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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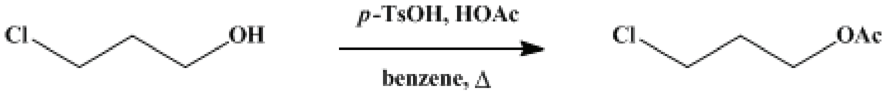
Organic Syntheses, Coll. Vol. 3, p.203 (1955); Vol. 29, p.33 (1949).

γ-CHLOROPROPYL ACETATE

[1-Propanol, 3-chloro-, acetate]



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1. Procedure

A 1-l. round-bottomed flask is fitted with a 30-cm. Vigreux column (Note 1) connected to a condenser. The condenser leads to an automatic separator arranged so that the lighter liquid is returned to the flask.[1] In the flask is placed a mixture of 189 g. (167 ml., 2 moles) of trimethylene chlorohydrin,[2] 180 g. (172 ml., 3 moles) of glacial acetic acid, 300 ml. of benzene, and 2 g. of *p*-toluenesulfonic acid monohydrate. The mixture is refluxed at such a rate that the temperature at the top of the column remains at 69° (boiling point of benzene-water azeotrope) during the time the greatest amount of water is distilling, and rises gradually to 80° (boiling point of benzene-acetic acid azeotrope) as the last of the water is removed. The volume of the aqueous layer collected varies with the temperature of the vapors and the length of time required for distillation, but it is approximately 50 ml. at the end of the reaction; the time required is 7–9 hours (Note 2).

The solution is cooled, then washed successively with two 500-ml. portions of 10% sodium carbonate solution, one 500-ml. portion of water, and one 100-ml. portion of saturated sodium chloride solution. The wash solutions are extracted successively with one 100-ml. portion of benzene, which is added to the main benzene solution. After removal of the benzene the ester is distilled at atmospheric pressure through a 30-cm. asbestos-wrapped Vigreux column, the fraction boiling at 166–170°, n_{D}^{2} 1.4295, being collected. The yield of colorless product is 257–260 g. (93–95%).

2. Notes

1. The submitters prefer to use the Clarke-Rahrs ester column,[3] for which they claim two distinct advantages: (1) dehydration requires no attention beyond occasionally noting the amount of distillate—when no more aqueous layer separates the reaction is over; (2) reagents do not need to be dry—any water present is removed during the heating.
2. Titration of an aliquot portion of the aqueous layer with standard alkali will give the amount of acetic acid carried over, from which the amount of water can be determined. The expected amount of water is 36 ml.

3. Discussion

γ-Chloropropyl acetate has been prepared by heating 1-bromo-3-chloropropane and potassium acetate in glacial acetic acid,[4] and by the action of acetyl chloride on trimethylene chlorohydrin.[5,6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 835

References and Notes

1. *Org. Syntheses* Coll. Vol. **1**, 422 (1941).

2. *Org. Syntheses* Coll. Vol. **1**, 533 (1941).
3. *Synthetic Org. Chemicals*, **9**, No. 3 (May, 1936), Eastman Kodak Company.
4. Henry, *Bull. acad. roy. Belg.*, **1906**, 738 [*C. A.*, **1**, 1969 (1907)].
5. Derick and Bissel, *J. Am. Chem. Soc.*, **38**, 2483 (1916).
6. Lespieau, *Bull. soc. chim. France*, **7**, 254 (1940).

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

benzene-acetic acid azeotrope

acetic acid (64-19-7)

Benzene (71-43-2)

acetyl chloride (75-36-5)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

1-bromo-3-chloropropane (109-70-6)

Trimethylene chlorohydrin (627-30-5)

γ-Chloropropyl acetate,
1-Propanol, 3-chloro-, acetate (628-09-1)

potassium acetate (127-08-2)

p-toluenesulfonic acid monohydrate (6192-52-5)