



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.

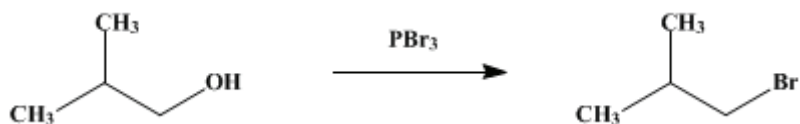
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 2, p.358 (1943); Vol. 13, p.20 (1933).

ISOBUTYL BROMIDE

[Propane, 1-bromo-2-methyl-]



Submitted by C. R. Noller and R. Dinsmore.

Checked by Frank C. Whitmore, D. E. Badertscher, and A. R. Lux.

1. Procedure

In a 2-l. three-necked flask, fitted with a mechanical stirrer, a thermometer, and a dropping funnel, is placed 518 g. (643 cc., 7 moles) of dry *isobutyl alcohol* (b.p. 106–108°). The alcohol is cooled to –10° by immersing the flask in an ice-salt bath, and 695 g. (244 cc., 2.56 moles) of *phosphorus tribromide* (Note 1) is slowly added with stirring at such a rate as to keep the temperature below 0° (about four hours). The cooling bath is removed, and stirring is continued until the mixture reaches room temperature; it is then allowed to stand overnight. The stirrer, funnel, and thermometer are removed, and the flask is fitted with a 30-cm. fractionating column and a condenser. The crude *isobutyl bromide* is distilled from the reaction mixture under diminished pressure, e.g., at about 50°/200 mm. (Note 2).

The distillate is cooled to about 0° and washed three times with 50-cc. portions of concentrated *sulfuric acid* cooled to 0°; it is then shaken with 25 g. of anhydrous *potassium carbonate* until the odor of *hydrobromic acid* disappears. It is distilled through a 1-m. fractionating column at atmospheric pressure collecting the portion boiling at 91–93° (88.5–90.5°/728 mm.), or under reduced pressure through a 70 by 2-cm. total reflux, adjustable take-off, adiabatic column (Note 3), b.p. 41–43°/135 mm. The product weighs 525–570 g. (55–60 per cent of the theoretical amount) (Note 4).

2. Notes

1. The *phosphorus tribromide* boiled at 171–173° (168–170°/725 mm.), and was prepared in 90–95 per cent yield by adding *bromine* to a stirred suspension of red phosphorus in *carbon tetrachloride*. A good fractionating column is necessary. Old, red phosphorus containing acids of *phosphorus* gives a poorer yield.
2. In some runs, the crude bromide was successfully distilled at atmospheric pressures; in others it decomposed violently. With reduced pressure no difficulty was experienced. A water pump with an adjustable leak in the vacuum line was used.
3. The column used with reduced pressure was similar to those described by Whitmore and Lux, *J. Am. Chem. Soc.* **54**, 3451 (1932). The product, fractionated under reduced pressure using a reflux ratio of 5:1, contained less than 1 per cent of *tertiary butyl bromide*.
4. By similar procedures, the following bromides can be prepared with the yields indicated: *sec.-butyl*, b.p. 90–93°, 80 per cent; *n-propyl*, b.p. 70–73°, 95 per cent; *isopropyl*, b.p. 60–63°, 68 per cent. In the preparation of these three bromides and *isobutyl bromide* as well, the *phosphorus tribromide* procedure described above gives purer products in better yields than the hydrobromic-sulfuric acid method described in *Org. Syn. Coll. Vol. I*, 1941, 25. The *phosphorus tribromide* method is not convenient for the preparation of *tertiary butyl bromide*; the product is difficult to purify.

3. Discussion

Isobutyl bromide has been prepared from *isobutyl alcohol* by the action of *bromine* and *phosphorus*,¹ aqueous *hydrobromic acid*,² and gaseous *hydrobromic acid*,³ from *isobutylene* and gaseous *hydrogen bromide*,⁴ or *hydrogen bromide* in glacial *acetic acid*,⁵ and by the rearrangement of *tertiary*

butyl bromide at 210–220°. ⁶ A number of bromides, including isobutyl bromide, have been prepared by the action of phosphorus tribromide on alcohols. ⁷ The procedure described above is a modification of one used for preparing cyclopentyl bromide. ⁸

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 366
- Org. Syn. Coll. Vol. 2, 406
- Org. Syn. Coll. Vol. 2, 476
- Org. Syn. Coll. Vol. 2, 547

References and Notes

1. Wurtz, Ann. **93**, 114 (1855).
2. Norris, Am. Chem. J. **38**, 640 (1907).
3. Fournier, Bull. soc. chim. (3) **35**, 623 (1906); Longinov and Lerman, Khim Farm. Prom. **1933**, 14 [C. A. **27**, 3443 (1933)].
4. Brunel, J. Am. Chem. Soc. **39**, 1978 (1917).
5. Ipatiew and Ogonowsky, Ber. **36**, 1988 (1903).
6. Faworsky, Ann. **354**, 343 (1907).
7. Reynolds and Adkins, J. Am. Chem. Soc. **51**, 280 (1929); Tseng and Hou, J Chinese Chem. Soc. **2**, 57 (1934) [C. A. **28**, 3711 (1934)].
8. Adams and Noller, J. Am. Chem. Soc. **48**, 1084 (1926).

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

red phosphorus

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

bromine (7726-95-6)

PHOSPHORUS (7723-14-0)

Isopropyl bromide (75-26-3)

n-PROPYL BROMIDE (106-94-5)

sec.-BUTYL BROMIDE (78-76-2)

tertiary butyl bromide,

t-butyl bromide (507-19-7)

phosphorus tribromide (7789-60-8)

carbon tetrachloride (56-23-5)

isobutyl alcohol (78-83-1)

Isobutyl bromide,
Propane, 1-bromo-2-methyl- (78-77-3)

isobutylene (9003-27-4)

cyclopentyl bromide (137-43-9)