



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.

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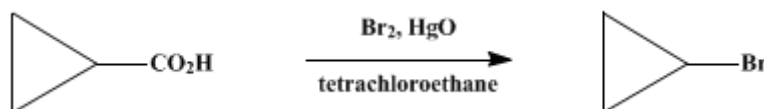
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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BROMOCYCLOPROPANE

[Cyclopropane, bromo-]



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Checked by F. S. Fawcett and B. C. McKusick.

1. Procedure

Twenty-four grams (0.11 mole) of red mercuric oxide (Note 1) and 60 ml. of freshly distilled 1,1,2,2-tetrachloroethane are placed in a 250-ml. three-necked flask equipped with a dropping funnel, a reflux condenser, and a stirrer. A solution of 32.2 g. (0.20 mole) of bromine and 17.2 g. (0.20 mole) of cyclopropanecarboxylic acid in 50 ml. of tetrachloroethane is added dropwise to the stirred suspension of mercuric oxide over a period of 45 minutes, the flask being kept in a water bath at 30–35° (Note 2). The mixture is stirred after the addition of the reactants until the evolution of carbon dioxide ceases.

The flask is then cooled in ice water, and the contents are filtered with as little suction as possible (Note 3). The filter cake is pressed dry and washed with three 15-ml. portions of tetrachloroethane first used to rinse out the flask. The combined filtrates are dried with a little calcium chloride. Sometimes the solution contains a little bromine; it is removed by adding allyl alcohol dropwise until the bromine color is discharged (usually 0.5–1.0 ml. suffices).

The solution is decanted into a 200-ml. round-bottomed flask containing a carborundum chip. The material is distilled through a 20-cm. column of glass helices or a 30-cm. spinning-band column. The fore-run boiling below 75°/760 mm. is bromocyclopropane pure enough for most purposes; weight 9.8–11.2 g. (41–46%); n_D^{25} 1.455–1.459; d_4^{26} 1.506 (Note 4). Redistillation of this product gives pure bromocyclopropane, b.p. 69°/760 mm., n_D^{25} 1.4570, with but slight loss (Note 5).

2. Notes

1. The mercuric oxide used was Mallinckrodt or Baker powdered red mercuric oxide, analytical reagent grade. Old mercuric oxide gives variable results and may lower the yield. The 1,1,2,2-tetrachloroethane used was a technical grade and was distilled to make sure no low-boiling impurities were present. Reagent-grade solvent has been used without distillation. The vapors of this chlorinated hydrocarbon are toxic, and its distillation as well as the reaction should be carried out in a hood. Suitable cyclopropanecarboxylic acid² is obtainable from Aldrich Chemical Company.
2. The reaction starts spontaneously and is mildly exothermic. Moderating the temperature by use of a water bath diminishes the amount of bromine and product carried off by the carbon dioxide evolved. The reaction can be followed by use of a tetrachloroethane bubbler, and at the end of the reaction the solvent in the bubbler can be used to wash the mercuric bromide. The checkers followed the reaction with a wet test meter presaturated with carbon dioxide; 52–60% of the theoretical amount of carbon dioxide was evolved.
3. The checkers used a sintered glass pressure filter (Corning Glass Works, Cat. No. 34020) rather than a suction filter in order to minimize evaporation losses. An ordinary water aspirator can cause the mixture to boil at room temperature. The flask and filter can be cleaned readily with a little acetone, which dissolves mercuric bromide rapidly.
4. Once the boiling point starts to rise, it goes up quite rapidly. The fractions collected between 75° and 90° contain a little product and can be reworked if a second distillation is carried out.
5. After publication of this procedure, the submitters increased the yield to 53–65% by the following modification. A Barrett distilling receiver and thermometer are added to the described apparatus. A mixture of 60 ml. of undistilled technical 1,1,2,2-tetrachloroethane, 27.5 g. (0.125 mole) of mercuric

