Organic Syntheses

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.

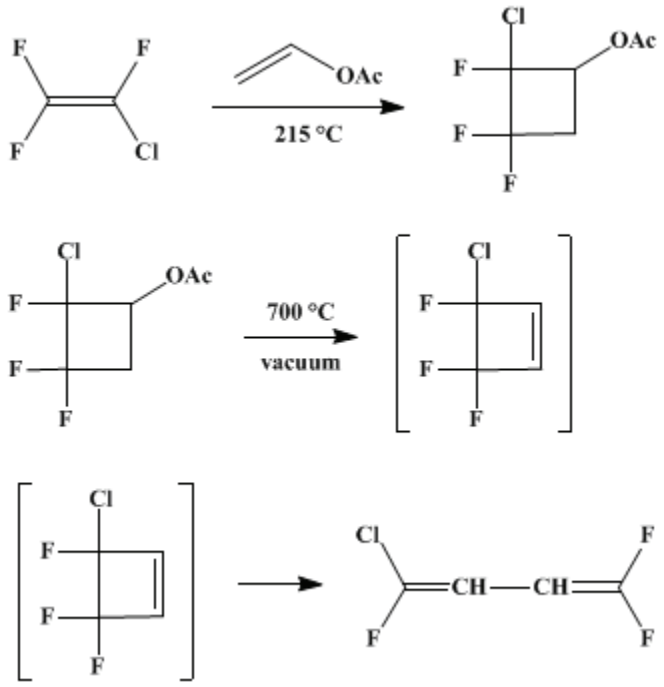
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.043.0017

Organic Syntheses, Coll. Vol. 5, p.235 (1973); Vol. 43, p.17 (1963).

1-CHLORO-1,4,4-TRIFLUOROBUTADIENE

[Butadiene, 1-chloro-1,4,4-trifluoro-]



Submitted by R. E. Putnam, B. C. Anderson, and W. H. Sharkey[1].
Checked by R. D. Birkenmeyer, M. A. Rebenstorf, and F. Kagan[2].

1. Procedure

A. *2-Chloro-2,3,3-trifluorocyclobutyl acetate* (Note 1). A mixture of 1.0 g. of hydroquinone, 3 drops of a terpene inhibitor (Note 2), and 140 g. (1.63 moles) of inhibited redistilled vinyl acetate (Note 3) is placed in a 400-ml. high-pressure shaker tube lined with stainless steel (Note 4). The shaker tube is closed, cooled in a mixture of solid carbon dioxide and acetone, evacuated, and charged with 47 g. (0.40 mole) of chlorotrifluoroethylene (Note 5). The shaker tube is heated with agitation to 215° in a period of about 1 hour and is then heated at 215° for 3 hours. The shaker tube is cooled to room temperature and is bled slowly to remove excess chlorotrifluoroethylene. The black, viscous reaction mixture (Note 6) is transferred to a distillation flask and heated on a steam bath. After a fore-run of dichlorohexafluorocyclobutane and vinyl acetate is collected at atmospheric pressure, a receiver cooled in solid carbon dioxide and acetone is attached, and crude 2-chloro-2,3,3-trifluorocyclobutyl acetate is rapidly distilled by gradually reducing the pressure to about 10 mm. (Note 7). Redistillation through a 30-cm. column packed with glass helices provides 22–30 g. (27–37%) (Note 8) of the acetate, b.p. 60–65°/100 mm., n_D^{25} 1.3916–1.3921.

B. *1-Chloro-1,4,4-trifluorobutadiene*. The apparatus is similar to that described in a previous volume.[3] It consists of a "Vycor" glass reaction tube, 60 cm. long by 25 mm. outside diameter, mounted vertically in an electric furnace about 35 cm. long (Note 9). Attached to the top of the tube is a graduated dropping funnel. A thermocouple well extending to the center of the heated section is inserted through the bottom of the tube. The heated section of the tube is packed with quartz tubing (8 mm. outside diameter), cut into 0.5-cm. lengths, and held in place by indentations in the tube. Ten centimeters from the bottom of the tube is a side arm leading successively to two traps cooled with solid carbon dioxide and acetone, an inlet tube for nitrogen, a manometer, and a vacuum pump.

