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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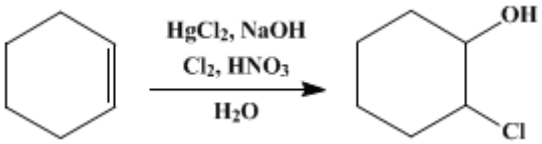
Organic Syntheses, Coll. Vol. 1, p.158 (1941); Vol. 5, p.31 (1925).

2-CHLOROCYCLOHEXANOL

[Cyclohexanol, 2-chloro-]



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1. Procedure

To a solution of 25 g. of mercuric chloride in 500 cc. of water in a 5-l. flask, 800 g. of cracked ice is added. A cold solution of 190 g. of sodium hydroxide in 500 cc. of water is added, and a rapid stream of chlorine is passed into the mixture, which must be kept below 5°. The addition of chlorine is continued in this way until the yellow precipitate of mercuric oxide just disappears. Then 1600 cc. of cold nitric acid (1.5 *N*) is added slowly, with stirring.

The concentration of the hypochlorous acid solution is determined by adding a measured volume to an excess of potassium iodide solution acidified with hydrochloric acid, and titrating with standard thiosulfate solution. Usually the concentration is found to be between 3.5 and 4 per cent. The amount necessary to react with 123 g. (1.5 moles) of cyclohexene is calculated.

In a 5-l. round-bottomed flask equipped with a good mechanical stirrer (Note 1) is placed 123 g. (1.5 moles) of cyclohexene (p. 183), and to it is added about one-fourth the calculated amount of the hypochlorous acid solution. The mixture is kept between 15° and 20°, and stirred vigorously until a 1-cc. test portion gives no yellow color when it is treated with potassium iodide solution and dilute hydrochloric acid. When the first portion of the hypochlorous acid has reacted, a second is added and the process is repeated. When all the hypochlorous acid has been added and the reaction is complete, the oily layer should be on the bottom and a very slight excess of hypochlorous acid should be present, as indicated by the potassium iodide test. If these conditions are not fulfilled, 100-cc. portions of the hypochlorous acid solution are added until the reaction is shown to be complete.

The solution is now saturated with salt and distilled with steam (Note 2). About 2 l. of distillate is required before all of the 2-chlorocyclohexanol passes over. The distillate is saturated with salt and the oily layer separated. The aqueous layer is extracted once with about 250 cc. of ether. This is added to the main portion, which is dried with anhydrous sodium sulfate. The ether is removed by distillation and the product distilled under reduced pressure. The fraction boiling at 88–90°/20 mm. (104–106°/45 mm.) is collected. The yield is 142–148 g. (70–73 per cent of the theoretical amount).

2. Notes

1. If a mechanical stirrer is not available, shaking the flask by hand will give as good results.
2. In the separation of the product from the hypochlorous acid solution, steam distillation seems to be desirable. In several runs in which this was not carried out, a larger amount of a dark-colored high-boiling residue remained in the flask after distillation, and the yield of 2-chlorocyclohexanol was smaller.

3. Discussion

2-Chlorocyclohexanol can be prepared by the action of hypochlorous acid on cyclohexene.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 185

References and Notes

1. Fortey, J. Chem. Soc. **73**, 948 (1898); Detoeuf, Bull. soc. chim. (4) **31**, 177 (1922); Osterberg and Kendall, J. Am. Chem. Soc. **42**, 2621 (1920).

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

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

Cyclohexene (110-83-8)

sodium sulfate (7757-82-6)

potassium iodide (7681-11-0)

mercuric oxide (21908-53-2)

chlorine (7782-50-5)

2-Chlorocyclohexanol,
Cyclohexanol, 2-chloro- (1561-86-0)

mercuric chloride (7487-94-7)

hypochlorous acid (7790-92-3)

thiosulfate