



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.

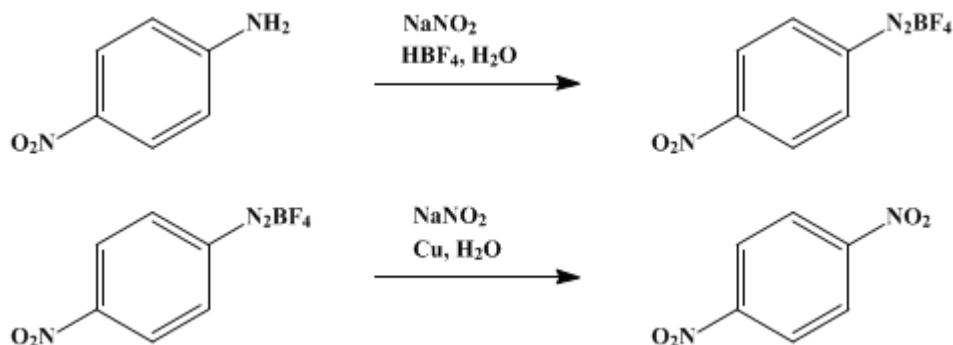
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 2, p.225 (1943); Vol. 19, p.40 (1939).

***p*-DINITROBENZENE**

[Benzene, *p*-dinitro-]



Submitted by E. B. Starkey

Checked by Lee Irvin Smith and H. E. Ungnade.

1. Procedure

Thirty-four grams (0.25 mole) of *p*-nitroaniline is dissolved in 110 cc. of fluoboric acid solution (Note 1) in a 400-cc. beaker. The beaker is placed in an ice bath and the solution stirred with an efficient stirrer. A cold solution of 17 g. (0.25 mole) of sodium nitrite in 34 cc. of water is added dropwise. When the addition is complete, the mixture is stirred for a few minutes and filtered by suction on a sintered glass filter. The solid diazonium fluoborate is washed once with 25–30 cc. of cold fluoboric acid, twice with 95 per cent alcohol, and several times with ether (Note 2). The product weighs 56–59 g. (95–99 per cent of the theoretical amount).

Two hundred grams of sodium nitrite is dissolved in 400 cc. of water in a 2-l. beaker, and 40 g. of copper powder is added (Note 3). The mixture is stirred with an efficient stirrer (Note 4), and a suspension of the *p*-nitrophenyldiazonium fluoborate in 200 cc. of water is added slowly. Much frothing occurs, and 4–5 cc. of ether is added from time to time to break the foam. The reaction is complete when all the diazonium compound has been added. The product is filtered with suction, washed several times with water, twice with dilute sodium hydroxide solution, and again with water. The solid is dried in an oven at 110°, powdered, and extracted with 300-cc., 200-cc., and 150-cc. portions of boiling benzene. The benzene is evaporated on a water bath, and the residue is crystallized from 120–150 cc. of boiling glacial acetic acid. The resulting reddish yellow crystals, melting at 172–173°, weigh 28–34.5 g. (67–82 per cent yield) (Note 5). Recrystallization from alcohol yields pale yellow crystals melting at 173°.

