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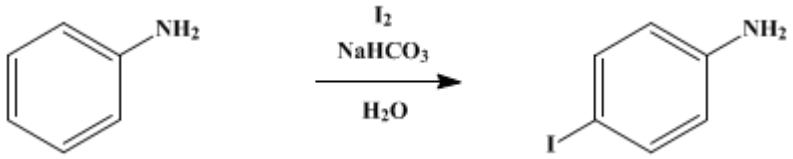
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.011.0062

Organic Syntheses, Coll. Vol. 2, p.347 (1943); Vol. 11, p.62 (1931).

p-IODOANILINE

[Aniline, *p*-iodo-]



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1. Procedure

In a 3-l. beaker are placed 110 g. (1.2 moles) of aniline, 150 g. (1.8 moles) of sodium bicarbonate, and 1 l. of water, and the mixture is cooled to 12–15° by the addition of a small amount of ice. The beaker is then fitted with an efficient mechanical stirrer. The blade of a large porcelain spatula should be inserted into the liquid to overcome the rotary motion and thus obtain better mixing. The stirrer is started and 254 g. (1 mole) of powdered iodine is added in 15–20 g. portions at intervals of two to three minutes so that all the iodine is introduced during one-half hour. Stirring is continued for twenty to thirty minutes. By this time the reaction is complete and the color of the free iodine in the solution has practically disappeared. The crude *p*-iodoaniline, which separates as a dark crystalline mass, is collected on a Büchner funnel, pressed as free from water as possible, and dried in the air. The filtrate may be saved for the recovery of iodine (Note 1).

For the purification of the *p*-iodoaniline, the crude product is placed in a 2-l. flask and 1 l. of gasoline (Note 2) is added. The flask is fitted with an air-cooled reflux condenser and heated in a water bath at a temperature of 75–80° (Note 3). The flask should be shaken frequently, and about fifteen minutes should be allowed for saturation of the solution. The hot gasoline solution is slowly decanted into a beaker set in an ice-salt mixture and stirred constantly. The *p*-iodoaniline crystallizes immediately in practically colorless needles which are filtered and dried in the air (Note 4) and (Note 5). The filtrate is returned to the flask for use in a second extraction (Note 6). The yield is 165–185 g. (75–84 per cent of the theoretical amount) of a product which melts at 62–63°.

2. Notes

1. The sodium iodide which remains in the aqueous solution may be converted into iodine as follows: To the aqueous filtrate from the *p*-iodoaniline are added 100 cc. of concentrated sulfuric acid and 200 g. of sodium dichromate in 200 cc. of water. The iodine is allowed to settle, washed three times with water by decantation, collected on a filter, and allowed to dry on a watch glass. The yield of crude iodine is 167–179 g.
2. The gasoline used was a fractionated product (b. p. 70–150°). Ordinary gasoline may be used, but it has the disadvantage that the higher-boiling hydrocarbons are removed very slowly from the *p*-iodoaniline.
3. If a higher temperature is used a tarry material is sometimes formed and a diminished yield results.
4. If rapid cooling is not obtained, the product often separates as an oil.
5. For drying purposes, a current of warm air from a commercial hair dryer is advantageous.
6. Two extractions are usually sufficient, but, if much undissolved organic material still remains, a third extraction should be made. The first fraction is practically colorless, but the second and third portions are light brown unless a little charcoal is used for decolorizing the solution.

3. Discussion

p-Iodoaniline has been prepared by the reduction of *p*-nitroiodobenzene;[1] by the hydrolysis of *p*-

iodoacetanilide formed by the action of iodine monochloride on acetanilide;[2] and by the direct iodination of aniline.[3] The method described here is an adaptation of the procedure used by Wheeler,[4] and by Hann and Berliner[5] for the iodination of the toluidines.

References and Notes

1. Griess, Zeit. für Chem. **1866**, 218; Kekulé, ibid. 687; Körner and Wender, Gazz. chim. ital. **17**, 489 (1887); Baeyer, Ber. **38**, 2762 (1905); Montagne, ibid. **51**, 1490 (1918).
2. Michael and Norton, ibid. **11**, 108 (1878); Chattaway and Constable, J. Chem. Soc. **105**, 125 (1914).
3. Hofmann, Ann. **67**, 65 (1848); Bradfield, Orton, and Roberts, J. Chem. Soc. **1928**, 783; Militzer, Smith, and Evans, J. Am. Chem. Soc. **63**, 436 (1941).
4. Wheeler and Liddle, Am. Chem. J. **42**, 501 (1909); Wheeler, ibid. **44**, 128, 500 (1910).
5. Hann and Berliner, J. Am. Chem. Soc. **47**, 1710 (1925).

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

gasoline

sulfuric acid (7664-93-9)

aniline (62-53-3)

Acetanilide (103-84-4)

sodium bicarbonate (144-55-8)

iodine (7553-56-2)

sodium dichromate (7789-12-0)

sodium iodide (7681-82-5)

iodine monochloride (7790-99-0)

p-nitroiodobenzene (636-98-6)

p-IODOANILINE,
Aniline, p-iodo- (540-37-4)

p-iodoacetanilide (622-50-4)