The system is evacuated to a pressure of 5–10 mm., and the tube is heated to 700°, measured at the

center of the heated zone. 2-Chloro-2,3,3-trifluorocyclobutyl acetate is admitted at the rate of 10–20 g. per hour. From 70 g. (0.35 mole) of the cyclobutyl acetate there is obtained 62–68 g. of mixed solid and liquid condensate (Note 10). Fractionation through a 30-cm. column packed with glass helices affords 30–35 g. (60–70%) of 1-chloro-1,4,4-trifluorobutadiene (Note 11), b.p. 50–51°, n_D^{25} 1.3870; 18–22 g. of acetic acid; and 7–18 g. of recovered 2-chloro-2,3,3-trifluorocyclobutyl acetate (Note 12).

2. Notes

1. The exact structure of the cyclobutane is not known. Any of the possible isomers would undergo pyrolysis to give 1-chloro-1,4,4-trifluorobutadiene. 2-Chloro-2,3,3-trifluorocyclobutyl acetate is now favored as the structure of the cycloadduct rather than 3-chloro-2,2,3-trifluorocyclobutyl acetate as originally proposed.[4] The basis for this preference is mass spectral data. Ions of *m/e* 64 [$(CF_2{=}CH_2)^+$, relative abundance 1.2%] and 138 [$(CFCl{=}CHOCOCH_3)^+$, relative abundance 0.96%] were much more abundant than ions of *m/e* 80 [$(CFCl{=}CH_2)^+$, relative abundance 0.10%] and 122 [$(CF_2{=}CHOCOCH_3)^+$, relative abundance 0.026%].
2. The purpose of the terpene is to inhibit polymerization of the fluoroölefin. Terpenes that are effective include dipentene and terpinolene.
3. Ordinary commercial-grade vinyl acetate is redistilled. One gram of hydroquinone per 100 g. of vinyl acetate is added to inhibit polymerization of the latter, which is then stored at 0–4° until needed.
4. A shaker tube equipped with a 1200-atm. rupture-disk assembly was used by the submitters. The checkers used a 1270-ml. stainless steel rocking autoclave fitted with a thermocouple well that extended into the reaction mixture and a stainless steel 5000-p.s.i. rupture disk. The agitation rate was 58 cycles per second. Attempts to use a magnetically stirred autoclave were unsuccessful.
5. Chlorotrifluoroethylene is available in 1-lb. and 5-lb. cylinders from the Matheson Company, East Rutherford, New Jersey.
6. The checkers found the reaction mixture to be dark but not viscous. In experiments in which a magnetically stirred autoclave was used, dark viscous reaction mixtures were obtained, but no product. Difficulties encountered by the checkers when they used a magnetically stirred autoclave led the submitters to re-examine the reaction. It was found that certain batches of vinyl acetate gave very poor yields. In these cases, 27–37% yields were obtained by heating to 175° in 1 hour followed by heating at 175° for 16 hours.
7. The quantity of fore-run depends on the amount of polymerization of vinyl acetate. Distillation of the product through a packed column goes more smoothly, with less heat having to be applied to the distillation flask, if the product has been separated from high-boiling material by a quick preliminary distillation.
8. Up to 25% by weight of the product is ethylidene diacetate. The diacetate can be detected by gas chromatographic analysis using a column of the diglyceride of 6,6,6-trifluorohexanoic acid on firebrick at 120°.[5] The checkers obtained yields ranging from 24% in a 0.75-scale experiment to 47% on a three-fold increase in scale.
9. A standard tube furnace such as the 120-volt "Multiple Unit" electric furnace manufactured by the Hevi Duty Electric Company was used.
10. Care must be taken to prevent plugging of the first cold trap by solid acetic acid because the back-pressure produced leads to greatly reduced yields and appreciable carbonization. Should plugging occur, the cooling bath is removed and the plug is melted with warm acetone. Some diene will distil into the second trap during this process.
11. 1-Chloro-1,4,4-trifluorobutadiene is a mixture of equal amounts of *cis* and *trans* isomers. This has been demonstrated by gas chromatographic analysis of the mixture on a packed column of high efficiency using Dow-Corning silicone 703 oil or 200 oil on firebrick, or on a capillary gas chromatographic column using squalane as the partitioning liquid.
12. The checkers did not isolate any recovered 2-chloro-2,3,3-trifluorocyclobutyl acetate.

