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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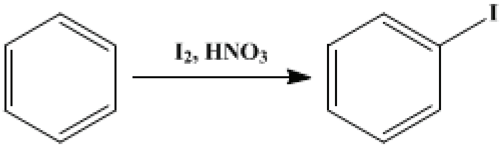
IODOBENZENE

[Benzene, iodo-]



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1. Procedure

In a 1-l. three-necked flask fitted with mechanical stirrer, reflux condenser, and separatory funnel, are placed 381 g. (1.5 moles) of iodine and 400 g. (455 cc., 5.1 moles) of benzene. The mixture is heated to about 50° on a water bath, and 275 cc. (6.15 moles) of nitric acid (sp. gr. 1.50) is added slowly from the separatory funnel; the time required for the addition should be about one and one-quarter hours. A copious evolution of oxides of nitrogen takes place, and the gases are carried off from the upper end of the condenser to an open window or hood, or absorbed by means of a gas trap (Fig. 7 on p. 97). The reaction proceeds smoothly (Note 1), and the temperature rises slowly without the application of heat until the mixture boils gently. When all the nitric acid has been added, the solution is refluxed for about fifteen minutes. If iodine still remains, more nitric acid should be added slowly to the warm solution until the purple color of the iodine has been discharged and the solution becomes brownish red.

The lower reddish oily layer is separated, mixed with an equal volume of 10 per cent sodium hydroxide solution, and steam-distilled from a 2-l. flask until no more oil passes over. Towards the end of the distillation a yellow solid begins to collect in the receiver; this consists of nitro compounds, which are removed by vigorously stirring the oil for about three hours with 20 cc. of concentrated hydrochloric acid, 300 cc. of water, and 200 g. of iron filings in a 2-l. flask connected with a reflux condenser.

The mixture is allowed to cool and is then filtered. The filtrate is rendered distinctly acid to Congo red with hydrochloric acid and again distilled with steam. The oil so obtained is separated and distilled under normal pressure with the use of a fractionating column (Note 2). The fraction boiling at 180–190° is redistilled, and the pure compound is collected at 184–186°. The yield is 523–531 g. (86–87 per cent of the theoretical amount) (Note 3).

2. Notes

1. The reaction proceeds smoothly without stirring; however, the time of addition is decreased somewhat by stirring. Ordinary rubber stoppers may be used; although they are somewhat attacked, this is not sufficiently serious to warrant any special apparatus. In very large runs it may be desirable to use stoppers made from asbestos paper and water glass. Rubber stoppers have been used in a run five times the size of that described.
2. A good separation is obtained by means of a 500-cc. modified Claisen flask (p. 130) without the use of diminished pressure.
3. Iodobenzene prepared by this procedure may contain traces of nitro compounds. The test for these is to reduce a sample with stannous chloride (or tin) and hydrochloric acid, and treat the resulting acid solution in the cold with a solution of sodium nitrite. If a phenolic odor is obtained on boiling the solution, nitro compounds are still present. A more delicate test can be made by adding the reduced solution, after treatment with sodium nitrite, to an alkaline solution of β-naphthol; an azo dye is formed if nitro compounds were originally present.

3. Discussion

The procedure described is essentially that of Datta and Chatterjee.[1] Oxidizing agents other than nitric acid can be used in the preparation of iodobenzene from benzene and iodine, but no one of them appears to be so effective and so convenient as nitric acid. Those that have been used are iodic acid,[2] fuming sulfuric acid,[3] mercuric oxide,[4] and ferric chloride.[5] It can also be made by the diazo reaction from aniline.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 351

References and Notes

1. Datta and Chatterjee, J. Am. Chem. Soc. **39**, 437 (1917).
2. Kekulé, Ann. **137**, 162 (1866); Klages and Liecke, J. prakt. Chem. (2) **61**, 311 (1900).
3. Rupp, Ber. **29**, 1629 (1896); Neumann, Ann. **241**, 84 (1887).
4. Weselsky, Ann. **174**, 99 (1874).
5. Meyer, Ann. **231**, 195 (1885); J. prakt. Chem. (2) **34**, 504 (1886).
6. Griess, Jahresber. 477 (1866); Org. Syn. **19**, 55.

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

fuming sulfuric acid

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

iron filings (7439-89-6)

nitric acid (7697-37-2)

sodium nitrite (7632-00-0)

β-naphthol (135-19-3)

tin (7440-31-5)

stannous chloride

mercuric oxide (21908-53-2)

iodine (7553-56-2)

ferric chloride (7705-08-0)

Iodobenzene,
Benzene, iodo- (591-50-4)

iodic acid (7782-68-5)