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.

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.

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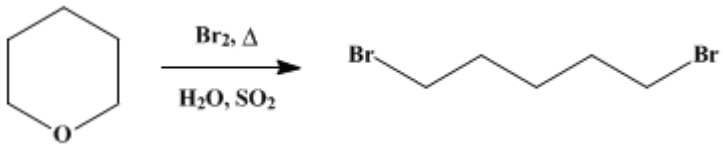
Organic Syntheses, Coll. Vol. 3, p.692 (1955); Vol. 23, p.67 (1943).

PENTAMETHYLENE BROMIDE

[Pentane, 1,5-dibromo-]



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1. Procedure

A hydrobromic acid solution [*Org. Syntheses* Coll. Vol. **1**, 26 (1941)] is prepared in a 500-ml. round-bottomed flask by passing sulfur dioxide into a mixture of 120 g. (37.7 ml., 0.75 mole) of bromine, 50 ml. of water, and 150 g. of crushed ice. This is equivalent to a mixture of 253 g. (1.5 moles) of 48% hydrobromic acid and 74 g. of concentrated sulfuric acid. To the mixture 21.5 g. (0.25 mole) of tetrahydropyran (p. 794) is added, a reflux condenser is attached to the flask, and the light-brown homogeneous mixture is refluxed for 3 hours (Note 1).

The heavy lower layer is separated (Note 2), washed once with a saturated solution of sodium bicarbonate and once with water, and then dried over 4–5 g. of anhydrous calcium chloride. The crude product is decanted from the calcium chloride, and the drying agent is rinsed once or twice with a small quantity of ethyl bromide which is added to the main product. The mixture is distilled under reduced pressure, and the pentamethylene bromide, which weighs 46–47 g. (80–82%), is collected at 104–106°/19 mm.

2. Notes

1. The submitter refluxed the mixture for 10 hours, but the checkers obtained equally good yields in 3 hours.
2. The upper aqueous layer contains considerable unchanged hydrobromic acid. If this layer is distilled, about 150 g. (0.9 mole) of constant-boiling hydrobromic acid (b.p. 123–124°/748 mm.) may be recovered.

3. Discussion

The methods of preparing pentamethylene bromide are given in *Org. Syntheses* Coll. Vol. **1**, 428 (1941), where the preparation of the dihalide from benzoylpiperidine and phosphorus pentabromide is described in detail. The procedure given above is based upon the work of Paul.[1]

References and Notes

1. Paul, *Bull. soc. chim. France*, (4) **53**, 1489 (1933).

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

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

sodium bicarbonate (144-55-8)

HYDROBROMIC ACID (10035-10-6)

bromine (7726-95-6)

sulfur dioxide (7446-09-5)

Ethyl bromide (74-96-4)

Benzoylpiperidine (776-75-0)

pentamethylene bromide,
Pentane, 1,5-dibromo- (111-24-0)

Tetrahydropyran (142-68-7)

phosphorus pentabromide (7789-69-7)