



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.

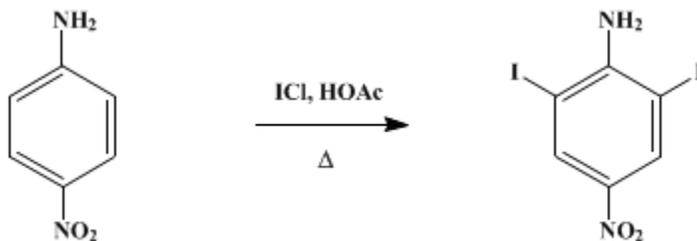
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.196 (1943); Vol. 12, p.28 (1932).

2,6-DIIODO-*p*-NITROANILINE

[Aniline, 2,6-diiodo-4-nitro-]



Submitted by R. B. Sandin, W. V. Drake, and Frank Leger.
Checked by Frank C. Whitmore and Marion M. Whitmore.

1. Procedure

One hundred thirty-eight grams (1 mole) of *p*-nitroaniline (East-man Technical grade) is dissolved in 370 cc. of boiling glacial acetic acid in a 2-l. three-necked flask provided with a mechanical stirrer, a reflux condenser, and a dropping funnel. The burner is removed, and a mixture of 325 g. (2 moles) of iodine monochloride (Note 1) in 100 cc. of glacial acetic acid is added slowly from the dropping funnel with rapid stirring during thirty minutes. Considerable heat is evolved. The mixture is heated on a rapidly boiling water bath for two hours and then transferred to a 1-l. beaker and allowed to cool. The solidified mixture is treated with 100 cc. of glacial acetic acid and any hard lumps are crushed thoroughly with a flat glass stopper (Note 2). The mixture is transferred to a large Büchner funnel and filtered by suction, two 25-cc. portions of glacial acetic acid being used to wash the last of the crystals into the funnel. The dark mother liquor is removed as completely as possible by suction. The crystals are returned to the beaker, thoroughly stirred with 200 cc. of cold glacial acetic acid, and transferred to the suction filter again. The beaker is rinsed with two 25-cc. portions of glacial acetic acid, and the crystals are sucked as dry as possible. The suction is shut off, and the crystals are wetted with 50 cc. of ether. The suction is again used to remove the ether. The product is air dried to constant weight (about twenty-four hours). The yield of air-dried diiodo-*p*-nitroaniline melting at 243–245° is 220–250 g. (56–64 per cent of the theoretical amount) (Note 3).

2. Notes

1. The iodine monochloride is made by passing dry chlorine gas into 254 g. (1 mole) of iodine in a tared 500-cc. Erlenmeyer flask until the gain in weight is 71 g. Frequent shaking is necessary. The iodine mono-chloride is used directly without distillation. Compare p. 344.
2. It is advisable to wear rubber gloves during these operations with glacial acetic acid.
3. It is reported that the following modifications increase the yield to 86 per cent: The reaction mixture is refluxed for two hours in an oil bath, cooled, filtered, and sucked as dry of solvent as possible. The cake is then made into a paste with 600 cc. of hot water, a little sodium bisulfite is added in order to remove excess iodine, and the product is filtered and dried. 2,6-Diiodo-4-nitroaniline can be crystallized from nitrobenzene followed by washing with alcohol; it then melts at 249–250°. [Carl Niemann and C. E. Redemann, private communication, and J. Am. Chem. Soc. 63, 1550 (1941)].

3. Discussion

2,6-Diiodo-*p*-nitroaniline has been made by the action of iodine chloride on a chloroform solution¹ and also on a glacial acetic acid solution² of *p*-nitroaniline.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 349](#)
- [Org. Syn. Coll. Vol. 2, 604](#)

References and Notes

1. Michael and Norton, Ber. **11**, 113 (1878).
 2. Willgerodt and Arnold, *ibid.* **34**, 3344 (1901).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[acetic acid \(64-19-7\)](#)

[ether \(60-29-7\)](#)

[chloroform \(67-66-3\)](#)

[sodium bisulfite \(7631-90-5\)](#)

[iodine \(7553-56-2\)](#)

[chlorine \(7782-50-5\)](#)

[Nitrobenzene \(98-95-3\)](#)

[Aniline, 2,6-diiodo-4-nitro-,
2,6-Diiodo-4-nitroaniline,
2,6-Diiodo-p-nitroaniline \(5398-27-6\)](#)

[iodine monochloride,
iodine mono-chloride,
iodine chloride \(7790-99-0\)](#)

[p-nitroaniline \(100-01-6\)](#)

[diiodo-p-nitroaniline](#)