



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.

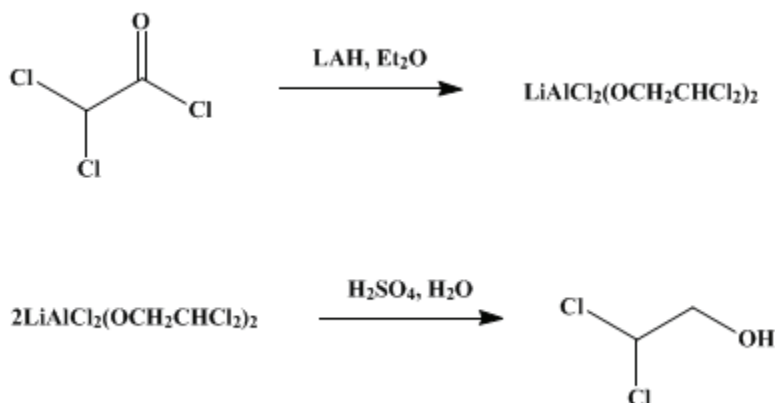
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.271 (1963); Vol. 32, p.46 (1952).

2,2-DICHLOROETHANOL

[Ethanol, 2,2-dichloro-]



Submitted by C. E. Sroog and H. M. Woodburn¹.

Checked by R. S. Schreiber and C. J. Lintner, Jr..

1. Procedure

Caution! This procedure should be carried out in a good hood, and a spark-proof motor should be used.

A 1-l. three-necked flask having ground-glass joints is fitted with an efficient reflux condenser, a dropping funnel, and a mercury-sealed stirrer, and all exits are protected by drying tubes (Note 1). In the flask are placed 300 ml. of rigorously dried ether (Note 2) and 13.6 g. (0.36 mole) of pulverized lithium aluminum hydride (Note 3). After the mixture has been stirred for 15 minutes, a milky suspension is produced. A solution of 88.6 g. (0.60 mole) of dichloroacetyl chloride in 75 ml. of dry ether is added from the dropping funnel (Note 4) at a rate such as to produce gentle reflux. The process is completed in about 2.5 hours (Note 5).

Agitation is continued for 30 minutes after all the chloride has been introduced, and the excess hydride is then destroyed by the careful, dropwise addition of water to the stirred and cooled reaction mixture. The hydrolysis is accompanied by the formation of a white curdy mass of aluminum hydroxide, and the mixture has a semisolid consistency when the hydride has been completely decomposed (Note 6). With constant stirring, 500 ml. of 10% sulfuric acid is then added slowly to the mass. Stirring is continued for 30 minutes, and the solution becomes clear during this period.

The ether layer is separated, and the solvent is removed by distillation under atmospheric pressure, and the dark-colored residue is fractionated under reduced pressure through a 25-cm. column packed with glass helices. The fraction boiling at 37–38.5°/6 mm. is collected; it weighs 44–45 g. (64–65%); n_D^{25} 1.4626; d_4^{25} 1.404 (Note 7).

2. Notes

1. To prevent partial hydrolysis of the lithium aluminum hydride, the checkers found it desirable to dry the glassware by flaming while dry nitrogen was being swept through the apparatus.
2. Anhydrous ether is recommended since a solvent containing moisture will react to coat the hydride with oxides which will retard its rate of solution. The checkers used ether dried over sodium wire.
3. The hydride can be pulverized rapidly and safely by breaking the large pieces with a spatula, followed by careful crushing with a mortar and pestle.
4. The acid chloride was obtained from the Eastman Kodak Company and was used without prior

treatment. The submitters report² that dichloroacetyl acid or [ethyl dichloroacetate](#) may be substituted for [dichloroacetyl chloride](#) but that the reaction appears to be smoother with the acid chloride.

5. The acid chloride should be added slowly since the reaction appears to have a short induction period and it is undesirable to accumulate a large quantity of unreacted material.

6. The decomposition of the hydride is accompanied by the vigorous evolution of [hydrogen](#). Cessation of [hydrogen](#) formation is evidence that the hydride is completely decomposed.

7. The following constants have been reported in the literature for [2,2-dichloroethanol](#): d_4^{15} 1.415;² d_4^{19} 1.416; $n_D^{17.3}$ 1.4752.³

3. Discussion

[2,2-Dichloroethanol](#) has been prepared by the reaction of [dichloroacetaldehyde](#) with zinc dialkyls⁴ and aluminum alkoxides.³

References and Notes

1. University of Buffalo, Buffalo, New York.
 2. Sroog, Chih, Short, and Woodburn, *J. Am. Chem. Soc.*, **71**, 1710 (1949).
 3. Boeseken, Tellegen, and Plusje, *Rec. trav. chim.*, **57**, 73 (1938).
 4. de Lacre, *Compt. rend.*, **104**, 1184 (1887).
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Appendix

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

dichloroacetyl acid

[sulfuric acid](#) (7664-93-9)

[ether](#) (60-29-7)

[hydrogen](#) (1333-74-0)

[nitrogen](#) (7727-37-9)

[sodium wire](#) (13966-32-0)

[2,2-Dichloroethanol](#),
[Ethanol, 2,2-dichloro-](#) (598-38-9)

[dichloroacetaldehyde](#) (16086-14-9)

[aluminum hydroxide](#)

[dichloroacetyl chloride](#) (79-36-7)

[lithium aluminum hydride](#) (16853-85-3)

[ethyl dichloroacetate](#) (535-15-9)

