



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.

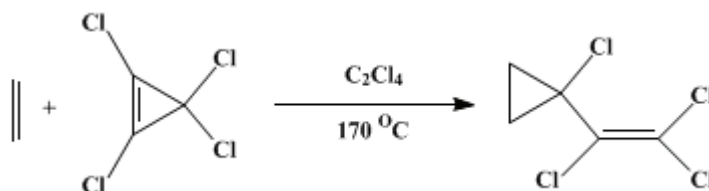
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1-CHLORO-1-(TRICHLOROETHENYL)CYCLOPROPANE

[Cyclopropane, 1-chloro-1-(trichloroethenyl)-]



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1. Procedure

A 1-L Hastelloy C-276 shaker tube (Note 1) fitted with a temperature sensor, a rupture-disk safety device, and a gas inlet valve attached to an ethylene cylinder is charged with 120.0 g (0.675 mol) of freshly distilled tetrachlorocyclopropene (Note 2), 350 mL of dry tetrachloroethylene (Note 3), and 10 g of anhydrous sodium carbonate (Note 4). The tube is pressurized to 20 atm with ethylene and shaken for 3 hr. The ethylene cylinder is disconnected, and the pressure vessel is gradually heated to 170°C over a 30-min period and is shaken at this temperature for 19.5 hr. The vessel is allowed to cool to room temperature, and the excess ethylene is slowly released and bubbled through a wash bottle containing methylene chloride (Note 5). The light-brown liquid in the shaker tube is decanted and the remaining solid washed twice with 50 mL of methylene chloride. The organic phases are combined and the methylene chloride is removed by distillation. The residual liquid is distilled at water-aspirator vacuum through a 40-cm Vigreux column. The solvent tetrachloroethylene, bp 35°C (27 mm), is collected (Note 6), followed by 104.1–105.6 g (75–76%) of 1-chloro-1-(trichloroethenyl)cyclopropane as a colorless liquid, bp 81–83°C (27 mm) (Note 7).

2. Notes

- The submitters used a 1-L autoclave lined with Hastelloy C-4. Hastelloy C materials are high nickel alloys. A highly resistant alloy is employed to avoid possible side reactions.
- Tetrachlorocyclopropene was prepared from sodium trichloroacetate and trichloroethylene.^{2,3} It is also available from the Aldrich Chemical Company, Inc., Eastman Organic Chemicals, and the Merck-Schuchardt Company (in Europe).
- Tetrachloroethylene was obtained from the Aldrich Chemical Company, Inc. and distilled from phosphorus pentoxide prior to use.
- Anhydrous sodium carbonate was obtained from the J. T. Baker Chemical Company and dried under vacuum at 130°C.
- The wash bottle serves to trap any product carried with the ethylene vapors, to monitor and control the release of ethylene pressure and to indicate when no excess pressure remains, and to diminish the release of toxic materials.
- The receiver was cooled in an ice bath to avoid loss of the tetrachloroethylene distillate.
- The submitters obtained 111–116 g of product, bp 72–75°C (14–18 mm). The spectral properties of 1-chloro-1-(trichloroethenyl)cyclopropane are as follows; IR (neat) cm^{-1} : 3100 (CH), 3020 (CH), 1585 (C=C), 1415, 1170, 1040, 1015, 940, 910, 875, 800, 750, 645; ¹H NMR (CDCl_3) δ : 1.42 (m, 2 H), 1.52 (m, 2 H).

3. Discussion

Tetrachlorocyclopropene has been known for some time to be a reasonably reactive dienophile.⁴ Its thermal ring opening to perchlorovinyl carbene is in accord with the behavior of other cyclopropenes under thermolytic conditions,⁵ but the efficiency with which this vinyl carbene intermolecularly adds to

a wide variety of olefins^{6,7} is unprecedented. The resulting 1-chloro-1-(trichloroethenyl)cyclopropanes^{6,7} can be reductively dechlorinated to vinylcyclopropanes,⁶ transformed into variously substituted cyclopropylacetylenes^{7,8} or cyclopropylidenacetates.⁹ The simple cyclopropyl derivatives, accessible from the reported 1-chloro-1-(trichloroethenyl)cyclopropane, like methyl 2-chloro-2-cyclopropylidenacetate (see accompanying procedure) and 1-trimethylsilyl-1-(trimethylsilylethynyl)cyclopropane (prepared by reductive silylation with magnesium/chlorotrimethylsilane in tetrahydrofuran¹⁰), are especially useful building blocks for the construction of complex organic molecules.^{11,12,13}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 8, 373](#)

References and Notes

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Appendix

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

[magnesium](#) (7439-95-4)

[sodium carbonate](#) (497-19-8)

ethylene (9002-88-4)

methylene chloride (75-09-2)

tetrachloroethylene (127-18-4)

Tetrahydrofuran (109-99-9)

trichloroethylene (79-01-6)

tetrachlorocyclopropene

sodium trichloroacetate (650-51-1)

CHLOROTRIMETHYLSILANE (75-77-4)

phosphorus pentoxide (1314-56-3)

1-CHLORO-1-(TRICHLOROETHENYL)CYCLOPROPANE,
Cyclopropane, 1-chloro-1-(trichloroethenyl)- (82979-27-9)

perchlorovinyl carbene

Methyl 2-chloro-2-cyclopropylidenacetate (82979-45-1)

1-trimethylsilyl-1-(trimethylsilylethynyl)cyclopropane