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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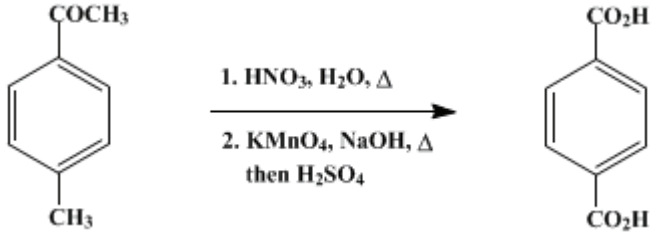
*Organic Syntheses, Coll. Vol. 3, p.791 (1955); Vol. 26, p.95 (1946).*

# TEREPHTHALIC ACID

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## 1. Procedure

One hundred grams (0.75 mole) of *p*-methylacetophenone[1] is added to a mixture of 250 ml. (4 moles) of concentrated nitric acid (sp. gr. 1.42) and 1 l. of water in a 3-l. flask, and the mixture is refluxed in a hood for 4 hours. After the mixture has been cooled, the sticky, yellow solid is collected on a 14-cm. Büchner funnel, pressed down well, and washed with 300 ml. of cold water.

The moist solid is mixed with 1 l. of water and 35 g. of sodium hydroxide in a 3-l. three-necked flask, fitted with a mechanical stirrer and a reflux condenser, and the stirred mixture is heated almost to its boiling point. Through the momentarily opened third neck of the flask is added, in portions of about 20 g., 300 g. (1.9 moles) of potassium permanganate, at such a rate that the boiling of the stirred mixture is maintained without external heating. After the addition has been completed, the mixture is refluxed for 2 hours; if any permanganate remains it is destroyed by the addition of 25 ml. of ethanol. The mixture is then filtered through a 14-cm. Büchner funnel, and the manganese dioxide is washed by removing it from the funnel, slurrying with 500 ml. of hot water (Note 1), and filtering.

The combined filtrates are heated nearly to boiling and acidified with a solution of 108 ml. of concentrated sulfuric acid (sp. gr. 1.84) in 400 ml. of water. After the mixture has been cooled to room temperature, the terephthalic acid is filtered and washed by stirring on the filter with three successive 100-ml. portions of cold water. The product is dried in an evaporating dish on a steam bath. The yield of terephthalic acid which sublimes at 300° or higher without melting is 105–109 g. (84–88%) (Note 2) and (Note 3).

## 2. Notes

1. This extraction yields 1–2 g. of the product.
2. The acid is analytically pure. There is no satisfactory solvent for the recrystallization of large amounts of terephthalic acid. Small quantities may be recrystallized from acetic acid, but the purity of a properly precipitated and washed sample is not thereby improved.
3. The high yields of ethyl ester obtainable from the product attest its purity. A mixture of 50 g. of terephthalic acid, 500 ml. of absolute ethanol, and 25 ml. of sulfuric acid was boiled for 16 hours and then distilled to half its volume and poured into dilute aqueous sodium carbonate. There was obtained 56.7 g. of diethyl terephthalate (m.p. 42–44°), and from the wash water there was recovered 4.6 g. of terephthalic acid; these materials account for 93.3% of the original substance.

## 3. Discussion

Terephthalic acid has been obtained from a great many *p*-disubstituted derivatives of benzene or cyclohexane by oxidation with permanganate, chromic acid, or nitric acid. The following routes appear to have preparative value: from *p*-toluic acid,[2] *p*-methylacetophenone,[3] or dihydro-*p*-tolualdehyde[4] by oxidation with permanganate; from *p*-cymene by oxidation with sodium dichromate and sulfuric acid;[5] from *p*-dibromobenzene or from *p*-chloro- or *p*-bromobenzoic acid by heating at 250° with potassium

and cuprous cyanides;[6] and from *p*-dibromobenzene[7] or *p*-iodobenzoic acid,[8] butyllithium, and carbon dioxide. It has been obtained also by the air oxidation of *p*-xylene in the presence of cobalt naphthenates.[9] Oxidations of *p*-toluic acid,[10] *p*-tolualdehyde,[11] and α-chloro-*p*-xylene[12] have been patented.

## References and Notes


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11. Brit. pat. 644,667 [*C. A.*, **45**, 4743 (1951)].
12. Brit. pat. 644,707 [*C. A.*, **45**, 4744 (1951)].


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

p-chloro- or p-bromobenzoic acid

potassium and cuprous cyanides

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

potassium permanganate (7722-64-7)

sodium carbonate (497-19-8)

carbon dioxide (124-38-9)

cyclohexane (110-82-7)

chromic acid (7738-94-5)

sodium dichromate (7789-12-0)

manganese dioxide (1313-13-9)

p-xylene (106-42-3)

p-cymene (99-87-6)

butyllithium (109-72-8)

Terephthalic acid (100-21-0)

diethyl terephthalate (636-09-9)

p-Toluic acid (99-94-5)

p-dibromobenzene (106-37-6)

p-Methylacetophenone (122-00-9)

p-iodobenzoic acid (619-58-9)

p-Tolualdehyde (104-87-0)

dihydro-p-tolualdehyde

α-chloro-p-xylene (104-82-5)