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.

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.

September 2014: The paragraphs above replace the section “Handling and Disposal of Hazardous Chemicals” in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.
CYCLOPROPENE: A NEW SIMPLE SYNTHESIS AND ITS DIELS-ALDER REACTION WITH CYCLOPENTADIENE

[ Tricyclo[3.2.1.0²,4]oct-6-ene, (1α,2α,4α,5α)- ]

A. Cyclopropene (1). A 250-mL, three-necked flask is equipped with a 25-mL dropping funnel, a Dimroth-type reflux condenser (Note 1), an immersed thermometer, a magnetic stirring bar, and a silicon oil gas bubbler with a short connection to the inlet tube of a cold trap (ampule). Argon flow (Note 2) is introduced from the top of the condenser. The flask is charged with sodium bis(trimethylsilyl)amide (Note 3), (Note 4) (35.05 g, 0.192 mol), which is dissolved in toluene (150 mL) (Note 5). The resulting solution is brought to a vigorous reflux (Note 6) at which time allyl chloride (Note 7), (Note 8) (13.8 mL, 0.169 mol) is added from the dropping funnel over a period of 45-60 min (Note 9). Cyclopropene (1) emerges from the flask and is condensed through the inlet tube into an ampule at −80°C. After an additional 30 min at reflux, 2.6 g (d = ca. 0.7 g/mL) (yield 39 %) of cyclopropene (1) is collected as a colorless liquid (purity > 95%) containing only traces of allyl chloride as determined by ¹H NMR spectroscopy at −80°C (Note 10).

B. Reaction of cyclopropene (1) with cyclopentadiene. A 50-mL, one-necked flask equipped with a rubber septum and a stirring bar is charged with pentane (10 mL) (Note 11) and cooled to −80°C, whereupon cyclopentadiene (3.81 g, 4.76 mL, 0.058 mol) (Note 12) is added. A 25-mL flask is equipped with a rubber septum and charged with pentane (10 mL). The pentane is cooled to −80°C, then transferred via cannula into the cold trap (ampule) containing cyclopropene (1) (2.1 g, 0.052 mol). The resulting cyclopropene solution is quickly transferred through a short capillary (steel, 1 mm i.d.) to the cyclopentadiene solution (Note 13) using a positive pressure of argon. The reaction mixture is allowed to warm to room temperature within 2 hr. The resulting colorless solution is distilled via a short-path still. At 125°C, 2.80 g of endo-tricyclo[3.2.1.0²,4]oct-6-ene (2) is collected. A second fraction furnished 1.16 g, providing a combined yield of 3.96 g (72 %) of 2; the purity is >99% as determined from its ¹H and ¹³C NMR spectra (Note 14).

2. Notes

1. An internal water-cooled coil allows for efficient condensation of low-boiling vapors and prevents condensation on the outside, which might seep into joints. The checkers used an Allihn condenser.
2. A stream of argon is added after the condenser is in place to drive the cyclopropene into the cold trap. If the argon stream is too strong, cyclopropene will be blown out of the cold trap, thereby affecting the yield.
3. Sodium bis(trimethylsilyl)amide is commercially available from Aldrich Chemical Company, Inc., or Fluka Chemical Corp., but can be prepared according to reference ³⁴.
4. Sodium bis(trimethylsilyl)amide was weighed in an air bag or glove box to minimize exposure to the air and moisture.
5. Toluene (Overlack) was dried over Na/K alloy and freshly distilled before use.
6. The oil bath should be kept between 140°C and 150°C.
7. Allyl chloride (98%, Fluka Chemical Corp.) was freshly distilled before use.
8. Optimal yields were obtained when using 0.85-0.90 equiv of allyl chloride.5
9. If the allyl chloride is added too quickly, some of the cyclopropene is not condensed and is blown out of the system. In addition, allyl chloride will condense in the cold trap, affecting the purity of the cyclopropene.
10. The following spectra were obtained: 1H NMR (500 MHz, toluene-d$_8$, −80°C, round-bottom tube, 5-mm wide) δ: 1.18-1.19 (m, 2 H), 6.69-6.70 (m, 2 H); 13C NMR (125 MHz, toluene-d$_8$, −80°C) δ: 3.0, 108.5 (2C).
11. Pentane (> 98%, Aldrich Chemical Company, Inc.) was distilled before use.
12. Cyclopentadiene (purity > 99%) was obtained by cracking the dimer (Aldrich Chemical Company, Inc.) at 180°C.
13. The NMR spectrum recorded at −80°C showed that no reaction takes place (even after 24 hr).
14. The spectra were as follows: 1H NMR (500 MHz, CDCl$_3$) δ: 0.37-0.39 (m, 1 H), 0.57-0.62 (m, 1 H), 1.33-1.36 (m, 2 H), 1.69-1.71 (m, 1 H), 1.80-1.82 (m, 1 H), 2.77 (s, 2 H), 5.70-5.71 (m, 2 H); 13C NMR (125 MHz, CDCl$_3$) δ: 12.3 (2C), 17.0, 42.3 (2C), 63.6, 130.4 (2C).

