



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.

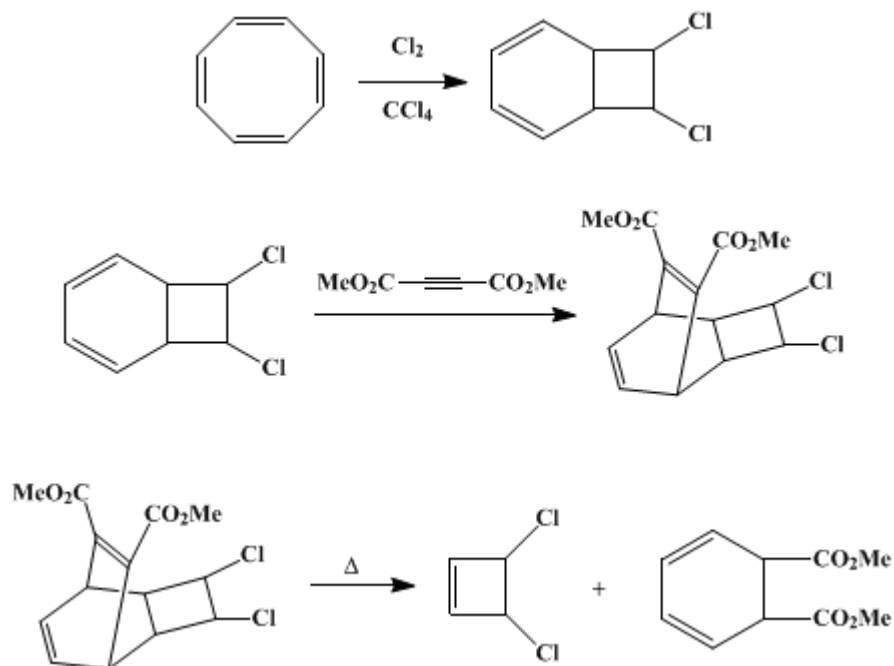
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.422 (1988); Vol. 50, p.36 (1970).

cis-3,4-DICHLOROCYCLOBUTENE

[Cyclobutene, 3,4-dichloro, *cis*-]



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1. Procedure

Dry chlorine gas is admitted into a solution of 104 g. (1.00 mole) of [cyclooctatetraene](#) in 150 ml. of dry [carbon tetrachloride](#) contained in a tared, 500-ml., three-necked flask equipped with a gas-inlet tube, a low-temperature thermometer, and a calcium chloride drying tube. The reaction mixture is maintained between -28° and -30° throughout the addition, which is terminated after 71 g. (1.0 mole) of [chlorine](#) has been added. After the addition, which takes approximately 1 hour, the reaction mixture is allowed to warm to 0° and 50 g. of powdered [sodium carbonate](#) is added, and the contents are shaken gently for several minutes. This treatment removes any [hydrochloric acid](#) which may have been produced during the reaction. The mixture is then filtered directly into a 1-l., round-bottomed flask containing 135 g. (0.951 mole) of [dimethyl acetylenedicarboxylate](#). A condenser is fitted to the flask and the solution is heated at gentle reflux for 3 hours ([Note 1](#)). The solvent is removed under reduced pressure ([Note 2](#)). The crude Diels-Alder adduct, which will slowly solidify on standing, is used directly in the next step.

The crude Diels-Alder adduct is transferred to a 500-ml., pressure-equalizing dropping funnel attached to a 1-l., three-necked, round-bottomed flask; the latter is immersed in an oil bath maintained at 200° and equipped with a distillation head, condenser, and receiving flask. The pressure inside the equipment is reduced to 20 mm. A magnetic stirrer in the pyrolysis flask is started, the Diels-Alder adduct ([Note 3](#)) is added slowly to the hot flask, and the pyrolysate collected in the receiving flask. The distillation temperature during the pyrolysis varies from 135° to 152° , depending on the rate of addition of the Diels-Alder adduct. After the addition is complete (about 1 hour), the pyrolysis is continued for a further 30 minutes or until very little material remains in the pyrolysis flask ([Note 4](#)). The crude pyrolysate is then redistilled at 12–15 mm., with all material boiling below 140° collected; this distillate consists mainly of a mixture of [dichlorocyclobutene](#) and [1,4-dichlorobutadiene](#), the residue being mainly [dimethylphthalate](#).

A Final distillation at 55 mm. through a 36-in., platinum spinning band column yields 49–52 g. (40–43%) of pure *cis*-3,4-dichlorocyclobutene (b.p. 70–71°, 55 mm.); the forerun (b.p. 58–62°, 55 mm.) consists mainly of 1,4-dichlorobutadiene (Note 5).

2. Notes

1. The reaction is very exothermic and usually it is necessary to remove the external source of heat for a short period as soon as reflux has started.
2. Slight warming and pressures of about 1 mm. are required to remove the last of the solvent.
3. A sun lamp situated close to the funnel may be required to prevent solidification of the Diels-Alder adduct.
4. It is necessary to keep the internal pressure close to 20 mm. (place a manometer in the line). If lower pressures are used, the Diels-Alder adduct itself will distill over; if higher pressures are maintained, the rate of removal of the dichlorocyclobutene from the hot reaction flask is reduced and extensive thermal rearrangement to 1,4-dichlorobutadiene will occur.
5. A good fractionating column is required to separate the 1,4-dichlorobutadiene from the dichlorocyclobutene. At 55 mm. the dichlorobutadiene will distill at 58–62°; after this material has been removed, the temperature will rise fairly sharply to 70°, and at this point the reflux ratio may then be reduced from 10:1 to zero and the dichlorocyclobutene collected quickly. It usually is necessary to apply heat frequently with a sun lamp to prevent solidification of the dichlorobutadiene in the exit tube of the distillation apparatus, especially if the receiving flask is kept cold.

3. Discussion

This method of preparation, due to Nenitzescu, Avram, Marica, Dinulescu, Farcasiu, Elian, and Mateescu,² is the only practical method available at this time for the preparation of 3,4-dichlorocyclobutene.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 6*, 310
- *Org. Syn. Coll. Vol. 6*, 1002

References and Notes

1. Deceased, December 10, 1981; work done at Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.
2. M. Avram, E. Marica, I. Dinulescu, M. Farcasiu, M. Elian, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

Appendix

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

hydrochloric acid (7647-01-0)

sodium carbonate (497-19-8)

carbon tetrachloride (56-23-5)

chlorine (7782-50-5)

Dimethyl acetylenedicarboxylate (762-42-5)

dichlorocyclobutene

3,4-dichlorocyclobutene

1,4-dichlorobutadiene

dimethylphthalate

dichlorobutadiene

cyclooctatetraene

cis-3,4-Dichlorocyclobutene,
Cyclobutene, 3,4-dichloro, cis- (2957-95-1)