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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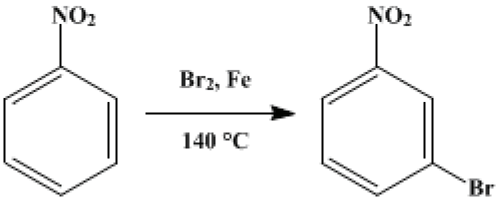
m-BROMONITROBENZENE

[Benzene, 1-bromo-3-nitro-]



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1. Procedure

In a 3-l. three-necked, round-bottomed flask, provided with an efficient reflux condenser bearing an outlet tube held above a surface of water, a 100-cc. separatory funnel, and a mercury-sealed mechanical stirrer (Note 1), is placed 270 g. (2.2 moles) of freshly distilled dry nitrobenzene (Note 2). The joints in the apparatus are made of asbestos paper covered with water glass (see Note 5, p. 19). The flask is heated in an oil bath maintained at 135–145°, and 26 g. of iron powder and 562 g. (180 cc., 3.5 moles) of dry bromine (Note 3) are added in the following manner: Eight grams of iron powder ("ferrum reductum") (Note 4) is added through the side neck to the stirred nitrobenzene. From the separatory funnel 60 cc. of bromine is added at such a rate that the bromine vapors do not traverse the condenser. This addition requires about one hour, and the mixture is stirred and heated for another hour before the addition of a second portion of iron and bromine. Two portions, each of 8 g. of iron powder and 60 cc. of bromine, are added under the same conditions as the first addition, and the mixture is stirred and heated for one hour between the completion of one addition and the beginning of another. The evolution of hydrogen bromide slackens considerably toward the last of the heating, and there is practically no more bromine vapor in the condenser. A final addition of 2 g. of iron powder is made, and the heating continued for one hour longer.

The reaction product, which is a dark reddish-brown liquid, is poured or siphoned (Note 5) into 1.5 l. of water to which 50 cc. of a saturated solution of sodium bisulfite has been added (Note 6). The mixture is distilled with steam (p. 479) and the first portion of the distillate is collected separately to remove a small amount of unchanged nitrobenzene. It is necessary to collect about 12 l. of distillate in order to obtain all the *m*-bromonitrobenzene. The yellow crystalline solid is filtered with suction and pressed well on the funnel to remove water and traces of nitrobenzene. The yield of crude product varies from 270 to 340 g. (60–75 per cent of the theoretical amount). It melts at 51.5–52° and boils at 117–118°/9 mm. This product is satisfactory for most purposes. If a purer material is desired, the crude *m*-bromonitrobenzene may be distilled under reduced pressure. The recovery on purification is about 85 per cent. Brühl recorded the b.p. as 138°/18 mm. and the m.p. as 56° for pure *m*-bromonitrobenzene.[1]

2. Notes

1. With small amounts, up to 90 g. of nitrobenzene, mechanical stirring is not essential, and occasional shaking is sufficient.
2. The nitrobenzene is dried by distillation under atmospheric or reduced pressure, by rejecting the first 5 per cent of the distillate.
3. The bromine is dried by shaking with an equal volume of concentrated sulfuric acid and separating.
4. A number of other forms of iron were used, but none gave as good results as the "ferrum reductum."
5. If a series of successive runs is to be made, it is convenient to siphon the reaction product, and carry out a second preparation in the same apparatus without dismantling it.
6. The sodium bisulfite is added to remove any free bromine. A large excess should not be used as secondary reactions may occur during the steam distillation.

3. Discussion

m-Bromonitrobenzene can be obtained through *m*-nitrobenzenediazonium salts[2] and by elimination of the amino group from 4-bromo-2-nitroaniline.[3] It has been prepared by the bromination of nitrobenzene in the presence of various catalysts.[4] The procedure given is adapted from that described by Wheeler and McFarland.[5]

References and Notes

1. Brühl, Z. physik. Chem. **22**, 379 (1897).
2. Griess, Phil. Trans. Roy. Soc. London **154**, III, 711 (1864); Jahresber. 457 (1866); Fittig and Mager, Ber. **8**, 364 (1875).
3. Wurster, Ber. **6**, 1543 (1873); Wurster and Grubenmann, Ber. **7**, 416 (1874).
4. Scheufelen, Ann. **231**, 165 (1885).
5. Wheeler and McFarland, Am. Chem. J. **19**, 366 (1897).

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

nitrobenzenediazonium salts

sulfuric acid (7664-93-9)

iron (7439-89-6)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

sodium bisulfite (7631-90-5)

Nitrobenzene (98-95-3)

Benzene, 1-bromo-3-nitro-,
m-Bromonitrobenzene (585-79-5)

Bromonitrobenzene (577-19-5)

4-bromo-2-nitroaniline (875-51-4)