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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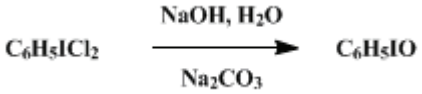
Organic Syntheses, Coll. Vol. 3, p.483 (1955); Vol. 22, p.70 (1942).

IODOSOBENZENE

[Benzene, iodoso-]



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1. Procedure

In a large mortar chilled in an ice bath are placed 55 g. (0.2 mole) of iodobenzene dichloride (p. 482), 50 g. of anhydrous sodium carbonate, and 100 g. of finely crushed ice. The mixture is ground thoroughly (Note 1) until all the ice has melted and a thick paste results. To this suspension 140 ml. of 5 *N* sodium hydroxide is added, in 20-ml. portions, with repeated trituration after each addition. Finally, 100 ml. of water is added to render the mixture more fluid and the material is allowed to stand overnight. The product is collected with suction, pressed thoroughly on the filter, transferred to a beaker, and washed thoroughly with 300 ml. of water (Note 2). The material is filtered with suction, washed again in a beaker with 300 ml. of water, collected with suction, and washed with about 250 ml. of water on the filter. After thorough drying in the air, the product is stirred to a thin mush with a little chloroform (Note 3), freed of solvent by suction, and spread on filter paper to dry in the air. The yield is 26–27 g. (60–62%) of a product having a purity of about 99%, as determined by titration (Note 4) and (Note 5).

2. Notes

1. The solid forms a caked mass, which is disintegrated by trituration.
2. The filtrate contains some diphenyliodonium salts, which may be recovered in the form of the sparingly soluble iodide by the addition of potassium iodide (p. 355). Usually 7–9 g. of diphenyliodonium iodide is obtained.
3. The chloroform removes iodobenzene, which may be recovered.
4. The following procedure is used in the analysis of iodoso and iodoxy compounds. In a 200-ml. iodine flask are placed 100 ml. of water, 10 ml. of 6 *N* sulfuric acid, 2 g. of iodate-free potassium iodide, 10 ml. of chloroform, and finally the sample, about 0.25 g. The flask is shaken for 15 minutes (or longer, if the reaction is not complete), and then the mixture is titrated with 0.1 *N* sodium thiosulfate. If the sample is pure the change of color in the chloroform layer may be taken as the end point, but if impurities are present starch must be used, for the impurities impart a brownish color to the chloroform. This solvent is desirable, as it facilitates the reaction with potassium iodide by dissolving the reaction products. Iodosobenzene may be differentiated from iodoxybenzene, for the former reduces iodide ion in a saturated sodium borate solution, whereas the latter does not.[1] The reactions involved are: $C_6H_5IO + 2HI \rightarrow C_6H_5I + H_2O + I_2$ $C_6H_5IO_2 + 4HI \rightarrow C_6H_5I + 2H_2O + 2I_2$
5. For use in the preparation of iodoxybenzene by the disproportionation method (p. 485) it is superfluous to dry the crude product and to wash it with chloroform to remove iodobenzene. The crude wet iodosobenzene may also be used directly for the preparation of diphenyliodonium iodide (p. 355), but it is desirable to assay the wet product by titration to determine the quantity of iodoxybenzene needed.

3. Discussion

Iodosobenzene has been prepared by the action of aqueous sodium or potassium hydroxide upon iodobenzene dichloride; [2] and by repeated additions of water to iodobenzene dichloride.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 355
- Org. Syn. Coll. Vol. 3, 485
- Org. Syn. Coll. Vol. 5, 658
- Org. Syn. Coll. Vol. 5, 660

References and Notes

1. Masson, Race, and Pounder, *J. Chem. Soc.*, **1935**, 1678.
2. Willgerodt, *Ber.*, **25**, 3495 (1892); **26**, 357, 1807 (1893); Askenasy and Meyer, *Ber.*, **26**, 1356 (1893); Hartmann and Meyer, *Ber.*, **27**, 505 (1894).
3. Willgerodt, *Ber.*, **26**, 357 (1893); Ortoleva, *Chem. Zentr.*, **1900**, I, 722.

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

sodium or potassium hydroxide

sulfuric acid (7664-93-9)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium carbonate (497-19-8)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

Iodobenzene (591-50-4)

iodobenzene dichloride (2401-21-0)

DIPHENYLIODONIUM IODIDE (2217-79-0)

Iodosobenzene,
Benzene, iodoso- (536-80-1)

Iodoxybenzene (696-33-3)

sodium borate