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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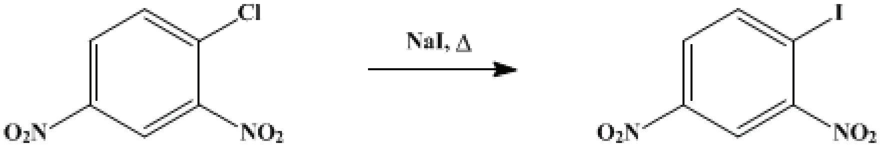
2,4-DINITROIODOBENZENE

[Benzene, 1-iodo-2,4-dinitro-]



Submitted by J. F. Bunnett and R. M. Conner[1].
Checked by Virgil Boekelheide and James S. Todd.

1. Procedure

Caution! 2,4-Dinitrochlorobenzene causes sever skin irritation to some individuals. Sensitive persons are advised to wear rubber gloves.

To 200 ml. of redistilled technical grade dimethylformamide (Note 1) in a 1-l. round-bottomed flask are added 150 g. (1 mole) of sodium iodide (Note 2) and 40.5 g. (0.2 mole) of 2,4-dinitrochlorobenzene (Note 3). The flask is fitted with a reflux condenser, and the red-brown mixture is refluxed for 15 minutes over a free flame arranged to impinge somewhat off-center (Note 4).

The hot reaction mixture is poured with stirring over about 0.75 l. of crushed ice in a 2-l. beaker. The beaker is filled with water, and the mixture is stirred to dissolve inorganic salts (Note 5). The insoluble red-brown solid is collected on a suction filter. This crude product, even while damp, is transferred to a 2-l. round-bottomed flask, and 500 ml. of a mixture of 75% (375 ml.) of petroleum ether (b.p. 90–100°) and 25% (125 ml.) of benzene is added. The flask is provided with a reflux condenser, and the mixture is heated at reflux for 15 minutes by means of an electric mantle (Note 6). The resulting solution is decanted into a second 2-l. flask, leaving in the first flask some water and a red-brown solid residue. To the slightly cooled liquor in the second flask is added cautiously 7 g. of powdered activated carbon. The carbon is dispersed by swirling, and the mixture is heated for an additional 5 minutes. The mixture is then filtered through a fluted filter into a 1-l. Erlenmeyer flask. This flask is stoppered and chilled to cause crystallization of the product (Note 7).

The product is collected on a suction filter. The yield of air-dried product, as yellow-orange crystals, m.p. 87–89°, is 38–42 g. (65–71%) (Note 8). A purer, lemon-yellow product, m.p. 88.5–90°, is obtained by an additional recrystallization from 1 l. of petroleum ether (b.p. 90–100°) with use of carbon; the yield after this second crystallization is 28–34 g. (48–58%).

2. Notes

1. Dimethylformamide is available from E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.
2. Reagent grade sodium iodide was used.
3. Eastman Kodak white label 2,4-dinitrochlorobenzene, which had a light tan color, was used without further purification.
4. The burner should be so arranged that the flame impinges upon the side of the flask in such a way as to dissolve the sodium iodide from the top downward. The flask should be shaken or swirled frequently during the onset of boiling. A small amount of white solid remains undissolved even at reflux.
5. At this point there may be a lumpy, dark-brown material mixed with the orange-brown crude precipitated product. There appears to be no need to break up the lumps.
6. Alternatively, the flask can be heated on an efficient steam bath with swirling until the crude product melts. After an additional 15 minutes of heating, the solution can be decanted as described.
7. The submitters placed the flasks of warm filtrate in the refrigerator for storage overnight or in a

freezing cabinet at −20° for at least 1 hour.
8. From a run of five times the scale described, the submitters obtained 219 g. (71%) of an orange-yellow crystalline product, m.p. 88–90°.

3. Discussion

2,4-Dinitroiodobenzene has been prepared by the nitration of *o*- or *p*-nitroiodobenzene,[2] by treatment of 2,4-dinitrobenzenediazonium sulfate with potassium iodide,[3] and by the reaction of sodium iodide with 2,4-dinitrochlorobenzene in refluxing ethylene glycol.[4] The present procedure is a modification[5] of the last-mentioned one.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 904

References and Notes

1. Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina.
2. W. Körner, *Gazz. Chim. Ital.*, **4**, 323 (1874).
3. A. L. Beckwith, J. Miller, and G. D. Leahy, *J. Chem. Soc.*, 3556 (1952).
4. G. M. Bennett and I. H. Vernon, *J. Chem. Soc.*, 1783 (1938).
5. J. F. Bunnett and R. M. Conner, *J. Org. Chem.*, **23**, 305 (1958).

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

petroleum ether

o- or p-nitroiodobenzene

Benzene (71-43-2)

potassium iodide (7681-11-0)

carbon,
activated carbon (7782-42-5)

ethylene glycol (107-21-1)

sodium iodide (7681-82-5)

2,4-dinitrochlorobenzene (97-00-7)

dimethylformamide (68-12-2)

2,4-Dinitroiodobenzene,
Benzene, 1-iodo-2,4-dinitro- (709-49-9)

2,4-dinitrobenzenediazonium sulfate