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.

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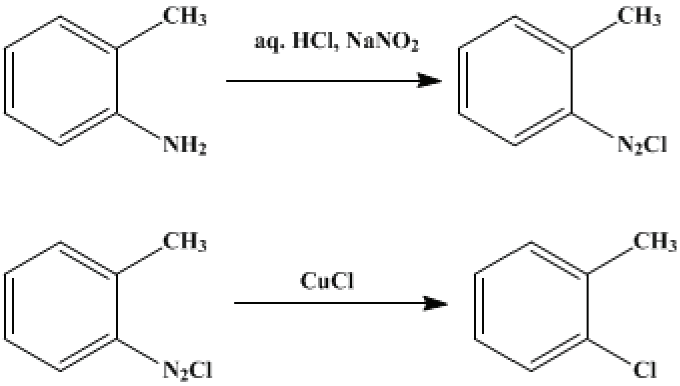
Organic Syntheses, Coll. Vol. 1, p.170 (1941); Vol. 3, p.33 (1923).

o-CHLOROTOLUENE AND *p*-CHLOROTOLUENE

[Toluene, *o*-chloro- and *p*-chloro-]



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1. Procedure

(*A*) *Preparation of Cuprous Chloride Solution* (Note 1).—A solution of 1250 g. (5 moles) of crystallized copper sulfate and 325 g. (5.6 moles) of sodium chloride in 4 l. of hot water is prepared in a 12-l. flask. The flask is fitted with a mechanical stirrer, and an alkaline solution of sodium sulfite (265 g. of sodium bisulfite and 175 g. of sodium hydroxide in 2 l. of water) is added during a period of five to ten minutes. The mixture is allowed to cool to room temperature and washed by decantation. The cuprous chloride is obtained as a white powder, which, however, darkens on exposure to the air. The crude product is dissolved in 2 kg. of commercial 28 per cent hydrochloric acid (sp. gr. 1.14) and the solution is used in the following preparation (Note 2).

(*B*) *o-Chlorotoluene*.—In a 10-l. stone jar fitted with a mechanical stirrer are placed 2 kg. (1755 cc.) of commercial 28 per cent hydrochloric acid (sp. gr. 1.14) and 428 g. (427 cc., 4 moles) of *o*-toluidine. The mixture is cooled to 0° by adding cracked ice (about 1 kg. is required). The *o*-toluidine hydrochloride separates as a finely divided precipitate. The stirrer is started, and to the cold suspension is added a solution of 280 g. (4.05 moles) of sodium nitrite in 800 cc. of water; the diazotization is carried out at 0–5° and requires about fifteen minutes. Cracked ice is added from time to time to keep the temperature within the proper limits. The volume of the final solution is 5–6 l.

While the diazotization is being carried out the cuprous chloride solution (*A*) is cooled to 0°. The cold diazonium solution is now poured rapidly into the well-stirred cuprous chloride solution. The solution becomes very thick, owing to the separation of an addition product between the diazonium salt and the cuprous chloride. The cold mixture is allowed to warm up to room temperature, and stirring is continued for two and one-half to three hours at this temperature (Note 3). When the temperature reaches about 15°, the solid addition compound begins to break down with the formation of nitrogen and *o*-chlorotoluene. After the specified time the solution is placed on a steam bath and heated to 60° to complete the decomposition of the addition product. The *o*-chlorotoluene forms a layer on top of the copper salt solution. The water solution is drawn off through a siphon until only 5–6 l. remains. The remaining material is steam-distilled from a 12-l. round-bottomed flask (Note 4) until about 3.5–4 l. is collected in the distillate. The *o*-chlorotoluene layer is separated from the water, washed with cold concentrated sulfuric acid (Note 5) and then with water, and finally dried over calcium chloride. The product boiling at 155–158° weighs 375–400 g. 74–79 per cent of the theoretical amount).

(*C*) *p-Chlorotoluene*.—*p*-Chlorotoluene is prepared in exactly the same way starting with *p*-toluidine. The yields are 70–79 per cent of the theoretical amount of a product which boils at 158–162°

and melts at 4–7°.

2. Notes

1. The cuprous chloride solution prepared as described is more satisfactory and less expensive than one prepared by reducing cupric chloride with copper turnings.
2. If less cuprous chloride is used the yield is lowered. It seems desirable to use 1 mole of cuprous chloride (CuCl) to 1 mole of diazonium salt. Increasing the amount of cuprous chloride beyond this point does not improve the yield.
3. The literature directions usually call for mixing the diazonium solution and the cuprous chloride solution at about 30–40°. This procedure gives a yield considerably lower than that obtained by mixing the solutions cold and allowing to warm up gradually. If the mixture obtained by adding the diazonium solution to the cuprous chloride solution is heated at once, the yield falls to 55–65 per cent.
4. The steam distillation can be conveniently carried out in the apparatus described on p. 479.
5. The treatment with sulfuric acid is necessary to remove cresol and a trace of azo compound that usually colors the crude product and cannot be removed by distillation.

3. Discussion

o-Chlorotoluene can be prepared by the action of chlorine[1] and of sulfuryl chloride[2] on toluene in the presence of various catalysts; by the chlorination of *p*-toluenesulfonyl chloride followed by hydrolysis;[3] and by the diazotization of *o*-toluidine followed by replacement of the diazonium salt group by chlorine.[4]

p-Chlorotoluene can be prepared by the action of chlorine[5] and of sulfuryl chloride[6] on toluene in the presence of various catalysts, and by the diazo reaction with *p*-toluidine.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 514
- Org. Syn. Coll. Vol. 2, 133
- Org. Syn. Coll. Vol. 2, 135
- Org. Syn. Coll. Vol. 2, 583

References and Notes

1. Hübner and Majert, Ber. **6**, 790 (1873); Seelig, Ann. **237**, 152 (1887); Seyewitz and Biot, Compt. rend. **135**, 1121 (1902).
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3. Gesellschaft Chem. Ind. Basel, Ger. Pat. 133,000 [Chem. Zentr. II, 313 (1902)]; Badische Anilin Soda-Fabrik, Ger. pat. 294,638 [Frdl. **12**, 908 (1914–16)]; McMaster and Carol, Ind. Eng. Chem. **23**, 218 (1931).
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7. Hübner and Majert, Ber. **6**, 794 (1873); Gasiorovski and Wayss, Ber. **18**, 1939 (1885); Gattermann, Ber. **23**, 1221 (1890); Heller and Tischner, Ber. **44**, 254 (1911); Heller, Z. angew. Chem. **23**, 392 (1910).

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

diazonium salt

copper salt

diazonium solution

Toluene, o-chloro- and p-chloro-

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

copper sulfate (7758-98-7)

sodium nitrite (7632-00-0)

sodium bisulfite (7631-90-5)

copper turnings (7440-50-8)

sulfuryl chloride (7791-25-5)

chlorine (7782-50-5)

toluene (108-88-3)

cuprous chloride (7758-89-6)

cupric chloride (7758-89-6)

o-Chlorotoluene (95-49-8)

p-Chlorotoluene (106-43-4)

cresol (95-48-7)

p-toluidine (106-49-0)

o-toluidine (95-53-4)

p-Toluenesulfonyl chloride (98-59-9)

o-toluidine hydrochloride (636-21-5)