



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.

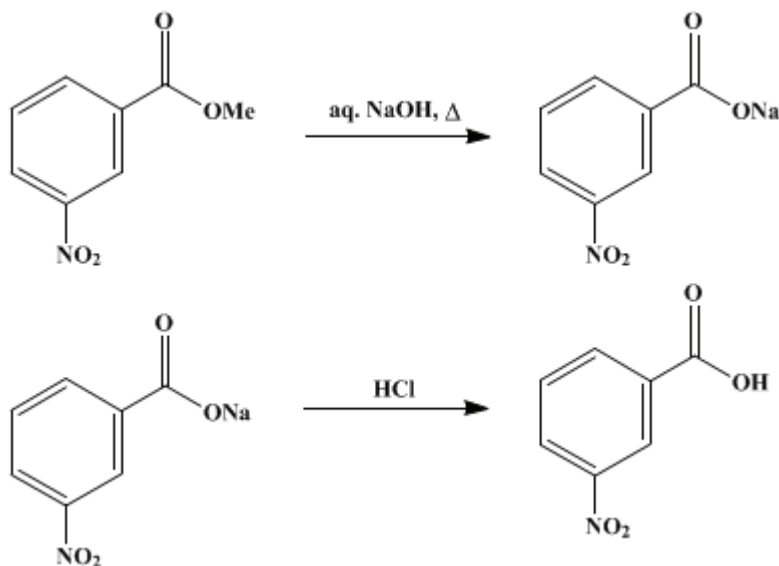
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.391 (1941); Vol. 3, p.73 (1923).*

## ***m*-NITROBENZOIC ACID**

[Benzoic acid, *m*-nitro-]



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### 1. Procedure

In a 2-l. round-bottomed flask fitted with a reflux condenser are placed a solution of 80 g. (2 moles) of sodium hydroxide in 320 cc. of water (Note 1) and 181 g. (1 mole) of methyl *m*-nitrobenzoate (not recrystallized, p. 372). The mixture is heated to boiling during five to ten minutes or until the saponification is complete as shown by the disappearance of the ester.

The reaction mixture is now diluted with an equal volume of water, and when cool is poured, with stirring, into 250 cc. of concentrated hydrochloric acid (Note 2). After the solution has cooled to room temperature, the *m*-nitrobenzoic acid is filtered off by means of suction. This crude acid when dry weighs 150–160 g. (90–96 per cent of the theoretical amount). It has a light brownish color, melts at 140°, and should be completely soluble in ether, thus showing the absence of salts. This acid is satisfactory for many purposes, but in order to prepare a perfectly pure product it must be crystallized once from 1 per cent aqueous hydrochloric acid (Note 3). A light cream-colored product is thus obtained with a loss of about 5 per cent of the material (Note 4).

### 2. Notes

1. The use of a more dilute sodium hydroxide solution than that recommended above has been found to yield unsatisfactory results in the saponification of the ester. Prolonged boiling may lead to the production of colored products.
2. After the hydrolysis of the methyl *m*-nitrobenzoate it is essential that the solution of the sodium salt be poured into the acid. If acid is added to the salt in the usual way, a less soluble acid salt separates; and, as this cannot be entirely removed from the *m*-nitrobenzoic acid even on long digestion with hydrochloric acid, a product is obtained which does not dissolve completely in ether.
3. *m*-Nitrobenzoic acid is soluble to the extent of 1 part in 300 parts of water at 20°, and 20 parts at 100°. The crystallization from water or dilute hydrochloric acid is therefore quite satisfactory.
4. *m*-Nitrobenzoic acid is obtained in a higher yield by nitration of methyl benzoate (p. 372) with subsequent hydrolysis than by the direct nitration of benzoic acid; this method is also preferable on

account of the laborious nature of the methods necessary for the separation of the meta acid from the small quantities of the para isomer formed in the latter process.

### 3. Discussion

*m*-Nitrobenzoic acid can be prepared by the nitration of benzoic acid by means of nitric acid,<sup>1</sup> a mixture of nitric and sulfuric acids,<sup>2</sup> or mixtures of nitrates and sulfuric acid;<sup>3</sup> all these methods lead to the production of a mixture containing principally the *m*-nitrobenzoic acid with a smaller proportion of the ortho and 1–2 per cent of the para isomer. Nitration of benzotrichloride with subsequent hydrolysis also furnishes *m*-nitrobenzoic acid.<sup>4</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 715](#)

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### References and Notes

1. Mulder, *Ann.* **34**, 297 (1840); Hübner, *Ann.* **222**, 72 (1884).
2. Gerland, *Ann.* **91**, 186 (1854); Varma and Kulkarni, *J. Am. Chem. Soc.* **47**, 143 (1925).
3. Gerland, *Ann.* **91**, 185 (1854); Liebermann, *Ber.* **10**, 862 (1877).
4. Sah, Lei, and Wang, *Science Repts. Natl. Tsinghua Univ.* **A2**, 137 (1933) [*C. A.* **28**, 118 (1934)].

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### Appendix

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

nitric and sulfuric acids

nitrates and sulfuric acid

[hydrochloric acid \(7647-01-0\)](#)

[ether \(60-29-7\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[nitric acid \(7697-37-2\)](#)

[Benzoic acid \(65-85-0\)](#)

[benzotrichloride \(98-07-7\)](#)

[methyl benzoate \(93-58-3\)](#)

[m-Nitrobenzoic acid,  
Benzoic acid, m-nitro- \(121-92-6\)](#)

[Methyl m-nitrobenzoate \(618-95-1\)](#)

