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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

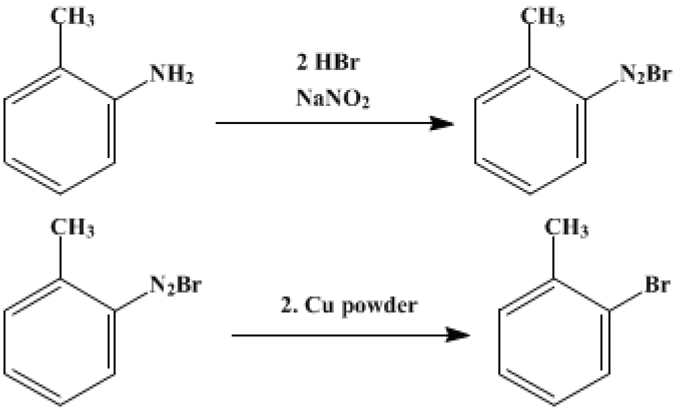
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.009.0022

Organic Syntheses, Coll. Vol. 1, p.135 (1941); Vol. 9, p.22 (1929).

o-BROMOTOLUENE

[Toluene, *o*-bromo-]



Submitted by L. A. Bigelow
Checked by C. S. Marvel and S. V. Puntambeker.

1. Procedure

A solution of 162 g. (1.5 moles) of commercial *o*-toluidine in 880 cc. (6 moles) of 40 per cent commercial hydrobromic acid (Note 1) in a 3-l. flask is cooled to 10° and diazotized with 116 g. (1.7 moles) of coarsely powdered commercial sodium nitrite, added about 10 g. at a time. After each addition the flask is stoppered and shaken until all the red fumes are absorbed. The temperature must be kept below 10°. When diazotization is complete, 5 g. of copper powder (Note 2) is added, the flask is attached to a reflux condenser and heated very cautiously. As soon as the first sign of reaction is observed, the flask is cooled with ice. Nitrogen is evolved vigorously. When the reaction subsides, the mixture is heated one-half hour on the steam bath.

Then 1 l. of water is added and the mixture is distilled with steam until about 1.5 l. has passed over. The distillate is made alkaline with about 10 g. of powdered sodium hydroxide and the lower red layer of crude *o*-bromotoluene separated (Note 3). This weighs about 140 g. It is washed with concentrated sulfuric acid, which removes almost all the color, and then twice with water. It is dried over a little calcium chloride, filtered and distilled twice from a modified Claisen flask (p. 130). The yield of pure product boiling at 178–181° is 110–120 g. (43–47 per cent of the theoretical amount).

2. Notes

1. If 48 per cent (constant boiling) hydrobromic acid is used the diazotization is very difficult to control. The reaction becomes very vigorous and forces out the stopper.
2. Either reduced copper or fine copper filings may be used.
3. This gives as good results as when the *o*-bromotoluene is extracted from the alkaline mixture with ether.

3. Discussion

o-Bromotoluene can be prepared by the bromination of toluene;[1] by the bromination of potassium *p*-toluenesulfonate and subsequent hydrolysis;[2] and by the diazotization of *o*-toluidine under different conditions.[3]

References and Notes

1. Jannasch and Hübner, Ann. **170**, 117 (1873); Varma and Narayan, Quart. J. Indian Chem. Soc. **4**, 283 (1927) [Chem. Zentr. I, 489 (1928)].
2. Miller, J. Chem. Soc. **61**, 1027 (1892).
3. Wroblevsky, Ann. **168**, 171 (1873); Körner, Gazz. chim. ital. **4**, 305 (1874); Jackson, Am. Chem. J. **1**, 100 (1879); Feitler, Z. physik. Chem. **4**, 72 (1889); Neogi and Mitra, J. Chem. Soc. 1332 (1928).

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium hydroxide (1310-73-2)

HYDROBROMIC ACID (10035-10-6)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

copper,
copper powder,
copper filings (7440-50-8)

toluene (108-88-3)

o-Bromotoluene,
Toluene, o-bromo- (95-46-5)

o-toluidine (95-53-4)

potassium p-toluenesulfonate