



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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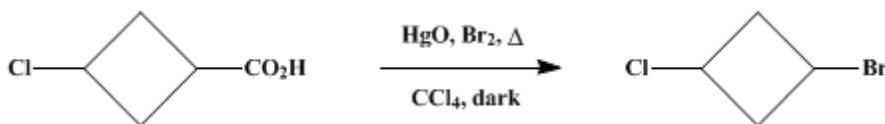
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.179 (1988); Vol. 51, p.106 (1971).

MERCURY(II) OXIDE-MODIFIED HUNSDIECKER REACTION: 1-BROMO-3-CHLOROCYCLOBUTANE



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1. Procedure

In a 1-l., three-necked, round-bottomed flask, wrapped with aluminum foil to exclude light, and equipped with a mechanical stirrer, a reflux condenser, and an addition funnel, is suspended 37 g. (0.17 mole) of red mercury(II) oxide (Note 1) in 330 ml. of carbon tetrachloride (Note 2). To the flask is added 30.0 g. (0.227 mole) of 3-chlorocyclobutanecarboxylic acid (Note 3). With stirring, the mixture is heated to reflux before a solution of 40 g. (0.25 mole) of bromine in 180 ml. of carbon tetrachloride is added dropwise, but as fast as possible (4–7 minutes) without loss of bromine from the condenser (Note 4). After a short induction period, carbon dioxide is evolved at a rate of 150–200 bubbles per minute (Note 5). The solution is allowed to reflux for 25–30 minutes, until the rate of carbon dioxide evolution slows to about 5 bubbles per minute (Note 5). The mixture is cooled in an ice bath, and the precipitate is removed by filtration. The residue is washed with carbon tetrachloride, and the filtrates are combined. The solvent is removed by distillation using a modified Claisen distillation apparatus with a 6-cm. Vigreux column; vacuum distillation of the residual oil gives 13–17 g. (35–46%) of 1-bromo-3-chlorocyclobutane, b.p. 67–72° (45 mm.), n_D^{23} 1.5065 (Note 7) and (Note 8).

2. Notes

1. Purified product is available from J. T. Baker Chemical Company.
2. Reagent grade carbon tetrachloride was used.
3. 3-Chlorocyclobutanecarboxylic acid was prepared as described in *Org. Synth.*, **Coll. Vol. 6**, 271 (1988).
4. The heating bath should be maintained at about 120° to ensure that the solution continues to reflux while the bromine solution is added.
5. The gas evolution can be monitored by conducting the gas through rubber tubing from the condenser into a small amount of water where the bubbling can be observed. A small amount of bromine is lost because of entrainment by the gas.
6. There is no increase in yield on heating the mixture under reflux for 3 hours.
7. The submitters reported a 48–52% yield (18–20 g.) using the indicated scale, and a 35% yield when the reaction was carried out using twice the scale. The checkers obtained the product in 28–29% yield when the reaction was conducted on a scale 10 times that indicated.
8. The product was analyzed by GC at 130° on a Beckman GC-2 chromatograph equipped with a 180 cm. × 6 mm. column (Beckman 17449) containing 42/60 Johns-Manville C-22 firebrick coated with Dow-Corning 550 silicone oil. The retention times are 12 and 14 minutes for the *trans* and *cis* compounds, respectively.

3. Discussion

This procedure, a modified Hunsdiecker reaction based upon the method of Cristol and Firth,² results in moderate to high yields of bromides and iodides from aliphatic^{2,3} and alicyclic carboxylic acids.^{4,5,6} Carbon tetrachloride is most frequently used as the solvent, but others can be employed.^{3,6} Attempts to prepare chlorides by the method have proved to be unsuccessful.⁷

The main advantage of this procedure over that of the standard method⁸ is one of convenience. For

example, the present method is a one-step reaction while the usual method is a two-step sequence involving an intermediate silver salt. In addition, the presence of water produced in the reaction apparently does not reduce the yield in the present method while water markedly reduces the yield in that involving the silver intermediate.

Some variations of the method have been used to prepare cyclopropyl and cyclobutyl halides. Simultaneous addition of bromine and 3-bromocyclobutanecarboxylic acid to the suspension of mercury (II) oxide gives 1,3-dibromocyclobutane in good yield.⁷ Similarly, cyclopropanecarboxylic acid gives bromocyclopropane,⁹ and 3-(bromomethyl)cyclobutanecarboxylic acid gives 1-bromo-3-(bromomethyl)cyclobutane.¹⁰ In the latter reaction, it was found desirable to remove the water from the reaction as it is formed in order to obtain high yields. Another variation is the addition of a mixture of the acid and mercury (II) oxide to excess bromine in bromotrichloromethane.⁶

The conversion of 1-bromo-3-chlorocyclobutane to bicyclo[1.1.0]butane is described in *Organic Syntheses*.¹¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 126](#)
- [Org. Syn. Coll. Vol. 6, 133](#)
- [Org. Syn. Coll. Vol. 6, 271](#)

References and Notes

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Appendix

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

[bromine \(7726-95-6\)](#)

[carbon tetrachloride \(56-23-5\)](#)

[carbon dioxide \(124-38-9\)](#)

[mercury\(II\) oxide,](#)
[mercury \(II\) oxide \(21908-53-2\)](#)

[Cyclopropanecarboxylic acid \(1759-53-1\)](#)

Bromocyclopropane (4333-56-6)

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

bromotrichloromethane (75-62-7)

Bicyclo[1.1.0]butane (157-33-5)

1-bromo-3-(bromomethyl)cyclobutane

3-Chlorocyclobutanecarboxylic acid (35207-71-7)

3-bromocyclobutanecarboxylic acid

1,3-dibromocyclobutane

3-(bromomethyl)cyclobutanecarboxylic acid