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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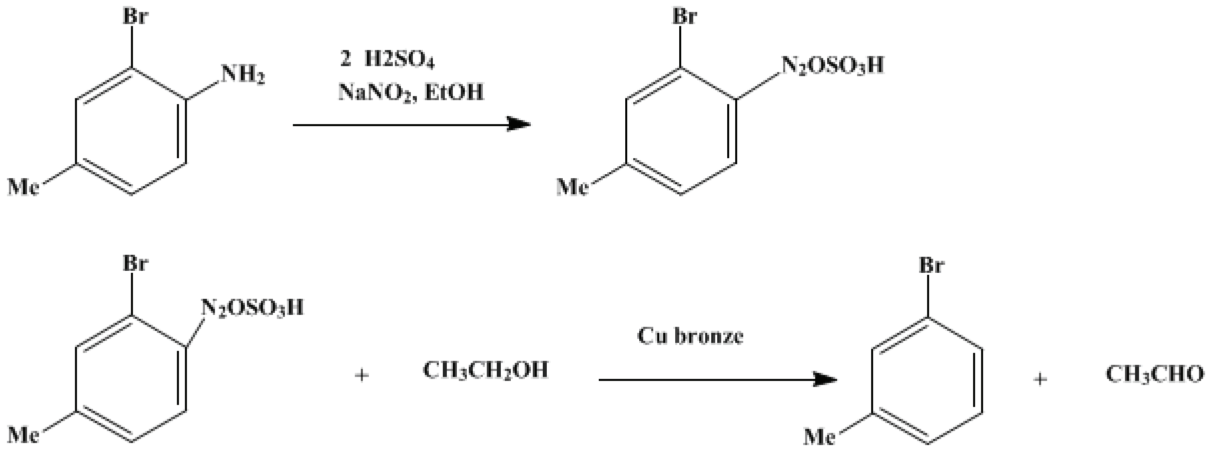
Organic Syntheses, Coll. Vol. 1, p.133 (1941); Vol. 6, p.16 (1926).

m-BROMOTOLUENE

[Toluene, *m*-bromo-]



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1. Procedure

To a cold mixture of 800 cc. of 95 per cent ethyl alcohol and 200 cc. of concentrated sulfuric acid (Note 1) in a 5-l. round-bottomed flask, provided with an efficient mechanical stirrer, is added 250 g. (1.33 moles) of crude 3-bromo-4-aminotoluene (p. 111). The solution is stirred and cooled to 10°, and a solution of 148 g. (2.05 moles) of u.s.p. sodium nitrite in 260 cc. of water is added from a separatory funnel. During this addition, the temperature of the mixture must not be allowed to rise above 10°. After all of the nitrite solution has been added, the mixture is stirred twenty minutes longer to complete the diazotization.

To the diazotized solution is added 35 g. (0.55 atom) of copper bronze (Note 2) which has been washed with ether. The stirrer is replaced by a long, efficient reflux condenser. A bath of ice water is prepared for cooling the flask when the reaction becomes too vigorous. The flask is warmed cautiously until a vigorous evolution of gas starts. It is then immersed in the ice water to prevent loss through the condenser by too rapid evolution of nitrogen and acetaldehyde. When the reaction has moderated, the flask is again warmed, and finally the mixture is heated for ten minutes on a steam bath. At the end of the reaction the color changes from reddish brown to yellow.

After the addition of 2 l. of water, the mixture is steam-distilled as long as any oil comes over. The crude, heavy, yellow oil is separated and washed with two 200-cc. portions of 10 per cent sodium hydroxide, once with 100 cc. of water, twice with 150-cc. portions of concentrated sulfuric acid, and finally with 100 cc. of 5 per cent sodium carbonate solution. It is dried with about 5 g. of calcium chloride, filtered through glass wool, and distilled using a long air condenser. Most of the product boils at 180–183°/750 mm. The yield of pure colorless material, b.p. 183°/760 mm., is 125–135 g. (36–39 per cent of the theoretical amount, based on the amount of *p*-toluidine originally used (p. 111), or 54–59 per cent based on the amount of 3-bromo-4-aminotoluene).

2. Notes

1. Proper care must be exercised in mixing the alcohol and sulfuric acid. The mixture is best cooled in the flask with stirring.
2. Reduced copper powder and various grades of copper bronze were used with practically the same results.

3. Discussion

m-Bromotoluene can be prepared by the diazotization of *m*-toluidine followed by treatment with cuprous bromide, potassium bromide and hydrobromic acid,[1] and by elimination of the amino group from 3-bromo-4-aminotoluene[2] and 5-bromo-2-aminotoluene.[3] The procedure described is a modification of the method of Feitler.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 111

References and Notes

1. Acree, Ber. **37**, 994 (1904).
2. Wroblevsky, Ann. **168**, 155, 158 (1873); Feitler, Z. physik. Chem. **4**, 77 (1889).
3. Wroblevsky, Ann. **168**, 164 (1873).

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

copper bronze

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium hydroxide (1310-73-2)

HYDROBROMIC ACID (10035-10-6)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

nitrite (14797-65-0)

copper powder (7440-50-8)

3-Bromo-4-aminotoluene (583-68-6)

potassium bromide (7758-02-3)

cuprous bromide (7787-70-4)

5-bromo-2-aminotoluene (583-75-5)

p-toluidine (106-49-0)

m-toluidine (108-44-1)

m-Bromotoluene,
Toluene, m-bromo- (591-17-3)