Organic Syntheses

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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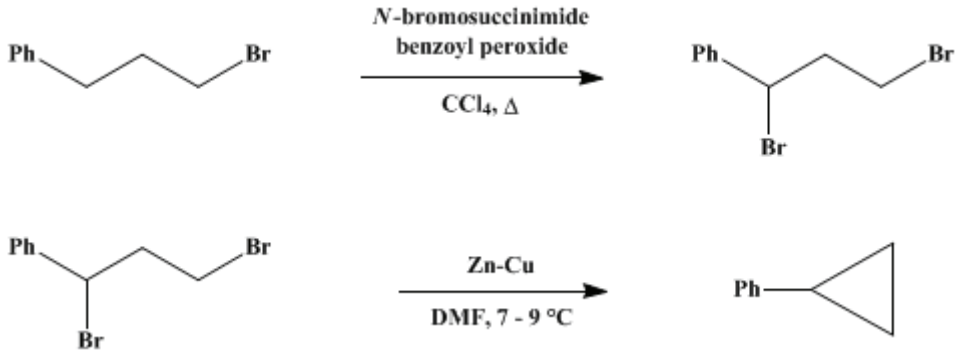
# CYCLOPROPYLBENZENE

## [Benzene, cyclopropyl-]

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Checked by William G. Dauben and Paul Laug.

## 1. Procedure

*Caution! N-Bromosuccinimide is a skin irritant.*

A. *1,3-Dibromo-1-phenylpropane*. In a 3-l. three-necked flask fitted with a sealed stirrer and two efficient reflux condensers are placed 199 g. (1.0 mole) of 1-bromo-3-phenylpropane (Note 1), 187 g. (1.05 moles) of N-bromosuccinimide (Note 2), 3 g. of benzoyl peroxide, and 1.2 l. of carbon tetrachloride. The mixture is heated cautiously with a flame to reflux until a spontaneous reaction starts; ice-bath cooling is then applied if necessary (Note 3). When the spontaneous reaction subsides, the stirring is stopped; if more than a negligible amount of N-bromosuccinimide remains in the bottom of the flask (succinimide rises to the surface of the solvent), heating and stirring are continued until an evolution of hydrogen bromide is noted. The mixture is cooled, and the solids are removed by suction filtration and washed with carbon tetrachloride. The washings are combined with the original filtrate, and the bulk of the carbon tetrachloride is removed (Note 4) by distillation at water aspirator pressure and a bath temperature of 40–50° (Note 5). The remainder of the solvent is removed at the same bath temperature and at 0.1 mm. pressure (Note 6). The orange-yellow residue (nearly 100% of the theoretical yield of 1,3-dibromo-1-phenylpropane) is used without further purification (Note 7) in the next step.

B. *Cyclopropylbenzene*. In a 1-l. three-necked flask equipped with a stirrer and a thermometer extending into the flask but free from the stirrer are placed 500 ml. of redistilled dimethylformamide and zinc-copper couple prepared from 131 g. (2 g. atoms) of zinc (Note 8). The mixture is cooled to 7° in an ice bath, and 1,3-dibromo-1-phenylpropane is added to the stirred mixture at a rate sufficient to maintain the reaction temperature at 7–9° (Note 9). The mixture is stirred for 30 minutes after the addition is completed, poured into 1 l. of water, and then steam-distilled until the condensate is homogeneous or 1 l. of water has been collected. The organic layer is separated from the distillate, and the aqueous layer is extracted with three 100-ml. portions of ether. The combined organic portions are washed with four 50-ml. portions of water and dried over anhydrous potassium carbonate. The ether is removed by distillation at atmospheric pressure at water bath temperature. The residue is distilled to give 88–100 g. (75–85%) of cyclopropylbenzene, b.p. 170–175° (Note 10), $n^{26}$D 1.5306–1.5318.

