



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](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.

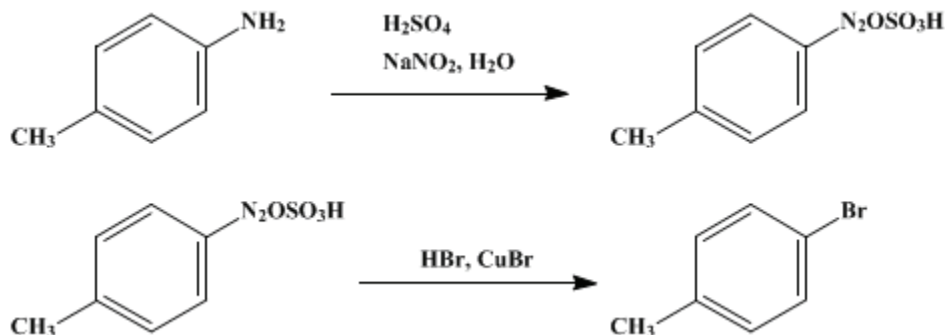
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.136 (1941); Vol. 5, p.21 (1925).*

## ***p*-BROMOTOLUENE**

[Toluene, *p*-bromo-]



Submitted by L. A. Bigelow

Checked by C. S. Marvel and A. E. Broderick.

### 1. Procedure

A mixture of 63 g. (0.25 mole) of crystallized [copper sulfate](#), 20 g. (0.31 atom) of [copper turnings](#), 154 g. (1.1 moles) of [sodium bromide dihydrate](#), 30 g. (16.3 cc., 0.28 mole) of concentrated [sulfuric acid](#) (sp. gr. 1.84), and 1 l. of water is refluxed over a flame for three to four hours until the color becomes yellowish ([Note 1](#)).

When the [hydrobromic acid-cuprous bromide](#) solution is ready for use, the diazonium solution is prepared. A solution of 107 g. (1 mole) of *p*-toluidine and 196 g. (107 cc., 1.9 moles) of concentrated [sulfuric acid](#) (sp. gr. 1.84) in 1 l. of water is cooled below 20° and diazotized with a solution of 70 g. (1 mole) of [sodium nitrite](#) in 125 cc. of water. This requires about twenty to thirty minutes when the temperature is maintained between 15° and 20° by means of an ice bath.

A 5-l. round-bottomed flask containing the [hydrobromic acid-cuprous bromide](#) solution, is arranged for steam distillation. After the copper solution is heated to boiling, the diazonium solution is gradually added from a separatory funnel and a vigorous current of steam is passed through the reaction mixture at the same time. This procedure requires about two hours.

The aqueous distillate is made alkaline with [sodium hydroxide](#) solution and the *p*-bromotoluene is separated from the water layer ([Note 2](#)). The crude product weighs 131–137 g. For purification the crude product is washed once with concentrated [sulfuric acid](#) ([Note 3](#)) and then with water. It is dried over a little [calcium chloride](#), filtered, and distilled. The yield of pure product amounts to 120–126 g. (70–73 per cent of the theoretical amount) boiling at 183–185° and melting at 25–26°.

### 2. Notes

1. If the color of the solution has not been discharged after heating for three to four hours, a few grams of [sodium sulfite](#) may be added to complete the reduction.
2. A small amount of [ether](#) or [benzene](#) may be used to aid in the separation if it is needed.
3. The [sulfuric acid](#) treatment is necessary if a colorless product is to be obtained. If ether is used in the extraction of the *p*-bromotoluene, it must be removed before washing with [sulfuric acid](#).

### 3. Discussion

*p*-Bromotoluene can be prepared by the bromination of [toluene](#) with [bromine](#)<sup>1</sup> or [hypobromous acid](#);<sup>2</sup> and, preferably, by the diazotization of *p*-toluidine followed by replacement of the diazonium group by [bromine](#).<sup>3</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 550](#)
- [Org. Syn. Coll. Vol. 2, 89](#)

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## References and Notes

1. Glinzer and Fittig, *Ann.* **136**, 301 (1865); Hübner and Wallach, *Ann.* **154**, 294 (1870); *Z. Chem.* **138** (1869); Michaelis and Genzken, *Ann.* **242**, 165 (1887); Schramm, *Ber.* **18**, 608 (1885); Gay, Ducelliez and Raynaud, *Compt. rend.* **158**, 1806 (1914); Varma and Narayan, *Quart. J. Indian Chem. Soc.* **4**, 283 (1927) [*Chem. Zentr. I*, 489 (1928)].
2. Stark, *Ber.* **43**, 673 (1910).
3. Acree, *Ber.* **37**, 994 (1904); Neogi and Mitra, *J. Chem. Soc.* 1332 (1928).

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## Appendix

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

[calcium chloride \(10043-52-4\)](#)

[sulfuric acid \(7664-93-9\)](#)

[Benzene \(71-43-2\)](#)

[ether \(60-29-7\)](#)

[sodium sulfite \(7757-83-7\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[bromine \(7726-95-6\)](#)

[copper sulfate \(7758-98-7\)](#)

[sodium nitrite \(7632-00-0\)](#)

[copper turnings \(7440-50-8\)](#)

[toluene \(108-88-3\)](#)

[hypobromous acid \(13517-11-8\)](#)

[sodium bromide dihydrate](#)

[hydrobromic acid-cuprous bromide](#)

[p-toluidine \(106-49-0\)](#)

p-Bromotoluene,  
Toluene, p-bromo- (106-38-7)

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