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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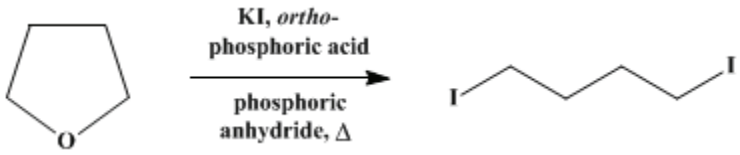
1,4-DIIODOBUTANE

[Butane, 1,4-diiodo-]



Submitted by Herman Stone and Harold Shechter[1].
Checked by Cliff S. Hamilton and R. C. Rupert.

1. Procedure

Tetrahydrofuran (36 g., 0.5 mole) (Note 1) is added to a mixture of potassium iodide (332 g., 2 moles), 85% orthophosphoric acid (231 g., 135 ml., 2 moles), and phosphoric anhydride (65 g.) (Note 2), (Note 3), and (Note 4) in a 1-l. three-necked flask equipped with a sealed mechanical stirrer, a reflux condenser, and a thermometer. The mixture is stirred and heated at its reflux temperature for 3 hours, during which time a dense oil separates from the acid layer. The stirred mixture is cooled to room temperature, and 150 ml. of water and 250 ml. of ether are added (Note 5). The ether layer is separated, decolorized with dilute aqueous sodium thiosulfate solution, washed with cold saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The ether is removed by distillation on a steam bath, and the residue is distilled under reduced pressure from a modified Claisen flask. The portion boiling at 108–110°/10 mm. is collected. The yield of colorless 1,4-diiodobutane (n_D^{20} 1.615; d_4^{20} 2.300) (Note 6) is 143–149 g. (92–96%).

2. Notes

1. Tetrahydrofuran was obtained by the submitters from E. I. du Pont de Nemours and Company.
2. The specified mixture of commercial 85% orthophosphoric acid and phosphoric anhydride corresponds to a 95% orthophosphoric acid solution. The phosphoric anhydride is placed in the dry flask, and the 85% orthophosphoric acid is added with stirring. After the mixture has cooled to room temperature, solid potassium iodide is added. The solution should be cooled, before addition of the potassium iodide, to prevent evolution of hydrogen iodide and formation of iodine. After the tetrahydrofuran is added, the mixture can be heated as desired since the hydrogen iodide reacts as rapidly as it is formed.
3. Orthophosphoric acid of 95% concentration is most efficient for effecting cleavage of tetrahydrofuran. Commercial orthophosphoric acid (85%) may be used; however, the yield drops to 82% and approximately 10% of the tetrahydrofuran is recovered. Anhydrous orthophosphoric acid and tetraphosphoric acid cannot be employed conveniently because of the limited solubility of hydrogen iodide in these reagents.
4. This procedure has been used successfully to convert simple aliphatic ethers into their corresponding iodides. Yields of iodides obtained in the reaction of di-*n*-butyl ether and diisopropyl ether with potassium iodide and 95% orthophosphoric acid were 81 and 90% respectively. Small quantities of the corresponding alcohols were also isolated as products from these reactions.
5. Usually one extraction with ether is sufficient to decolorize the acid layer; if this fails, an additional extraction with 100 ml. of ether is recommended.
6. The checkers obtained values of: n_D^{25} 1.619; d_4^{26} 2.349. The product darkens slowly on standing.

3. Discussion

1,4-Diiodobutane has been prepared in 51% yield by the reaction of phosphorus, iodine, and tetrahydrofuran.[2] It has also been prepared by the reaction of hydriodic acid with phenoxybutyl iodide[3,4] and with the diisoamyl ether of 1,4-butanediol.[5] Sulfuric acid has been used in place of phosphoric acid

in the reaction described in the present procedure.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 368

References and Notes

1. Ohio State University, Columbus, Ohio.
2. Heisig, *J. Am. Chem. Soc.*, **61**, 525 (1939).
3. von Braun and Beschke, *Ber.*, **39**, 4357 (1906).
4. Marvel and Tannenbaum, *J. Am. Chem. Soc.*, **44**, 2650 (1922).
5. Hamonet, *Compt. rend.*, **132**, 345 (1901).
6. Bräuniger and Mengering, *Pharmazie*, **14**, 191 (1959) [*C. A.*, **54**, 548 (1960)].

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

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium chloride (7647-14-5)

PHOSPHORUS (7723-14-0)

sodium sulfate (7757-82-6)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

iodine (7553-56-2)

orthophosphoric acid (7664-38-2)

hydriodic acid,
hydrogen iodide (10034-85-2)

di-n-butyl ether (142-96-1)

Tetrahydrofuran (109-99-9)

diisopropyl ether (108-20-3)

phosphoric anhydride (2466-09-3)

1,4-Diiodobutane,

Butane, 1,4-diiodo- (628-21-7)

tetraphosphoric acid

phenoxybutyl iodide

diisoamyl ether of 1,4-butanediol