## 2. Notes

1. The 1-bromo-3-phenylpropane was obtained from Columbia Organic Chemicals Co., Inc., Columbia, South Carolina, and from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. Redistillation of the

commercial material does not noticeably affect yields.
2. N-Bromosuccinimide was obtained from Arapahoe Chemicals, Inc., Boulder, Colorado, and from Coleman and Bell, Norwood, Ohio. The material utilized by the checkers was shown to be 98.6% pure by iodometric analyses.
3. This reaction may become vigorously exothermic; two condensers and a highly mobile setup, allowing quick (5 seconds) removal of heat and application of cooling, are then necessary to contain it. *Caution* must be taken to control but not stop the reaction.
4. Any bromine present at this point is entrained by the carbon tetrachloride; the separated carbon tetrachloride may be purified by shaking with a small quantity of sodium bisulfite, drying over anhydrous potassium carbonate, and distilling.
5. Higher bath temperatures cause darkening of the residue with evolution of hydrogen bromide.
6. An efficient dry ice trap is essential to protect the vacuum pump.
7. Attempts to distil the residue usually cause evolution of large amounts of hydrogen bromide.
8. Zinc powder, obtainable from Mallinckrodt Chemical Works, St. Louis, Missouri, and Merck and Co., Rahway, New Jersey, is placed in a beaker and is washed consecutively and *rapidly* (~10 seconds) with three 100-ml. portions of 3% hydrochloric acid, two 100-ml. portions of water, two 200-ml. portions of 2% aqueous copper sulfate (until blue color disappears), two 200-ml. portions of water, two 100-ml. portions of acetone, two 100-ml. portions of dimethylformamide, and is washed into the reaction vessel with dimethylformamide. This procedure is a modification of one described by Hennion and Sheehan.[3]
9. This *highly exothermic* reaction often has an induction period the end of which is characterized by a rapid temperature rise dependent on the amount of dibromide already added. At the first sign of reaction (*watch the thermometer closely*), addition of dibromide should be stopped and should be resumed only after the temperature has stopped rising. Careful purification of the dimethylformamide appears to minimize the induction period.
10. Analysis of this product by gas liquid chromatography (QF-1 coated column, 130°) showed it to be >98.5% pure. The boiling point of a sample collected by chromatography was 169–171°.

## 3. Discussion

Cyclopropylbenzene has been prepared by decomposition of 5-phenylpyrazoline,[4] addition of hydrogen bromide to cinnamyl bromide followed by cyclization with zinc,[5] decarboxylation of 1-phenylcyclopropanecarboxylic acid,[6] reaction of magnesium with 3-bromo-3-phenyl methyl ether followed by decomposition of the intermediate Grignard reagent,[7] reaction of styrene with methylene iodide and zinc-copper couple,[8] reaction of sodium amide with 3-phenylpropyltrimethylammonium iodide in liquid ammonia,[9] decarbonylation of 1-phenylcyclopropanecarboxaldehyde,[10] and reaction of sodium hydroxide with (1-phenylcyclopropyl)-diphenylphosphine oxide.[11]

## 4. Merits of the Preparation

Because of the unique properties of the cyclopropane ring, cyclopropylbenzene is a compound of considerable interest. Only one of the alternative methods[9] for the preparation of this compound has been reported to give more than 32% yield; the procedure described affords an olefin-free product without a relatively laborious purification process. By its utilization of readily available starting materials, and by its applicability to the preparation of large quantities of product, this method of synthesis provides easy access to many cyclopropylbenzene derivatives.[12]

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## References and Notes


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

3-bromo-3-phenyl methyl ether

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

copper sulfate (7758-98-7)

sodium bisulfite (7631-90-5)

acetone (67-64-1)

zinc,
zinc powder (7440-66-6)

Methylene iodide (75-11-6)

styrene (100-42-5)

benzoyl peroxide (94-36-0)

zinc-copper

sodium amide (7782-92-5)

dimethylformamide (68-12-2)

N-bromosuccinimide (128-08-5)

Cinnamyl bromide (4392-24-9)

Cyclopropylbenzene,
Benzene, cyclopropyl- (873-49-4)

1-bromo-3-phenylpropane (637-59-2)

1,3-Dibromo-1-phenylpropane (17714-42-0)

5-phenylpyrazoline

1-phenylcyclopropanecarboxylic acid (6120-95-2)

3-phenylpropyltrimethylammonium iodide (2125-48-6)

1-phenylcyclopropanecarboxaldehyde

(1-phenylcyclopropyl)-diphenylphosphine oxide