



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](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.

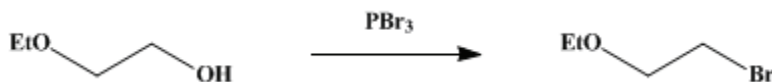
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.370 (1955); Vol. 23, p.32 (1943).*

## β-ETHOXYETHYL BROMIDE

[Ethane, 1-bromo-2-ethoxy-]



Submitted by George C. Harrison and Harvey Diehl.

Checked by R. L. Shriner and C. H. Tilford.

### 1. Procedure

In a 2-l. three-necked flask, fitted with a mechanical stirrer (Note 1), a reflux condenser, and a dropping funnel, is placed 630 g. (670 ml., 7 moles) of β-ethoxyethyl alcohol (Note 2). The stirrer is started, and 600 g. (210 ml., 2.2 moles) (Note 3) of phosphorus tribromide is added from the dropping funnel over a period of 1.5–2 hours. The temperature is permitted to rise until the reaction mixture refluxes gently.

The mixture is then distilled, and the distillate boiling below 150° is collected in a 2-l. flask containing 1 l. of water. The lower layer of crude β-ethoxyethyl bromide is separated and dried over 10 g. of calcium chloride. The liquid is decanted and distilled through a 25-cm. fractionating column, and the fraction boiling at 125–127°/760 mm. is collected (Note 4). The yield of pure product is 660–670 g. (65–66% based on the phosphorus tribromide).

### 2. Notes

1. A rubber sleeve lubricated with a drop of oil provides an effective seal for the stirrer.
2. Technical β-ethoxyethyl alcohol is marketed commercially as Cellosolve; it should be dried over calcium oxide and distilled.
3. A slight excess of β-ethoxyethyl alcohol gives the best results.
4. The first fraction, boiling at 38–40°, is ethyl bromide, and it weighs 120–130 g. Lower yields (56–59%) of β-ethoxyethyl bromide are obtained by distillation without a fractionating column. The residue, however, should not be overheated, for at high temperatures phosphorous acid decomposes to give phosphine and perhaps even elementary phosphorus, and then, when air is admitted to the apparatus an explosion may occur. A minor explosion in connection with this preparation has been reported (N. L. Drake, private communication) and a similar situation has been observed in reactions with phosphorus trichloride.<sup>1</sup>

### 3. Discussion

β-Ethoxyethyl bromide has been prepared by the action of sodium ethoxide upon ethylene bromide;<sup>2</sup> by the action of bromine upon β-ethoxyethyl iodide;<sup>3</sup> and by the procedure adopted here, which was first used by Chalmers.<sup>4</sup> The action of sodium bromide and sulfuric acid on β-ethoxyethyl alcohol cleaves the ether linkage.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3, 372*

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### References and Notes

1. Coghill, *J. Am. Chem. Soc.*, **60**, 488 (1938).
2. Foran, *J. Soc. Chem. Ind.*, **44**, 173 (1925).

3. Henry, *Jahresb.*, **1885**, 1163.
  4. Chalmers, *Can. J. Research*, **7**, 464 (1932).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ether (60-29-7)

bromine (7726-95-6)

sodium bromide (7647-15-6)

PHOSPHORUS (7723-14-0)

phosphorus tribromide (7789-60-8)

sodium ethoxide (141-52-6)

phosphorus trichloride (7719-12-2)

ethylene bromide (106-93-4)

calcium oxide

phosphorous acid (13598-36-2)

$\beta$ -Ethoxyethyl bromide,  
Ethane, 1-bromo-2-ethoxy- (592-55-2)

$\beta$ -ethoxyethyl alcohol (110-80-5)

phosphine (7723-14-0)

$\beta$ -ethoxyethyl iodide