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.

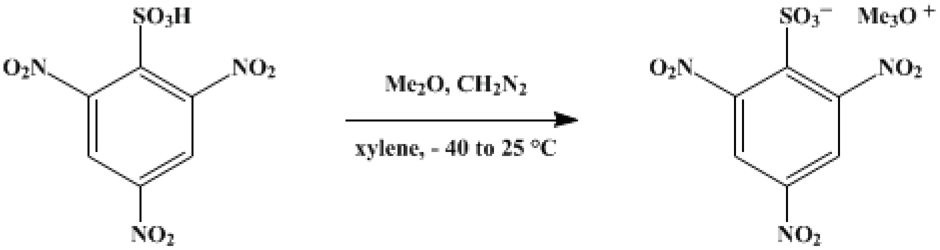
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.046.0122

Organic Syntheses, Coll. Vol. 5, p.1099 (1973); Vol. 46, p.122 (1966).

TRIMETHYLOXONIUM 2,4,6-TRINITROBENZENESULFONATE

[Oxonium compounds, trimethyloxonium 2,4,6-trinitrobenzenesulfonate]



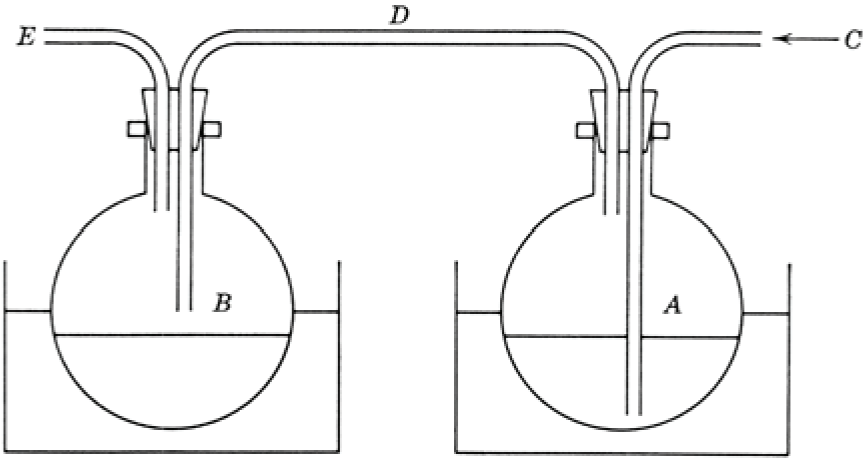
Submitted by G. K. Helmkamp and D. J. Pettitt[1] [2].
Checked by O. Vogl, B. C. Anderson, and B. C. McKusick.

1. Procedure

Caution! Diazomethane is hazardous. Follow the directions for safe handling of diazomethane given in earlier volumes.[3,4] All operations are carried out in a hood.

The apparatus is shown in Fig. 1. Two 500-ml. round-bottomed flasks *without standard-taper joints* (which could cause diazomethane to detonate) are used. The gas inlet *C* is connected to a cylinder of dimethyl ether. Gas inlet *C* is long enough to reach near the bottom of flask *A*, but tubing *D* extends only about halfway into flask *B*. A calcium chloride drying tube is attached to the gas outlet *E*. Flask *B* contains a Teflon®-covered stirring bar. The pieces of the apparatus are dried in an oven at 110°; well-dried apparatus is essential for a good yield.

Fig. 1.



A solution of diazomethane in 200 ml. of xylene is prepared from 15.0 g. (0.146 mole) of nitrosomethylurea[5] (Note 1). The diazomethane solution is decanted into flask *A*, and about 20 g. of potassium hydroxide pellets is added to the solution. The mixture is swirled for a few seconds to ensure removal of most of the water. About 4.2 g. (0.10 mole) of diazomethane is present. Flask *A* is then immersed in a water bath at 20–25°.

2,4,6-Trinitrobenzenesulfonic acid (14.7 g., 0.050 mole) (Note 2), previously dried for at least 1 hour at 80–100° (1 mm.), is placed in flask *B*, which is then immersed to the level shown in Fig. 2 in a bath of acetone maintained at −35° to −40° by addition of small amounts of dry ice (Note 3). About 200 ml. of dimethyl ether is rapidly poured from an ampoule into flask *B* (Note 3). Flasks *A* and *B* are connected as shown in Fig. 2, and magnetic stirring is started in flask *B*. When most of the sulfonic acid has dissolved, gaseous dimethyl ether is introduced through *C* at such a rate that a rapid stream of individual bubbles passes through the diazomethane solution in flask *A*. In the course of the reaction all the acid goes into soution and is replaced by a fluffy precipitate of the oxonium salt. The introduction of dimethyl ether is discontinued as soon as the supernatant solution in flask *B* turns yellow (Note 5) and (Note 6).

Flask *B* is separated from the apparatus but kept in the cooling bath, and 200 ml. of anhydrous ethyl acetate is added; addition is slow so as to avoid excessive boiling of the dimethyl ether (Note 7). The flask, with a tube of calcium chloride attached, is gradually brought to room temperature; most of the dimethyl ether evaporates during this operation. Crystalline trimethyloxonium 2,4,6-trinitrobenzenesulfonate is separated on a coarse sintered-glass funnel, washed with two 25-ml. portions of ethyl acetate and with 50 ml. of high-boiling petroleum ether, and dried over phosphorus pentoxide at 25° (<1 mm.) (Note 8); yield 12–14 g. (68–79%) (Note 9), m.p. 181–183° (Note 10).

2. Notes

1. Xylene is used as the solvent instead of diethyl ether because of its considerably lower vapor pressure.
2. 2,4,6-Trinitrobenzenesulfonic acid from Nutritional Bio-chemical Corp., Cleveland, Ohio, can be used without any purification other than drying. The checkers observed m.p. 174–177° for the dried acid.

The acid can be prepared from picryl chloride according to the method described by Golumbic, Fruton, and Bergmann,[6] but the following modifications are recommended: sodium metabisulfite should be used in place of sodium bisulfite; the crude sodium salt is not recrystallized but is converted directly to the acid by the addition of hydrochloric acid to its acetone solution; the product is recrystallized by dissolving it in a minimum amount of hot acetone, adding chloroform until crystallization starts, and cooling to about 0°. Two recrystallizations yield a product with m.p. 194–196°.

3. If the level of the cooling bath is too high, or if the bath temperature is less than −40°, unnecessary condensation of dimethyl ether occurs. If the level of the bath is too low, a brownish ring of decomposition product forms in the flask. Since the brown material is soluble in dimethyl ether and ethyl acetate, it does not contaminate the trimethyloxonium salt.
4. The submitters first transferred the dimethyl ether from a cylinder to an ampoule in order to avoid the accumulation of excess water. The ampoule should have a moderately wide mouth in order to facilitate rapid transfer of dimethyl ether.

The checkers made a mark on flask *B* corresponding to a volume of 220 ml., added the acid and stirrer, immersed the flask in liquid nitrogen, and passed in gaseous dimethyl ether from a cylinder until the volume of condensate reached the mark.

5. Diazomethane reacts with 2,4,6-trinitrobenzenesulfonic acid with ring opening similar to that observed with 1,3,5-trinitrobenzene.[7] Hence an excess of the reagent is to be avoided. The yellow color is not due to the presence of diazomethane itself. The reaction time is highly sensitive to the temperature of the xylene solution and to the flow rate of gaseous dimethyl ether. The reaction time is usually 20–40 minutes.
6. The excess diazomethane in flask A should be destroyed by adding a few drops of glacial acetic acid.
7. The ethyl acetate acts only as a high-boiling material that makes the subsequent vacuum filtration easier to control.
8. If the product is air-dried for more than a few seconds on the filter, it may pick up a significant amount of water. Most of the solvent that remains with the crystals should be removed under vacuum.
9. The product at this stage of purification is sufficiently pure for synthetic applications. As measured by the amount of dimethyl ether evolved on heating, its purity is about 95%.
10. On very rapid heating, the compound effervesces at about 120–130°. It then resolidifies and melts again at 181–183°, which is the melting point of methyl 2,4,6-trinitrobenzenesulfonate. At low heating rates, the effervescence may not be noticed.

3. Discussion

This method for the preparation of trimethyloxonium 2,4,6-trinitrobenzenesulfonate is an adaptation of that described by the submitters.[8] The salt can also be prepared from trimethyloxonium fluoborate by anion exchange.[8] Trimethyloxonium fluoborate[9] and hexachloroantimonate[10,11,12] have been prepared by other methods.

4. Merits of the Preparation

Like triethyloxonium fluoborate,[13] trimethyloxonium 2,4,6-trinitrobenzenesulfonate is a potent alkylating agent. Trimethyloxonium 2,4,6-trinitrobenzenesulfonate is nonhygroscopic and hence keeps better than trimethyloxonium fluoborate,[9] but it is more laborious to make.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1080
- Org. Syn. Coll. Vol. 5, 1096
- Org. Syn. Coll. Vol. 6, 1019

References and Notes

1. Department of Chemistry, University of California, Riverside, California.
2. Pioneering Research Laboratory, Textile Fibers Department, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington 98, Delaware. This work was supported in part by grant AM-08185 of the National Institutes of Health, U. S. Public Health Service.
3. Th. J. de Boer and H. J. Backer, *Org. Syntheses*, Coll. Vol. **4**, 250 (1963).
4. J. A. Moore and D. R. Reed, this volume, p. 351.
5. F. Arndt, *Org. Syntheses*, Coll. Vol. **2**, 165 (1943).
6. C. Golumbic, J. S. Fruton, and M. Bergmann, *J. Org. Chem.*, **11**, 518 (1946).
7. Th. J. de Boer and J. C. van Velzen, *Rec. Trav. Chim.*, **78**, 947 (1959).
8. D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963).
9. H. Meerwein, this volume, p. 1096.
10. F. Klages and H. Meuresch, *Ber.*, **85**, 863 (1952).
11. F. Klages and H. Meuresch, *Ber.*, **86**, 1322 (1953).
12. H. Teichmann and G. Hilgetag, *Naturwissenschaften*, **47**, 39 (1960).
13. H. Meerwein, this volume, p. 1080; T. J. Curphey, *Org. Syntheses*, **51**, 142 (1971).

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

petroleum ether

sodium metabisulfite

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ethyl acetate (141-78-6)

diethyl ether (60-29-7)

chloroform (67-66-3)

nitrogen (7727-37-9)

sodium bisulfite (7631-90-5)

dimethyl ether (115-10-6)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

xylene (106-42-3)

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

Diazomethane (334-88-3)

Nitrosomethylurea

picryl chloride (88-88-0)

Triethyloxonium fluoborate (368-39-8)

trimethyloxonium fluoborate (420-37-1)

Trimethyloxonium 2,4,6-trinitrobenzenesulfonate (13700-00-0)

2,4,6-Trinitrobenzenesulfonic acid (2508-19-2)

methyl 2,4,6-trinitrobenzenesulfonate

hexachloroantimonate

phosphorus pentoxide (1314-56-3)

Oxonium compounds, trimethyloxonium 2,4,6-trinitrobenzenesulfonate

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved