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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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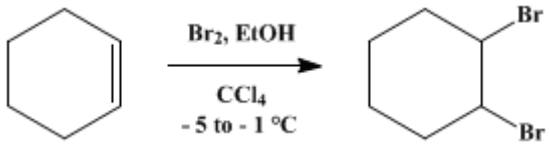
Organic Syntheses, Coll. Vol. 2, p.171 (1943); Vol. 12, p.26 (1932).

1,2-DIBROMOCYCLOHEXANE

[Cyclohexane, 1,2-dibromo-]



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1. Procedure

In a 2-l. three-necked, round-bottomed flask, fitted with a 500-cc. separatory funnel, a mechanical stirrer, and a thermometer, is placed a solution of 123 g. (1.5 moles) of cyclohexene (Note 1) in a mixture of 300 cc. of carbon tetrachloride and 15 cc. of absolute alcohol. The flask is surrounded by an ice-salt bath. The stirrer is started, and, when the temperature has reached −5°, a solution of 210 g. (67 cc., 1.3 moles) of bromine in 145 cc. of carbon tetrachloride is added from the separatory funnel at such a rate that the temperature of the reaction mixture does not exceed −1° (Note 2). The addition requires about three hours.

When the bromine has been added the contents of the flask are transferred directly to a 1-l. modified Claisen flask and the carbon tetrachloride and excess cyclohexene are distilled from a water bath (Note 3), (Note 4), and (Note 5). The water bath is replaced by an oil bath and the product distilled under reduced pressure. There is a small low-boiling fraction, and then pure dibromocyclohexane distils at 99–103°/16 mm. (108–112°/25 mm.). The yield is 303 g. (95 per cent of the theoretical amount) (Note 6) and (Note 7).

2. Notes

1. Cyclohexene boiling over a two-degree range is satisfactory for this preparation. Directions for preparing cyclohexene are given in Org. Syn. Coll. Vol. I, **1941**, 183 and on p. 152 above.
2. Unless the temperature is controlled carefully, the yield is poor because of substitution reactions. Even at this low temperature some substitution occurs unless the excess of cyclohexene is used.
3. The three-necked flask may be rinsed with a little carbon tetrachloride.
4. The dibromide decomposes on continued exposure to the air and becomes very dark. Hence the product should be distilled at once.
5. The low-boiling distillate contains a trace of the dibromide as shown by the fact that it darkens on exposure to the air.
6. The product is stored best in sealed bottles with as little exposure to the air as possible.
7. A product which will not darken may be obtained by the following purification: The crude dibromide is shaken for five minutes with about one-third its volume of 20 per cent ethyl alcoholic potassium hydroxide. The mixture is diluted with its own volume of water and the organic layer is washed free of alkali, dried, and distilled. Material so treated will stay clear indefinitely. The loss in the purification is about 10 per cent. (Wm. Von Eggers Doering and Aldrich Durant, Jr., private communication.)

3. Discussion

1,2-Dibromocyclohexane has been prepared from cyclohexene by the addition of bromine in chloroform,[1] carbon tetrachloride,[2] ether,[3] glacial acetic acid,[4] aqueous sodium bromide,[5] and in the absence of a solvent.[6] The bromination in carbon tetrachloride containing a little alcohol is more satisfactory than the bromination in carbon tetrachloride which is described in an earlier volume.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 285

References and Notes

1. Baeyer, Ann. **278**, 108 (1894); Hofmann and Damm, Mitt. schlesischen Kohlenforsch. Kaiser Wilhelm Ges. **2**, 97 (1925) [C. A. **22**, 1249 (1928)]; Rothstein, Ann. chim. (10) **14**, 542 (1930).
2. Coffey, Rec. trav. chim. **42**, 398 (1923); Greengard, Org. Syn. **12**, 27.
3. Fortey, J. Chem. Soc. **73**, 948 (1898).
4. Harries and Splawa-Neyman, Ber. **42**, 695 (1909).
5. Markownikoff, Ann. **302**, 29 (1898); Swarts, Bull. soc. chim. Belg. **46**, 13 (1937):
6. Truffault, Bull. soc. chim. (5) **1**, 398 (1934).

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

ethyl alcoholic potassium hydroxide

alcohol (64-17-5)

acetic acid (64-19-7)

ether (60-29-7)

chloroform (67-66-3)

Cyclohexene (110-83-8)

bromine (7726-95-6)

sodium bromide (7647-15-6)

carbon tetrachloride (56-23-5)

1,2-Dibromocyclohexane,
Cyclohexane, 1,2-dibromo- (5401-62-7)

dibromocyclohexane