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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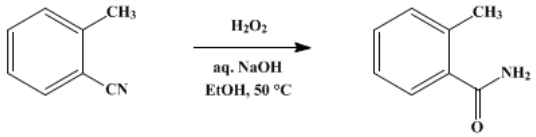
o-TOLUAMIDE



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1. Procedure

Caution! See the discussion in Org. Synth. 1973, Coll. Vol. 5, 1054 with regard to potential hazards associated with this procedure.

In a 2-l. round-bottomed flask are placed 88 g. (0.75 mole) of *o*-tolunitrile (Org. Syn. Coll. Vol. I, **1941**, 514), 300 cc. (2.6 moles) of 30 per cent hydrogen peroxide, 400 cc. of 95 per cent alcohol, and 30 cc. of 6 *N* sodium hydroxide solution (Note 1). The mixture evolves oxygen and soon warms up owing to the heat of reaction; the temperature is kept at 40–50° by external cooling (Note 2). After about one hour, heat is no longer evolved; the temperature is then maintained at 50° by external heating for an additional three hours. The mixture, while still warm, is made exactly neutral to litmus with 5 per cent sulfuric acid and distilled with steam until 1 l. of distillate is collected. The residue, which has a volume of about 600 cc. (Note 3), is poured while hot into a 1-l. beaker and cooled to 20°. The crystals which form are filtered with suction. They are transferred to a mortar and ground to a paste with 100 cc. of cold water, filtered again, and then washed on the filter with an additional 100 cc. of cold water. The *o*-toluamide is obtained in the form of white crystals melting at 141–141.5°. The yield of air-dried product is 91–93 g. (90–92 per cent of the theoretical amount) (Note 4). The product may be recrystallized from water (10 g. per 100 cc.). The recovery is 92 per cent, and the melting point is not changed (Note 5).

2. Notes

1. This amount of alcohol is sufficient to provide a homogeneous solution.
2. If the temperature is allowed to rise much above 50° the evolution of oxygen will be sufficiently rapid to cause the mixture to foam out of the flask.
3. The volume of the solution in the flask is kept down by applying a small flame to the flask after most of the alcohol has been distilled.
4. An additional 3–4 g. of low-melting material may be obtained by concentrating the filtrate, but this is hardly worth while.
5. In general, amides may be prepared by this method from aliphatic nitriles in yields of 50–60 per cent and from aromatic nitriles in yields of 80–95 per cent. Slight variations in the above procedure may be necessary for carrying out the reaction and for isolating the amide, depending on the solubility of the nitriles and amides. Except for difficulty hydrolyzable nitriles such as the *o*-substituted aromatic nitriles, an equivalent amount of 6 to 12 per cent hydrogen peroxide gives better yields than the 30 per cent reagent.[1]

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3. Discussion

o-Toluamide has been prepared by the action of ammonia on *o*-toluyl chloride,[2] and by the action of alcoholic potassium hydroxide[3] or of an alkaline solution of hydrogen peroxide[4], [1] on *o*-tolunitrile.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1054

References and Notes

1. McMaster and Noller, Wash. Univ. Studies **13**, 23 (1925); J. Indian Chem. Soc. **12**, 652 (1935) [C. A. **30**, 1736 (1936)].
2. Remsen and Reid, Am. Chem. J. **21**, 289 (1899).
3. Weith, Ber. **6**, 419 (1873).
4. Kattwinkel and Wolffenstein, ibid. **37**, 3224 (1904); Dubsky, J. prakt. Chem. (2) **93**, 137 (1916).

Appendix

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

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

sodium hydroxide (1310-73-2)

oxygen (7782-44-7)

potassium hydroxide (1310-58-3)

hydrogen peroxide (7722-84-1)

o-toluyl chloride (95-49-8)

o-Tolunitrile (529-19-1)

o-Toluamide (527-85-5)