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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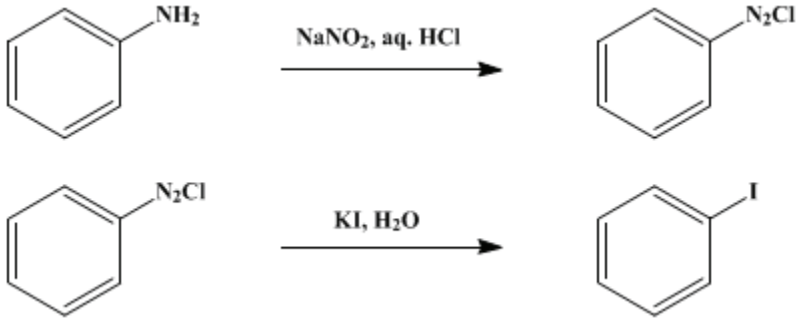
Organic Syntheses, Coll. Vol. 2, p.351 (1943); Vol. 19, p.55 (1939).

IODOBENZENE

[Benzene, iodo-]



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1. Procedure

In a 3- or 5-gallon stoneware crock are placed 950 cc. (1130 g., 11.7 moles) of concentrated hydrochloric acid (sp. gr. 1.19), 950 cc. of water, 200 g. (196 cc., 2.15 moles) of aniline, and 2 kg. of ice (Note 1). The mixture is agitated by a mechanical stirrer, and, as soon as the temperature drops below 5°, a chilled solution of 156 g. (2.26 moles) of sodium nitrite in a measured volume (700–1000 cc.) of water is introduced fairly rapidly from a separatory funnel, the stem of which projects below the surface of the reaction mixture. The addition should not be fast enough to cause the temperature to rise to 10° or to cause evolution of oxides of nitrogen. The last 5 per cent of the nitrite solution is added more slowly, and the reaction mixture is tested with starch-iodide paper at intervals until an excess of nitrous acid is indicated.

Stirring is continued for ten minutes, and if necessary the solution is filtered rapidly through a loose cotton plug in a large funnel. An aqueous solution of 358 g. (2.16 moles) of potassium iodide is added and the reaction mixture allowed to stand overnight. The mixture is transferred to a large flask (or two smaller flasks) and heated on a steam bath, using an air-cooled reflux condenser, until no more gas is evolved, then allowed to cool and stand undisturbed until the heavy organic layer has settled thoroughly. A large part of the upper aqueous layer is siphoned off, and discarded (Note 2). The residual aqueous and organic layers are made alkaline by the cautious addition of strong sodium hydroxide solution (100–125 g. of solid technical sodium hydroxide is usually required) and steam-distilled at once. The last one-third of the steam distillate is collected separately and combined with the aqueous layer separated from the earlier portions of the distillate. This mixture is acidified with 5–10 cc. of concentrated sulfuric acid and steam-distilled again. The iodobenzene from this operation is combined with the main portion and dried with 10–15 g. of calcium chloride (Note 3) and (Note 4). Distillation under reduced pressure gives 327–335 g. (74–76 per cent of the theoretical amount) of iodobenzene, b.p. 77–78°/20 mm. or 63–64°/8 mm. (Note 5).

2. Notes

1. If more ice is used a portion remains unmelted after the diazotization is completed.
2. If a good separation has been made not more than 1–2 g. of iodobenzene is lost with the upper layer.
3. An appreciable amount of iodobenzene is retained by the solid calcium chloride. By treating the spent drying agent with water 8–12 g. of iodobenzene can be recovered.
4. The crude iodobenzene weighs 350–355 g. (80 per cent of the theoretical amount) and is pure enough for many purposes without redistillation.
5. If the distillation is carried too far, the distillate will be colored.

3. Discussion

The preparation of iodobenzene by iodination of benzene, with iodine and nitric acid, and a survey of preparative methods have been given in an earlier volume.[1] The present procedure, based upon the method of Gattermann,[2] gives a purer product.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 660
- Org. Syn. Coll. Vol. 5, 665

References and Notes

1. Org. Syn. Coll. Vol. I, **1941**, 323.
2. Gattermann-Wieland, "Laboratory Methods of Organic Chemistry," p. 283. Translated from the twenty-fourth German edition by W. McCartney, The Macmillan Company, New York, 1937.

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

oxides of nitrogen

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

potassium iodide (7681-11-0)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

iodine (7553-56-2)

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