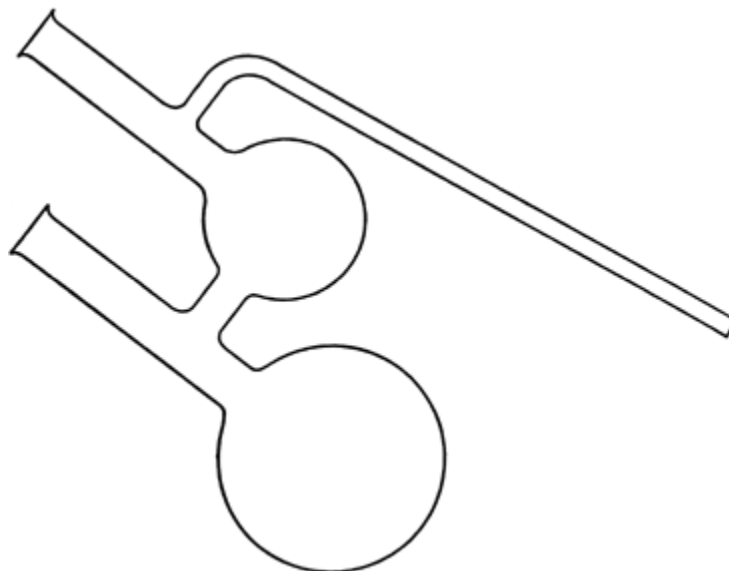
2. Notes

1. Fluoboric acid is made by adding 184 g. of boric acid slowly, with constant stirring, to 450 g. of hydrofluoric acid (48–52 per cent) in a copper, lead, or silver-plated container placed in an ice bath. *Hydrofluoric acid causes very painful burns. Exposed parts of the body must be protected when working with this material.* Compare Note 3, p. 297. Fluoboric acid (40 per cent) is now a commercial product.
2. A sintered glass filter should be used for filtering, and the fluoborate stirred well on the filter with each washing, before suction is applied. The diazonium fluoborate is stable and may be dried in a vacuum desiccator over phosphorus pentoxide.
3. The copper used was "Copper metal, precipitated powder."
4. In the decomposition reaction, efficient stirring is quite essential. An off-center stirrer is best suited for the purpose. The reaction should require about two hours. Less efficient stirring and a shorter reaction time cause the formation of an impure product which is not readily purified by crystallization.
5. *o*-Dinitrobenzene may be prepared from *o*-nitroaniline by the same general method. From 34 g. (0.25

mole) of the amine there is obtained 38 g. (63 per cent yield) of dry *o*-nitrobenzenediazonium fluoborate. After carrying out the reaction of the diazonium fluoborate with sodium nitrite and copper, the *o*-dinitrobenzene is separated by steam distillation instead of filtration and extraction. A little paraffin is added to diminish the troublesome foaming and creeping during distillation, and a special flask (Note 6) designed for such operations may be used advantageously. The crystalline product is filtered from the steam distillate and recrystallized from alcohol. The yield of *o*-dinitrobenzene, m.p. 116–116.5°, is 14–16 g. (33–38 per cent of the theoretical amount).

6. A Claisen flask modified as shown in Fig. 8 is used in the synthetic laboratories of the Eastman Kodak Company for the distillation of liquids which foam and creep badly. The large bulb inserted in the side arm should have a capacity about one-third that of the distillation flask. During distillation the flask is supported at the angle shown in the figure.

Fig. 8



3. Discussion

p-Dinitrobenzene has been prepared from *p*-nitrosonitrobenzene by treatment with nitric acid;¹ from *p*-nitroaniline by the Sandmeyer reaction;² and by the oxidation of *p*-nitroaniline in concentrated sulfuric acid with ammonium persulfate.³ *o*-Dinitrobenzene has been prepared in similar fashion from *o*-nitroaniline by the Sandmeyer reaction⁴ and by oxidation with persulfate.³ The preparation described above has been published.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 665

References and Notes

1. Bamberger and Hübner, Ber. **36**, 3808 (1903).
 2. Meisenheimer and Patzig, ibid. **39**, 2528 (1906).
 3. Witt and Kopetschni, ibid. **45**, 1134 (1912).
 4. Körner and Contardi, Atti acad. Lincei (5) **23**, I, 283 (1914) [C. A. **8**, 3020 (1914)].
 5. Starkey, J. Am. Chem. Soc. **59**, 1479 (1937).
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**Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)**

fluoboric acid

alcohol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

sodium nitrite (7632-00-0)

hydrofluoric acid (7664-39-3)

copper,
copper powder (7440-50-8)

boric acid (10043-35-3)

ammonium persulfate (7727-54-0)

o-Dinitrobenzene (528-29-0)

o-NITROANILINE (88-74-4)

phosphorus pentoxide (1314-56-3)

p-nitroaniline (100-01-6)

p-Dinitrobenzene,
Benzene, p-dinitro- (100-25-4)

p-nitrophenyldiazonium fluoborate (456-27-9)

o-Nitrobenzenediazonium fluoborate

p-nitrosnitrobenzene