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.

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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.*

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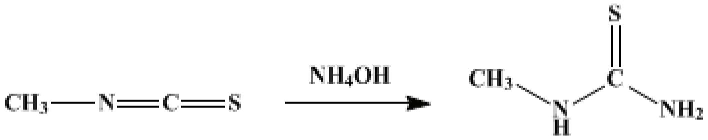
# METHYLTHIOUREA

## [Urea, 1-methyl-2-thio-]



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## 1. Procedure

In a 500-ml. three-necked flask, equipped with a stirrer, a reflux condenser, and a dropping funnel, is placed 140 ml. (34 g.; 2 moles of ammonia) of concentrated ammonium hydroxide solution, and 95 g. (1.3 moles) of methyl isothiocyanate (p. 599), b.p. 115–121°, is added, with stirring, over a period of 1 hour (Note 1). After the addition has been completed, the condenser is removed and the solution is heated on a water bath for 30 minutes to remove excess ammonia. The solution is then boiled with 2 g. of Norit and filtered, and the filtrate is chilled in an ice bath. The methylthiourea crystallizes as a colorless, compact, solid mass, which is collected on a filter, washed three times with 25-ml. portions of ice water, and dried. The first crop of crystals weighs 65–75 g. A second crop amounting to 15–20 g. is obtained by concentrating the mother liquor and washings to a volume of 75 ml. and again chilling in the ice bath. The total yield of methylthiourea, m.p. 119–120.5° (Note 2), is 85–95 g. (74–81%) (Note 3) and (Note 4).

## 2. Notes

1. The addition of the methyl isothiocyanate should be maintained at a constant rate since the reaction is slow to start; when the mixture has warmed up, the reaction becomes very vigorous and hard to control.
2. Further purification by crystallizing from boiling anhydrous ethanol yields a product melting at 120.5–121°.
3. The yield is only slightly higher if purer methyl isothiocyanate is used.
4. This is a general method for the preparation of alkyl thioureas. Ethylthiourea, m.p. 103–106°, has been prepared from ethyl isothiocyanate in the same manner. Di- and trialkyl thioureas may be prepared from alkyl isothiocyanates in a similar manner by substituting an equivalent amount of an amine solution in place of the ammonium hydroxide. Thus, *sym*-dimethylthiourea is prepared from methyl isothiocyanate and methylamine solution. A solution of dimethylamine and methyl isothiocyanate gives trimethylthiourea.

## 3. Discussion

Methylthiourea has been prepared from methyl isothiocyanate and ammonia in ethanolic[1] or aqueous[2] solution, from methylammonium thiocyanate,[3] and by heating the methyl or ethyl ester of N-methyldithiocarbamic acid with alcoholic ammonia.[4]

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## References and Notes

1. *Näf, Ann.*, **265**, 108 (1891).
2. Andreasch, *Monatsh.*, **2**, 276 (1881).
3. Salkowski, *Ber.*, **26**, 2497 (1893).
4. Delépine, *Compt. rend.*, **134**, 1222 (1902); *Bull. soc. chim. France*, (3) **27**, 812 (1902).

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

sym-dimethylthiourea

methyl or ethyl ester of N-methyldithiocarbamic acid

ethanol (64-17-5)

ammonia (7664-41-7)

Norit (7782-42-5)

ammonium hydroxide (1336-21-6)

dimethylamine (124-40-3)

methylamine (74-89-5)

ethyl isothiocyanate (542-85-8)

Methyl isothiocyanate (556-61-6)

METHYLTHIOUREA,
Urea, 1-methyl-2-thio- (598-52-7)

Ethylthiourea (625-53-6)

trimethylthiourea (2489-77-2)

methylammonium thiocyanate