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of Reliable Methods
for the Preparation
of Organic Compounds

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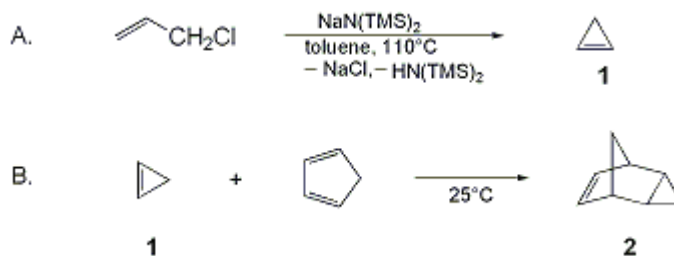
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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CYCLOPROPENE: A NEW SIMPLE SYNTHESIS AND ITS DIELS-ALDER REACTION WITH CYCLOPENTADIENE

[Tricyclo[3.2.1.0^{2,4}]oct-6-ene, (1 α ,2 α ,4 α ,5 α)-]



Submitted by Paul Binger¹, Petra Wedemann¹, and Udo H. Brinker².
Checked by Wenyong Wang and Amos B. Smith, III.

1. Procedure

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 ($d = \text{ca. } 0.7 \text{ g/mL}$) (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[3.2.1.0^{2,4}]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 ^{13}C 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 ^{3,4}.
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-d₈, -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-d₈, -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, CDCl₃) 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, CDCl₃) 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[3.2.1.0^{2,4}]oct-6-ene (2)** in 70% yield.^{14,15,16,18,19}

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References and Notes

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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- (9); (107-05-1)

endo-Tricyclo[3.2.1.0^{2,4}]oct-6-ene:
 Tricyclo[3.2.1.0^{2,4}]oct-6-ene, endo- (8);

Tricyclo[3.2.1.0^{2,4}]oct-6-ene, (1 α ,2 α ,4 α ,5 α)- (9); (3635-94-7)