



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](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.

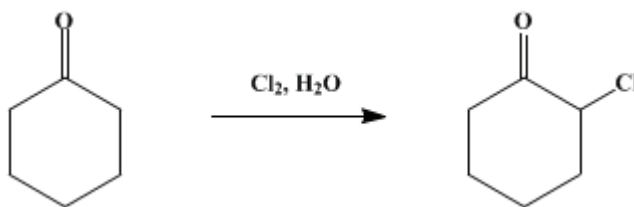
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.*

*Organic Syntheses, Coll. Vol. 3, p.188 (1955); Vol. 25, p.22 (1945).*

## 2-CHLOROCYCLOHEXANONE

[Cyclohexanone, 2-chloro-]



Submitted by M. S. Newman, M. D. Farbman, and H. Hipsher.

Checked by C. S. Hamilton and C. W. Whitehead.

### 1. Procedure

In a 3-l. three-necked round-bottomed flask, fitted with a gas inlet tube reaching almost to the bottom, a sealed mechanical stirrer (Note 1), and a gas outlet tube connected to a mercury valve (Note 2), are placed 294 g. (3 moles) of cyclohexanone (Note 3) and 900 ml. of water. After the reaction vessel has been swept out with chlorine, the gas outlet tube is connected to the mercury valve, the flask is cooled in an ice bath, the stirrer is started, and 215 g. (slightly more than 3 moles) of chlorine is bubbled in as rapidly as the gas is absorbed (about 45 minutes) (Note 4).

The heavier chlorocyclohexanone layer is separated and combined with three 150-ml. ether extracts of the aqueous phase, and washed with 150 ml. of water and then with 200 ml. of saturated sodium chloride solution. After filtration (gravity) through anhydrous sodium sulfate the ether is removed and the residue vacuum-distilled in a modified Claisen flask. The fraction (300–340 g.) boiling below 100° at 10 mm. (Note 5) is collected (Note 6). This material is then fractionated carefully under reduced pressure by means of a 42-in. modified Vigreux column (heated) with a total-condensation variable take-off head (Note 7). The yield of 2-chlorocyclohexanone boiling at 90–91°/14–15 mm. is 240–265 g. (61–66%) (Note 8) and (Note 9).

### 2. Notes

1. A large propeller-type stirrer is satisfactory. The blades should be pitched to drive the liquid upwards, and the propeller should be located just below the surface of the liquid to provide splashing. The checkers used a glycerol-lubricated rubber-tube seal.<sup>1</sup>
2. The mercury valve consists of a tube dipping about 0.5 in. into some mercury in a vented test tube. This allows the reaction to be carried out under a slight pressure of chlorine. The checkers found a water valve to be more satisfactory. The outlet tube was made to dip about 7 in. into water in a vented glass tube. A trap (125-ml. suction flask) was placed between the water valve and the reaction flask to prevent water from being sucked into the reaction mixture.
3. The checkers used Eastman's cyclohexanone boiling at 154–156°. The submitters report that the practical grade gives just as good yields.
4. Careful control of the temperature is unnecessary as approximately the same results are obtained when the temperature is allowed to rise to about 50° or is kept below 20°. However, at the lower temperature a greater amount of cyclohexanone is recovered.
5. Or below 110°/13 mm., or 92°/4 mm.
6. This preliminary purification is advisable before careful fractionation.
7. The head used was similar to that described by Turk and Matuszak<sup>2</sup> except for the stopcock, which was of the variety described by Newman.<sup>3</sup>
8. This material shows a long flat at 23.2° cor. in a time-temperature cooling curve. It can be stored in a refrigerator in paraffin-covered stoppered bottles for long periods of time without discoloration.
9. About 15–40 g. (5–13%) of cyclohexanone, b.p. 52°/14–15 mm., is recovered.

### 3. Discussion

2-Chlorocyclohexanone can be prepared by chlorinating cyclohexanone in glacial acetic acid as the solvent,<sup>4</sup> by passing chlorine into a mixture of cyclohexanone<sup>5</sup> or cyclohexanol<sup>6</sup> and water in the presence of powdered calcium carbonate, by the electrochemical chlorination of cyclohexanone in hydrochloric acid,<sup>7</sup> by the action of monochlorourea in acetic acid on the ketone,<sup>8</sup> by the oxidation of 2-chlorocyclohexanol,<sup>9</sup> and by the chlorination of the sodio derivative of cyclohexanone with ethyl hypochlorite.<sup>10</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 928
- Org. Syn. Coll. Vol. 7, 456
- Org. Syn. Coll. Vol. 10, 584

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### References and Notes

1. *Org. Syntheses Coll. Vol. 3*, 368 (1954).
2. Turk and Matuszak, *Ind. Eng. Chem., Anal. Ed.*, **14**, 72 (1942).
3. Newman, *Ind. Eng. Chem., Anal. Ed.*, **14**, 902 (1942).
4. Bartlett and Rosenwald, *J. Am. Chem. Soc.*, **56**, 1992 (1934).
5. Kotz and Grethe, *J. prakt. Chem.*, (2) **188**, 487 (1909).
6. Ebel, *Helv. Chim. Acta*, **12**, 9 (1929); Bouveault and Chereau, *Compt. rend.*, **142**, 1086 (1906); Meyer, *Helv. Chim. Acta*, **16**, 1291 (1933); Vavon and Mitchovitch, *Bull. soc. chim. France*, (4) **45**, 961 (1929).
7. Szper, *Bull. soc. chim. France*, (4) **51**, 653 (1932).
8. Godchot and Mousseron, *Bull. soc. chim. France*, (4) **51**, 361 (1932).
9. Detoef, *Bull. soc. chim. France*, (4) **31**, 178 (1922).
10. Mousseron and Froger, *Bull. soc. chim. France*, **12**, 69 (1945).

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### Appendix

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

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

Cyclohexanol (108-93-0)

Cyclohexanone (108-94-1)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

mercury (7439-97-6)

calcium carbonate (471-34-1)

chlorine (7782-50-5)

2-Chlorocyclohexanol (1561-86-0)

2-Chlorocyclohexanone,  
Cyclohexanone, 2-chloro-,  
chlorocyclohexanone (822-87-7)

monochlorourea

ethyl hypochlorite (624-85-1)