**Waste Disposal Information**

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

A variety of diverse synthetic methods have been employed for the preparation of cyclopropene (1).6 7 8 9 10 11 Schlatter12 and Demjanov and Dojarenko13 pyrolyzed cyclopropyltrimethylammonium hydroxide at 320°C using platinized asbestos as the catalyst. About equal amounts of cyclopropene (1) and cyclopropyldimethylamine are formed, contaminated with some dimethyl ether and ethylene. Treatment with dilute hydrochloric acid removed the amine from the gas stream and 1 was separated from the other products by gas chromatography. Alder-Rickert cleavage of the Diels-Alder adduct formed from cycloheptatriene and dimethyl acetylenedicarboxylate resulted only in the formation of a polymer and trace amounts of 1.14 15 A simple approach by Closs and Krantz16 based on the synthesis of 1-methylcyclopropene 5 17 involved the addition of allyl chloride to a suspension of sodium amide in mineral oil at 80°C. Under the conditions employed, 1 could readily escape from the reaction mixture.16 Though a number of variations were tried, the yield of 1 never exceeded 10%.

From a preparative point of view, previous attempts at preparing cyclopropene (1) are either very laborious or low yielding. Over the last 25 years, the submitters have developed simple syntheses for substituted cyclopropenes on a multigram scale.6,5 17 Here they present their efforts towards an improved synthesis of the parent compound 1.

When allyl chloride (Note 7), (Note 8), (Note 9) was dropped into a solution of sodium bis (trimethylsilyl)amide (Note 3), (Note 4) in boiling toluene (Note 5), (Note 6), cyclopropene (1) could be isolated in a trap/ampule at −80°C.18 19 Compared with the published procedure,16 these conditions proved superior, affording 1 in about 40% yield. Furthermore, as could be established by NMR spectroscopy at −80°C, the cyclopropene (1) was nearly pure (>95%) (Note 10), containing only traces of allyl chloride. Compound 1, prepared in this manner, was found to be stable in toluene solution at −78°C for at least 1 week. Upon warming to −30°C, 1 begins to oligomerize (NMR control).

When 1 was reacted with cyclopentadiene (Note 12) at −80°C or −30°C, no reaction took place, as determined by NMR spectroscopy. At room temperature, however, the Diels-Alder reaction afforded exclusively endo-tricyclo[3.2.1.0²⁴]oct-6-ene (2) in 70% yield.14,15,16,18,19

**Acknowledgments** U.H.B. thanks the State University of New York at Binghamton for a sabbatical leave and those at the Max-Planck-Institut für Kohlenforschung for their generous hospitality.

---

**References and Notes**
Appendix

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

Cyclopropene (8,9); (2781-85-3)

Cyclopentadiene:
1,3-Cyclopentadiene (8,9); (542-92-7)

Sodium bis(trimethylsilyl)amide:
Disilazane, 1,1,1,3,3,3-hexamethyl-, sodium salt (8);
Silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-, sodium salt (9); (1070-89-9)

Allyl chloride:
Propene, 3-chloro- (8);
1-Propene, 3-chloro- (8); (107-05-1)

endo-Tricyclo[3.2.1.0²,4]oct-6-ene:
Tricyclo[3.2.1.0²,4]oct-6-ene, endo- (8);

Tricyclo[3.2.1.0²,4]oct-6-ene, (1α,2α,4α,5α)- (9); (3635-94-7)