



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.

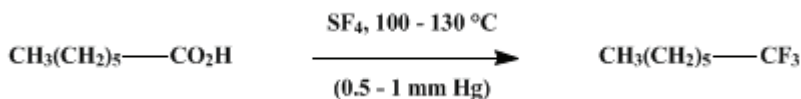
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

Organic Syntheses, Coll. Vol. 5, p.1082 (1973); Vol. 41, p.104 (1961).

1,1,1-TRIFLUOROHEPTANE

[Heptane, 1,1,1-trifluoro-]



Submitted by W. R. Hasek¹

Checked by John E. Baldwin and John D. Roberts.

1. Procedure

Caution! Sulfur tetrafluoride is toxic. This procedure should be carried out in a good hood. The pressure vessel should be heated in a well-ventilated area.

Twenty-six grams (0.20 mole) of **heptanoic acid** is placed in a 145-ml. pressure vessel lined with Hastelloy-C (**Note 1**). The air in the vessel is displaced with **nitrogen**, and the head of the vessel is secured in place. The vessel is cooled in a bath of acetone and solid **carbon dioxide**, and the **nitrogen** in the vessel is evacuated with a vacuum pump to a pressure of 0.5–1.0 mm. Sixty-five grams (95% pure, 0.57 mole) of **sulfur tetrafluoride** (**Note 2**) is transferred to the cold vessel. This is conveniently done by connecting a cylinder containing 65 g. of **sulfur tetrafluoride** to the pressure vessel by a length of copper tubing having a 1/16-in. bore and 1/8-in. outside diameter (**Note 3**).

The pressure vessel is heated with agitation at 100° for 4 hours and at 130° for 6 hours. The vessel is allowed to cool to room temperature and the volatile by-products [**Caution! Toxic!** (**Note 4**)] are vented. The crude, fuming, liquid product (**Note 5**) is poured into a stirred suspension of 10 g. of finely divided **sodium fluoride** in 60 ml. of **pentane** (**Note 6**), the mixture is filtered, and the filtrate is fractionated through a 6-in. Vigreux column. **1,1,1-Trifluoroheptane** is collected at 100–101°/760 mm., n_D^{25} 1.3449. The yield is 21.7–24.6 g. (70–80%).

2. Notes

1. The pressure vessel should be lined with Hastelloy-C, stainless steel, or other metal resistant to attack by **hydrogen fluoride**, because the latter substance is a by-product of the reaction. The pressure vessel employed should be safe for use at 500 atm. pressure and should be equipped with a rupture disk rated at 500 atm. If the equipment available is rated for use only at lower pressure, the size of the charge should be reduced appropriately.

2. Directions for the synthesis of **sulfur tetrafluoride** by the action of **sodium fluoride** on **sulfur dichloride** in **acetonitrile** have been published,² and a more detailed version of these directions appears in *Inorganic Syntheses*, 7, 119 (1963).

3. It is also possible to connect the supply cylinder of **sulfur tetrafluoride** to the pressure vessel by a short length of butyl rubber vacuum tubing.

If the supply cylinder of **sulfur tetrafluoride** contains more than 65 g., it may be placed on a balance in order to determine when the required amount has been transferred to the pressure vessel.

4. Since the volatile gases include **sulfur tetrafluoride** and **thionyl fluoride**, which possess toxicities comparable to that of **phosgene**, caution must be exercised in their disposal. A suitable procedure is to condense the volatile gases in a trap cooled in a mixture of **acetone** and solid **carbon dioxide**, and then to allow this material to pass slowly through an empty polyethylene bottle, which serves as a safety trap, and into a stirred aqueous **potassium hydroxide** solution.

5. If it is found necessary to retain the crude product for any period of time before working it up, it may be conveniently stored in a polyethylene bottle or other container resistant to attack by **hydrogen fluoride**.

6. As indicated above, the crude product contains **hydrogen fluoride**. The **sodium fluoride** disposes of

this by-product by the reaction $\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2$. An alternative procedure is to pour the crude product into water and to separate the product by extraction with [pentane](#).

3. Discussion

[1,1,1-Trifluoroheptane](#) has been prepared only by the action of [sulfur tetrafluoride](#) on [heptanoic acid](#).³

4. Merits of Preparation

The described procedure is useful for the preparation of a wide variety of compounds containing trifluoromethyl groups from the corresponding carboxylic acids.³ The yields are generally 60–90%. Some representative examples are listed in Table I. In the cases of the difunctional acids, only 0.1 mole of the compound should be used in the procedure.

TABLE I

Product	B.P., °C.	n_D^{25}
1,1,1-Trifluorododecane	92 (12 mm.)	1.3896
1,1,1-Trifluorohexadecane	107 (0.3 mm.)	1.4148
1,1,1-Trifluoro-3,5,5-trimethylhexane	121–122	1.3657
(4,4,4-Trifluorobutyl)cyclohexane	172–173	1.3987
1,1,1,10,10,10-Hexafluorodecane	183–184	1.3519
1,1,1,6,6,6-Hexafluoro-3-hexene	90–91	1.3131
<i>p</i> -Bis(trifluoromethyl)benzene	113–115	1.3767
2,4-Bis(trifluoromethyl)chlorobenzene	147	1.4130
<i>p</i> -Trifluoromethylnitrobenzene	(m.p. 41–43°)	

Carboxylic anhydrides and esters react with [sulfur tetrafluoride](#) to give the same products as the acids only at elevated temperatures, i.e., 200° to 300°.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 396](#)

References and Notes

1. Contribution No. 572 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del.
2. C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).
3. W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960); W. C. Smith, U.S. pat. 2,859,245 (1958).

Appendix

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

[acetonitrile](#) (75-05-8)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

hydrogen fluoride (7664-39-3)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

phosgene (75-44-5)

Pentane (109-66-0)

sulfur dichloride (10545-99-0)

Heptanoic acid (111-14-8)

sodium fluoride (7681-49-4)

sulfur tetrafluoride (7783-60-0)

1,1,1-Trifluoroheptane,
Heptane, 1,1,1-trifluoro- (693-09-4)

thionyl fluoride (7783-42-8)

1,1,1-Trifluorododecane

1,1,1-Trifluorohexadecane

1,1,1-Trifluoro-3,5,5-trimethylhexane

(4,4,4-Trifluorobutyl)cyclohexane

1,1,1,10,10,10-Hexafluorodecane

1,1,1,6,6,6-Hexafluoro-3-hexene

2,4-Bis(trifluoromethyl)chlorobenzene (327-76-4)

p-Bis(trifluoromethyl)benzene (433-19-2)

p-Trifluoromethylnitrobenzene (402-54-0)