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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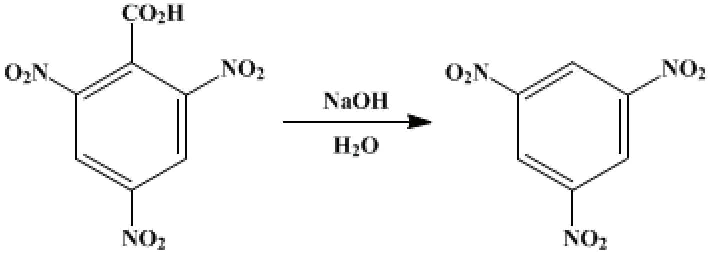
Organic Syntheses, Coll. Vol. 1, p.541 (1941); Vol. 2, p.93 (1922).

1,3,5-TRINITROBENZENE

[Benzene, 1,3,5-trinitro-]



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1. Procedure

The crude trinitrobenzoic acid obtained by oxidation of 360 g. (1.6 moles) of trinitrotoluene (p. 543) is mixed with 2 l. of water at 35° (Note 1) in a 5-l. flask provided with a stirrer. Fifteen per cent sodium hydroxide solution is added, with continuous stirring, until a *faint* red color is just produced (Note 2). The color is then immediately discharged by means of one or two drops of acetic acid, and the liquid is filtered from unchanged trinitrotoluene. The filtrate is transferred to a 5-l. flask, and 70 cc. of glacial acetic acid is added.

The mixture is then gently heated (Note 3), with continuous stirring, when trinitrobenzene separates in crystalline condition and floats on the surface of the liquid as a frothy layer. After about one and one-half hours the evolution of gas ceases; at this point the crystals begin to stir into the solution. The heating and stirring are continued for three-quarters of an hour, when the mixture is allowed to cool, and the crystals filtered off. A sample of the filtrate should be tested for undecomposed trinitrobenzoic acid: if a precipitate is produced by the addition of sulfuric acid the process must be continued. After recrystallization from glacial acetic acid, the product melts at 121–122°. The yield is 145–155 g. (43–46 per cent of the theoretical amount calculated from the trinitrotoluene).

2. Notes

1. During the solution of the trinitrobenzoic acid, the temperature should not be below 35°, owing to the slight solubility of trinitrobenzoic acid in cold water. The heat of neutralization raises the temperature to 45–55°, but 55° should not be exceeded, since any trinitrobenzene formed at this point would later be removed with the unreacted trinitrotoluene.
2. Care must be taken that no more alkali is added than is just sufficient to produce the faint red color. If an excess of alkali is added it produces a permanent color, which is not removed by acid and colors the final product.
3. When once the evolution of carbon dioxide sets in, the flame must be cut down so as to avoid the formation of a thick layer of froth which might foam over.

3. Discussion

1,3,5-Trinitrobenzene can be prepared by nitrating *m*-dinitrobenzene,[1] and by heating 2,4,6-trinitrobenzoic acid or its sodium salt with water, alcohol, dilute sodium carbonate, or other suitable solvent.[2] 2,4,6-Trinitrobenzaldehyde[3] and 2,4,6-trinitrobenzoic acid[4] both furnish trinitrobenzene on treatment with alcoholic ammonia—the yield from the aldehyde is reported to be quantitative.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 219
- Org. Syn. Coll. Vol. 1, 455
- Org. Syn. Coll. Vol. 1, 543

References and Notes

1. Hepp, Ber. **9**, 402 (1876), Ann. **215**, 344 (1882); Drummond, J. Soc. Chem. Ind. **41**, 338T (1922).
2. Chemische Fabrik Griesheim, Ger. pat. 77,353 [Frdl. **4**, 34 (1894–97)], Desvergnes, Chimie & industrie, **25**, 3, 291 (1931) [C. A. **25**, 2699 (1931)], which contains a comparative study of methods of preparation.
3. Secareanu, Bull. soc. chim. (4) **51**, 596 (1932).
4. Secareanu, ibid. **53**, 1399 (1933).

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

2,4,6-trinitrobenzoic acid or its sodium salt

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ammonia (7664-41-7)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

carbon dioxide (124-38-9)

1,3,5-Trinitrobenzene,
Benzene, 1,3,5-trinitro- (99-35-4)

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

trinitrotoluene (118-96-7)

trinitrobenzoic acid

trinitrobenzene

2,4,6-Trinitrobenzaldehyde (606-34-8)

m-dinitrobenzene (99-65-0)