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.

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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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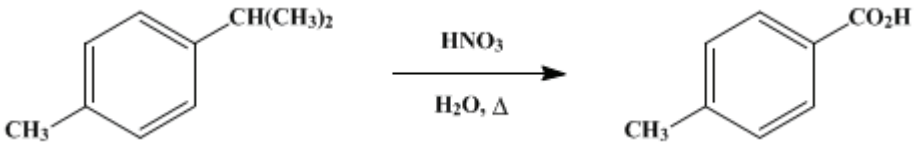
Organic Syntheses, Coll. Vol. 3, p.822 (1955); Vol. 27, p.86 (1947).

p-TOLUIC ACID



Submitted by W. F. Tuley and C. S. Marvel.
Checked by H. T. Clarke and D. Blumenthal.

1. Procedure

In a 5-l. round-bottomed flask are mixed 2.7 l. of water and 750 ml. of concentrated nitric acid (sp. gr. 1.42). The flask is fitted with an efficient stirrer (Note 1) and a reflux condenser whose outlet is connected with a trap to remove oxides of nitrogen. One hundred and five grams (125 ml., 0.78 mole) of *p*-cymene (Note 2) is added, the stirrer is started, and the reaction mixture is boiled gently for 8 hours. It is then allowed to cool, and the solid which crystallizes is collected on a hardened filter paper in a Büchner funnel (Note 3). The crude product (Note 4) is washed with 200 ml. of water in small portions and then dissolved in 850 ml. of 1 *N* sodium hydroxide. The alkaline solution is placed in a 2-l. flask with 20 g. of zinc dust (Note 5) and distilled until the distillate runs clear (Note 6). The undissolved zinc is removed by filtration, and the yellowish filtrate is poured in a thin stream with vigorous stirring into 500 ml. of boiling 5 *N* hydrochloric acid. After cooling, the precipitated acid is filtered, washed with cold water until substantially free of chloride, and dried. About 80 g. of a light-brown powder is thus obtained.

The product is extracted for 6 hours with 300 ml. of toluene in the apparatus described in a previous volume[1] (Note 7). The toluene extract is chilled to 0°, and the light-brown crystals of *p*-toluic acid are filtered. This material weighs 56–58 g.; an additional 5 g. is obtained by concentrating the filtrate to 100 ml. The total yield of product melting at 174–177° is 60–63 g. (56–59%). The acid may be purified further with very little loss by dissolving it in 0.5 *N* sodium hydroxide, treating the solution with Norit, precipitating the acid by pouring the alkaline solution into excess hot hydrochloric acid, and recrystallizing the product from toluene (Note 8). The purified *p*-toluic acid melts at 176–177° and weighs about 55 g. (51%).

2. Notes

1. A stirrer of the tubular type, running in a bearing consisting of a glass tube which extends well below the surface of the liquid, is recommended.
2. The fraction of spruce turpentine which boils at 175–178° is satisfactory.
3. The filtrate contains too little dissolved product (about 4 g.) to repay extraction. It can be employed for a subsequent run by adding sufficient concentrated nitric acid (about 300 ml.) to restore the specific gravity to its initial value, 1.115.
4. The crude product consists of *p*-toluic acid contaminated with small amounts of terephthalic acid, methyl *p*-tolyl ketone, and nitration products.
5. The zinc serves to reduce nitration products that are otherwise difficult to remove. The resulting amines remain in the filtrate after acidification.
6. About 300 ml. of distillate is collected, of which 5 ml. consists of methyl *p*-tolyl ketone.
7. About 4 g. of light-tan terephthalic acid remains on the filter paper.
8. The last traces of color are removed only with considerable difficulty by Norit. An alternative procedure consists in distilling the toluic acid under reduced pressure from a two-bulbed flask with a wide connecting tube and crystallizing the distillate from toluene.

3. Discussion

p-Toluic acid has been prepared by the oxidation of cymene,[2] *p*-xylene,[3,4] or dihydro-*p*-tolualdehyde;[5] by reaction of *p*-chlorotoluene and metallic sodium[6] or *p*-bromotoluene and butyllithium followed by carbonation;[7] by hydrolysis of *p*-tolunitrile;[8] by fusing *p*-tolyl phenyl ketone or di-*p*-tolyl ketone with potassium hydroxide;[9] and by reaction of oxalyl chloride with toluene in the presence of aluminum chloride.[10]

References and Notes

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

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

nitrogen (7727-37-9)

Norit (7782-42-5)

aluminum chloride (3495-54-3)

potassium hydroxide (1310-58-3)

toluene (108-88-3)

zinc (7440-66-6)

sodium (13966-32-0)

p-Chlorotoluene (106-43-4)

p-xylene (106-42-3)

p-Tolunitrile (104-85-8)

cymene,
p-cymene (99-87-6)

butyllithium (109-72-8)

oxalyl chloride (79-37-8)

Terephthalic acid (100-21-0)

toluic acid,
p-Toluic acid (99-94-5)

p-Bromotoluene (106-38-7)

methyl p-tolyl ketone (122-00-9)

dihydro-p-tolualdehyde

p-tolyl phenyl ketone (134-84-9)

di-p-tolyl ketone (611-97-2)

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