



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.

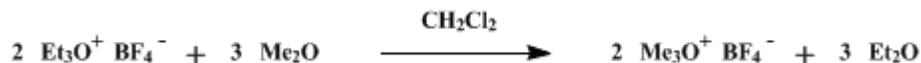
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.1096 (1973); Vol. 46, p.120 (1966).

TRIMETHYLOXONIUM FLUOBORATE

[Oxonium compounds, trimethyloxonium tetrafluoroborate]



Submitted by H. Meerwein¹

Checked by O. Vogl, B. C. Anderson, and B. C. McKusick.

1. Procedure

Freshly prepared triethyloxonium fluoborate² (170 g., 0.90 mole) is dissolved in 500 ml. of anhydrous methylene chloride in a 1-l. three-necked flask equipped with a stirrer, gas-inlet tube, and drying tube (Note 1). The reaction flask is immersed in an ice bath, the stirrer is started, and 138 g. (3.00 moles) of dry dimethyl ether is passed into the solution from a tared cylinder over a period of about 2 hours. The reaction mixture is allowed to stand overnight at room temperature. An hour after the addition of dimethyl ether is complete, trimethyloxonium fluoborate begins to separate. The initially liquid product solidifies slowly.

The stirrer is replaced by a filter stick, and the supernatant methylene chloride is withdrawn from the crystalline mass of trimethyloxonium fluoborate; nitrogen is admitted through a bubbler during this operation to prevent atmospheric moisture from entering the flask. The crystals are washed with three 100-ml. portions of anhydrous methylene chloride. The flask is transferred to a dry box, and trimethyloxonium fluoborate is collected on a sintered-glass filter, dried for 2 hours in a vacuum desiccator at 25° (1 mm.), and bottled in a stream of dry nitrogen. The fluoborate is colorless; yield 114–124 g. (86–94%). Rapidly heated in an open capillary tube, it sinters and darkens, with decomposition, at 141–143° (Note 3).

2. Notes

1. In order to obtain maximum yields, all operations must be carried out under rigorously dry conditions. The apparatus should be dried in an oven at 110°, assembled while hot, and cooled in a stream of dry nitrogen. The checkers dried the methylene chloride over PA 100 silica gel (12–28 mesh) obtained from Davison Chemical Co., Baltimore, Maryland.
2. Trimethyloxonium fluoborate is less hygroscopic and keeps better than triethyloxonium fluoborate, but it should be stored at 0–5° in a tightly closed screw-cap bottle.² So stored, it can be kept at least a few weeks.
3. The decomposition point varies widely, depending on rate of heating and apparatus. Professor S. H. Pine, California State College at Los Angeles, informed the checkers that he observed decomposition at 210–220°, with the salt totally disappearing and (CH₃)₂OBF₃ forming on the wall of the capillary tube above the bath. This prompted the checkers to study the decomposition by differential thermal analysis. At a heating rate of 30°/min., there was an endotherm peak at 142°, with sample all gone by 200°. At 15°/min., the peak was at 155°, with sample all gone by 180°.

3. Discussion

The procedure used is essentially that described by Meerwein and co-workers.³ The salt has also been prepared from the same reagents in a sealed tube.⁴

Curphey has described a convenient synthesis from boron trifluoride diethyl etherate, dimethyl ether, and epichlorohydrin.⁵

4. Merits of the Preparation

This facile preparation is suitable for preparation of large amounts of salt. Like [triethyloxonium fluoborate](#),² [trimethyloxonium fluoborate](#) is a potent alkylating agent. In comparison with [trimethyloxonium 2,4,6-trinitrobenzenesulfonate](#),⁶ [trimethyloxonium fluoborate](#) is easier to make but does not keep quite as well on storage.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 1080](#)
- [Org. Syn. Coll. Vol. 5, 1099](#)
- [Org. Syn. Coll. Vol. 6, 1019](#)

References and Notes

1. Deceased October 24, 1965; formerly at University of Marburg, Marburg, Germany.
2. [H. Meerwein, this volume, p. 1080.](#)
3. H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, *Ber.*, **89**, 2071 (1956).
4. H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, [2] **154**, 143 (1939).
5. T. J. Curphey, *Org. Syntheses*, **51**, 142 (1971).
6. G. K. Helmakamp and D. J. Pettitt, this volume, p. 1099.

Appendix

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

[Epichlorohydrin \(106-89-8\)](#)

[nitrogen \(7727-37-9\)](#)

[dimethyl ether \(115-10-6\)](#)

[methylene chloride \(75-09-2\)](#)

[boron trifluoride diethyl etherate \(109-63-7\)](#)

[Triethyloxonium fluoborate \(368-39-8\)](#)

[trimethyloxonium fluoborate \(420-37-1\)](#)

[Trimethyloxonium 2,4,6-trinitrobenzenesulfonate \(13700-00-0\)](#)

[Oxonium compounds, trimethyloxonium tetrafluoroborate](#)