganates,<sup>3</sup> and electrolytically.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 394
- Org. Syn. Coll. Vol. 3, 334

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### References and Notes

1. Fischer, Ann. **127**, 137 (1863); Wilbrand and Beilstein, Ann. **128**, 257 (1863); Lloyd and Gershon, U. S. pat. 1,458,715 [C. A. **17**, 2587 (1923)].
  2. Beilstein and Geitner, Ann. **139**, 335 (1866).
  3. Bigelow, J. Am. Chem. Soc. **41**, 1575 (1919).
  4. Boehringer and Sons, Ger. pat. 117,129 [Frdl. **6**, 112 (1900–02)]; Dumbrook and Lowy, Trans. Am. Electrochem. Soc. **45** (pre-print) (1924) [C. A. **18**, 1088 (1924)].
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

permanganates

sulfuric acid (7664-93-9)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

chromic acid (7738-94-5)

sodium dichromate (7789-12-0)

nitrotoluene (88-72-2)

chromium hydroxide

nitrobenzoic acid (552-16-9)

**p-NITROBENZOIC ACID,**  
Benzoic acid, p-nitro- (62-23-7)

*p*-nitrotoluene (99-99-0)

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