



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.

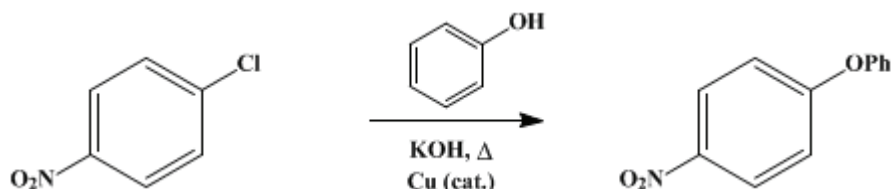
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.445 (1943); Vol. 14, p.66 (1934).

***p*-NITRODIPHENYL ETHER**

[Ether, *p*-nitrophenyl phenyl,]



Submitted by Ray Q. Brewster and Theodore Groening.

Checked by W. W. Hartman and J. B. Dickey.

1. Procedure

One hundred sixty grams (1.7 moles) of a good grade of phenol and 80 g. (1.43 moles) of potassium hydroxide are placed in a 2-l. flask, and the mixture is heated to 130–140° until all the alkali has dissolved. The potassium phenoxide is cooled to 100–110°, and 0.5 g. of copper catalyst (Note 1) and 78.8 g. (0.5 mole) of *p*-nitrochlorobenzene are added. The flask is then fitted with a mechanical stirrer, thermometer, and a reflux condenser. The stirrer is started, and the contents of the flask are warmed with a Bunsen burner to 150–160°, at which temperature a spontaneous reaction begins with ebullition and the separation of potassium chloride. The flame should be removed during this stage of the reaction. Boiling nearly ceases within five to seven minutes, and another 78.8 g. (0.5 mole) of *p*-nitrochlorobenzene is added. The mixture is again heated as before until a second spontaneous reaction begins. This also proceeds for about five minutes without the application of heat. When boiling due to the exothermic reaction has ceased, heat is applied and a temperature of 150–160° is maintained for an additional thirty minutes. The dark-colored melt is then poured into 1.5 l. of ice water containing 50 g. of sodium hydroxide and stirred well to remove excess phenol. The crude *p*-nitrodiphenyl ether separates as a dark brown crystalline mass which is allowed to settle. The product is filtered on a Büchner funnel, washed with 2 l. of water, and pressed as free from water as possible. After drying in the air it is distilled from a 500-cc. Claisen flask. The small fraction boiling up to 170°/8 mm., which contains *p*-nitrochlorobenzene, is discarded. A fraction boiling at 170–188°/8 mm. and weighing 14 g. is collected (Note 2). The main fraction boiling at 188–193°/8 mm. boils at 188–190°/8 mm. on redistillation with no fore-run and practically no residue. *p*-Nitrodiphenyl ether solidifies on cooling to diamond-shaped crystals melting at 56–58°. The yield is 173–177 g. (80–82 per cent of the theoretical amount) (Note 3).

2. Notes

1. An active copper powder can be prepared from copper sulfate. One hundred grams (0.4 mole) of copper sulfate (CuSO₄·5H₂O) is dissolved in 350 cc. of hot water in a 1-l. beaker. After cooling to room temperature 35 g. (0.53 gram atom) of zinc dust (more if necessary) is gradually added until the solution is decolorized. The precipitated copper is washed by decantation with water. Dilute hydrochloric acid (5 per cent) is added to the precipitate to remove the excess of the zinc, and agitation is continued until the escape of hydrogen ceases. The copper powder is filtered, washed with water, and kept in a moist condition in a carefully stoppered bottle.
2. This fraction on redistillation yields 4 g. of *p*-nitrodiphenyl ether.
3. A yield of 84 per cent of *o*-nitrodiphenyl ether boiling at 183–185°/8 mm. is obtained when *o*-nitrochlorobenzene is used. For the preparation of *m*-nitrodiphenyl ether, the method of Ullmann and Sponagel,¹ using *m*-bromonitrobenzene, seems to be the best, since *m*-chloronitrobenzene gives large amounts of tarry matter.

3. Discussion

p-Nitrodiphenyl ether has been prepared by the nitration of diphenyl ether² and by heating *p*-nitrochlorobenzene³ or *p*-nitrofluorobenzene⁴ with potassium phenoxide and phenol.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 62
- Org. Syn. Coll. Vol. 3, 566

References and Notes

1. Ullmann and Sponagel, Ber. **38**, 2211 (1905).
 2. Suter, J. Am. Chem. Soc. **51**, 2583 (1929).
 3. Haeussermann and Teichmann, Ber. **29**, 1446 (1896).
 4. Rarick, Brewster, and Dains, J. Am. Chem. Soc. **55**, 1289 (1933).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrochloric acid (7647-01-0)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

phenol (108-95-2)

copper sulfate (7758-98-7)

copper,
copper powder (7440-50-8)

potassium hydroxide (1310-58-3)

zinc (7440-66-6)

m-Bromonitrobenzene (585-79-5)

m-Chloronitrobenzene (121-73-3)

o-nitrochlorobenzene (88-73-3)

potassium chloride (7447-40-7)

potassium phenoxide

diphenyl ether (101-84-8)

p-nitrochlorobenzene (100-00-5)

p-Nitrodiphenyl ether,
Ether, p-nitrophenyl phenyl (620-88-2)

o-Nitrodiphenyl ether (2216-12-8)

m-nitrodiphenyl ether (620-55-3)

p-nitrofluorobenzene (350-46-9)