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.

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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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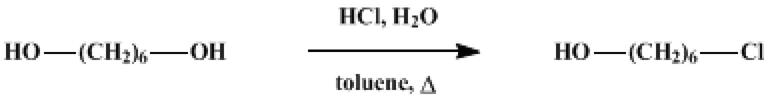
Organic Syntheses, Coll. Vol. 3, p.446 (1955); Vol. 28, p.65 (1948).

HEXAMETHYLENE CHLOROHYDRIN

[1-Hexanol, 6-chloro-]



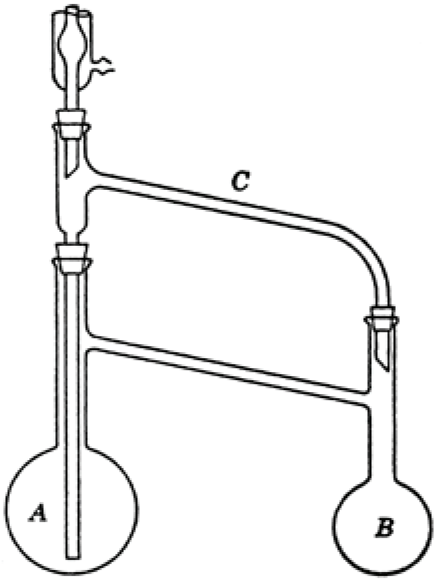
$$HO—(CH_2)_6—OH \xrightarrow[\text{toluene, } \Delta]{HCl,\ H_2O} HO—(CH_2)_6—Cl$$

Submitted by Kenneth N. Campbell and Armiger H. Sommers[1].
Checked by Richard T. Arnold and Roger Amidon.

1. Procedure

The apparatus shown in Fig. 14 is constructed from a 1-l. distilling flask (*A*) and a 500-ml. distilling flask (*B*) the side arm of which has been replaced by 10-mm. Pyrex tubing sealed at an upward angle to the side arm of the larger flask (*A*). Charred cork stoppers are used, and a hydrogen chloride trap[2] is connected to the water-cooled reflux condenser. The bent side arm (*C*) is insulated by a wrapping of cloth. Reaction flask *A* is charged with 105 g. (0.89 mole) of hexamethyleneglycol,[3] 785 ml. (9.5 moles) of concentrated hydrochloric acid, 130 ml. of water (Note 1), and 55 ml. of toluene (Note 2) and (Note 3). In flask *B* are put 350 ml. toluene and a few boiling chips. The apparatus is assembled, and the flasks are heated in oil baths. The bath covering about two-thirds of flask *A* is kept at 95°; the one surrounding most of flask *B* is kept between 160° and 165° (Note 4). As the reaction proceeds and the products are removed by the continuous flow of toluene through the mixture, the organic-aqueous interface in *A* falls steadily. After 9 hours the heating baths and condensers are removed, and water is added to *A* to force the upper layer of toluene into *B*. The aqueous solution is siphoned out of *A*, and then the toluene extract in *B* is poured into a dropping funnel inserted through a stopper in the neck of a 500-ml. Claisen flask. Some of the extract is run into the flask, and most of the toluene is removed by distillation at atmospheric pressure while the remainder of the solution is slowly run into the flask. To remove the last of the solvent, the pressure is lowered to 65 mm. while the bath temperature is kept at 100°.

Fig. 14.



The material obtained from two such runs is combined and fractionated through a Fenske-Whitmore column[4] packed with glass helices. Distillation is carried out at a pressure of 8–12 mm., with a reflux ratio of 5:1. After a fore-run of 5–15 g., about 45 g. (16%) of hexamethylene dichloride distils at 80–84°/9 mm., n_D^{20} 1.4585–1.4565. An intermediate fraction of 10–20 g. distils at 84–100° /9 mm., and then 108–122 g. (45–50%) of hexamethylene chlorohydrin boiling at 100–104° /9 mm., n_D^{20} 1.4551–1.4557, is collected. If several runs are made the residues may be distilled from a Claisen flask and the distillate combined with the intermediate fractions for refractionation. In this way the average yield may be raised to 50–55%.

2. Notes

1. The use of concentrated hydrochloric acid without dilution results in violent bubbling during the reaction.
2. In the original work of Bennett and Turner[5] a petroleum fraction of b.p. 90–120° was used. When the submitters used Skellysolve L, b.p. 90–100°, the hexamethylene chlorohydrin was not sufficiently soluble in it to be removed from the reaction mixture. A study of the solubility of hexamethylene chlorohydrin in various commonly available solvents was made, and toluene was found to be the most satisfactory.
3. The exact volume of free space below the side arm of *A* will vary somewhat according to the exact dimensions of the flask and the adapter tube, and it may be desirable to make corresponding changes in the volumes of hydrochloric acid and water used. In the apparatus constructed by the checkers the aqueous phase expanded during the heating to such an extent that only about 5 ml. of toluene remained in the neck below the side arm; this apparatus operated satisfactorily when the volumes of hydrochloric acid and water were reduced to 720 ml. and 115 ml., respectively.
4. The bath temperature may be controlled by heating with an immersed loop of Nichrome resistance coil, such as the heating element from an electrical appliance. The coil is connected to a 110-volt line in series with a 27-ohm 5-ampere variable resistor and a 600-watt heater element, which may be cut out of the circuit to lower the fixed resistance. An ammeter in the circuit helps to determine the proper adjustment of the sliding contact of the resistor. To avoid an excessive load on the coil, the bath about *B* should be heated in addition by a hot plate adjusted to give a temperature somewhat below 160°.

3. Discussion

Hexamethylene chlorohydrin has been prepared by the reaction of hydrochloric acid with hexamethylene glycol, without a catalyst[5,6,7] or in the presence of cuprous chloride.[8]

References and Notes

1. Work done under contract with the Office of Scientific Research and Development.
2. *Org. Syntheses* Coll. Vol. **2**, 4 (1943).
3. *Org. Syntheses* Coll. Vol. **2**, 325 (1943).
4. *Org. Syntheses*, **25**, 2 (1945).
5. Bennett and Turner, *J. Chem. Soc.*, **1938**, 814.
6. Müller and Vanc, *Monatsh.*, **77**, 259 (1947).
7. Campbell, Sommers, Kerwin, and Campbell, *J. Am. Chem. Soc.*, **68**, 1556 (1946).
8. Coleman and Bywater, *J. Am. Chem. Soc.*, **66**, 1821 (1944).

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

hydrochloric acid (7647-01-0)

toluene (108-88-3)

cuprous chloride (7758-89-6)

Hexamethylene glycol,
hexamethyleneglycol (629-11-8)

Hexamethylene chlorohydrin,
1-Hexanol, 6-chloro- (2009-83-8)

hexamethylene dichloride (2163-00-0)