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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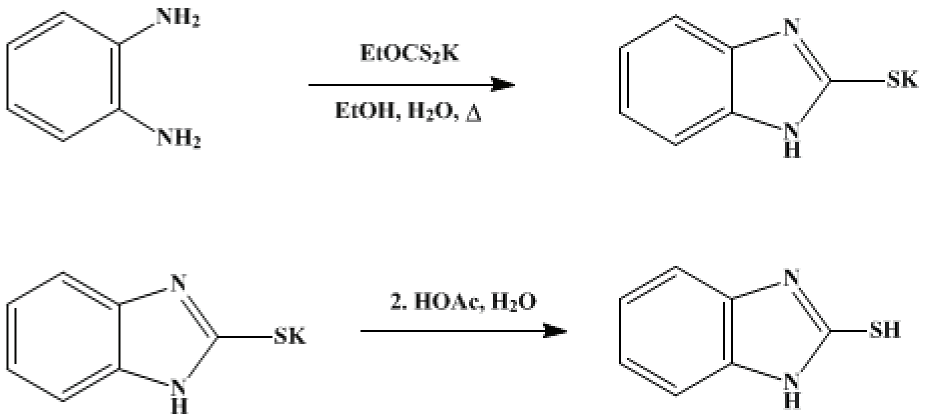
2-MERCAPTOBENZIMIDAZOLE

[2-Benzimidazolethiol]



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1. Procedure

A mixture of 32.4 g. (0.3 mole) of *o*-phenylenediamine,[2] 52.8 g. (0.33 mole) of potassium ethyl xanthate (Note 1), 300 ml. of 95% ethanol, and 45 ml. of water in a 1-l. flask is heated under reflux for 3 hours. Norit (12 g.) is then added cautiously, and after the mixture has been heated at the reflux temperature for 10 minutes the Norit is removed by filtration. The filtrate is heated to 60–70°, 300 ml. of warm tap water (60–70°) is added, and then 25 ml. of acetic acid in 50 ml. of water is added with good stirring. The product separates as glistening white crystals, and the mixture is placed in a refrigerator for 3 hours to complete the crystallization. The product is collected on a Büchner funnel and dried overnight at 40°. The yield is 37.8–39 g. (84–86.5%) of 2-mercaptobenzimidazole melting at 303–304° (cor.) (Note 2) and (Note 3).

2. Notes

1. The potassium ethyl xanthate may be replaced by 19 g. of potassium hydroxide and 26 g. (21 ml., 0.34 mole) of carbon disulfide. The yield and quality of the product are the same.
2. The quality of the product is excellent. Recrystallization may be effected from 95% ethanol as a solvent. Recovery is about 90%; there is no change in the melting point.
3. 2-Mercaptobenzoxazole, m.p. 193–195°, can be prepared in 80% yield by a similar procedure, using *o*-aminophenol in place of *o*-phenylenediamine.

3. Discussion

2-Mercaptobenzimidazole has also been prepared from *o*-phenylenediamine by heating the thiocyanate to 120–130°;[3] by heating with aqueous potassium thiocyanate (in which case 2-aminophenylthiourea is a by-product);[4] by the action of thiophosgene in chloroform;[5] by heating with carbon disulfide in alcohol[6] or in water;[7] and by heating the hydrochloride with thiourea to 170–180°.[8]

References and Notes

1. Eastman Kodak Company, Rochester, New York.
2. *Org. Syntheses Coll. Vol* **2**, 501 (1943).
3. Lellmann, *Ann.*, **221**, 9 (1883).

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5. Billeter and Steiner, *Ber.*, **20**, 231 (1887).
6. Gucci, *Gazz. chim. ital.*, [1] **23**, 295 (1893).
7. Kawaoka, *J. Soc. Chem. Ind., Japan* **43**, Suppl. binding 223 (1940) [*C. A.*, **35**, 2368 (1941)].
8. Kym, *J. prakt. Chem.*, [2] **75**, 324 (1907).

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

ethanol (64-17-5)

acetic acid (64-19-7)

chloroform (67-66-3)

o-aminophenol (95-55-6)

Norit (7782-42-5)

potassium hydroxide (1310-58-3)

carbon disulfide (75-15-0)

Thiophosgene (463-71-8)

potassium thiocyanate (333-20-0)

thiocyanate

potassium ethyl xanthate (140-89-6)

thiourea (62-56-6)

o-Phenylenediamine (95-54-5)

2-Mercaptobenzimidazole,
2-Benzimidazolethiol (583-39-1)

2-Mercaptobenzoxazole (2382-96-9)

2-aminophenylthiourea (3394-09-0)