Organic Syntheses

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.

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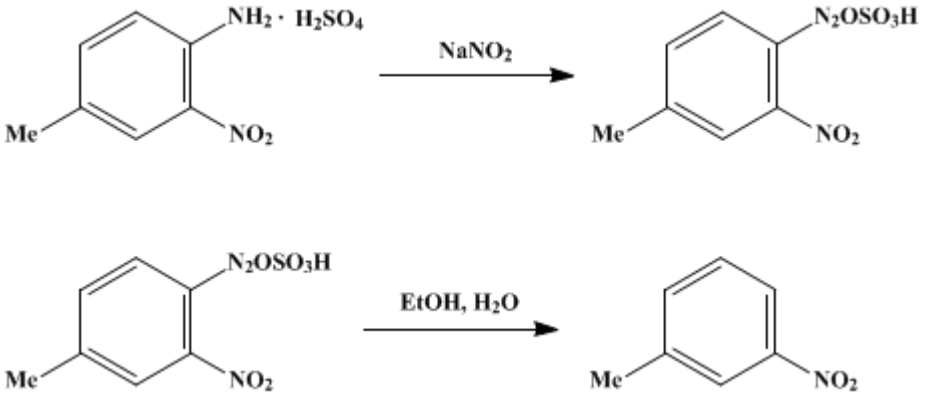
m-NITROTOLUENE

[Toluene, *m*-nitro-]



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1. Procedure

To 500 g. of 95 per cent ethyl alcohol in a 5-l. flask are added 170 g. (1.1 moles) of "*m*-nitro-*p*-toluidine" (3-nitro-4-aminotoluene, m.p. 112–114°, (Note 1)) and 250 g. of concentrated sulfuric acid. The solution is chilled to 10° by means of an ice bath, and a solution of 85 g. (1.2 moles) of technical sodium nitrite in the minimum quantity of water is slowly added, with stirring, the temperature being kept below 10°. The mixture is now warmed very gently on the water bath under an efficient reflux condenser (from the upper end of which a tube leads to a hood or through water) until evolution of gas ceases (Note 2). The alcohol and aldehyde are then carefully distilled off, using a fractionating column and heating in an oil or brine bath (Note 3); when the temperature of the vapors reaches 80° fractionation is stopped and the residue is distilled in a current of steam.

The oil is separated from the distillate, and the aqueous portion is shaken out once with 150–200 cc. of benzene. The united oil and extract are dried with a small quantity of calcium chloride and distilled, first under atmospheric pressure to remove the benzene, and finally under reduced pressure. The *m*-nitrotoluene passes over entirely at 113–114°/15 mm. On cooling, it forms a pale yellow solid which melts at 16°. The yield of pure material is 95–110 g. (62–72 per cent of the theoretical amount).

2. Notes

1. "*m*-Nitro-*p*-toluidine" of good quality is readily available, since it is employed as an intermediate in the preparation of certain important pigments.
2. The decomposition of the diazonium sulfate in the presence of alcohol may take place with considerable violence, and it is necessary to watch the reaction carefully so as to be able to check it, if necessary, by the external application of cold water. Acetaldehyde is rapidly evolved, and some will generally escape from the condenser. It is therefore advisable to lead the escaping gases through water, not only in order to avoid possibility of fire, but also to retain any nitrotoluene which may be entrained.
3. If, after the reaction, the alcohol is distilled off without the use of a column it will contain an appreciable quantity of *m*-nitrotoluene, amounting to 5 or more per cent of the yield. The use of an oil or brine bath is recommended on account of the presence of solid inorganic salts in the mixture.

3. Discussion

The procedure described is substantially that of Buchka.[1] *m*-Nitrotoluene can also be prepared by a similar process from 5-nitro-2-aminotoluene.[2]

References and Notes

1. Buchka, Ber. **22**, 829 (1889); Bigelow, J. Am. Chem. Soc. **41**, 1565 (1919).
2. Beilstein and Kuhlberg, Ann. **158**, 348 (1871).

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

diazonium sulfate

ethyl alcohol (64-17-5)

calcium chloride (10043-52-4)

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

sodium nitrite (7632-00-0)

nitrotoluene (88-72-2)

3-nitro-4-aminotoluene (89-62-3)

5-nitro-2-aminotoluene (99-52-5)

m-Nitrotoluene,
Toluene, m-nitro- (99-08-1)

m-nitro-p-toluidine (119-32-4)