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.

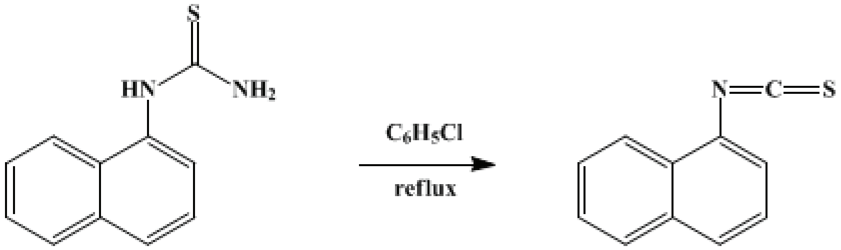
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.036.0056

Organic Syntheses, Coll. Vol. 4, p.700 (1963); Vol. 36, p.56 (1956).

α-NAPHTHYL ISOTHIOCYANATE

[Isothiocyanic acid, 1-naphthyl ester]



Submitted by J. Cymerman-Craig, M. Moyle, and R. A. White[1].
Checked by N. J. Leonard and F. H. Owens.

1. Procedure

In a 500-ml. round-bottomed flask fitted with a reflux condenser are placed 16.2 g. (0.08 mole) of dry α-naphthylthiourea (Note 1) and 180 ml. of redistilled chlorobenzene. The flask is heated at the reflux temperature by means of an electric heating mantle. Evolution of ammonia begins almost at once, and all of the solid dissolves after 30–45 minutes. The solution is maintained at reflux for 8 hours (Note 2) and then is evaporated on a steam bath at water-pump pressure to remove all of the chlorobenzene. The residue crystallizes on cooling and is extracted with four 30-ml. portions of boiling hexane (Note 3). Removal of solvent from the combined hexane extracts affords pale yellow crystals of α-naphthyl isothiocyanate, m.p. 58–59°. The yield is 12.7–13.0 g. (86–88%). Recrystallization from hexane (9 ml. of hexane for 1 g. of solute) gives colorless needles, melting point unchanged (Note 4).

2. Notes

1. α-Naphthylthiourea may be prepared by the method of Frank and Smith, *Org. Syntheses Coll. Vol.* **3**, 735 (1955), or by the method of de Clermont, *Ber.*, **9**, 446 (1876), and Bertram, *Ber.*, **25**, 48 (1892).
2. The checkers found that a 24-hour heating period increased the yield of α-naphthyl isothiocyanate to 95%.
3. A fifth extraction yields no further product. The residue insoluble in hexane was found by the submitters to consist of 1.3–1.9 g. of a mixture of equal parts of di-α-naphthylthiourea and α-naphthylthiourea, m.p. 178–181°.
4. The method is generally applicable to the preparation of aryl isothiocyanates. Using this procedure, the submitters have prepared the following isothiocyanates, with the yields and times of refluxing indicated: phenyl, 44%, 8 hours; *o*-chlorophenyl, 46, 8; *p*-bromophenyl, 73, 8; *p*-biphenylyl, 49, 6; β-naphthyl, 70, 10; 9-phenanthryl, 70, 10; 1-pyrenyl, 72, 10.

3. Discussion

Aryl isothiocyanates can be prepared by the action of thiophosgene on the arylamine[2] (this reaction fails with naphthyl compounds),[3] by fission of a *sym*-diarylthiourea with acidic reagents[4] (this reaction involves the loss of half the amine used), and by the decomposition of an ammonium aryldithiocarbamate[5] (low yields are reported for naphthyl and other compounds).[5,6] The procedure described here is that of Baxter, Cymerman-Craig, Moyle, and White.[7]

References and Notes

1. University of Sydney, Sydney, Australia.
2. *Org. Syntheses Coll. Vol.* **1**, 165 (1941).

3. Connolly and Dyson, *J. Chem. Soc.*, **1935**, 679.
4. Werner, *J. Chem. Soc.*, **59**, 396 (1891).
5. *Org. Syntheses Coll. Vol.* **1**, 447 (1941).
6. Dains, Brewster, and Olander, *Univ. Kansas Sci. Bull.*, **13**, 1 (1922) [*C. A.*, **17**, 543 (1923)].
7. Baxter, Cymerman-Craig, Moyle, and White, *Chem. & Ind.* (*London*), **1954**, 785; *J. Chem. Soc.*, **1956**, 659.

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

α-naphthylthiourea

ammonia (7664-41-7)

chlorobenzene (108-90-7)

Thiophosgene (463-71-8)

PHENYL ISOTHIOCYANATE (103-72-0)

hexane (110-54-3)

α-Naphthyl isothiocyanate,
Isothiocyanic acid, 1-naphthyl ester (551-06-4)

di-α-naphthylthiourea

p-bromophenyl isothiocyanate (1985-12-2)

o-chlorophenyl isothiocyanate (2740-81-0)

p-biphenylyl isothiocyanate

2-naphthyl isothiocyanate

9-phenanthryl isothiocyanate

1-pyrenyl isothiocyanate

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved