



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.

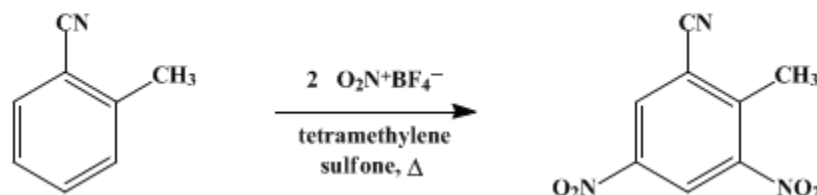
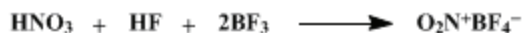
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 5, p.480 (1973); Vol. 47, p.56 (1967).*

## 3,5-DINITRO-*o*-TOLUNITRILE

[Benzonitrile, 2-methyl-3,5-dinitro-]



Submitted by George A. Olah<sup>1</sup> and Stephen J. Kuhn<sup>2</sup>.  
Checked by J. Lazar and B. C. McKusick.

### 1. Procedure

A. *Nitronium tetrafluoroborate* (Note 1). *Caution! Hydrogen fluoride is very hazardous. Caution is also called for in the use of boron trifluoride. All operations must be carried out in a hood, and the precautions outlined in (Note 2) should be followed.* A 1-l. three-necked polyolefin flask (Note 3) is provided with a short inlet tube for nitrogen, a long inlet tube for gaseous boron trifluoride, a drying tube, and a magnetic stirring bar (Note 4). The flask is immersed in an ice-salt bath and flushed with dry nitrogen. Under a gentle stream of nitrogen and with stirring, the flask is charged with 400 ml. of methylene chloride, 41 ml. (65.5 g., 1.00 mole) of red fuming nitric acid (95%), and 22 ml. (22 g., 1.10 moles) of cold, liquid, anhydrous hydrogen fluoride (Note 5).

Gaseous boron trifluoride (136 g., 2.00 moles) from a cylinder mounted on a scale is bubbled into the stirred, cooled reaction mixture (Note 6). The first mole is passed in rather quickly (in about 10 minutes). When approximately 1 mole has been absorbed, copious white fumes begin to appear at the exit, and the rate of flow is diminished so that it takes about 1 hour to pass in the second mole; even at this slow rate, there is considerable fuming at the exit. After all the boron trifluoride has been introduced, the mixture is allowed to stand in the cooling bath under a slow stream of nitrogen for 1.5 hours. The mixture is swirled, and the suspended product is separated from the supernatant liquid by means of a medium-porosity, sintered-glass Buchner funnel (Note 7). The gooey solid remaining in the flask is transferred to the funnel with the aid of two 50-ml. portions of nitromethane. The solid on the funnel, nitronium tetrafluoroborate, is washed successively with two 100-ml. portions of nitromethane and two 100-ml. portions of methylene chloride. In order to protect the salt from atmospheric moisture during the washing procedure, suction is always stopped while the salt is still moist. The moist salt is transferred to a round-bottomed flask and dried by evaporating the solvent (Note 8). At the end of the procedure the flask can be gently heated to 40–50° (Note 9). The yield of colorless nitronium tetrafluoroborate is 85–106 g. (64–80%) (Note 10), (Note 11), (Note 12). It is stored in a wide-mouthed polyolefin bottle with a screw cap. The edge of the cap is sealed with paraffin wax after it is screwed on.

B. *3,5-Dinitro-*o*-tolunitrile*. A 500-ml. four-necked flask is equipped with a mechanical stirrer, a dropping funnel, a thermometer and an inlet for dry nitrogen (Note 13). It is baked thoroughly by means of a Bunsen flame and allowed to cool to room temperature with a slow stream of dry nitrogen passing through it. The flask is charge, preferably in a dry box, with 335 g. of tetramethylene sulfone (Note 14) and 73.1 g. (0.55 mole) of nitronium tetrafluoroborate. The thermometer is adjusted so that the bulb is immersed in the liquid. The reaction mixture is stirred well and kept at 10–20° by means of an ice bath while 58.5 g. (0.50 mole) of freshly distilled *o*-tolunitrile<sup>3</sup> is added dropwise. The nitronium tetrafluoroborate only partially dissolves in the tetramethylene sulfone (Note 15), but through good stirring a homogeneous suspension can be obtained. As the dissolved nitronium salt reacts with the nitrile, more and more salt dissolves until all of it is in solution. The addition of *o*-tolunitrile requires

25–35 minutes.

After the addition is complete, the cooling bath is removed and stirring is continued for 15 minutes at 35°. The dropping funnel is removed, 74.5 g. (0.56 mole) of **nitronium tetrafluoroborate** is added, and the opening of the flask is closed with a glass stopper. The well-stirred reaction mixture is heated by an electric heating mantle to 100° in 15 minutes and kept at 100–115° for 1 hour. The reaction mixture is allowed to cool to room temperature with continued stirring and is then poured into 800 g. of ice water. Crude **3,5-dinitro-*o*-tolunitrile** separates on top of the aqueous mixture as a dark oil that solidifies after standing a few minutes. The solid is collected on a Buchner funnel. It is triturated on the funnel with five 50-ml. portions of cold water and with 40 ml. of ice-cold **ethanol**. After being dried in a vacuum desiccator, the crude nitrile weighs 75–84 g., m.p. 60–65°. Recrystallization from about 110 ml. of hot **methanol** gives 50–55 g. (48–53%) of **3,5-dinitro-*o*-tolunitrile**, m.p. 82–84° (Note 16).

## 2. Notes

1. **Nitronium tetrafluoroborate** is commercially available from the Ozark-Mahoning Co., Tulsa, Oklahoma.
2. *Because of the hazardous nature of anhydrous hydrogen fluoride, adequate precautions should be taken to protect the head, eyes, and skin.* Rubber gloves, an apron, and a plastic face mask are strongly recommended. All operations should be carried out in a hood. If **hydrogen fluoride** comes in contact with the skin, the contacted area should be thoroughly washed with water and then immersed in ice water while the patient is taken to a physician. After completion of the reaction, all equipment should be washed with liberal quantities of water. *Note! Burns caused by hydrogen fluoride may not be noticed for several hours, by which time serious tissue damage may have occurred.*
3. All operations involving liquid **hydrogen fluoride** must be carried out with equipment resisting **hydrogen fluoride** (fused silica, polyolefin, etc.).
4. An egg-shaped stirrer seems to work best. As the reaction proceeds, the precipitating **nitronium tetrafluoroborate** prevents the stirring bar from operating. This is not serious if the reaction mixture is shaken occasionally.
5. It is convenient to condense anhydrous **hydrogen fluoride**, b.p. 19.5°, from a cylinder into a small calibrated polyolefin flask immersed in a mixture of dry ice and **acetone**. As **hydrogen fluoride** is very hygroscopic, it should be carefully protected from atmospheric moisture, preferably by maintaining an atmosphere of dry **nitrogen** over it, otherwise by means of a drying tube. The **hydrogen fluoride** is then simply poured into the reaction flask.
6. The temperature of the reaction is not critical, but the reaction is slower at higher temperatures because of the lower solubility of **boron trifluoride** in the solvent.
7. Since free **hydrogen fluoride** is no longer present, filtration can be carried out with glass or porcelain equipment. However, commercially available polyolefin Buchner funnels and filter flasks are preferred.
8. Kel-F grease is recommended for ground-glass joints. **Nitronium tetrafluoroborate** slowly attacks silicone stopcock grease, causing air to enter the flask.
9. **Nitronium tetrafluoroborate** is thermally stable up to 170°. Above this temperature it starts to dissociate into nitryl fluoride and **boron trifluoride**.
10. **Nitronium tetrafluoroborate** is very hygroscopic. It is stable as long as it is anhydrous, but it is decomposed by moisture, and all transfers should be in a dry box. Its purity can be checked by conventional elemental analysis. However, because of the hygroscopic nature of the salt, the submitters have found it convenient to use neutron activation analysis (B, F, N, O) of samples sealed into polyolefin sample holders. Lange's method<sup>4</sup> for the determination of  $\text{BF}_4^-$  as the nitron salt gives good results but requires considerable care to achieve reproducibility.
11. The last part of the procedure can be used to purify **nitronium tetrafluoroborate** that has picked up water on standing. The impure salt is washed twice with **nitromethane**, twice with **methylene chloride**, and is dried under reduced pressure.
12. **Nitronium tetrafluoroborate** slowly attacks polyethylene and polypropylene, but apparatus made of these materials will last for several preparations of the salt.
13. The entire operation should be carried out in an atmosphere of dry **nitrogen**. If dry **nitrogen** is not available, rigorously anhydrous conditions should be maintained with the help of a drying tube.
14. **Tetramethylene sulfone** is commercially available from the Shell Chemical Company and the Phillips Petroleum Company.

15. A saturated solution at 25° contains 7 g. of **nitronium tetrafluoroborate** per 100 g. of **tetramethylene sulfone**.  
16. This is pure enough for most purposes. An analytical sample melted at 86.5–88.4°.

### 3. Discussion

**Nitronium tetrafluoroborate** has been prepared by interaction of **nitric acid**, **hydrogen fluoride**, and **boron fluoride** in **nitromethane**.<sup>5</sup> However, mixtures of **nitric acid** and **nitromethane** are extremely explosive.<sup>6,7</sup> The present modification of the procedure, in which the medium is **methylene chloride** instead of **nitromethane**, was developed to avoid this hazard. It has not been published before.

The preparation of **3,5-dinitro-*o*-tolunitrile** is based on previously published work.<sup>8</sup> The nitration of ***o*-tolunitrile** using fuming **nitric acid** has been reported by Candea and Macovski.<sup>9</sup>

### 4. Merits of the Preparation

Nitration of aromatic rings by **nitronium tetrafluoroborate** is a general method. Fifty-seven arenes, haloarenes, nitroarenes, arenecarboxylic esters, arenecarbonyl halides, and arenecarbonitriles have been nitrated in high yield by this reagent.<sup>8</sup> The method is particularly convenient for nitrating aromatic compounds susceptible to acid-catalyzed hydrolysis. For example, although mononitration of arenecarbonitriles is easily accomplished by conventional nitrating agents, dinitration is not. The reason is that the forcing conditions required for dinitration (strongly acid media and higher temperatures) bring about hydrolysis (and oxidation) of the nitrile group. In contrast, nitrations with **nitronium tetrafluoroborate** can be carried out in nonaqueous acid-free systems, where the only acid originates from proton elimination during nitration. In the basic solvent used, this acid concentration generally is not sufficient to cause any detectable hydrolysis (or oxidation).

---

### References and Notes

1. Western Reserve University, Cleveland, Ohio.
2. Dow Chemical of Canada, Limited, Sarnia, Ontario.
3. H. T. Clarke and R. R. Read, *Org. Syntheses*, Coll. Vol. 1, 514 (1941).
4. W. Lange, *Ber.*, **59**, 2107, 2432 (1926).
5. S. J. Kuhn, *Can. J. Chem.*, **40**, 1660 (1962).
6. D. W. Coillet and S. D. Hamann, *Trans. Faraday Soc.*, **57**, 2232 (1961).
7. J. A. Herickes, J. Ribovich, G. H. Damon, and R. W. Van Dolah, "Shock-Sensitivity Studies of Liquid Systems," Preprint, Second Conference on Explosives Sensitivity, Washington, D. C., September 16–17, 1957.
8. S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961); G. A. Olah, S. Kuhn, and A. Mlinko, *J. Chem. Soc.*, 4257 (1956).
9. C. Candea and E. Macovski, *Bull. Soc. Chim. France*, [5] **5**, 1350 (1938).

---

### Appendix

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

BF<sub>4</sub>

polyethylene

polypropylene

ethanol (64-17-5)

methanol (67-56-1)

nitric acid (7697-37-2)

nitrogen (7727-37-9)

hydrogen fluoride (7664-39-3)

acetone (67-64-1)

Nitromethane (75-52-5)

methylene chloride (75-09-2)

o-Tolunitrile (529-19-1)

boron fluoride,  
boron trifluoride (7637-07-2)

Benzonitrile, 2-methyl-3,5-dinitro-,  
3,5-Dinitro-o-tolunitrile (948-31-2)

nitronium tetrafluoroborate

tetramethylene sulfone (126-33-0)