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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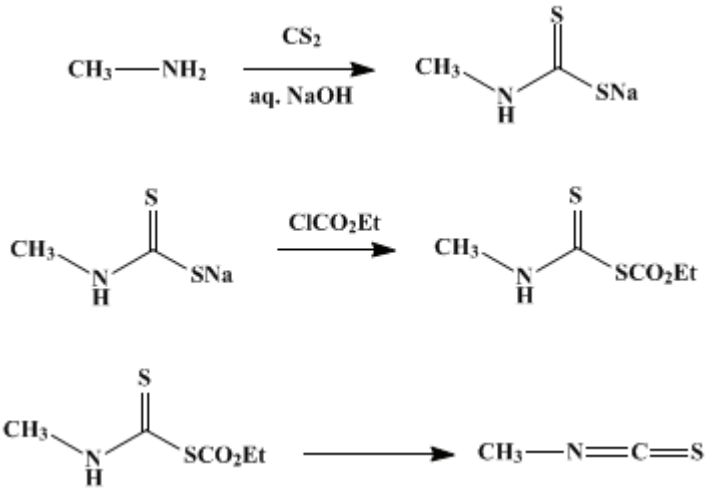
METHYL ISOTHIOCYANATE

[Isothiocyanic acid, methyl ester)]



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1. Procedure

In a 1-l. round-bottomed three-necked flask, surrounded by an ice bath and fitted with a mechanical stirrer, a reflux condenser, thermometer, and a 250-ml. dropping funnel, are placed 137 g. (110 ml., 1.8 moles) of carbon disulfide and a cold solution of 72 g. (1.8 moles) of sodium hydroxide in 160 ml. of water. To this mixture, cooled to 10–15°, is added, with stirring, 180 ml. (56 g., 1.8 moles of methylamine) of 35% aqueous methylamine solution (Note 1) and (Note 2) over a period of 30 minutes. Stirring is continued, and the mixture is warmed gently on a steam bath for 1–2 hours to ensure complete reaction (Note 3). The bright red solution is cooled to 35–40°, and to it is added over a period of 1 hour, with stirring, 196 g. (175 ml., 1.8 moles) of ethyl chlorocarbonate (Note 4). The stirring is continued for 30 minutes after all the ethyl chlorocarbonate has been added, at which time the temperature should have fallen to 30–40°. The methyl isothiocyanate, which separates on top, is removed from the reaction mixture and weighs 170–190 g.

The product is dried over 10 g. of sodium sulfate and distilled under atmospheric pressure through a short Vigreux column; the fraction which boils at 115–121° is collected. The yield is 85–100 g. (65–76%) (Note 5) and (Note 6). The product may be further purified by refractionation. The portion which boils at 117–119° is collected.

2. Notes

1. The monomethylamine used in this preparation was a "Commercial Special 35% Solution" obtained from Rohm and Haas Company.
2. Methylamine hydrochloride can be used in place of the commercial aqueous methylamine solution by a slight modification of the above procedure. The carbon disulfide and a solution of 122 g. (1.8 moles) of methylamine hydrochloride in 200 ml. of water are mixed together in the flask, and a cold solution of 144 g. (3.6 moles) of sodium hydroxide in 320 ml. of water is added, with stirring, over a period of 30 minutes. Two equivalents of sodium hydroxide must be used in this case. The remainder of the procedure is the same as with the free base.
3. The temperature gradually rises from 25°, which is that noted at the end of the addition of the methylamine solution, to 75–85°.
4. The temperature may rise rather rapidly during this addition; it is advisable to maintain the rate of

addition constant so that the reaction does not become too vigorous.
5. Larger runs, up to 5.4 moles of carbon disulfide, have been made with only a slight reduction in yield.
6. This reaction is general for the preparation of alkyl isothiocyanates in good yields; thus, according to the submitters, ethyl isothiocyanate is obtained in yields of 60–70% from ethylamine hydrochloride.

3. Discussion

Methyl isothiocyanate has been prepared from methyl thiocyanate by rearrangement with heat[1] and from N,N'-dimethylthiuramdisulfide by the action of iodine[2] or by heating with water or methanol.[3] The most useful method of preparation has been the reaction of methylamine with carbon disulfide to form methyldithiocarbamic acid which is decomposed by steam distillation of the lead salt,[4] or by reaction with ethyl chlorocarbonate.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 617

References and Notes

1. Hofmann, *Ber.*, **13**, 1349 (1880).
2. v. Braun, *Ber.*, **35**, 817 (1902).
3. Freund and Asbrand, *Ann.*, **285**, 166 (1895).
4. Delépine, *Bull. soc. chim. France*, (4) **3**, 641 (1908); Delépine, *Compt. rend.*, **144**, 1125 (1907); Worrall, *J. Am. Chem. Soc.*, **50**, 1456 (1928).
5. Slotta and Dressler, *Ber.*, **63**, 888 (1930).

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

lead salt

methanol (67-56-1)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

iodine (7553-56-2)

carbon disulfide (75-15-0)

Methylamine hydrochloride (593-51-1)

methylamine,
monomethylamine (74-89-5)

ethyl chlorocarbonate (541-41-3)

ethyl isothiocyanate (542-85-8)

Methyl isothiocyanate,
Isothiocyanic acid, methyl ester (556-61-6)

ethylamine hydrochloride (557-66-4)

methyl thiocyanate (556-64-9)

methyldithiocarbamic acid

N,N'-dimethylthiuramdisulfide