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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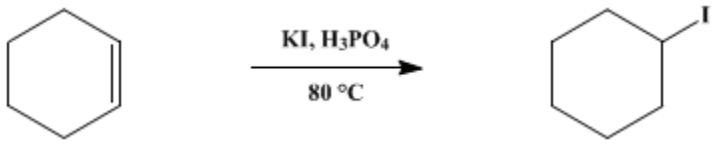
IODOCYCLOHEXANE

[Cyclohexane, iodo-]



Submitted by Herman Stone and Harold Shechter[1].
Checked by T. L. Cairns and V. A. Engelhardt.

1. Procedure

Forty-one grams (0.5 mole) of cyclohexene (Note 1) is added to a mixture of 250 g. (1.5 moles) of potassium iodide in 221 g. (2.14 moles) of 95% orthophosphoric acid (Note 2), (Note 3), and (Note 4) contained in a 1-l. three-necked flask equipped with a reflux condenser, a sealed mechanical stirrer, and a thermometer. The mixture is stirred and heated at 80° for 3 hours, after which it is allowed to cool and treated with 150 ml. of water and 250 ml. of ether with continued stirring (Note 5) and (Note 6). The ether extract is separated, decolorized with 50 ml. of 10% aqueous sodium thiosulfate solution, washed with 50 ml. of saturated sodium chloride solution, and dried with anhydrous sodium sulfate (50 g.). The ether is evaporated on a steam bath, and the product is distilled from a modified Claisen flask under reduced pressure. The portion boiling at 48–49.5°/4 mm. is collected. The yield of iodocyclohexane is 93–95 g. (88–90%), n_D^{20} 1.551, d_4^{20} 1.625.

2. Notes

1. Cyclohexene was obtained from Eastman Kodak Company.
2. The 95% orthophosphoric acid is prepared by adding 174 g. (102 ml., 1.5 moles) of 85% phosphoric acid with stirring to 47 g. of phosphoric anhydride. The solution should be cooled to room temperature before the addition of potassium iodide; otherwise evolution of hydrogen iodide and formation of iodine will take place. After the cyclohexene has been added, the mixture can be heated as desired, since the hydrogen iodide reacts as rapidly as it is generated.
3. Although 95% orthophosphoric acid is recommended for this method, commercial phosphoric acid (85%) may be used, but the reaction proceeds more slowly and the yield is lower.
4. This procedure has been used for the conversion of other olefins to iodides in excellent yield. Yields of 2-iodohexane and 2,3-dimethyl-2-iodobutane from 1-hexene and 2,3-dimethyl-2-butene were 94.5 and 91.4%, respectively.
5. Excess potassium iodide can be recovered by filtering the acid layer, after adding sufficient water to dissolve precipitated inorganic phosphates.
6. If the acid layer has an iodine color, another extraction with 100 ml. of ether is recommended.

3. Discussion

Iodocyclohexane has been prepared by the action of phosphorus and iodine on cyclohexanol,[2] and from hydrogen iodide and cyclohexanol,[3] chlorocyclohexane,[4] or cyclohexyl ether.[5] It has also been prepared by reaction of potassium iodide and chlorocyclohexane,[6] by the reaction of iodine with cyclohexyldiphenyl phosphite,[7] and by the condensation of triphenyl phosphite, methyl iodide, and cyclohexanol.[8]

References and Notes

1. Ohio State University, Columbus, Ohio.

2. Freundler and Damon, *Compt. rend.*, **141**, 593 (1905).
3. Baeyer, *Ann.*, **278**, 107 (1894).
4. Markownikoff, *Ann.*, **302**, 12 (1898).
5. Lacourt, *Bull. soc. chim. Belges*, **36**, 353 (1927).
6. Conant and Hussey, *J. Am. Chem. Soc.*, **47**, 476 (1925).
7. Forsman and Lipkin, *J. Am. Chem. Soc.*, **75**, 3145 (1953).
8. Rydon and Landauer (to National Research Development Corp.), Brit. pat. 695,468 [*C. A.*, **48**, 10047 (1954)]; Landauer and Rydon, *J. Chem. Soc.*, **1953**, 2224.

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

ether (60-29-7)

Cyclohexanol (108-93-0)

Cyclohexene (110-83-8)

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)

phosphoric acid,
orthophosphoric acid (7664-38-2)

hydrogen iodide (10034-85-2)

chlorocyclohexane (542-18-7)

Methyl iodide (74-88-4)

2,3-dimethyl-2-butene (563-79-1)

phosphoric anhydride (2466-09-3)

1-hexene (592-41-6)

Iodocyclohexane,
Cyclohexane, iodo- (626-62-0)

2-iodohexane

2,3-dimethyl-2-iodobutane

cyclohexyl ether

cyclohexyldiphenyl phosphite

triphenyl phosphite (101-02-0)