



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). 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.

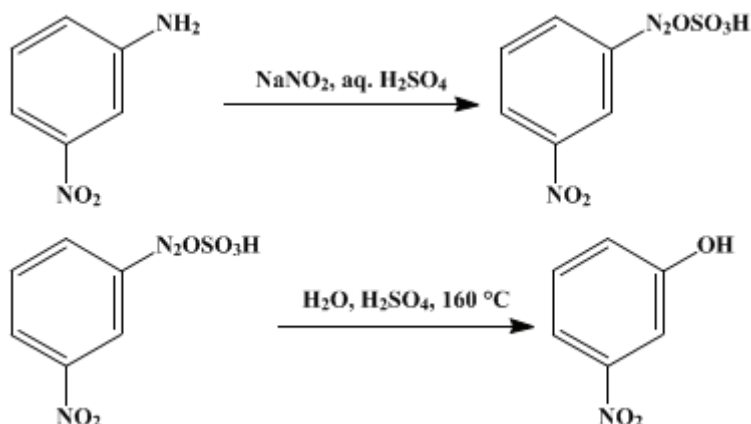
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.404 (1941); Vol. 8, p.80 (1928).

m-NITROPHENOL

[Phenol, *m*-nitro-]



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1. Procedure

In a 4-l. beaker is placed 210 g. (1.5 moles) of finely powdered *m*-nitroaniline (Note 1). A cold mixture of 450 cc. of water and 330 cc. of concentrated sulfuric acid is added with hand or mechanical stirring, and then about 800 g. of finely crushed ice. When a homogeneous mixture has resulted, a solution of 105 g. (1.52 moles) of sodium nitrite in 250 cc. of water is added rapidly over a period of eight to ten minutes at the bottom of the mixture through a separatory funnel (Note 2) until a permanent color is given to starch-iodide paper (about 25–30 cc. of nitrite solution remains unused). The temperature during diazotization should be maintained at 0–5°. Stirring is continued for five to ten minutes longer, and the solution allowed to settle for another five minutes. A heavy crystalline deposit of *m*-nitrobenzenediazonium sulfate settles at the bottom of the beaker, from which the supernatant liquid is decanted (Note 3).

While the diazotization is in progress, 1 l. of concentrated sulfuric acid is added to 750 cc. of water in a 5-l. round-bottomed flask and the mixture heated to boiling (160°) with a large ring burner. The liquor from the diazotization is then added from a separatory funnel at such a rate that the acid mixture boils very vigorously. About fifty minutes is required for this addition. The crystalline diazonium sulfate is then added in small portions at such a rate that the evolved nitrogen does not cause loss of material by excessive foaming. Boiling is continued for a few minutes longer, and the contents of the flask are poured into a large beaker (Note 4) set in running cold water, and vigorously stirred to obtain a homogeneous crystal magma.

When completely cold, the nitrophenol is filtered, thoroughly pressed out, drained with suction, and washed with several portions of iced water, 450 cc. in all being used. It is spread on large sheets of filter paper and dried in a warm room. As thus prepared it has a yellowish brown appearance with darker particles intermixed. The yield is 170–180 g. (81–86 per cent of the theoretical amount) (Note 5).

It may be purified by recrystallization from hot hydrochloric acid, as recommended in Org. Syn. 3, 89, but on account of the difficulty of filtration this procedure is satisfactory on a small scale only. It is preferably distilled in 200-g. lots from a 500-cc. Claisen flask under 10–15 mm. pressure, b.p. 160–165°/12 mm. It is important that no air inlet be used to prevent bumping, since under these conditions the nitrophenol partly sublimes and causes trouble by stopping up the connections. A filter or distilling flask is used as a receiver, and only a short but wide-bore (10-mm.) air condenser is necessary (Note 6). The product is pale yellow and melts at 95–96°. The yield from 200 g. of crude product is 180–185 g.

2. Notes

1. The *m*-nitroaniline used in these experiments was a commercial specimen of 98.4 per cent purity. A less pure specimen did not give a greatly decreased yield. The *m*-nitroaniline may also be added to the mixture prepared by adding the ice to the diluted acid, but this procedure is not quite so satisfactory.
2. The addition of the sodium nitrite solution should be as rapid as possible. If it is too rapid, however, considerable foaming occurs.
3. The filtration of this solution is slow and usually unnecessary. Occasionally undetermined impurities are present, and then washing of the diazonium salt with iced water by decantation, followed by filtration, becomes desirable.
4. In the first part of the addition the solution remains pale yellow to brown, but when the solution becomes saturated with the nitrophenol the nitrophenol separates as a dark oil which is not filtered off. The final volume of the solution is about 3.5 l., and the boiling temperature about 120°.
5. By using the same molecular proportions the following *m*-nitrophenols were prepared in equally good yields from the corresponding *m*-nitroanilines: 3-methoxy-5-nitrophenol and 3-nitro-4,6-xylenol. For the first compound it is advisable to use slightly more ice in the diazotization and add the diazonium solution to a mixture of equal volumes of sulfuric acid and water.
6. After the *m*-nitrophenol has been distilled the flask should be allowed to cool before air is admitted. Otherwise the residue may decompose with explosive violence (W. E. Bachmann and B. W. Rottschaefel, private communication).

3. Discussion

m-Nitrophenol can be prepared by diazotizing *m*-nitroaniline and subsequently heating with a large volume of water;¹ by treating benzene with mercury nitrate and nitric acid in an atmosphere of carbon dioxide;² and by boiling *m*-nitrophenetole (from phenacetin by nitration, hydrolysis, and diazotization in alcohol) with hydrobromic acid,³ a method which is better than that given in Org. Syn. **3**, 87, but far inferior to the present procedure.

References and Notes

1. Fittig, Ber. **7**, 179 (1874); Henriques, Ann. **215**, 323 (1882); De Bruyn, Rec. trav. chim. **2**, 216 (1883); Holleman and Wilhelmy, ibid. **21**, 433 (1902); Adams and Wilson, Org. Syn. **3**, 87 (1923).
2. Macdonald and Calvert, U. S. pat. 1,320,076 [C. A. **14**, 71 (1920)]; Davis, U. S. pat. 1,417,368 [C. A. **16**, 2518 (1922)].
3. Unpublished experiments by one of the editors.

Appendix

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

m-nitrophenols

m-nitroanilines

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

nitric acid (7697-37-2)

HYDROBROMIC ACID (10035-10-6)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

nitrite (14797-65-0)

carbon dioxide (124-38-9)

phenacetin (62-44-2)

nitrophenol (88-75-5)

3-Methoxy-5-nitrophenol

3-Nitro-4,6-xylenol

mercury nitrate

m-nitroaniline (99-09-2)

m-Nitrophenol,
Phenol, m-nitro- (554-84-7)

m-nitrobenzenediazonium sulfate

m-nitrophenetole (621-52-3)