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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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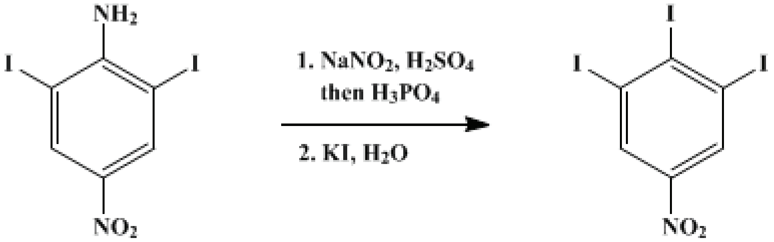
1,2,3-TRIIODO-5-NITROBENZENE

[Benzene, 1,2,3-triiodo-5-nitro-]



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1. Procedure

Fifty grams (0.13 mole) of 2,6-diiodo-4-nitroaniline (p. 196) is dissolved in 200 cc. of concentrated sulfuric acid (sp. gr. 1.84) in a 1-l. two-or three-necked flask provided with a mechanical stirrer. The solution is cooled to 5° in an ice-salt mixture, and to it is added with stirring a mixture of 100 cc. of concentrated sulfuric acid and 12 g. (0.17 mole) of sodium nitrite, also cooled to 5° (Note 1). To liberate nitrous acid from the nitrosylsulfuric acid, there is then added slowly from a separatory funnel, with rapid stirring, 200 cc. of 85 per cent phosphoric acid (151 cc. of u.s.p. phosphoric acid diluted to 200 cc.). During the addition the temperature is kept below 10°. The mixture is removed from the ice-salt bath and stirred until diazotization is complete (one to two hours) (Note 2). At the end of this time the solution is poured, with stirring, into 2 l. of a mixture of cracked ice and water in a 4-l. beaker. To destroy excess nitrous acid about 15 g. of urea is added in small portions, with stirring, as long as gas is produced. The mixture is filtered if it is not clear and is then treated gradually with a solution of 30 g. (0.18 mole) of potassium iodide in 200 cc. of water. To complete the reaction the mixture is heated until no more gas is evolved. Any free iodine is removed by sodium bisulfite, and the mixture is then filtered on a Büchner funnel, washed free from sulfuric acid and inorganic salts, pressed, and sucked as dry as possible. The product is then air dried to constant weight. The yield of light brown, crude material, m.p. 160–162°, is 60–61 g. (94–95 per cent of the theoretical amount). The pure product can be obtained by dissolving the crude material in 200 cc. of boiling benzene, filtering, and cooling the filtrate to 10°. The yield of yellow crystals melting at 161–162° is 40–42 g. (65–70 per cent recovery) (Note 3).

2. Notes

1. The sodium nitrite must be finely powdered and added slowly with vigorous stirring to the sulfuric acid, which is kept at 5° in an ice-salt mixture. The evolution of oxides of nitrogen during the addition of the nitrite must be avoided.
2. During this time the temperature of the mixture gradually rises to that of the room. When diazotization is complete a drop of the mixture will form a clear yellow solution if added to 10 cc. of cold water.
3. It has been reported that the procedure of Hodgson and Walker[1] is preferable to that described above, and that crude triiodonitrobenzene is best purified by crystallization from cellosolve. [Carl Niemann and C. E. Redemann, private communication, and J. Am. Chem. Soc. **63**, 1550 (1941).]

3. Discussion

1,2,3-Triiodo-5-nitrobenzene has been prepared by the diazotization of 2,6-diiodo-4-nitroaniline (without the use of phosphoric acid) and subsequent treatment with potassium iodide.[1] The present procedure is an example of a general method developed by Schoutissen[2] for diazotization of weakly basic amines, such as the 2,6-dihalogen derivatives of *p*-nitroaniline.

References and Notes

1. Willgerodt and Arnold, Ber. **34**, 3343 (1901); Kalb, Schweizer, Zellner, and Berthold, ibid. **59**, 1866 (1926); Harington and Barger, Biochem. J. **21**, 175 (1927); Hodgson and Walker, J. Chem. Soc. **1933**, 1620.
2. Schoutissen, J. Am. Chem. Soc. **55**, 4531 (1933).

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

oxides of nitrogen

2,6-dihalogen derivatives of p-nitroaniline

sulfuric acid (7664-93-9)

Benzene (71-43-2)

potassium iodide (7681-11-0)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

sodium bisulfite (7631-90-5)

iodine (7553-56-2)

phosphoric acid (7664-38-2)

cellosolve (107-21-1)

urea (57-13-6)

nitrosylsulfuric acid (7782-78-7)

2,6-Diiodo-4-nitroaniline (5398-27-6)

1,2,3-TRIIODO-5-NITROBENZENE,
Benzene, 1,2,3-triiodo-5-nitro- (53663-23-3)

triiodonitrobenzene