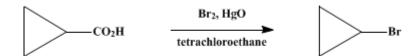
Organic Syntheses, Coll. Vol. 5, p.126 (1973); Vol. 43, p.9 (1963).

BROMOCYCLOPROPANE

[Cyclopropane, bromo-]



Submitted by John S. Meek and David T. Osuga¹. 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 <u>bromine</u> and 17.2 g. (0.20 mole) of <u>cyclopropanecarboxylic acid</u> in 50 ml. of <u>tetrachloroethane</u> is added dropwise to the stirred suspension of <u>mercuric oxide</u> over a period of 45 minutes, the flask being kept in a water bath at $30-35^{\circ}$ (Note 2). The mixture is stirred after the addition of the reactants until the evolution of <u>carbon dioxide</u> ceases.

The flask is then cooled in ice water, and the contents are filtered with as little suction as possible (<u>Note 3</u>). The filter cake is pressed dry and washed with three 15-ml. portions of <u>tetrachloroethane</u> first used to rinse out the flask. The combined filtrates are dried with a little <u>calcium chloride</u>. Sometimes the solution contains a little <u>bromine</u>; it is removed by adding <u>allyl</u> <u>alcohol</u> dropwise until the <u>bromine</u> 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 <u>bromocyclopropane</u> 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 <u>bromocyclopropane</u>, b.p. 69°/760 mm., n_D^{25} 1.4570, with but slight loss (Note 5).

2. Notes

1. The <u>mercuric oxide</u> used was Mallinckrodt or Baker powdered red mercuric oxide, analytical reagent grade. Old <u>mercuric oxide</u> gives variable results and may lower the yield. The <u>1,1,2,2-tetrachloroethane</u> 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 <u>bromine</u> and product carried off by the <u>carbon dioxide</u> 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 <u>mercuric</u> <u>bromide</u>. The checkers followed the reaction with a wet test meter presaturated with <u>carbon dioxide</u>; 52–60% of the theoretical amount of <u>carbon dioxide</u> 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 <u>acetone</u>, which dissolves <u>mercuric bromide</u> 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 <u>1,1,2,2-tetrachloroethane</u>, 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 <u>silver</u> cyclopropanecarboxylate to <u>bromine</u> in <u>dichlorodifluoromethane</u> at -29° (53% yield) or in <u>tetrachloroethane</u> at -20° to -25° (15–20% yield).³ Decomposition of the peroxide of cyclopropanecarboxylic acid in the presence of <u>carbon tetrabromide</u> gave <u>bromocyclopropane</u> 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 <u>cyclopropane</u>⁵ and the photochemical rearrangement of <u>allyl bromide</u>.⁶ Treatment of <u>1,1,3-tribromopropane</u> with <u>methyllithium</u> prepared from <u>methyl bromide</u> furnishes a 60–65% yield of <u>bromocyclopropane</u>.

4. Merits of the Preparation

The present procedure is substantially simpler and quicker than the best previous procedure³ based on using <u>cyclopropanecarboxylic acid</u>, 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.²

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

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

This preparation is referenced from:

- <u>Org. Syn. Coll. Vol. 6, 179</u>
- <u>10</u>

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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)

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potassium iodide (7681-11-0)
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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)

<u>Cyclopropanecarboxylic acid</u>, <u>cyclopropane-carboxylic acid</u> (1759-53-1)

Methyllithium (917-54-4)

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

<u>1,1,2,2-tetrachloroethane</u> (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)

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