



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.

Organic Syntheses, Coll. Vol. 2, p.588 (1943); Vol. 11, p.96 (1931).

***o*-TOLUIC ACID**



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1. Procedure

In a 5-l. flask, equipped with a mechanical stirrer, a reflux condenser, and a separatory funnel, is placed 3 kg. of 75 per cent **sulfuric acid** (sp. gr. 1.67). The solution is heated to about 150°, the stirrer is started, and 1 kg. (8.54 moles) of *o*-tolunitrile (*Org. Syn. Coll. Vol. I, 1941, 514*) is added during two hours. The temperature is maintained at 150–160° and the mixture is stirred for two hours after the addition of the nitrile is complete. The temperature is then raised to 190° and stirring is continued for another hour. Usually some crystalline material appears in the condenser at this stage. The reaction mixture is cooled, poured into ice water, and filtered. The crude material is dissolved in an excess of 10 per cent **sodium hydroxide** solution (*Note 1*), filtered hot, and the filtrate acidified with dilute **sulfuric acid**. The product is collected on a Büchner funnel, dried, and recrystallized from about 3 l. of **benzene** (*Note 2*). The yield is 930–1030 g. (80–89 per cent of the theoretical amount) of *o*-toluic acid which melts at 102–103° (*Note 3*).

2. Notes

1. Any insoluble material which separates on conversion into the sodium salt is **toluamide**, which may be isolated. The appearance of this substance indicates too short a period of heating or too low a temperature.

The reaction can be stopped readily so that a considerable quantity of the amide is produced. The amide purified by recrystallization from water, melts at 139–140°.

2. An additional amount of pure *o*-toluic acid may be obtained by distilling the **benzene** mother liquor to a small volume and allowing to cool.

3. *p*-Toluic acid (m.p. 178°) may be obtained from *p*-tolunitrile by the same process and in the same yields. This acid is less soluble in **benzene**, and about 9 l. is needed for recrystallization.

3. Discussion

o-Toluic acid has been prepared by heating 1,3-naphthalenedisulfonic acid, 1,3-dihydroxynaphthalene, 1-naphthol-3-sulfonic acid, or 1-naphthylamine-3-sulfonic acid with **sodium hydroxide**;¹ by reduction of **phthalide** with **hydriodic acid** and **phosphorus**;² by electrolytic oxidation of *o*-xylene;³ by oxidation of *o*-xylene with dilute **nitric acid**;⁴ by catalytic hydrogenation of **phthalic anhydride**;⁵ by hydrolysis of *o*-tolunitrile with 75 per cent **sulfuric acid**;⁶ and by carbonating the ether solution of the reaction product from **butyl lithium** and *o*-bromotoluene.⁷

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3, 820*
- *Org. Syn. Coll. Vol. 3, 822*

References and Notes

1. Kalle and Company, Ger. pat. 79,028 [*Frld. 4, 147 (1894-97)*]; Friedlaender and Rüdts, *Ber.* **29**,

- 1611 (1896).
2. Hessert, *ibid.* **11**, 238 (1878); *Racine, Ann.* **239**, 72 (1887).
 3. Fichter and Rinderspacher, *Helv. Chim. Acta* **10**, 41 (1927).
 4. Fittig and Bieber, *Ann.* **156**, 242 (1870).
 5. Willstätter and Jaquet, *Ber.* **51**, 771 (1918).
 6. Cahn, *Ann.* **240**, 280 (1887).
 7. Gilman, Langham, and Moore, *J. Am. Chem. Soc.* **62**, 2330 (1940).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

PHOSPHORUS (7723-14-0)

phthalic anhydride (85-44-9)

toluamide (55-21-0)

hydriodic acid (10034-85-2)

o-Tolunitrile (529-19-1)

p-Tolunitrile (104-85-8)

o-Bromotoluene (95-46-5)

butyl lithium (109-72-8)

Phthalide (87-41-2)

1-naphthylamine-3-sulfonic acid

1,3-dihydroxynaphthalene (132-86-5)

1-naphthol-3-sulfonic acid (3771-14-0)

1,3-naphthalenedisulfonic acid

p-Toluic acid (99-94-5)

[o-Toluic acid \(118-90-1\)](#)

[o-Xylene \(95-47-6\)](#)