



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.

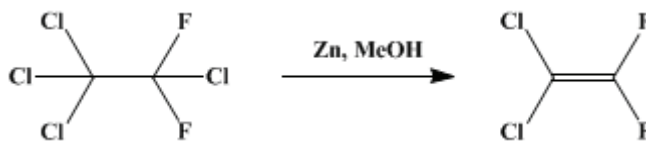
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,1-DICHLORO-2,2-DIFLUOROETHYLENE

[Ethylene, 1,1-dichloro-2,2-difluoro-]



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Checked by Charles C. Price and Maseh Osgan.

1. Procedure

In a 500-ml. three-necked round-bottomed flask equipped with a 100-ml. separatory funnel, a thermometer, and a short fractionating column (Note 1) leading through a condenser to a 100-ml. tared receiver are charged 150 ml. of methanol, 42.2 g. (0.65 g. atom) of powdered zinc, and 0.2 g. of zinc chloride. Acetone cooled in a Dry Ice-acetone bath is circulated through the condenser, and the distillation receiver is immersed in ice water (Note 2). The mixture in the flask is heated to 60–63°, and a 10–15-ml. portion of a solution consisting of 122.4 g. (0.6 mole) of 1,1,1,2-tetrachloro-2,2-difluoroethane (Note 3) in 50 ml. of methanol is added dropwise over a period of a few minutes. The reaction generally becomes moderately vigorous at this point, and refluxing of 1,1-dichloro-2,2-difluoroethylene part-way up the column is observed. The heating bath is removed at this time. Addition of the ethane derivative is continued at such a rate that the temperature of the refluxing liquid at the head of the column is maintained at 18–22°. The flask may require occasional shaking to prevent the zinc dust from agglomerating. The take-off rate of the ethylene derivative is adjusted to about one-half the rate of input of the ethane derivative. During this addition, the temperature in the distillation flask drops to 45–50°. The addition of the ethane derivative requires 45 minutes to 1 hour. The heating bath is replaced, and another hour is required to complete the dehalogenation and to distil the last of the product. The temperature in the distillation flask during this period gradually rises to 69–70°. There is collected in the receiver 71–76 g. (89–95% yield) (Note 4) of 1,1-dichloro-2,2-difluoroethylene, distilling at 18–21° (Note 5), n_D^{20} , 1.3730–1.3746.

2. Notes

1. A 16-in. column packed with platinum gauze and fitted with a variable take-off was used by the submitter. The checkers used a $20 \times \frac{3}{4}$ -in. jacketed column packed with 1/16-in. glass helices.
2. The checkers used a Dry Ice-acetone-cooled cold-finger condenser fitted with a partial take-off adapter.
3. Tetrachlorodifluoroethane ($\text{CCl}_3\text{-CClF}_2$) is sold under the trade name "Genetron-131" by the General Chemical Division, Allied Chemical and Dye Corporation, 40 Rector Street, New York 6, N. Y. The sample, as received, melted at 38–40°. According to infrared data, the compound was 95–99% pure. Distillation through a high-precision, spinning band column showed about 10% distilling at 86–90° (mostly 90°), another 10% at 90–90.5°, and the remainder at 91°. All fractions were essentially the same by infrared analysis. The first fraction melted at about 35°, and the main fraction melted at 40.5°.²
4. This product contains 1–1.7% methanol and a trace of the starting material.
5. This figure is slightly above the true boiling point of 1,1-dichloro-2,2-difluoroethylene. Upon redistillation in a low-temperature still fitted with a thermocouple, about 95% of this material distilled at 17°,³ n_D^{20} 1.3710.

3. Discussion

1,1-Dichloro-2,2-difluoroethylene has been prepared by the zinc dehalogenation method in ethanol.^{2,3} This compound also has been prepared by dehydrochlorination of 1,2,2-trichloro-1,1-difluoroethane by sodium hydroxide,⁴ by a solution of potassium hydroxide in aqueous methanol,⁵ by

passing it over active carbon containing barium chloride or strontium chloride,⁶ or by thermal cleavage at 590°.⁷ In addition, it has been obtained by the thermal cleavage of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane at 650° over aluminum fluoride.⁸

References and Notes

1. Contribution No. 285 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
2. Locke, Brode, and Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934).
3. Henne and Wiest, *J. Am. Chem. Soc.*, **62**, 2051 (1940).
4. Frederick (to B. F. Goodrich Co.), U. S. pat. 2,709,181 [*C. A.*, **50**, 5017 (1956)].
5. McBee, Hill, and Bachman, *Ind. Eng. Chem.*, **41**, 70 (1949).
6. Alexander Wacker Gesellschaft für electrochemische Industrie G.m.b.H., Brit. pat. 723,715 [*C. A.*, **50**, 5720 (1956)].
7. Padbury and Tarrant (to American Cyanamid Company), U. S. pat. 2,566,807 [*C. A.*, **46**, 2561 (1952)].
8. Miller and Calfee (to Allied Chemical and Dye Corp.), U. S. pat. 2,674,631 [*C. A.* **49**, 4007 (1955)].

Appendix

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

ethanol (64-17-5)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

barium chloride (10361-37-2)

acetone (67-64-1)

carbon (7782-42-5)

potassium hydroxide (1310-58-3)

zinc (7440-66-6)

zinc chloride (7646-85-7)

1,1-Dichloro-2,2-difluoroethylene,
Ethylene, 1,1-dichloro-2,2-difluoro- (79-35-6)

1,1,1,2-tetrachloro-2,2-difluoroethane,
Tetrachlorodifluoroethane (76-11-9)

1,2,2-trichloro-1,1-difluoroethane (354-21-2)

strontium chloride (10476-85-4)

1,1,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (336-50-5)

aluminum fluoride

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