3. Discussion

The procedure for chlorotrifluorocyclobutyl acetate[4] is a modification of one used by Coffman, Barrick, Cramer, and Raasch[6] for the preparation of tetrafluorocyclobutanes from tetrafluoroethylene.

The method for the pyrolysis of chlorotrifluorocyclobutyl acetate to chlorotrifluorobutadiene is that

of Anderson, Putnam, and Sharkey.[4]

4. Merits of the Preparation

The synthesis of 2-chloro-2,3,3-trifluorocyclobutyl acetate illustrates a general method of preparing cyclobutanes by heating chlorotrifluoroethylene, tetrafluoroethylene, and other highly fluorinated ethylenes with alkenes. The reaction has recently been reviewed.[7] Chlorotrifluoroethylene has been shown to form cyclobutanes in this way with acrylonitrile,[8] vinylidene chloride,[9] phenylacetylene,[10] and methyl propiolate.[4] A far greater number of cyclobutanes have been prepared from tetrafluoroethylene and alkenes;[6,7] *when tetrafluoroethylene is used, care must be exercised because of the danger of explosion.* The fluorinated cyclobutanes can be converted to a variety of cyclobutanes, cyclobutenes, and butadienes.

The synthesis of chlorotrifluorobutadiene illustrates a general method that has been used to make tetrafluorobutadiene[4,11] and substituted fluorodienes.[4,11,12] The same procedure can be used to transform fluorocyclobutenes and chlorofluorocyclobutenes to the isomeric dienes; 2-methyl-1,1,4,4-tetrafluorobutadiene, 2-chloro-1,1,4,4-tetrafluorobutadiene, and 1-chloro-1,4,4-trifluoro-2-phenylbutadiene have been made thus.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 28

References and Notes

1. Contribution No. 597 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.
2. Upjohn Co., Kalamazoo, Michigan.
3. R. E. Benson and B. C. McKusick, *Org. Syntheses*, Coll. Vol. **4**, 746 (1963).
4. J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961).
5. J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 844 (1961).
6. D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).
7. J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).
8. A. L. Barney and T. L. Cairns, *J. Am. Chem. Soc.*, **72**, 3193 (1950).
9. M. S. Raasch, R. E. Miegel, and J. E. Castle, *J. Am. Chem. Soc.*, **81**, 2678 (1959).
10. E. J. Smutny and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 3420 (1955).
11. J. L. Anderson and K. L. Berry, U.S. Patent pending.
12. J. L. Anderson, U.S. Patent 2,754,323 (1956) [C.A., **51**, 2026 (1957)].

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

terpene

diglyceride of 6,6,6-trifluorohexanoic acid

acetic acid (64-19-7)

hydroquinone (123-31-9)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

acetone (67-64-1)

ethylidene diacetate (542-10-9)

Phenylacetylene (536-74-3)

acrylonitrile (107-13-1)

vinyl acetate (108-05-4)

Chlorotrifluoroethylene (79-38-9)

cyclobutane (287-23-0)

1-Chloro-1,4,4-trifluorobutadiene,
Butadiene, 1-chloro-1,4,4-trifluoro- (764-14-7)

dichlorohexafluorocyclobutane

2-Chloro-2,3,3-trifluorocyclobutyl acetate

cyclobutyl acetate

3-chloro-2,2,3-trifluorocyclobutyl acetate

squalane (111-01-3)

chlorotrifluorocyclobutyl acetate

tetrafluoroethylene (9002-84-0)

chlorotrifluorobutadiene

vinylidene chloride (75-35-4)

methyl propiolate (922-67-8)

tetrafluorobutadiene

2-methyl-1,1,4,4-tetrafluorobutadiene

2-chloro-1,1,4,4-tetrafluorobutadiene

1-chloro-1,4,4-trifluoro-2-phenylbutadiene