



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.

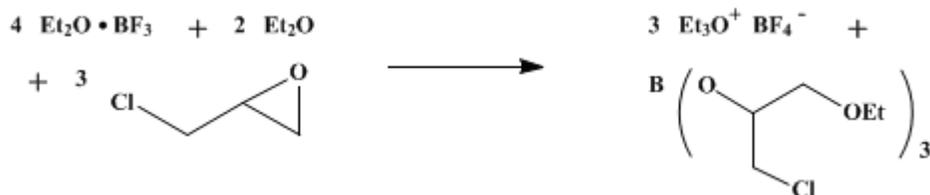
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.1080 (1973); Vol. 46, p.113 (1966).

TRIETHYLOXONIUM FLUOBORATE

[Oxonium compounds, triethyloxonium tetrafluoroborate]



Submitted by H. Meerwein¹

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

1. Procedure

A 2-l. three-necked flask, a stirrer, a dropping funnel, and a condenser provided with a drying tube are dried in an oven at 110°, assembled while hot, and cooled in a stream of dry nitrogen. Sodium-dried ether (500 ml.) and 284 g. (252 ml., 2.00 moles) of freshly distilled boron fluoride etherate (Note 1) and (Note 2) are placed in the flask. Epichlorohydrin (140 g., 119 ml., 1.51 moles) is added dropwise to the stirred solution at a rate sufficient to maintain vigorous boiling (about 1 hour is needed). The mixture is refluxed an additional hour and allowed to stand at room temperature overnight. The stirrer is replaced by a filter stick, and the supernatant ether is withdrawn from the crystalline mass of triethyloxonium fluoborate; nitrogen is admitted through a bubbler during this operation to prevent atmospheric moisture from entering the flask. The crystals are washed with three 500-ml. portions of sodium-dried ether. The flask is transferred to a dry box, and triethyloxonium fluoborate is collected on a sintered-glass filter and bottled in a stream of dry nitrogen. The fluoborate is colorless; m.p. 91–92° (dec.), yield 244–272 g. (85–95%) (Note 3).

2. Notes

1. The checkers obtained boron fluoride etherate and epichlorohydrin from Eastman Organic Chemicals and redistilled each through a 23-cm. Vigreux column immediately before use.
2. It is convenient to measure the liquids with syringes using the densities: epichlorohydrin d_4^{25} 1.179; boron fluoride etherate, d_4^{25} 1.125.
3. Triethyloxonium fluoborate is very hygroscopic. It should be stored in a tightly closed screw-cap bottle at 0–5° and should be used within a few days of the time it is made. It should be weighed and transferred in a dry box. It can be stored indefinitely under ether or at –80°.

3. Discussion

The procedure used is essentially that described by Meerwein and co-workers.^{2,3} The salt also has been prepared from ethyl fluoride and boron fluoride etherate, and from silver fluoborate, ethyl bromide, and ether.⁴

4. Merits of the Preparation

This simple procedure easily provides large amounts of triethyloxonium fluoborate. Triethyloxonium fluoborate readily ethylates such compounds as ethers, sulfides, nitriles, ketones, esters, and amides on oxygen, nitrogen, or sulfur to give onium fluoborates (often isolable) that can react with nucleophilic reagents to give useful products.⁵ For example, dimethylformamide gives the imino ether fluoborate $[(\text{CH}_3)_2\text{NCH-OC}_2\text{H}_5]^+ \text{BF}_4^-$, which is converted to $(\text{CH}_3)_2\text{NCH}(\text{OC}_2\text{H}_5)_2$ by sodium ethoxide.⁵ Since an imino ether fluoborate is easily hydrolyzed to the corresponding amine and ester, triethyloxonium fluoborate is a useful reagent for converting amides to amines under mild conditions.⁶ Curphey provides a fuller discussion of the alkylating properties of trialkyloxonium

fluoborates.⁷

If there is no advantage in ethylation over methylation, [trimethyloxonium fluoborate](#)⁸ or [trimethyloxonium 2,4,6-trinitrobenzenesulfonate](#)⁹ may be preferable alkylating agents; their preparation is more laborious, but they may be stored for a longer period of time.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 1096](#)
- [Org. Syn. Coll. Vol. 5, 1099](#)
- [Org. Syn. Coll. Vol. 6, 576](#)
- [Org. Syn. Coll. Vol. 6, 1019](#)

References and Notes

1. Deceased October 24, 1965; formerly at University of Marburg, Marburg, Germany.
2. H. Meerwein, E. Bettenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, [2] **154**, 83 (1940).
3. H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, [2] **147**, 257 (1937).
4. H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, **291**, 552 (1958).
5. H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, *Ber.*, **89**, 2060 (1956).
6. H. Muxfeldt and W. Rogalski, *J. Am. Chem. Soc.*, **87**, 933 (1965).
7. T. J. Curphey, *Org. Syntheses*, **51**, 142 (1971).
8. H. Meerwein, this volume, p. 1096.
9. G. K. Helmkamp and D. J. Pettitt, this volume, p. 1099.

Appendix

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

Sodium-dried ether

epichlorohydrin d_4^{25}

BF_4^-

ether (60-29-7)

Epichlorohydrin (106-89-8)

Ethyl bromide (74-96-4)

oxygen (7782-44-7)

nitrogen (7727-37-9)

sulfur (7704-34-9)

sodium ethoxide (141-52-6)

dimethylformamide (68-12-2)

silver fluoborate (14104-20-2)

boron fluoride etherate (109-63-7)

Triethyloxonium fluoborate (368-39-8)

ethyl fluoride (353-36-6)

trimethyloxonium fluoborate (420-37-1)

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

Oxonium compounds, triethyloxonium tetrafluoroborate