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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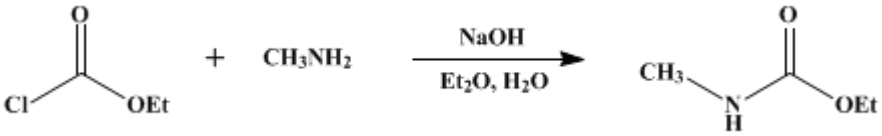
Organic Syntheses, Coll. Vol. 2, p.278 (1943); Vol. 12, p.38 (1932).

ETHYL N-METHYLCARBAMATE

[Carbamic acid, methyl-, ethyl ester]



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1. Procedure

In a 2-l. flask, provided with a mechanical stirrer and cooled by an ice-salt mixture, are placed 300 cc. of ether and 186 g. (2 moles) of a 33 per cent aqueous methylamine solution. When the stirred mixture has cooled to 5°, 217 g. (2 moles) of ethyl chloroformate (Note 1) is added without allowing the temperature to rise above 5°. When almost half of the chloroformate has been added a cold solution of 80 g. (2 moles) of pure sodium hydroxide in 120 cc. of water is added gradually along with the rest of the chloroformate at such a rate that the last portions of the two solutions are added simultaneously. Constant mechanical stirring throughout the addition is essential (Note 2). After standing for fifteen minutes, the ether layer is separated and the aqueous solution is extracted with 100 cc. of ether. The combined ether layers are rapidly dried by shaking for a short time with about 8 g. of potassium carbonate in two portions. The ether is then distilled and the residue distilled under reduced pressure, the distillate being collected at 55–60°/12 mm. The yield of colorless oil is 182–185 g. (88–90 per cent of the theoretical amount).

2. Notes

1. Technical ethyl chloroformate (chlorocarbonate) is manufactured by the U. S. Industrial Chemicals Company.
2. The rate of addition is determined by the efficiency with which the heat is removed from the reaction mixture. Five hours was required, using an ice-salt mixture outside.

3. Discussion

Ethyl N-methylcarbamate has been prepared by adding aqueous methylamine to ethyl chloroformate;[1] and from methylcarbamyl chloride and ethyl alcohol.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 464
- Org. Syn. Coll. Vol. 4, 780

References and Notes

1. Schreiner, J. prakt. Chem. (2) **21**, 124 (1880); Pechmann, Ber. **28**, 855 (1895); Eistert, Angew. Chem. **54**, 124 (1941).
2. Gattermann, Ann. **244**, 35 (1888).

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

ethyl alcohol (64-17-5)

potassium carbonate (584-08-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

methylamine (74-89-5)

ethyl chloroformate (541-41-3)

Ethyl N-methylcarbamate,
Carbamic acid, methyl-, ethyl ester (105-40-8)

methylcarbamyl chloride

chlorocarbonate