



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.

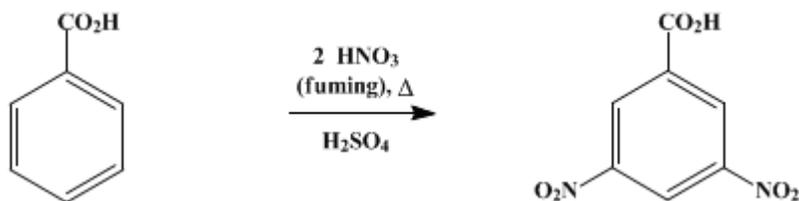
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 3, p.337 (1955); Vol. 22, p.48 (1942).*

## 3,5-DINITROBENZOIC ACID

[Benzoic acid, 3,5-dinitro-]



Submitted by (A) R. Q. Brewster, Bill Williams, and (B) Ross Phillips.  
Checked by Homer Adkins and James Ruhoff.

### 1. Procedure

A. In a 2-l. round-bottomed flask are placed 61 g. (0.5 mole) of benzoic acid and 300 ml. of concentrated sulfuric acid (sp. gr. 1.84). To this mixture is added 100 ml. of fuming nitric acid (sp. gr. 1.54) in portions of 2 or 3 ml. The temperature during the addition of the acid is kept between 70° and 90° by means of external cooling with cold water (Note 1), and the addition should be carried out in a good hood. The flask is covered with a watch glass and allowed to stand for an hour, or overnight, in the hood. The flask is then heated on a steam bath in the hood for 4 hours, during which time considerable amounts of brown fumes are evolved. The reaction mixture is then allowed to cool to room temperature (Note 2), whereupon yellow crystals separate from the solution. An additional 75 ml. of fuming nitric acid is added, and the mixture is heated on the steam bath for 3 hours and then in an oil bath at 135–145° for 3 hours (hood). Brown fumes are evolved continuously, especially during the heating in the oil bath. The color of the reaction mixture is light to reddish yellow.

The mixture is allowed to cool and is poured into 800 g. of ice and 800 ml. of water. After standing for 30 minutes the 3,5-dinitrobenzoic acid is filtered with suction and washed with water until free of sulfates. The crude product weighs 62–65 g. and melts at 200–202°. This product is recrystallized from 275 ml. of hot 50% ethanol. The purified 3,5-dinitrobenzoic acid weighs 57–61 g. (54–58%) and melts at 205–207° (Note 3).

B. Two hundred grams of benzoic acid (1.6 moles) is stirred into 1 l. of concentrated sulfuric acid contained in a 3-l. round-bottomed flask. The flask is surrounded by cold water, and the temperature is maintained below 45° while 80 ml. of fuming nitric acid is added. When the temperature of the reaction mixture has fallen to 30°, 240 ml. of fuming nitric acid is added, a beaker is inverted over the neck of the flask, and the mixture is allowed to stand for 6 weeks.

The flask is heated on a steam bath for 4 hours and then in an oil bath at 145° until all the crystals are dissolved. A mush of crystals separates when the mixture is cooled to room temperature. These are filtered on a Büchner funnel without any filtering medium. After the crystals are pressed dry, they are placed in 1.5 l. of cold water, washed thoroughly, filtered through paper, and dried in the air. The yield is 200–213 g. (60%), and the product melts at 205–207° (cor.) (Note 4) and (Note 5).

### 2. Notes

1. The temperature is so controlled that evolution of brown fumes, in other than small quantities, is avoided.
2. Mechanical stirring is advantageous but not necessary.
3. The melting points were taken with a short-stem total-immersion thermometer.
4. Procedure B has been carried out on ten times the scale specified, with yields a few per cent higher than those given above.
5. A purification procedure which gives material suitable for use in the determination of creatinine has

been reported.<sup>1</sup>

### 3. Discussion

3,5-Dinitrobenzoic acid has been prepared by nitration of benzoic acid with sulfuric acid and fuming nitric acid;<sup>2</sup> by nitration of 3-nitrobenzoic acid;<sup>3</sup> and by oxidation of 3,5-dinitrotoluene.<sup>2,4,5</sup> It has been obtained as a product of the action of nitric acid on 1,5-dinitronaphthalene.<sup>6</sup>

---

### References and Notes

1. Jansen, Sombrock, and Noyons, *Chem. Weekblad*, **43**, 731 (1947).
  2. Cahours, *Jahresber. Fortsch. Chem.*, **1847–1848**, 533; Voit, *Ann.*, **99**, 104 (1856); Michler, *Ann.*, **175**, 152 (1875); Hübner, *Ann.*, **222**, 72 (1884); Saunders, Stacey, and Wilding, *Biochem. J.*, **36**, 368 (1942)
  3. Tiemann and Judson, *Ber.*, **3**, 224 (1870).
  4. Staedel, *Ann.*, **217**, 194 (1883).
  5. Goldstein and Voegeli, *Helv. Chim. Acta*, **26**, 475 (1943)
  6. Beilstein and Kuhlberg, *Ann.*, **202**, 220 (1880)
- 

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

fuming nitric acid

ethanol (64-17-5)

sulfuric acid (7664-93-9)

nitric acid (7697-37-2)

Benzoic acid (65-85-0)

Creatinine (60-27-5)

3,5-Dinitrobenzoic acid,  
Benzoic acid, 3,5-dinitro- (99-34-3)

3-nitrobenzoic acid (121-92-6)

3,5-dinitrotoluene (618-85-9)

1,5-dinitronaphthalene (605-71-0)