



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.

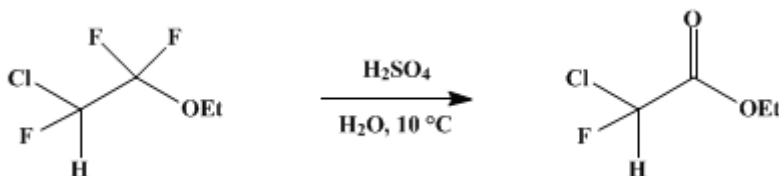
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.423 (1963); Vol. 34, p.49 (1954).

ETHYL CHLOROFLUOROACETATE

[Acetic acid, chlorofluoro-, ethyl ester]



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Checked by R. S. Schreiber and Burris D. Tiffany.

1. Procedure

Hydrogen fluoride vapors are highly corrosive and poisonous. An efficient hood should be used, and rubber gloves should be worn when dismantling the equipment.

A 2-l. three-necked round-bottomed flask is fitted with a mechanical stirrer and a 500-ml. dropping funnel (Note 1). The third neck is fitted with a thermometer and a length of rubber tubing to lead evolved hydrogen fluoride to the rear of the hood away from the operator. The flask is charged with 340 g. (2.09 moles) of crude 2-chloro-1,1,2-trifluoroethyl ethyl ether (p. 184) and cooled in an ice bath until the temperature of the halo ether is below 5°. From the dropping funnel, 228 ml. of 96% sulfuric acid (420 g., 4.1 moles) is added at such a rate that the temperature can be maintained at 5–15°. The addition requires 30–45 minutes, during which evolution of hydrogen fluoride begins. The reaction mixture is stirred at 10° for 2 hours, then carefully poured onto a mixture of 1 kg. of crushed ice and 500 ml. of water. The product, a nearly white oil, settles out as the lower layer. It is separated, washed until free of acid with three 25-ml. portions of saturated sodium bicarbonate solution (Note 2), then with four 25-ml. portions of water, and dried over 10 g. of Drierite. The weight of crude dried ester is 200–210 g. (68–71%). Fractional distillation gives 190–200 g. (65–68% yield) of pure ethyl chlorofluoroacetate, b.p. 129–130°, n_D^{25} 1.3925 (Note 3).

2. Notes

1. The hydrogen fluoride evolved etches the glass reaction vessel, but the same equipment may be used for 4–6 runs.
2. If the crude product is not washed free of acid considerable decomposition occurs during distillation with consequent reduction in yield.
3. The checkers found it necessary to use a moderately efficient (2 by 12 cm. helix-packed) column to effect satisfactory fractionation.

3. Discussion

Ethyl chlorofluoroacetate has been prepared by the action of sulfuric acid² or silica³ on 2-chloro-1,1,2-trifluoroethyl ethyl ether, and by the reaction of sulfuryl chloride with ethyl fluoroacetate in the presence of benzoyl peroxide.⁴ The procedure given is essentially that of Young and Tarrant.²

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 184

1. Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
 2. Young and Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949).
 3. Hanford and Rigby, U. S. pat. 2,409,274 [*C. A.*, **41**, 982 (1947)].
 4. Bergmann, Moses, Neeman, Cohen, Kaluszynier, and Reuter, *J. Am. Chem. Soc.*, **79**, 4174 (1957).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

silica

Drierite

sulfuric acid (7664-93-9)

sodium bicarbonate (144-55-8)

hydrogen fluoride (7664-39-3)

sulfuryl chloride (7791-25-5)

benzoyl peroxide (94-36-0)

2-Chloro-1,1,2-trifluoroethyl ethyl ether (310-71-4)

ethyl chlorofluoroacetate,
Acetic acid, chlorofluoro-, ethyl ester (401-56-9)

ethyl fluoroacetate (459-72-3)