



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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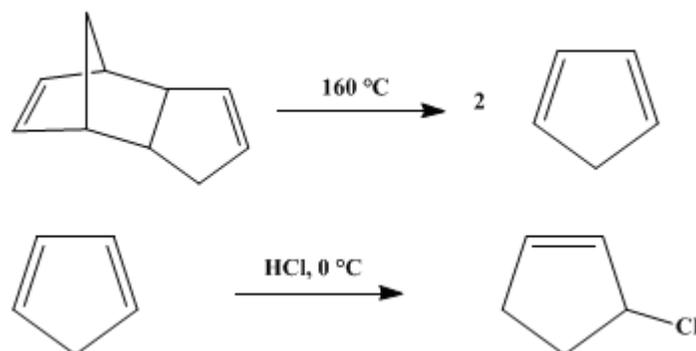
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.238 (1963); Vol. 32, p.41 (1952).

CYCLOPENTADIENE AND 3-CHLOROCYCLOPENTENE

[Cyclopentene, 3-chloro-]



Submitted by Robert Bruce Moffett¹
Checked by R. T. Arnold and George P. Scott.

1. Procedure

A. *Cyclopentadiene*. Two hundred milliliters (195 g.) of technical dicyclopentadiene (Note 1) is placed in a 500-ml. two-necked round-bottomed flask equipped with thermometer and an upright Friedrichs-type condenser (through which water at 50° (Note 2) is circulated). The ground-glass (Note 3) outlet of the Friedrichs condenser is connected to the side arm of a simple distilling head fitted with a thermometer and attached to an efficient water-cooled condenser held in a vertical position. At the lower end of this condenser is a receiver which consists of a carefully weighed 500-ml. two-necked round-bottomed flask immersed in a Dry Ice bath (Note 4) and protected from the air by a calcium chloride drying tube.

The flask containing dicyclopentadiene is now heated by means of an electric heating mantle or oil bath to approximately 160°, or until cyclopentadiene distils smoothly at 38–46° and a little dicyclopentadiene refluxes from the cold-finger (Friedrichs) condenser. After two-thirds of the dicyclopentadiene has been pyrolyzed (during the course of 4–5 hours), the residue in the flask may tend to become viscous and a higher temperature for the pyrolysis will be required in order to obtain rapid distillation of cyclopentadiene. In such an event it is desirable to discard the residue while it is still hot and mobile.

Cyclopentadiene dimerizes rapidly at room temperature and should be used immediately (Note 5) or stored at Dry Ice temperatures. As obtained above, the product has a refractive index of about 1.433 at 25° and is quite satisfactory as a starting material for the following preparation (Note 6). The yield, which is determined by weighing the receiving flask plus product, depends upon the quality of dicyclopentadiene employed (Note 7).

B. *3-Chlorocyclopentene*. The flask containing cyclopentadiene is weighed and the quantity of cyclopentadiene determined (Note 8). A thermometer and gas inlet tube are passed through a two-holed rubber stopper which is fitted to the center neck of the flask; the side neck is fitted with a calcium chloride drying tube. While the flask containing cyclopentadiene is being cooled in a Dry Ice bath (Note 9), dry hydrogen chloride (Note 10) is passed in rapidly. During this operation the temperature of the reaction mixture must be kept below 0° and the flask swirled to ensure good mixing. From time to time the flask is detached, wiped dry, and weighed quickly in order to determine the amount of hydrogen chloride that has been added. An excess is to be avoided, and it is advisable to stop the addition about 10% short of the theoretical quantity.

For many purposes, this crude 3-chlorocyclopentene, either as such or in solution (Note 5), may be

used without purification (Note 11) and (Note 12). If a purer product is desired, however, it may be distilled according to the following procedure.

The flask containing the crude product is equipped with a capillary tube and distilling head and surrounded by a water bath, which may be heated by a hot plate or steam cone. A water-cooled condenser connects the distilling head with the center neck of a two-necked receiver which is surrounded by a Dry Ice bath. The outer neck of the receiver is fitted with a Dry Ice condenser arranged in such a way that vapors which first escape the receiver are condensed and returned to it. This apparatus is connected through a second Dry Ice trap and soda-lime tower (Note 13) to a vacuum pump. A fore-run is removed at a bath temperature of 20° and a pressure of about 15 mm. The receiver is changed, and the product is distilled at 18–25°/5 mm. The temperature of the water bath should not exceed 30°. 3-Chlorocyclopentene is obtained as a colorless liquid in a yield of 70–90% based on cyclopentadiene; n_D^{20} 1.4708.

