



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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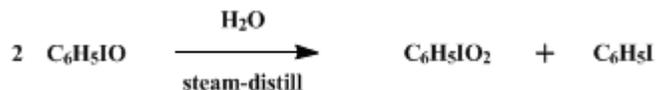
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.485 (1955); Vol. 22, p.72 (1942).

IODOXYBENZENE

[Benzene, iodoxy-]

[A. DISPROPORTIONATION OF IODOSOBENZENE]



Submitted by H. J. Lucas and E. R. Kennedy.
Checked by John R. Johnson and M. W. Formo.

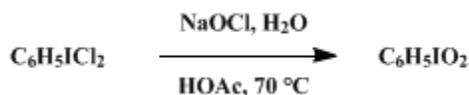
1. Procedure

In a 5-l. flask (Note 1), 110 g. (0.5 mole) of *iodosobenzene* (p. 483) is made into a thin paste with water, and the mixture is rapidly steam-distilled (Note 2) until almost all the *iodobenzene* (Note 3) is removed. The distillation should not be continued any longer than necessary, and the contents of the flask should be cooled at once. The white solid is filtered with suction and dried in the air at room temperature. It is then washed with *chloroform*, again dried, and the resulting cake is ground lightly in a mortar to facilitate removal of moisture in a final drying. The yield is 54–56 g. (92–95%). The product has a purity of about 99%, as determined by iodimetry (Note 4). The solid may be crystallized from hot water (Note 5).

2. Notes

1. Because of a tendency to froth, a large flask should be used.
2. Direct heating must be avoided, as the solid reactant and product may decompose with explosive violence on heating, especially when dry.
3. The recovered *iodobenzene* is quite pure and may be used for the preparation of *iodobenzene dichloride*. The recovery is about 46 g. (90%).
4. The iodimetric method described under *iodosobenzene* (p. 484) is applicable here. The main impurity in the *iodoxybenzene* is *iodosobenzene*.
5. The solubility of *iodoxybenzene*, per liter of water, is 2.8 g. at 12°, and about 12 g. at 100°.

[B. HYPOCHLORITE OXIDATION OF IODOBENZENE DICHLORIDE]



Submitted by M. W. Formo and John R. Johnson.
Checked by Lee Irvin Smith, R. T. Arnold, and Louis E. Demytt.

1. Procedure

In a 2-l. round-bottomed flask equipped with an efficient mechanical stirrer (Note 1) are placed 110 g. (0.4 mole) of freshly prepared, pulverized *iodobenzene dichloride* (p. 482) (Note 2), 1.0 mole of *sodium hypochlorite* solution (Note 3), and 2 ml. of glacial *acetic acid*. The vigorously stirred mixture is heated on a water bath maintained at 65–75°. After 10–15 minutes the heated mixture becomes frothy and the yellow color of *iodobenzene dichloride* is displaced by the white color of *iodoxybenzene*. The stirring is stopped after 1 hour, and the flask is cooled in an ice bath. The product is filtered with suction, pressed with a glass stopper, and transferred to an 800-ml. beaker. The material is stirred thoroughly with 300 ml. of water, filtered with suction, washed on the filter with 100 ml. of water, pressed, and dried in the air. The crude product weighs 85–89 g. (90–94%) and has a purity, as

determined iodimetrically, of 97–99% (Note 4). The air-dried material may be washed with 50–60 ml. of chloroform, air-dried, and finally dried in a vacuum desiccator. This product weighs 82–87g. (87–92%) and has a purity of 99.0–99.9% as determined by iodimetry (Note 5).

2. Notes

1. A Hershberg stirrer is well suited for stirring the pasty suspension.
2. Any lumps of iodobenzene dichloride should be broken up by pressing with a spatula; otherwise the reaction may be incomplete.
3. Stabilized hypochlorite solutions, commercially available, are satisfactory. The submitters used 1.15 l. of "Clorox" solution, containing 5.25% sodium hypochlorite by weight.
4. The iodimetric method as described under iodobenzene (p. 484) is applicable here. The crude product is satisfactory for the preparation of diphenyliodonium iodide (p. 355).
5. The checkers obtained the yields claimed, but the purity of the product was 90% before, and 95.7% after, washing with chloroform.

3. Discussion

Iodoxybenzene has been prepared by oxidizing iodobenzene with Caro's acid;^{1,2} by treating iodobenzene with hypochlorous acid or with aqueous sodium hydroxide and bromine;³ by action of chlorine upon iodobenzene dissolved in pyridine;⁴ by oxidation of iodobenzene with hypochlorous acid or bleaching powder;⁵ by heating iodobenzene;⁶ by steam distillation of iodobenzene;⁷ by heating iodobenzene dichloride with aqueous sodium hypochlorite containing some acetic acid;⁸ and by oxidation of iodobenzene with concentrated chloric acid solution.⁹

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 355
- Org. Syn. Coll. Vol. 3, 483
- Org. Syn. Coll. Vol. 5, 665

References and Notes

1. Bamberger and Hill, *Ber.*, **33**, 534 (1900).
2. Masson, Race, and Pounder, *J. Chem. Soc.*, **1935**, 1678.
3. Willgerodt, *Ber.*, **29**, 1571, 1572 (1896).
4. Ortoleva, *Chem. Zentr.*, **1900**, I, 723.
5. Willgerodt, *Ber.*, **29**, 1568, 1569 (1896).
6. Willgerodt, *Ber.*, **25**, 3500 (1892); **26**, 1806 (1893); Askenasy and Meyer, *Ber.*, **26**, 1356 (1893).
7. Willgerodt, *Ber.*, **26**, 358, 1307 (1893).
8. Willgerodt and Wiegand, *Ber.*, **42**, 3765 (1909).
9. Datta and Choudhury, *J. Am. Chem. Soc.*, **38**, 1085 (1916).

Appendix

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

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

bromine (7726-95-6)

pyridine (110-86-1)

chlorine (7782-50-5)

hypochlorous acid (7790-92-3)

sodium hypochlorite (7681-52-9)

Iodobenzene (591-50-4)

iodobenzene dichloride (2401-21-0)

DIPHENYLIODONIUM IODIDE (2217-79-0)

Iodosobenzene (536-80-1)

Iodoxybenzene,
Benzene, iodoxy- (696-33-3)