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.

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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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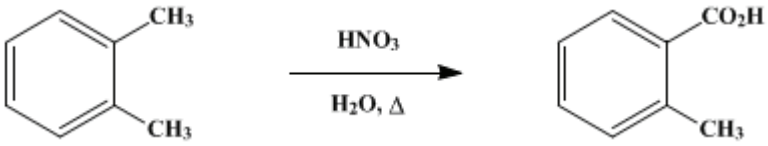
Organic Syntheses, Coll. Vol. 3, p.820 (1955); Vol. 27, p.84 (1947).

o-TOLUIC ACID



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1. Procedure

In a 5-l. round-bottomed flask are placed 1.6 l. of water, 800 ml. of concentrated nitric acid (sp. gr. 1.42), and 400 ml. (364 g., 3 moles) of commercial 90% *o*-xylene (Note 1). A reflux condenser (40 cm. or longer) is fitted to the flask with a cork, and a gas-absorption trap is attached to the top of the condenser. The mixture is refluxed by heating in an oil bath kept between 145° and 155° for 55 hours (Note 2). At the end of this time the organic layer has settled to the bottom of the flask. The hot reaction mixture is poured with stirring into 1 kg. of ice in a 4-l. beaker. After cooling, the solid product is filtered, suspended in 2 l. of cold water, and filtered again. The wet product is dissolved by warming in 1 l. of 10% sodium hydroxide solution. After cooling, any unreacted xylene is separated by extraction with 250 ml. of ether. The aqueous layer is then heated on the steam bath with 5–10 g. of Norit and filtered hot with suction through a layer of Norit. The warm, clear red alkaline solution is added with vigorous mechanical stirring to 225 ml. of concentrated hydrochloric acid. The product is filtered from the warm solution, washed with cold water, and sucked as dry as possible on a Büchner funnel (Note 3).

The crude product is dissolved in 350 ml. of 95% ethanol and heated on the steam bath with 5 g. of Darco for 1 hour. The hot solution is filtered by gravity through a heated funnel. The filter paper is heated with an additional 70-ml. portion of 95% ethanol, and the mixture is filtered hot through a fresh paper, into the main solution. To the ethanolic solution, adjusted to a temperature of 55–60°, is added 480 ml. of warm (55–60°) water. After being cooled first to room temperature and then to ice-bath temperature, the crystallized product is filtered, washed with 250 ml. of cold 50% ethanol, and dried (Note 4). The yield of light-tan product melting at 99–101° amounts to 218–225 g. (53–55%) (Note 5) and (Note 6).

2. Notes

1. The *o*-xylene (90–92% purity) may be obtained from the Barrett Division of the Allied Chemical and Dye Corporation, 40 Rector Street, New York 6, New York.
2. It is not necessary that this heating be continuous. Longer times of refluxing or mechanical stirring do not improve the yield.
3. The crude product after air drying for 24–30 hours weighs between 250 g. and 300 g. and melts at 94–98°.
4. If the humidity is low, the product may be air-dried; otherwise, it is best to dry in a vacuum desiccator overnight at room temperature. *o*-Toluic acid sublimes at higher temperatures.
5. The yield depends on the *o*-xylene content of the starting material. The yields stated are based on 90% *o*-xylene.
6. This product is pure enough for most purposes. Pure white needles of *o*-toluic acid may be obtained by recrystallization from water (2 l. of water for 20 g. of acid), Darco being used for decolorization. The recovery is about 85% of white needles melting at 101–103°.

3. Discussion

References to methods of preparation are given in earlier volumes.[1] *o*-Toluic acid has been prepared by the catalytic oxidation of *o*-xylene.[2]

References and Notes

1. *Org. Syntheses*, **11**, 97 (1931); Coll. Vol. **2**, 589 (1943).
2. Emerson, Lucas, and Heimsch, *J. Am. Chem. Soc.*, **71**, 1742 (1949).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

Norit (7782-42-5)

xylene (106-42-3)

o-Toluic acid (118-90-1)

o-Xylene (95-47-6)