



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.

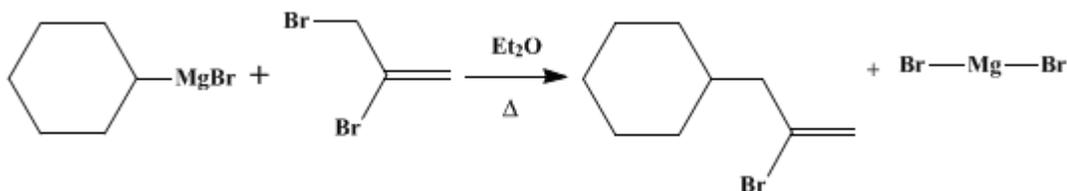
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 1, p.186 (1941); Vol. 6, p.20 (1926).

3-CYCLOHEXYL-2-BROMOPROPENE

[Propene, 2-bromo-3-cyclohexyl-]



Submitted by R. Lespieau and M. Bourguel.

Checked by Roger Adams and M. M. Brubaker.

1. Procedure

A 3-l. three-necked round-bottomed flask is fitted with a mechanical stirrer through a mercury seal, a reflux condenser and a 1-l. separatory funnel. A mixture of 200 g. (1 mole) of 2,3-dibromopropene (p. 209) and 200 cc. of dry ether is added. The flask is now cooled in an ice bath, the stirrer is started, and one molecular equivalent of cyclohexylmagnesium bromide, prepared from 31 g. (1.28 atoms) of magnesium, 204 g. (1.25 moles) of cyclohexyl bromide, and 400 cc. of dry ether (Note 1), is added at such a rate that the mixture refluxes gently (Note 2). The addition takes about one-half to three-quarters of an hour. Two layers are formed, and magnesium bromide may separate.

The stirring should be continued and the ice bath replaced by a hot-water bath, and the mixture refluxed gently for two hours. The flask is again cooled, and 30 cc. of concentrated hydrochloric acid in 350 cc. of water is added through the separatory funnel. This should be added slowly as long as heat is evolved. The contents of the flask are then transferred to a separatory funnel, the ether layer separated and dried over calcium chloride.

The ether is distilled on a steam bath (Note 3) and the residue fractionated under reduced pressure by means of a 20-cm. column (p. 130). After three fractionations, there is obtained 32–44 g. of a product boiling up to 100° /25 mm., which is mainly unchanged dibromopropene (b.p. 42–43° /18 mm.), and 123–130 g. (60.5–64 per cent of the theoretical amount, not taking into account recovered dibromopropene) of cyclohexylbromopropene (Note 4) boiling at 100–105° /25 mm. This material is satisfactory for most purposes. On redistillation it boils at 88–89° /14 mm.

2. Notes

1. The preparation of cyclohexylmagnesium chloride is described on p. 188. The solution may be standardized by titrating against 0.5 N hydrochloric acid, and exactly one mole equivalent is used in the preparation. Five cubic centimeters of cyclohexylmagnesium bromide solution is slowly added to 20 cc. of water, an excess of the standard acid is added, and the excess acid titrated with sodium hydroxide. If 85 g. (3.5 atoms) of magnesium, 1 l. of dry ether, and 571 g. of cyclohexyl bromide (3.5 moles) are used, a solution results which is about 2 molar.

Excess of Grignard reagent may be employed and the same yield obtained, so that the titration is an aid to conserving Grignard reagent. About an 80 per cent yield of cyclohexylmagnesium bromide from cyclohexyl bromide and magnesium can generally be depended upon. Superior yields for both cyclohexylmagnesium chloride and bromide have been reported.¹ Directions for the preparation of cyclohexylmagnesium chloride in superior yields are given in the preparation of cyclohexylcarbinol on p. 188.

2. The reaction is instantaneous and is not stopped by moderate cooling. The cooling may be dispensed with and the cyclohexylmagnesium bromide added more slowly (two hours).

3. The ether solution may be added in several portions to a 500-cc. modified Claisen flask (p. 130) and the ether distilled after each addition.

4. By a similar procedure² benzylmagnesium chloride and 2,3-dibromopropene give 4-phenyl-2-bromobutene in about 45 per cent yield, b.p. 119° /20 mm.; and heptylmagnesium bromide and 2,3-dibromopropene give 2-bromodecene in 60–65 per cent yields, b.p. 76–77° /3 mm.

3. Discussion

3-Cyclohexyl-2-bromopropene can be prepared by the action of cyclohexylmagnesium bromide on 2,3-dibromopropene³

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 191
- Org. Syn. Coll. Vol. 6, 488

References and Notes

1. Gilman and Zoellner, J. Am. Chem. Soc. **53**, 1945 (1931).
 2. Johnson and McEwen, J. Am. Chem. Soc. **48**, 469 (1926).
 3. Lespieau, Bull. soc. chim. (4) **29**, 528 (1921).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

cyclohexylmagnesium chloride and bromide

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

3-Cyclohexyl-2-bromopropene,
Propene, 2-bromo-3-cyclohexyl- (53608-85-8)

2,3-Dibromopropene (513-31-5)

cyclohexylmagnesium bromide

Cyclohexyl bromide (108-85-0)

magnesium bromide (7789-48-2)

dibromopropene (13195-80-7)

cyclohexylbromopropene

cyclohexylmagnesium chloride

Cyclohexylcarbinol (100-49-2)

benzylmagnesium chloride (6921-34-2)

4-phenyl-2-bromobutene

heptylmagnesium bromide (13125-66-1)

2-bromodecene