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.

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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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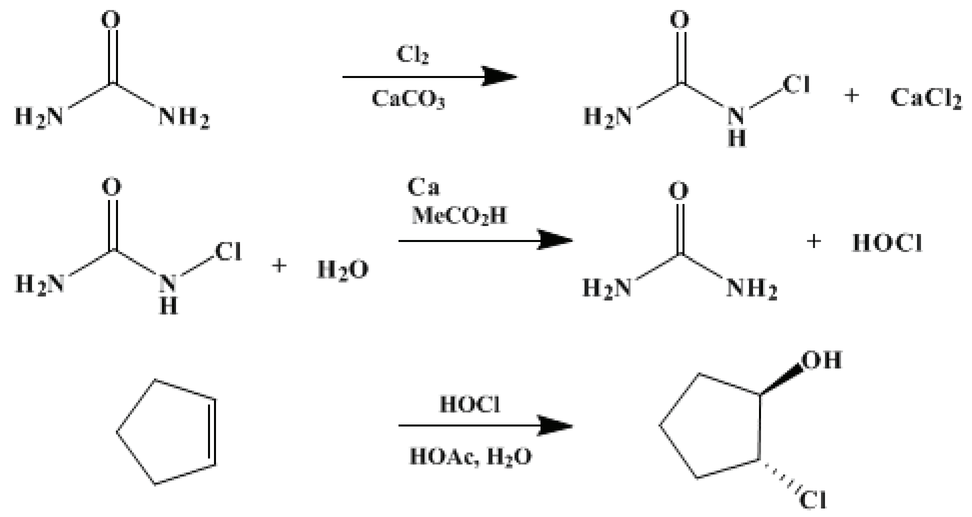
Organic Syntheses, Coll. Vol. 4, p.157 (1963); Vol. 30, p.24 (1950).

trans-2-CHLOROCYCLOPENTANOL

[Cyclopentanol, 2-chloro-, trans-]



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1. Procedure

A mixture of 150 g. (2.5 moles) of urea, 125 g. (1.25 moles) of reprecipitated calcium carbonate, and 150 ml. of water in a 2-l. three-necked flask is tared and cooled in an ice-salt bath. The flask is equipped with a thermometer which extends into the reaction mixture, a gas inlet tube, an outlet tube leading to a gas-absorption trap,[2] and a slip- or mercury-sealed mechanical stirrer which will disperse chlorine gas below the surface of the liquid (Note 1).

A rapid stream of chlorine gas is bubbled into the mixture at 0–15° with vigorous stirring until an increase in weight of about 95 g. has occurred (30–40 minutes) (Note 2). A 250-ml. portion of water at room temperature is added to the suspension, which is then filtered by suction through rather porous filter paper on a 16-cm. Büchner funnel. The filtrate is removed and cooled in an ice bath, and the filter cake is washed on the funnel with a 250-ml. portion of water at room temperature. The filtrate is poured back in the funnel and sucked through the filter cake repeatedly until no more solid appears to dissolve, and then is combined with the original filtrate (Note 3).

The cold filtrates (solutions of monochlorourea) are transferred to a 3-l. two-necked flask immersed in an ice-salt bath. The flask is equipped with a slip- or mercury-sealed mechanical stirrer and an efficient reflux condenser. To the flask are added 500 g. of ice, 100 ml. of glacial acetic acid, and 136 g. (2.0 moles) of cyclopentene (or 1.43 times the weight increase in grams during introduction of the chlorine) (Note 4). Mechanical stirring is begun and is continued while the flask is kept packed in ice until the cyclopentene (the top layer) disappears and a heavy oil settles to the bottom (Note 5).

The solution is saturated with sodium chloride and distilled with steam until all the 2-chlorocyclopentanol is collected, which requires distillation of a volume of about 2 l. The distillate is saturated with sodium chloride, the oily layer separated, and the aqueous layer extracted four times with 300-ml. portions of ether. The ether extracts are added to the oil, and the solution is washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. The ether is removed by distillation, and the product is distilled under reduced pressure through a total condensation, variable take-off, 15 by 1.5 cm. column packed with glass helices. A trap cooled with Dry Ice is placed in the vacuum line between the column and the pump. Low-boiling fractions, b.p. 43–81°/15 mm., amount to

19–40 g. (Note 6). The *trans*-2-chlorocyclopentanol is collected at 81–82°/15 mm. in a yield of 126–135 g. (52–56%); n_{D}^{25} 1.4770 (Note 7).

2. Notes

1. Rapid absorption of chlorine depends on efficient stirring and dispersal of the gas through the liquid phase. A stirrer which disperses the gas through the solution by vigorous agitation may be used (p.891) or the gas may be introduced through the stirrer.[3]
2. The actual weight of chlorine absorbed is equal to the sum of the weight increase noted plus the weight of carbon dioxide formed minus the relatively small weight of carbon dioxide that remains dissolved in the reaction mixture.
3. The combined filtrates may be titrated with 1*N* sodium thiosulfate solution to determine the yield of monochlorourea.[4] This preparation of monochlorourea is a modification of procedures previously described.[4,5]
4. Best yields result when an excess of cyclopentene is used, as specified. The weight increase should be roughly 95 g., and the amount of cyclopentene should be varied proportionately by using 1.43 times the weight increase in grams.
5. The stirring time is about 12–15 hours. It is advantageous to allow the ice to melt and the reaction mixture to come to room temperature during the last 2–3 hours.
6. The fractions boiling at 43–48°/15 mm. and 48–81°/15 mm. contain a mixture of 1,2-dichlorocyclopentane and *cis*- and *trans*-2-chlorocyclopentanol.[6,7]
7. The yield is based on the weight of cyclopentene, although this reagent is used in slight excess.

3. Discussion

2-Chlorocyclopentanol has been prepared by the reaction of dry hydrogen chloride[8] or thionyl chloride[9] with 1,2-cyclopentanediol, and by the addition of hypochlorous acid to cyclopentene.[6,7,8,10]

References and Notes

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10. Mousseron, Granger, Winternitz, and Combes, *Bull. soc. chim. France*, **1946**, 610.

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

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

thionyl chloride (7719-09-7)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

sodium thiosulfate (7772-98-7)

carbon dioxide (124-38-9)

calcium carbonate (471-34-1)

chlorine (7782-50-5)

urea (57-13-6)

hypochlorous acid (7790-92-3)

Cyclopentene (142-29-0)

monochlorourea

Cyclopentanol, 2-chloro-, trans-,
trans-2-Chlorocyclopentanol (20377-80-4)

2-chlorocyclopentanol,
cis- and trans-2-chlorocyclopentanol

1,2-dichlorocyclopentane (31025-65-7)

1,2-cyclopentanediol

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