



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

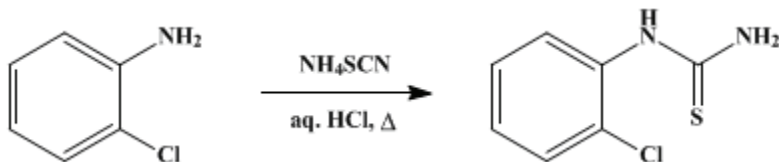
## Working with Hazardous Chemicals

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](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, CV 4, 180****o*-CHLOROPHENYLTHIOUREA****[Urea, 1-(*o*-chlorophenyl)-2-thio-]**Submitted by Frederick Kurzer<sup>1</sup>

Checked by Cliff S. Hamilton and David B. Capps.

**1. Procedure**

To a suspension of 38.3 g. (31.5 ml., 0.30 mole) of *o*-chloroaniline in 300 ml. of warm water is added, with stirring, 27.5 ml. (0.33 mole) of concentrated hydrochloric acid (12*N*). The resulting solution is placed in a 500-ml. porcelain evaporating dish, 25 g. (0.33 mole) of ammonium thiocyanate is added (Note 1), and the mixture is heated on the steam bath for 1 hour (Note 2). The liquid, from which a mass of large needles of *o*-chloroaniline thiocyanate separates, is allowed to cool, set aside at room temperature for 1 hour (Note 3), and then evaporated slowly to dryness over a period of 2–3 hours. The crystalline residue is crushed finely, 300 ml. of water is added, and again the mixture is evaporated slowly. The dry grayish white residual powder is heated finally on the steam bath for 4–5 hours.

The resulting mixture of crude *o*-chlorophenylthiourea and ammonium chloride (58–62 g.) is powdered finely and suspended in 300 ml. of water. The mixture is warmed slowly to 70° with mechanical stirring, then allowed to cool to 35°, and the solid is filtered with suction. The yield of crude *o*-chlorophenylthiourea, melting at 140–144°, is 30–35 g. (54–63%).

The crude material is dissolved in 60 ml. of absolute ethanol, the solution boiled with decolorizing carbon for a few minutes, and the clear, nearly colorless filtrate (Note 4) diluted with 100 ml. of hot benzene and 20 ml. of light petroleum ether (b.p. 60–80°). The white crystalline mass of *o*-chlorophenylthiourea, which separates gradually on cooling and standing, is separated by filtration under reduced pressure, washed with light petroleum ether, and dried, m.p. 144–146°. The yield of purified material is 20–24 g. (36–43%). Evaporation of the mother liquors and crystallization of the residue from a proportionally smaller volume of solvents yields a second crop (6–8 g.) (Note 5).

**2. Notes**

1. A good commercial grade of *o*-chloroaniline and pure ammonium thiocyanate are satisfactory for this preparation.
2. Comparable results are obtained when three times the quantities specified are used.
3. Uninterrupted evaporation of the initial reaction mixture sometimes tends to give a partly oily product from which only smaller yields can be obtained.
4. The filtration is best effected by the use of reduced pressure employing a preheated Büchner funnel and filter flask.
5. According to the submitter the method is generally applicable to the synthesis of aromatic thioureas. For example, phenylthiourea may be prepared in yields of 37–42%.

**3. Discussion**

*o*-Chlorophenylthiourea has been prepared from *o*-chlorophenylisothiocyanate and ammonia,<sup>2</sup> by the interaction of *o*-chloroaniline hydrochloride<sup>3</sup> or sulfate<sup>4</sup> with sodium thiocyanate in chlorobenzene, or with ammonium thiocyanate in aqueous solution.<sup>4,5</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 172](#)

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## References and Notes

1. University of London, London, England.
  2. Dyson and George, *J. Chem. Soc.*, **125**, 1705 (1924).
  3. Dalglish and Mann, *J. Chem. Soc.*, **1945**, 900.
  4. Elderfield and Short, *J. Org. Chem.*, **18**, 1092 (1953).
  5. Kurzer, *J. Chem. Soc.*, **1949**, 3033.
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## Appendix

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

petroleum ether

[ethanol \(64-17-5\)](#)

[hydrochloric acid \(7647-01-0\)](#)

[ammonia \(7664-41-7\)](#)

[Benzene \(71-43-2\)](#)

[ammonium chloride \(12125-02-9\)](#)

[ammonium thiocyanate \(1762-95-4\)](#)

[carbon \(7782-42-5\)](#)

[chlorobenzene \(108-90-7\)](#)

[phenylthiourea \(103-85-5\)](#)

[sodium thiocyanate \(540-72-7\)](#)

[o-Chlorophenylthiourea,  
Urea, 1-\(o-chlorophenyl\)-2-thio- \(5344-82-1\)](#)

[o-chloroaniline \(95-51-2\)](#)

[o-chloroaniline hydrochloride \(137-04-2\)](#)

[o-chloroaniline thiocyanate](#)

[o-chlorophenylisothiocyanate \(2740-81-0\)](#)

