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.

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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.

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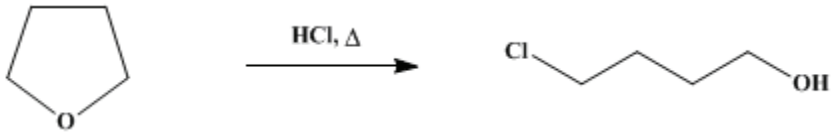
TETRAMETHYLENE CHLOROHYDRIN

[1-Butanol, 4-chloro-]



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1. Procedure

A 500-cc. three-necked flask containing 114 g. (1.58 moles) of tetrahydrofuran (p. 566) is fitted with a reflux condenser, a thermometer dipping into the liquid, and a bent glass tube arranged to introduce gaseous hydrogen chloride (Note 1) near the bottom of the flask. The upper end of the reflux condenser is connected to a 150-cc. distilling flask cooled in an ice-salt mixture to trap material entrained by the hydrogen chloride.

The tetrahydrofuran is heated to the boiling point (64–65°), and a slow stream of hydrogen chloride is bubbled into the liquid. As the reaction proceeds the temperature of the boiling liquid increases, slowly at first and then more rapidly, until it is above 100° (after about four hours' heating). At the end of about five hours the temperature remains practically constant in the range 103.5–105.5°, and the reaction is stopped. The light brown liquid is cooled, transferred to a 250-cc. Claisen flask having a 20-cm. fractionating side arm, and fractionated at reduced pressure, using a water aspirator. A large quantity of hydrogen chloride is evolved at the start of the distillation and a low pressure cannot be obtained until this has been removed. Throughout the fractionation a trap cooled to −15° in an ice-salt mixture is used to collect the recovered tetrahydrofuran.

After removal of a small amount of low-boiling material the main fraction distils in the range 80–90°/14 mm. or 65–75°/7 mm. (Note 2) and weighs 95–100 g. A small amount (5–10 g.) of high-boiling material remains. The crude product on refractionation yields 93–98 g. (54–57 per cent of the theoretical amount) of pure tetramethylene chlorohydrin boiling over a one-degree interval, 81–82°/14 mm. or 70–71°/7 mm. (Note 3) and (Note 4).

2. Notes

1. Hydrogen chloride prepared by dropping concentrated sulfuric acid into a mixture of sodium chloride and concentrated hydrochloric acid may be used directly without drying.
2. It has been reported[1] that tetramethylene chlorohydrin undergoes loss of hydrogen chloride when distilled at pressures appreciably above 15 mm. If an oil pump is used for the distillation of the main fraction, it should be protected from hydrogen chloride by means of soda-lime towers.
3. For recovery of tetrahydrofuran, the condensate from the cooling traps and the low-boiling material from the fractionations are combined, cooled in an ice bath, and treated carefully with 15–20 cc. of 40 per cent alkali. The upper layer is separated, dried with a little calcium chloride, and distilled. The recovered tetrahydrofuran, b.p. 64–67°, weighs 20–22 g. (17–19 per cent of the original material). The residue (12–14 g.) remaining after distillation of the tetrahydrofuran distils at 43–45°/10 mm. and is tetramethylene dichloride.
4. Tetramethylene chlorohydrin may be converted to the chlorobromide in excellent yields by the action of phosphorus tribromide.[2]

3. Discussion

Tetramethylene chlorohydrin has been prepared by the action of thionyl chloride on tetramethylene

glycol in the presence of pyridine,[1] and by the method described above.[2]

References and Notes

1. Kirner and Richter, J. Am. Chem. Soc. **51**, 2503 (1929).
2. Starr and Hixon, ibid. **56**, 1595 (1934).

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

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

thionyl chloride (7719-09-7)

sodium chloride (7647-14-5)

phosphorus tribromide (7789-60-8)

pyridine (110-86-1)

Tetrahydrofuran (109-99-9)

tetramethylene glycol

TETRAMETHYLENE CHLOROHYDRIN,
1-Butanol, 4-chloro- (928-51-8)

tetramethylene dichloride (110-56-5)