



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.

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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. 5, p.249 (1973); Vol. 48, p.51 (1968).

CINNAMYL BROMIDE

[Benzene, 3-bromopropenyl-]



Submitted by John P. Schaefer, J. G. Higgins, and P. K. Shenoy¹.
Checked by R. Breslow and J. T. Groves.

1. Procedure

A 1-l., three-necked, round-bottomed flask equipped with a Trubore stirrer, a pressure-equalizing dropping funnel, and a reflux condenser with a drying tube is charged with 350 ml. of **acetonitrile** (Note 1) and 106.4 g. (0.41 mole) of **triphenylphosphine** (Note 2). The flask is cooled in an ice-water bath (Note 3), and 64 g. (0.40 mole) of **bromine** is added dropwise over a period of *ca.* 15–20 minutes (Note 4) and (Note 5). The ice-water bath is removed, and a solution of 54 g. (0.40 mole) of **cinnamyl alcohol** in 50 ml. of **acetonitrile** is added in portions over a period of 5–10 minutes with continued stirring (Note 6). The solvent is removed by distillation with the use of a water aspirator (30–40 mm.) and an oil bath until the bath temperature reaches 120°. The water aspirator is replaced by a vacuum pump and the water-cooled condenser with an air condenser, and the distillation is continued with rapid stirring (Note 7), (Note 8), and (Note 9). Most of the product (Note 10) distills at 91–98° (2–4 mm.), and about 59 g. of product crystallizes in the receiving flask (63–75% yield) (Note 11).

The product is dissolved in 200 ml. of **ether**, and the solution is washed with 75 ml. of saturated aqueous **sodium carbonate**, dried over anhydrous **magnesium sulfate**, and distilled to give 47–56 g. (60–71%) of product, b.p. 66–68° (0.07 mm.), 84–86° (0.8 mm.); m.p. 29°.

2. Notes

1. The **acetonitrile** was distilled from **phosphorus pentoxide**.
2. **Triphenylphosphine** was obtained from M and T Chemicals, Inc., and used without further purification.
3. The **triphenylphosphine** is only partially dissolved.
4. If a slight excess of **bromine** persists after addition, a small amount of **triphenylphosphine** should be added until the color of **bromine** disappears.
5. The solid **triphenylphosphine** disappears, but at the same time the adduct, $(\text{C}_6\text{H}_5)_3\text{PBr}_2$, precipitates as a white solid.
6. This addition is mildly exothermic, and the temperature rises to 50–60°. All the precipitate should dissolve at this point; warming by external heat may be necessary.
7. To protect the vacuum pump from damage a dry ice-acetone trap and two liquid nitrogen traps are necessary to condense and solidify the **hydrogen bromide** evolved.
8. The receiving flask is placed in an ice-water bath.
9. The distillation is continued until the **triphenylphosphine oxide** solidifies and no more product distills. The oil bath is maintained at 130–140° during the distillation.
10. Some product is carried over by the **hydrogen bromide** in the initial stages of the distillation.
11. When this distillation was replaced by a procedure in which the **acetonitrile** was removed with a rotary evaporator and steam bath, and the product was extracted from the **triphenylphosphine oxide** with

small portions of [acetonitrile](#) totaling *ca.* 250 ml., the checkers obtained an improved yield (79%) of [cinnamyl bromide](#).

3. Discussion

[Cinnamyl bromide](#) has been prepared from [cinnamyl alcohol](#) by the action of [hydrogen bromide](#) in cold [acetic acid](#)² and of [phosphorus tribromide](#) in boiling [benzene](#).³ It has also been prepared by the action of [N-bromosuccinimide](#) on [3-phenylpropene](#)⁴ and on [1-phenylpropene](#).⁵

4. Merits of the Preparation

The method described is general for converting alcohols to alkyl halides and is stereospecific.⁶

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 142](#)

References and Notes

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Appendix

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

[acetic acid](#) (64-19-7)

[Benzene](#) (71-43-2)

[ether](#) (60-29-7)

[acetonitrile](#) (75-05-8)

[hydrogen bromide](#) (10035-10-6)

[sodium carbonate](#) (497-19-8)

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

[phosphorus tribromide](#) (7789-60-8)

1-phenylpropene

magnesium sulfate (7487-88-9)

cinnamyl alcohol (104-54-1)

N-bromosuccinimide (128-08-5)

3-phenylpropene (300-57-2)

triphenylphosphine (603-35-0)

Cinnamyl bromide,
Benzene, 3-bromopropenyl- (4392-24-9)

triphenylphosphine oxide (791-28-6)

phosphorus pentoxide (1314-56-3)