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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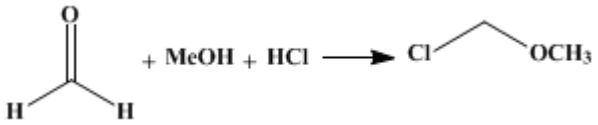
Organic Syntheses, Coll. Vol. 1, p.377 (1941); Vol. 9, p.58 (1929).

MONOCHLOROMETHYL ETHER

[Ether, chloromethyl methyl]



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1. Procedure

In a 2-l. round-bottomed flask fitted with a stopper carrying a reflux condenser and a glass tube reaching nearly to the bottom of the flask are placed 350 g. (438 cc., 10.9 moles) of methyl alcohol and 900 g. of technical formalin containing 252 g. (8.4 moles) of formaldehyde (Note 1).

A rapid stream of hydrogen chloride (Note 2) is run into the mixture, which is cooled with running water. In about two hours a layer of chloromethyl ether begins to appear. The stream of hydrogen chloride is continued for two or three hours longer until the solution is saturated. The layer of chloromethyl ether is then separated. The water layer is saturated with calcium chloride (Note 3), and more ether separates. This is added to the main portion, which is then dried over calcium chloride and fractionally distilled. The yield of product boiling at 55–60° is 580–600 g. (86–89 per cent of the theoretical amount based on the formaldehyde).

2. Notes

1. The following table, showing the relation between the density of formalin solutions and their formaldehyde content, has been found useful. It is copied from Beilstein's "Handbuch der organischen Chemie," 4th Ed., Julius Springer, Berlin, 1918, Vol. I, p. 561.

d_4^{18}	g. CH_2O in 100 cc.	g. CH_2O in 100 g.
1.0054	2.24	2.23
1.0126	4.66	4.60
1.0311	11.08	10.74
1.0410	14.15	13.59
1.0568	19.89	18.82
1.0719	25.44	23.73
1.0853	30.17	27.80
1.1057	37.72	34.11
1.1158	41.87	37.53

The values in this table are affected by the presence of methyl alcohol in the formalin solution; since it has been pointed out that technical formalin contains 8–10 per cent of methyl alcohol, the table is not satisfactory for determining the formaldehyde content of *technical* formalin solutions. For example, a solution containing 37 per cent of formaldehyde and 10 per cent of methyl alcohol would have a density of 1.09 and correspond to 28 per cent of formaldehyde in pure water. In view of this the percentage yield in the preparation described above should probably be 64–66 instead of 86–89 (Norman D. Scott, private communication).

2. The hydrogen chloride was generated by the method described on p. 293. About 390–420 g. of hydrogen chloride is required for saturation.

3. Chloromethyl ether is soluble in the aqueous hydrochloric acid used so that the salting-out with

calcium chloride is necessary to obtain the maximum yield.

3. Discussion

Monochloromethyl ether can be prepared by saturating an aqueous solution of formaldehyde and methyl alcohol with hydrogen chloride[1] and by saturating a solution of trioxymethylene in methyl alcohol with hydrogen chloride.[2] The procedure described is essentially that developed by Henry.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 54
- Org. Syn. Coll. Vol. 1, 214
- Org. Syn. Coll. Vol. 1, 347
- Org. Syn. Coll. Vol. 1, 355
- Org. Syn. Coll. Vol. 2, 610
- Org. Syn. Coll. Vol. 3, 436

References and Notes

1. Henry, Bull. sci. acad. roy. Belg. (3) **25**, 439 (1893) [Ber. **26** (2), 933 (1893)]; Litterscheid and Thimme, Ann. **334**, 10 (1904).
2. Wedekind, Ger. pat. 135,310 [Chem. Zentr. II, 1164 (1902)]; Ber. **36**, 1384 (1903); Houben and Arnold, Ber. **40**, 4307 (1907); Litterscheid, Ann. **330**, 109 (1904); Reychler, Bull. soc. chim. (4) **1**, 1195 (1907).

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

trioxymethylene

calcium chloride (10043-52-4)

hydrogen chloride,
hydrochloric acid (7647-01-0)

methyl alcohol (67-56-1)

hydrogen (1333-74-0)

formaldehyde,
formalin (50-00-0)

MONOCHLOROMETHYL ETHER,
chloromethyl ether (542-88-1)

Ether, chloromethyl methyl (107-30-2)