oxide, and 21.5 g. (0.25 mole) of cyclopropane-carboxylic acid is heated to remove 10 ml. of solvent and water; during the distillation the mercuric oxide dissolves to form a solution of mercuric cyclopropanecarboxylate. The solution is cooled to about 70°, the distilling receiver is removed, and 40 g. (0.25 mole) of bromine is added dropwise with swirling over a period of 15–20 minutes. Mercuric bromide starts to precipitate when 50–75% of the bromine has been added and may cause frothing if the last of the bromine is added too rapidly. The evolution of carbon dioxide tapers off and ceases about 15 minutes after addition is complete; the reaction temperature is about 55° at this point. Any bromine color is discharged with allyl alcohol as described above. The condenser is replaced by one of the distillation columns specified above, and the reaction mixture is distilled without filtration. Stirring helps, but is not essential, for the finely divided mercuric bromide does not cause bumping. The yield of bromocyclopropane having the properties given above is 16–17 g. (53–56%).

3. Discussion

Bromocyclopropane has been prepared by the Hunsdiecker reaction by adding silver cyclopropanecarboxylate to bromine in dichlorodifluoromethane at –29° (53% yield) or in tetrachloroethane at –20° to –25° (15–20% yield).³ Decomposition of the peroxide of cyclopropanecarboxylic acid in the presence of carbon tetrabromide gave bromocyclopropane in 43% yield.⁴ An attempt to prepare the bromide via the von Braun reaction was unsuccessful.³ Ten percent yields are reported for the photobromination of cyclopropane⁵ and the photochemical rearrangement of allyl bromide.⁶ Treatment of 1,1,3-tribromopropane with methyllithium prepared from methyl bromide furnishes a 60–65% yield of bromocyclopropane.

4. Merits of the Preparation

The present procedure is substantially simpler and quicker than the best previous procedure³ based on using cyclopropanecarboxylic acid, which requires 4 days instead of 4 hours. It is also safer, for no explosions have been encountered; whereas care must be taken to prevent explosion of the intermediate hypobromite when the Hunsdiecker method is used,³ and one detonation has been reported.⁷

Although the treatment of 1,1,3-tribromobutane with methyllithium is a safe procedure offering an attractive yield, it suffers from the fact that the tribromide is not commercially available while cyclopropanecarboxylic acid is.

A recent illustration of the generality of this method for preparing alkyl bromides from acids is provided by an *Organic Syntheses* procedure for 1-bromo-3-chlorocyclobutane.⁸ To aid in isolating higher boiling or solid products, solvents such as carbon tetrachloride and cyclohexane can be used.⁹ In preparing a solid, mercuric bromide can be removed by extraction with 5% potassium iodide. It should also be noted that mercuric bromide can be converted back to mercuric oxide easily with alkali

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 6*, 179

References and Notes

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

red mercuric oxide

peroxide of cyclopropanecarboxylic acid

calcium chloride (10043-52-4)

bromine (7726-95-6)

Allyl bromide (106-95-6)

Allyl alcohol (107-18-6)

carbon tetrachloride (56-23-5)

potassium iodide (7681-11-0)

carbon dioxide (124-38-9)

mercuric oxide (21908-53-2)

cyclohexane (110-82-7)

acetone (67-64-1)

methyl bromide (74-83-9)

cyclopropane (75-19-4)

carbon tetrabromide (558-13-4)

tetrachloroethane (630-20-6)

mercuric bromide (7789-47-1)

Cyclopropanecarboxylic acid,
cyclopropane-carboxylic acid (1759-53-1)

Methylithium (917-54-4)

Bromocyclopropane,
Cyclopropane, bromo- (4333-56-6)

1,1,2,2-tetrachloroethane (79-34-5)

mercuric cyclopropanecarboxylate

silver cyclopropanecarboxylate

dichlorodifluoromethane (75-71-8)

1,1,3-tribromopropane

1,1,3-tribromobutane

1-Bromo-3-chlorocyclobutane (4935-03-9)