



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.

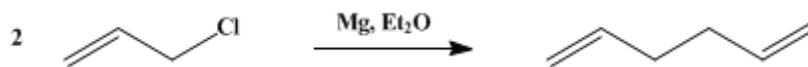
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 3, p.121 (1955); Vol. 27, p.7 (1947).

BIALLYL

[1,5-Hexadiene]



Submitted by Amos Turk and Henry Chanan.

Checked by Arthur C. Cope and Frank S. Fawcett.

1. Procedure

In a 5-l. three-necked flask fitted with a mercury-sealed stirrer (Note 1), a dropping funnel, and an efficient reflux condenser protected by a calcium chloride drying tube is placed 82 g. (3.5 gram atoms) of magnesium turnings. A solution of 459 g. (6 moles) of dry, freshly distilled allyl chloride in 2.4 l. of anhydrous ether is added to the flask through the dropping funnel in the following manner: A 100- to 200-ml. portion of the solution and a small crystal of iodine are added, and the mixture is warmed, if necessary, until the reaction starts. The remainder of the solution is added with stirring and cooling in an ice bath as rapidly as possible without loss of material through the condenser (Note 2). By sponging the upper part of the flask with ice water from the cooling bath, the addition can be completed in 1–1.5 hours. When the addition is complete, the thick slurry is allowed to stand at room temperature for 5 hours with stirring for as much of that period as is practicable (Note 1). The flask is again cooled in an ice bath, and a cold 5% solution of hydrochloric acid is added through the dropping funnel until the evolution of heat has practically ceased (Note 2) and the magnesium chloride is in solution. The mechanical stirrer is started again when the mixture becomes sufficiently fluid (Note 1).

The contents of the flask are transferred to a separatory funnel; the ether layer is separated and distilled without washing or drying through a small packed column (Note 3) until the distillation temperature begins to rise (38–40°). The residue is transferred to a separatory funnel, washed with two 500-ml. portions of water, dried over 10 g. of calcium chloride, and fractionated through the small packed column. After distillation of ether and some allyl chloride (b.p. 45°) biallyl is collected as a colorless liquid in a yield of 135–160 g. (55–65%), b.p. 59–60°/760 mm.; n_D^{20} 1.4040; n_D^{25} 1.4012.

2. Notes

- Efficient stirring is essential during the early part of the reaction. The submitters used a double-loop-type Hershberg wire (Nichrome, Chromel, or tantalum) stirrer¹ and a motor² powerful enough to stir the mixture during the entire preparation. The checkers used the simpler Hershberg wire (No. 16 B and S gauge Chromel or stainless-steel) stirrer³ and an ordinary good laboratory motor. Although the slurry became so thick that it could not be stirred with this equipment, the yield of pure biallyl obtained equaled that reported by the submitters.
- Care must be taken to avoid loss of material (and reduction in yield) through evaporation of allyl chloride or biallyl, both of which are very volatile.
- A simple total-condensation partial take-off column with a 2.2 by 25 cm. section packed with 3/32-in. single-turn glass helices was used with a reflux ratio of 7 or 8 to 1.

3. Discussion

This procedure is a modification of one described by Cortese.⁴ Allyl chloride is employed rather than allyl bromide because of its low cost. Biallyl has been prepared by the action of sodium⁵ or aluminum⁶ on allyl iodide; from allyl mercuric iodide by dry distillation⁷ or by the action of potassium cyanide solution;⁸ by the action of magnesium on allyl bromide,^{4,9} allyl chloride,^{4,10} allyl iodide,¹¹ or 1,2,3-tribromopropane;¹² and from diallyl ether by the action of sodium.¹³

References and Notes

1. *Org. Syntheses Coll. Vol. 2*, 117 (1943).
 2. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 293 (1940).
 3. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).
 4. Cortese, *J. Am. Chem. Soc.*, **51**, 2266 (1929).
 5. Berthelot and Luca, *Ann. chim. et phys.*, (3) **48**, 294 (1856).
 6. Domanitzkii, *J. Russ. Phys. Chem. Soc.*, **46**, 1078 (1914) [*C. A.*, **9**, 1899 (1915)].
 7. Linnemann, *Ann.*, **140**, 180 (1866).
 8. Oppenheim, *Ber.*, **4**, 670 (1871).
 9. Lespieau, *Ann. chim. et phys.*, (8) **27**, 149 (1912); Gilman and McGlumphy, *Bull. soc. chim. France*, **43**, 1322 (1928).
 10. Henne, Chanan, and Turk, *J. Am. Chem. Soc.*, **63**, 3474 (1941).
 11. Meisenheimer and Casper, *Ber.*, **54**, 1655 (1921).
 12. Krestinskii, *J. Russ. Phys. Chem. Soc.*, **58**, 1078 (1926) [*C. A.*, **22**, 1324 (1928)].
 13. U. S. pat. 2,405,347 [*C. A.*, **41**, 148 (1947)].
-

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

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ether (60-29-7)

magnesium,
magnesium turnings (7439-95-4)

Allyl bromide (106-95-6)

potassium cyanide (151-50-8)

allyl chloride (107-05-1)

allyl iodide (556-56-9)

aluminum (7429-90-5)

iodine (7553-56-2)

sodium (13966-32-0)

1,2,3-Tribromopropane (96-11-7)

magnesium chloride (7786-30-3)

diallyl ether (557-40-4)

Biallyl,
1,5-Hexadiene (592-42-7)

allyl mercuric iodide

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved