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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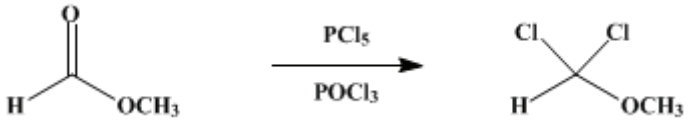
DICHLOROMETHYL METHYL ETHER



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1. Procedure

In a 2-l. three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel (Note 1) 832 g. (4.0 moles) of phosphorus pentachloride is stirred with 250 ml. of phosphorus oxychloride (Note 2). To this is added with stirring 264 g. (272 ml., 4.4 moles) of methyl formate (Note 3). During the addition the reaction vessel is cooled in an ice bath to maintain a reaction temperature of 10–20°. The addition requires about 1.75 hours. When the addition is complete, the solution is stirred at a temperature under 30° until all the phosphorus pentachloride has dissolved (about 1 hour). Then the stirrer is removed, the reflux condenser is replaced by a distilling head, and the reaction mixture is distilled under a pressure of 80–120 mm. with a bath temperature of 50–65° (Note 4). During the distillation the receiver is cooled to −10° to −20° by an ice-salt bath.

The material which is collected is redistilled through a 90-cm. vacuum-jacketed column packed with glass beads (5 mm.) using a 1:10 reflux ratio. The fraction, b.p. 80–100°, is redistilled through the same column to give 353–386 g. (77–84%) of dichloromethyl methyl ether, b.p. 82–85.5°, n^{20}D 1.4303 (Note 5).

2. Notes

1. The reflux condenser and dropping funnel must be provided with calcium chloride tubes.
2. Phosphorus oxychloride serves only as a suspension medium for phosphorus pentachloride and makes possible a homogeneous reaction. The phosphorus oxychloride obtained during workup may be recycled in this preparation.
3. Commercial methyl formate was dried over sodium sulfate and used without special purification.
4. If it is not first distilled under reduced pressure, extensive decomposition will occur during fractional distillation.
5. The product must be protected from moisture when stored.

3. Discussion

Dichloromethyl methyl ether has been prepared by the chlorination of chlorodimethyl ether in the liquid[2,3,4] or gas phase,[5] by the reaction of chlorodimethyl ether with sulfuryl chloride and benzoyl peroxide,[6,7] and by the treatment of methyl formate with phosphorus pentachloride.[8,9,10]

4. Merits of the Preparation

Dichloromethyl methyl ether may be employed preparatively in various ways. Thus it effects the replacement of carbonyl and hydroxyl oxygens by chlorine,[11] and may be used in the preparation of α-acetochlorosugars[12] and acid chlorides, particularly those derived from acetylated monocarboxylic acid sugars[12,13] and acetylated amino acids.[14] In addition, the *ortho* derivatives of formic acid may be prepared from dichloromethyl methyl ether.[15] With aromatic compounds, dichloromethyl methyl ether reacts under Friedel-Crafts conditions followed by hydrolysis to give the corresponding aromatic aldehydes.[10,16,17]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 49
- Org. Syn. Coll. Vol. 7, 467

References and Notes

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

phosphorus pentachloride (10026-13-8)

sodium sulfate (7757-82-6)

formic acid (64-18-6)

Phosphorus Oxychloride (21295-50-1)

sulfuryl chloride (7791-25-5)

methyl formate (107-31-3)

chlorodimethyl ether (107-30-2)

benzoyl peroxide (94-36-0)

Dichloromethyl methyl ether (4885-02-3)