



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](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.

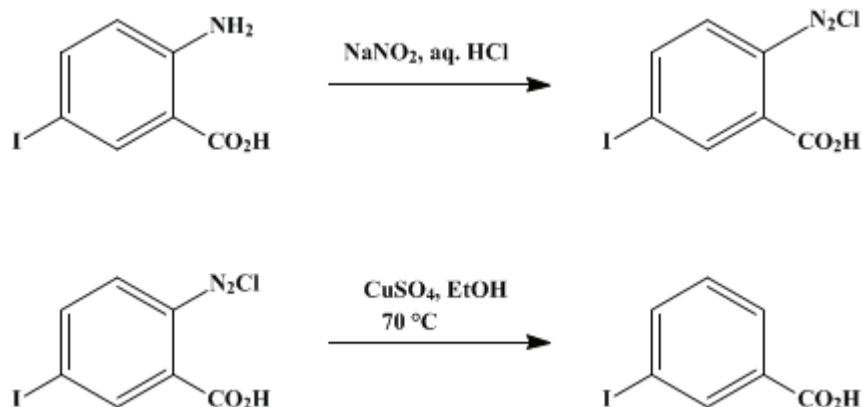
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.353 (1943); Vol. 19, p.57 (1939).*

## ***m*-IODOBENZOIC ACID**

[Benzoic acid, *m*-iodo-]



Submitted by V. H. Wallingford and Paul A. Krueger.  
Checked by Frank C. Whitmore and L. H. Sutherland.

### 1. Procedure

In a 1-l. flask 132 g. (0.5 mole) of *5*-iodoanthranilic acid (p. 349) and 35 g. (0.5 mole) of sodium nitrite are dissolved in a mixture of 500 cc. of warm water and 60 cc. of 30 per cent sodium hydroxide solution. After cooling to 20° the solution is added from a dropping funnel, over a period of fifteen to twenty minutes, to a well-stirred mixture of 250 cc. of concentrated hydrochloric acid (sp. gr. 1.18) and 250 g. of ice in a 2-l. beaker; more ice is added, as required, to keep the temperature below 20°. The insoluble, yellow diazonium compound separates before completion of the diazotization. After all the solution has been added from the dropping funnel, the reaction mixture is stirred for five minutes and tested for excess nitrous acid with starch-iodide paper. If required, small amounts of solid sodium nitrite are added and the test is repeated at three-minute intervals until a slight excess is definitely established. The diazonium compound is allowed to settle and as much as possible of the supernatant liquor is decanted, leaving a slurry of diazonium compound.

In a 3-l. beaker are placed 750 cc. of 95 per cent ethyl alcohol and 1.5 g. of finely ground copper sulfate, and the mixture is heated on a hot plate or steam bath to 70°. The diazonium slurry is added in about 30-cc. portions to the well-stirred alcohol; the temperature is kept between 60° and 70°, and the nitrogen evolution is allowed to subside considerably between additions. The final traces of diazonium slurry are washed into the alcohol with small amounts of the decanted solution, the remainder of which is then added to the alcohol in 100-cc. portions. The reaction mixture is heated and stirred at 65–70° for half an hour, and then cooled without agitation to 5°. The *m*-iodobenzoic acid which separates is filtered with suction on a Büchner funnel, washed with three 50-cc. portions of cold water, and dried at 90–110°. There is obtained 107–116 g. of crude, brown *m*-iodobenzoic acid (86–93 per cent of the theoretical amount) (Note 1).

The crude *m*-iodobenzoic acid is purified by recrystallization of its ammonium salt. To 100 g. of the acid in a 250-cc. beaker is added 75 cc. of hot water, and the acid is partially neutralized with 24 cc. of concentrated ammonia (sp. gr. 0.9). After stirring at 80° until no more acid dissolves, neutralization is completed by adding 2–5 cc. of ammonia, until the acid is completely dissolved. The solution is heated to 90°, 1 g. of decolorizing charcoal is added, and the mixture is filtered with suction using a preheated Büchner funnel and filter flask. The residue on the filter is washed with 15 cc. of boiling water. The combined washings and filtrate are transferred to a 250-cc. beaker and allowed to cool without agitation to 25–35°, then cooled by any convenient means to 5°. The ammonium *m*-iodobenzoate crystals are filtered and pressed as dry as possible on a Büchner funnel, spread in a thin layer on a glass or enameled

tray, and dried at a temperature not above 60°. There is obtained 86–90 g. of faintly yellow to tan prisms of the ammonium salt, a recovery of 80–84 per cent (Note 2).

The ammonium salt thus obtained is recrystallized until white by dissolving it in an equal weight of water at 80° and cooling to 5°. The recovery in this purification averages 75–85 per cent (Note 3).

*m*-Iodobenzoic acid melting at 187–188° is obtained by dissolving pure ammonium *m*-iodobenzoate in four times its weight of hot water, precipitating the acid by acidifying the solution to Congo red with concentrated hydrochloric acid, adding ice to reduce the temperature to 20°, filtering by suction, washing the acid freely with cold water, and drying at 90–110° (Note 4).

## 2. Notes

1. Evaporation of the mother liquors to incipient turbidity and cooling the concentrate to 5° will produce a few grams of acid, but this is usually very impure and tarry.

2. Ammonium *m*-iodobenzoate is not stable under these drying conditions. The product at this point contains some free acid.

3. In some runs as many as five recrystallizations failed to furnish white crystals of the ammonium salt, but, in these runs, precipitation of the acid after three or four crystallizations gave a product having the correct melting point.

Mother liquors from the crystallization are best worked up by acidifying to Congo red with concentrated hydrochloric acid, filtering, washing, drying, and reworking the recovered acid.

4. The total overall yield of pure acid from the crude depends on the amount of crude acid taken, the care exercised to avoid material losses, and the number of recrystallizations required to attain the desired purity. Without recoveries from mother liquors, 100 g. of crude acid, after conversion to the ammonium salt, and three recrystallizations of the latter, gave 40–45 g. of pure acid. Overall recovery of pure acid from 100 g. of the crude gave 50 g. of pure acid melting at 187–188°, 10 g. of less pure acid melting at 184–186°, and about 10 g. of a tarry solid residue.

## 3. Discussion

*m*-Iodobenzoic acid has been prepared by diazotization of *m*-aminobenzoic acid and treatment with potassium iodide in acid solution,<sup>1, 2, 3</sup> and by the action of concentrated nitric acid on a glacial acetic acid solution of iodine and benzoic acid.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 349

---

## References and Notes

1. Griess, Ann. **113**, 336 (1860).
2. Cohen and Raper, J. Chem. Soc. **85**, 1273 (1904).
3. Cattelain, Bull. soc. chim. (4) **41**, 1546 (1927).
4. Datta and Chatterjee, J. Am. Chem. Soc. **41**, 294 (1919).

---

## Appendix

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

Congo red

ethyl alcohol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

potassium iodide (7681-11-0)

nitrogen (7727-37-9)

copper sulfate (7758-98-7)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

Benzoic acid (65-85-0)

iodine (7553-56-2)

5-IODOANTHRANILIC ACID (5326-47-6)

m-iodobenzoic acid,  
Benzoic acid, m-iodo- (618-51-9)

ammonium m-iodobenzoate

m-aminobenzoic acid (99-05-8)