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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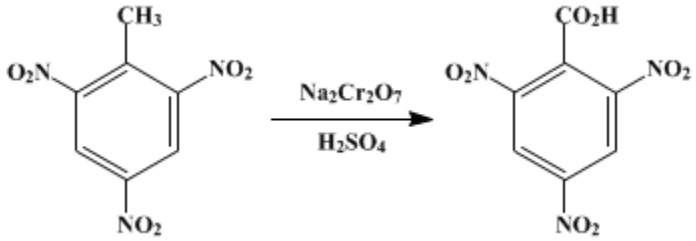
Organic Syntheses, Coll. Vol. 1, p.543 (1941); Vol. 2, p.95 (1922).

2,4,6-TRINITROBENZOIC ACID

[Benzoic acid, 2,4,6-trinitro-]



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1. Procedure

To 3600 g. (1960 cc.) of concentrated sulfuric acid, in a 5-l. flask placed in an empty water bath, is added 360 g. (1.6 moles) of technical trinitrotoluene, while the mixture is stirred mechanically (Note 1). Sodium dichromate is now added in small quantities (Note 2), with constant stirring, until the temperature of the mixture reaches 40°; the empty water bath is now filled with cold water and the addition of sodium dichromate continued at such a rate that the temperature remains at 45–55°. In all, 540 g. (1.8 moles) of sodium dichromate is added, the addition taking one to two hours. When all has been added, the mixture, which has now become very thick, is stirred for two hours at 45–55°, and poured into a crock containing 4 kg. of crushed ice. The insoluble trinitrobenzoic acid is filtered off and carefully washed with cold water until free from chromium salts. On drying it weighs 320–340 g.

The product is now mixed with 2 l. of distilled water at 35° in a 5-l. flask provided with a stirrer, and 15 per cent sodium hydroxide solution is dropped in with continuous stirring until a *faint* red color is just produced (Note 3). Should this disappear, it is restored by the addition of a few drops more. When it has persisted for five minutes, the color is discharged by the addition of a few drops of acetic acid, and the insoluble unattacked trinitrotoluene filtered off and washed with a little water. The trinitrobenzoic acid is precipitated from the filtrate by the addition of a slight excess of 50 per cent sulfuric acid. The solution is chilled, and the acid filtered and washed free from salts with ice water (Note 4). When dried in air it weighs 230–280 g. (57–69 per cent of the theoretical amount).

2. Notes

1. It is essential that the stirring should be most efficient, so that when the mixture becomes thick the dichromate will be evenly distributed throughout the liquid, as rapidly as it is added. If the stirring is not efficient, local reactions of extreme violence (in certain cases leading to conflagration) will occur. An iron stirrer may be employed in the oxidation reaction, but not in the purification.
2. Technical sodium dichromate generally contains a certain amount of chlorides, and the chlorine liberated from these tends to cause a troublesome foam towards the end of the reaction. Only a very efficient stirrer, which draws down the surface of the liquid, is able to combat this difficulty. The amount of solid sodium dichromate given is for the dry crystalline compound containing two molecules of water of crystallization.
3. Great care should be taken in dissolving the crude acid in the alkali. If an excess of alkali persists for any length of time, a permanent color is produced which will discolor the final product. The acid is fairly soluble in cold water and should be washed with care.
4. The mother liquors and washings lose carbon dioxide on boiling, and the insoluble trinitrobenzene separates (p. 541); after filtering, washings, and drying, it weighs 15–20 g. (4–6 per cent of the theoretical amount).

3. Discussion

2,4,6-Trinitrobenzoic acid can be prepared by the oxidation of trinitrotoluene with a mixture of concentrated nitric and sulfuric acids,[1] a method which is unsuitable in the laboratory owing to the difficulty of devising suitable apparatus; by oxidation in nitric acid solution by means of potassium chlorate,[2] a method which has been found difficult to control on a laboratory scale; and by the procedure described, a modification of a patented process,[3] in which trinitrotoluene suspended in sulfuric acid is oxidized by chromic anhydride.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 455
- Org. Syn. Coll. Vol. 1, 541
- Org. Syn. Coll. Vol. 3, 334

References and Notes

1. Chemische Fabrik Griesheim, Ger. pat. 77,559 [Frdl. **4**, 34 (1894–97)].
2. Lüttgen, Ger. pat. 226,225 [Frdl. **10**, 167 (1910–12)].
3. Chemische Fabrik Griesheim, Ger. pat. 127,325 [Frdl. **6**, 148 (1900–02)].

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

nitric and sulfuric acids

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

carbon dioxide (124-38-9)

chlorine (7782-50-5)

sodium dichromate (7789-12-0)

potassium chlorate (3811-04-9)

2,4,6-Trinitrobenzoic acid,
Benzoic acid, 2,4,6-trinitro- (129-66-8)

trinitrotoluene (118-96-7)

trinitrobenzoic acid

trinitrobenzene

chromic anhydride