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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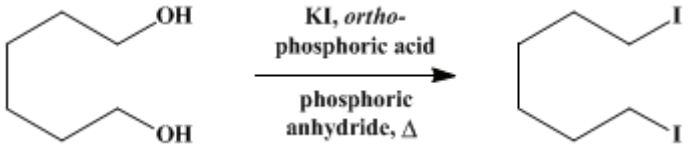
1,6-DIIODOHEXANE

[Hexane, 1,6-diiodo-]



Submitted by Herman Stone and Harold Shechter[1].
Checked by T. L. Cairns, B. C. McKusick, and G. V. Mock.

1. Procedure

In a 1-l. three-necked flask, equipped with a short reflux condenser, a sealed mechanical Hershberg stirrer, and a thermometer, is placed 65 g. (0.46 mole) of phosphoric anhydride, and 231 g. of 85% orthophosphoric acid (135 ml., 2 moles) is added (Note 1). After the stirred mixture has cooled to room temperature, 332 g. (2 moles) of potassium iodide and 59 g. (0.5 mole) of recrystallized 1,6-hexanediol (Note 2), (Note 3), and (Note 4) are added. The mixture is stirred and heated at 100–120° for 3–5 hours, during which time the homogeneous solution separates into two phases, and finally a dense oil settles through 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 by shaking with 50 ml. of 10% sodium thiosulfate solution, washed with 200 ml. of cold saturated sodium chloride solution, and dried with 50 g. of anhydrous sodium sulfate. The ether is removed by distillation on a steam bath, and the product is distilled from a modified Claisen flask under reduced pressure. The fraction boiling at 123–128°/4 mm. is collected. The yield of 1,6-diiodohexane is 140–144 g. (83–85%), n_D^{15} 1.585, m.p. 10° (Note 6) and (Note 7).

2. Notes

1. The specified mixture of commercial 85% orthophosphoric acid and phosphoric anhydride corresponds to 95% orthophosphoric acid. Ninety-five per cent orthophosphoric acid is recommended for this reaction. If 85% orthophosphoric acid is used, the reaction proceeds more slowly and the yield is reduced.
2. 1,6-Hexanediol,[2] m.p. 40–41°, was prepared by catalytic reduction of diethyl adipate with hydrogen over copper chromite catalyst. It can also be purchased from Columbia Organic Chemicals Company, Inc.
3. The solution must be cool before the potassium iodide is added to avoid the evolution of hydrogen iodide and formation of iodine. After the 1,6-hexanediol has been added, the mixture can be heated as desired since the hydrogen iodide reacts as rapidly as it is formed.
4. This procedure has been used successfully for conversion of various aliphatic and alicyclic alcohols to the corresponding iodides. Yields of iodides from 1-propanol, 2-methyl-1-propanol, 2-methyl-2-propanol, and cyclohexanol were 95, 88, 90, and 79.5%, respectively.
5. Usually one extraction of the reaction product with ether is sufficient to remove the color from the acid layer.
6. Slightly yellow 1,6-diiodohexane crystallizes as white needles when cooled in an ice-water mixture. The addition of a few drops of mercury to the yellow product produces a nearly colorless liquid.
7. The submitters reported yields of 93–95% and a melting point of 8.5–9.0°.

3. Discussion

1,6-Diiodohexane has been prepared in 73% yield by the reaction of 1,6-hexanediol, red phosphorus, and iodine.[3] It has also been prepared by reactions of hydrogen iodide and 1,6-diphenoxyhexane[4] and 1,6-diethoxyhexane,[5] respectively. Physical constants have been reported by

Dionneau.[6] The method described here has been published.[7]

This preparation is referenced from:

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

References and Notes

1. Ohio State University, Columbus, Ohio.
2. *Org. Syntheses Coll. Vol.* **2**, 325 (1943).
3. Müller and Rölz, *Ber.*, **61**, 571 (1928).
4. Salonina, *Ber.*, **26**, 2988 (1893); Gol'mov, *Zhur, Obschlei Khim (J. Gen. Chem.)*, **22**, 809 (1952) [*C. A.*, **47**, 3251 (1953)].
5. Farmer, Laroia, Switz, and Thorpe, *J. Chem. Soc.*, **1927**, 2951.
6. Dionneau, *Ann. chim.*, [9] **3**, 257 (1915).
7. Stone and Shechter, *J. Org. Chem.*, **15**, 491 (1950).

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

red phosphorus

ether (60-29-7)

hydrogen (1333-74-0)

Cyclohexanol (108-93-0)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

mercury (7439-97-6)

iodine (7553-56-2)

orthophosphoric acid (7664-38-2)

1-propanol (71-23-8)

hydrogen iodide (10034-85-2)

2-methyl-1-propanol (78-83-1)

COPPER CHROMITE

1,6-Hexanediol (629-11-8)

diethyl adipate (141-28-6)

1,6-Diiodohexane,
Hexane, 1,6-diiodo- (629-09-4)

phosphoric anhydride (2466-09-3)

2-methyl-2-propanol (75-65-0)

1,6-diphenoxyhexane (10125-18-5)

1,6-diethoxyhexane