2. Notes

1. Coarse iron filings or turnings may be added to speed up the rate of depolymerization,² but they are of questionable value.
2. Water at 50° may be obtained by carefully mixing streams of hot and cold water taps. A more elegant method is to circulate water from a thermostatically controlled constant-temperature bath. It has been suggested³ that a modification of the equipment described for the preparation of dehydroacetic acid,⁴ but without the fractionating column, is very convenient for the depolymerization of dicyclopentadiene. The partial condenser is filled with methylene chloride or other liquid with a boiling point in this range, and attached directly to the flask which contains the dicyclopentadiene. This arrangement eliminates the inconvenience of maintaining a supply of water at 50°.
3. It is desirable to use ground-glass jointed equipment throughout.
4. An ice-salt bath may be used but is not so effective. A very convenient fluid for use in Dry Ice baths is ethylene glycol monomethyl ether (methyl Cellosolve, Carbide and Carbon Chemicals Corporation, New York, New York).
5. If the cyclopentadiene is to be used in solution, it is convenient to collect it directly in a flask containing a weighed amount of the desired solvent (e.g., toluene or ether).
6. Further purification, if desired, may be accomplished by distillation at about 20 mm. while collecting the product in a Dry Ice cooled receiver.
7. The checkers used Eastman Kodak Company blue label grade dicyclopentadiene and obtained yields approximating 87%.
8. This reaction should be carried out with undiluted cyclopentadiene if reasonably pure distilled 3-chlorocyclopentene is to be isolated. However, if a distilled product is not required, a solution of cyclopentadiene (Note 5) may be used. 3-Chlorocyclopentene is somewhat more stable in solution.
9. If Dry Ice is not available, an ice-salt bath may be used but then the hydrogen chloride must be added at a much slower rate.
10. Hydrogen chloride gas from a cylinder is most convenient; however, it may be generated if desired.²
11. If the temperature has been kept sufficiently low and an excess of hydrogen chloride avoided, the product will be a clear (or only slightly turbid) colorless, mobile liquid. If an excess of hydrogen chloride seems to be present, or if the product is dark, distillation is advisable.
12. 3 Chlorocyclopentene is unstable at room temperature and soon polymerizes to a black tar which is very difficult to remove from the apparatus. It should be used at once or stored at temperatures well below 0°. All apparatus must be cleaned as soon as possible after completion of the experiment. Ground-glass joints, if not separated soon after the reaction is completed, may become cemented together.
13. In spite of the Dry Ice cooled trap and soda-lime tower, some low-boiling material (as evidenced by the odor) often reaches the pump. It is therefore recommended that an old pump be used and the oil changed immediately after the experiment.

3. Discussion

The only practical laboratory preparation of cyclopentadiene is by the depolymerization of dicyclopentadiene.^{5,6,7,8} 3-Chlorocyclopentene has been prepared by the addition of hydrogen chloride to

cyclopentadiene.^{9,10,11,12,13}

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 738
- Org. Syn. Coll. Vol. 5, 60
- Org. Syn. Coll. Vol. 5, 96
- Org. Syn. Coll. Vol. 7, 339
- Org. Syn. Coll. Vol. 8, 31
- Org. Syn. Coll. Vol. 8, 298
- Org. Syn. Coll. Vol. 9, 67

References and Notes

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 3. Kittila, Private communication.
 4. *Org. Syntheses Coll. Vol. 3*, 231 (1955).
 5. Perkins and Cruz, *J. Am. Chem. Soc.*, **49**, 518 (1927).
 6. Stobbe and Reuss, *Ann.*, **391**, 151 (1912).
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 9. Kraemer and Spilker, *Ber.*, **29**, 552 (1896).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrogen chloride (7647-01-0)

ether (60-29-7)

iron (7439-89-6)

toluene (108-88-3)

methylene chloride (75-09-2)

Dehydroacetic acid (520-45-6)

methyl Cellosolve,
ethylene glycol monomethyl ether (109-86-4)

CYCLOPENTADIENE (542-92-7)

3-Chlorocyclopentene,
Cyclopentene, 3-chloro-,
3 Chlorocyclopentene (96-40-2)

dicyclopentadiene (77-73-6)

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