



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.

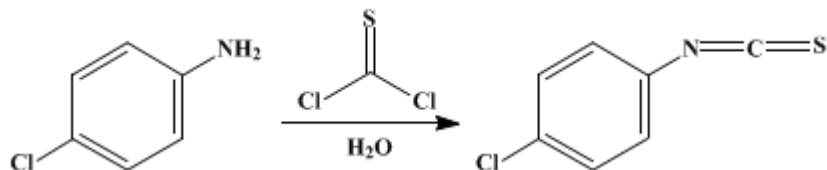
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

Organic Syntheses, Coll. Vol. 1, p.165 (1941); Vol. 6, p.18 (1926).

***p*-CHLOROPHENYL ISOTHIOCYANATE**

[Isothiocyanic acid, *p*-chlorophenyl ester]



Submitted by G. Malcolm Dyson

Checked by Frank C. Whitmore and P. L. Cramer.

1. Procedure

In a 5-l. crock or battery jar, provided with a powerful mechanical stirrer, are placed 3.5 l. of water and 249 g. (165 cc., 2.16 moles) of [thiophosgene](#) (p. 506) ([Note 1](#)). To the vigorously stirred ([Note 2](#)) mixture is added slowly 255 g. (2 moles) of *p*-chloroaniline during about one-half hour. The stirring is continued for about an additional one-half hour. The dark brown oil is separated, washed with 50 cc. of 10 per cent [hydrochloric acid](#), and placed in a flask for steam distillation.

The flask is immersed in an oil bath heated to 120° and dry steam is then passed through the reaction mixture. The first few cubic centimeters of distillate contain the excess of [thiophosgene](#) and are discarded. The [isothiocyanate](#) passes over with the water as an oil that solidifies on cooling. The steam distillation requires about four hours. The crude material is crystallized from two parts of [ethyl alcohol](#) at 50°, from which it separates as white needles melting at 44–45°. The yield is 245–275 g. (72–81 per cent of the theoretical amount) ([Note 3](#)).

2. Notes

1. Because of the objectionable properties of [thiophosgene](#), care should be exercised in its use.
2. The stirring at the start must be very vigorous or the yield is decreased.
3. The method is general for alkyl- and halogen-substituted aromatic amines. An alternative procedure which gives lower yields but avoids the use of [thiophosgene](#) will be found on p. 447.

3. Discussion

p-Chlorophenyl isothiocyanate can be prepared by treating an alcoholic solution of *sym*-di-*p*-chlorophenyl thiourea with [iodine](#);¹ from ammonium *p*-chlorophenyldithiocarbamate and [lead nitrate](#);² and by the action of [thiophosgene](#) on *p*-chloroaniline.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 700](#)
- [Org. Syn. Coll. Vol. 5, 223](#)

References and Notes

1. Losanitsch, Ber. **5**, 156 (1872).
 2. Dains, Brewster and Olander, Univ. Kansas Sci. Bull. **13**, 1 (1922) [C.A. **17**, 543 (1923)].
 3. Dyson and George, J. Chem. Soc. **125**, 1702 (1924).
-

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

ethyl alcohol (64-17-5)

hydrochloric acid (7647-01-0)

iodine (7553-56-2)

lead nitrate (10099-74-8)

Thiophosgene (463-71-8)

isothiocyanate (302-04-5)

p-Chlorophenyl isothiocyanate,
Isothiocyanic acid, p-chlorophenyl ester (2131-55-7)

p-chloroaniline (106-47-8)

di-p-chlorophenyl thiourea

ammonium p-chlorophenyldithiocarbamate