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.

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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.

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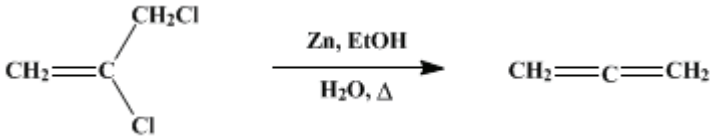
ALLENE



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1. Procedure

A 1-l. three-necked flask is equipped with a Hershberg stirrer operating in a ground-glass bearing (Note 1), a 250-ml. pressure-equalizing dropping funnel, and a coil condenser. The exit from the condenser is connected to a train consisting of a trap (of at least 50-ml. capacity below the bottom of the inlet tube) cooled in ice, a drying tube (about 6 in. long by 1 in. I.D.) filled with indicating Drierite and calcium chloride, an efficient trap of at least 150-ml. capacity cooled in Dry Ice-acetone to −70° or below, and a drying tube containing Drierite. A mixture of 95% ethanol (400 ml.), water (80 ml.), and 300 g. (4.6 g. atoms) of zinc dust is placed in the reaction flask. The addition funnel is charged with 260 g. (2.34 moles) of 2,3-dichloropropene (Note 2), the reaction mixture is stirred and heated to reflux, and the 2,3-dichloropropene is added dropwise at such a rate that reflux is maintained without external heating (2–3 hours). After the addition is complete, heating is resumed for 1 hour. The ice-cooled trap is warmed to about 25°, and the residual allene is purged from the reaction flask with a very slow stream of nitrogen.

The trap cooled in Dry Ice-acetone contains about 105 g. of crude product which, when distilled through a column packed with glass helices (Note 3), yields about 75 g. (80%) of allene (Note 4). No external heat is needed during the distillation. The distillation flask is allowed to warm to room temperature, the distillation beginning at a liquid temperature of −34° and virtually stopping at about 10°. The distilled product contains no detectable ethanol, water, 2,3-dichloropropene, or methylacetylene as determined by gas-liquid chromatography (Note 5).

2. Notes

1. The stirrer should be smooth running and gas-tight. The stirring motor (air-driven) should have a high torque because the reaction mixture tends to agglomerate as the reaction proceeds.
2. 2,3-Dichloropropene from Distillation Products or Columbia Chemicals was employed.
3. A vacuum-jacketed column 1 ft. long by 1 in. I.D. packed with glass helices (4 mm. O.D.) is satisfactory for this distillation. It is fitted with a cold finger in the top of the column cooled by means of acetone that has been cooled in a Dry Ice bath. The fraction cutter is jacketed and similarly cooled. A small circulating pump is used to circulate acetone successively through copper coils in a Dry Ice bath, the fraction cutter, and the cold finger. When the fraction cutter is full, the bottom may be attached to a cooled, evacuated gas cylinder and the allene sucked into the cylinder.
4. The allene contains up to 3% of 2-chloropropene, determined by its vapor-phase infrared spectrum and by vapor-phase chromatography (Note 5).
5. The checkers used an F and M Model 500 gas chromatographic apparatus (F and M Scientific Corporation, P. O. Box 245, Avondale, Penn.) equipped with a polyester column (pentaerythritol adipate, 20% W/W on Chromasorb P, LAC-2-R446) 1 ft. by ¼ in. O.D., helium flow 45 cc. per minute, column temperature 50°, block temperature 215°, injector temperature 225°. This system was able to separate allene from methylacetylene and 2-chloropropene.

3. Discussion

Although many routes to allene are described in the literature, most preparations give a mixture of allene and methylacetylene. The virtue of the present preparation, which is essentially that described by

Gustavson and Demjanoff,[4] is that it gives allene in a reproducible manner with 2-chloropropene as its only impurity.

Allene is an extremely useful reagent for cycloaddition reactions giving cyclobutane derivatives.[5] Allene dimer is also a useful and versatile starting material.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 459

References and Notes

1. Contribution No. 566 from the Central Research Department, Experimental Station, E.I. du Pont de Nemours and Co., Wilmington, Delaware.
2. Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Present Address: Department of Chemistry, University of Hawaii, Honolulu, Hawaii.
3. The Upjohn Company, Kalamazoo, Michigan.
4. G. Gustavson and N. Demjanoff, *J. Prakt. Chem.*, [2] **38**, 202 (1888).
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6. J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4269 (1959); S. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913) [C. A., 8, 320 (1914)].

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

ethanol (64-17-5)

nitrogen (7727-37-9)

copper (7440-50-8)

acetone (67-64-1)

zinc (7440-66-6)

2,3-dichloropropene (78-88-6)

Allene (463-49-0)

methylacetylene (74-99-7)

2-chloropropene (557-98-2)

pentaerythritol adipate

helium (7440-59-7)