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.

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.

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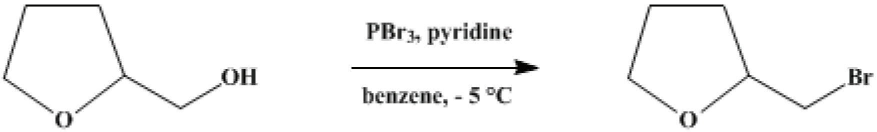
TETRAHYDROFURFURYL BROMIDE

[Furan, 2-(bromomethyl)tetrahydro-]



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1. Procedure

In a 500-ml. three-necked flask, fitted with a mechanical stirrer, thermometer, separatory funnel, and calcium chloride tube, are placed 96 g. (56.5 ml., 0.36 mole) of redistilled phosphorus tribromide (b.p. 174–175°/740 mm.) and 50 ml. of dry benzene. From the separatory funnel, 15 g. of dry pyridine is added with stirring over a period of 15 minutes. The flask is then surrounded by an ice-salt mixture, and the contents are cooled to −5°. A mixture of 102 g. (1 mole) of redistilled tetrahydrofurfuryl alcohol (b.p. 79–80°/20 mm.) and 5 g. of dry pyridine (total pyridine, 20 g., 0.25 mole) is added slowly from the dropping funnel with stirring over a period of 4 hours. During this time the internal temperature is kept at −5° to −3°. Stirring is continued for 1 hour longer, and the cooling bath is then allowed to warm up to room temperature.

The mixture is allowed to stand for 24–48 hours (Note 1) and is then transferred to a 500-ml. Claisen flask. Two small portions of benzene are used for rinsing the flask. The benzene is distilled by reducing the pressure gradually to about 60 mm. and heating the flask gently in an oil bath (not above 90°). After the benzene has been removed, the pressure is reduced to 5–10 mm. and the bath is heated slowly to 150–155° until no more material distils (Note 2). The crude distillate (110–126 g.) is redistilled through an efficient column, and the purified tetrahydrofurfuryl bromide is collected at 69–70°/22 mm. (61–62°/13 mm., 49–50°/4 mm.) (Note 3). The yield is 90–102 g. (53–61%).

2. Notes

1. The yields were slightly higher when the mixture was allowed to stand for 48 hours.
2. Most of the material distils while the bath is at 100–120°. When the bath reaches 155–160° the mixture begins to decompose and white fumes are copiously evolved.
3. Unless a good fractionation is obtained, the material will contain some pyridine and will discolor in a few days. Carefully fractionated material will remain colorless for 2 months or more. A considerable amount of dark, viscous residue remains in the distilling flask.

3. Discussion

Tetrahydrofurfuryl bromide has been obtained in low yields by the action of hydrobromic acid, or of phosphorus tribromide, on the corresponding alcohol.[1] The yield is improved markedly by use of phosphorus tribromide and pyridine.[2,3] The bromide has also been prepared by the action of potassium hydroxide on 4,5-dibromopentanol-1.[4]

References and Notes

1. Dox and Jones, *J. Am. Chem. Soc.*, **50**, 2033 (1928).
2. Paul, *Bull. soc. chim. France*, (4) **53**, 417 (1933).
3. Robinson and Smith, *J. Chem. Soc.*, **1936**, 195.
4. Paul, *Ann. chim.*, (10) **18**, 303 (1932).

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

Benzene (71-43-2)

HYDROBROMIC ACID (10035-10-6)

phosphorus tribromide (7789-60-8)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

tetrahydrofurfuryl alcohol (97-99-4)

Tetrahydrofurfuryl bromide,
Furan, 2-(bromomethyl)tetrahydro- (1192-30-9)

4,5-dibromopentanol-1