Journal of Fluorine Chemistry, 12 (1978) 471–479

Received: May 16, 1978

SYNTHESIS OF 3,3,3-TRIFLUOROPROPENE FROM VINYLIDENE FLUORIDE†

A. E. FEIRING

Central Research & Development Department,
Experimental Station, E. I. du Pont de Nemours & Co., Inc.
Wilmington, Delaware 19898

SUMMARY

3,3,3-Trifluoropropene is obtained under mild conditions via 3,3,3-trifluoropropyl acetate or 3,3,3-trifluoropropyl methyl ether as key intermediates. The intermediates were prepared by conjugate addition of FCH_2OR ($R = COCH_3$, CH_3) generated <u>in situ</u> from HF, paraformaldehyde and HOR to vinylidene fluoride.

INTRODUCTION

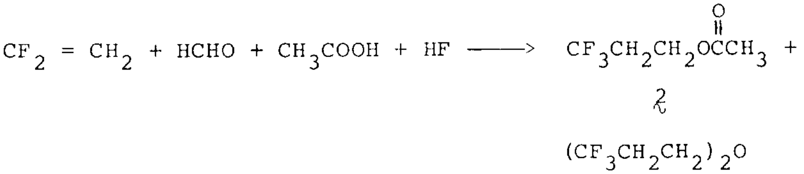
3,3,3-Trifluoropropene (**1**) is a useful starting material for the preparation of a variety of fluorinated compounds. Many syntheses of **1** have been reported, often based on the fluorination of 1,1,1,3-tetrachloropropane or related compounds[1,2] or on the reaction of acrylic acid with sulfur tetrafluoride.[3] These reactions often require highly specialized equipment and are inconvenient to run, especially on laboratory scale. In this paper, alternative syntheses of **1** based on vinylidene fluoride are reported.

---

† Contribution No. 2575

RESULTS

The first approach to **1** was based on the known[4,5] reaction of vinylidene fluoride with paraformaldehyde and acetic acid in hydrogen fluoride to give 3,3,3-trifluoropropyl acetate in 30% yield together with about 15% of 3,3,3-trifluoropropyl ether (**3**).



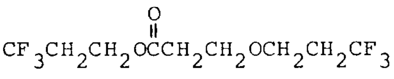
$$CF_2 = CH_2 + HCHO + CH_3COOH + HF \longrightarrow CF_3CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3 + (CF_3CH_2CH_2)_2O$$

2

3

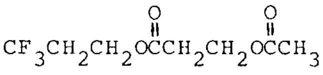
These compounds were difficult to separate by distillation. However, pyrolysis of the mixture in a flow system at 450° gave an essentially quantitative yield of **1** from **2** plus unchanged **3** and acetic acid.

Although short and convenient, this synthesis of **1** clearly suffers from the low yield of acetate **2** in the first step Efforts to increase the yield were unsuccessful. By-products isolated from this reaction included, in addition to **3**, the polycondensation products **4**, **5**, and **6**.



$$CF_3CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_2OCH_2CH_2CF_3$$

4



$$CF_3CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$$

5

$CF_3CH_2CH_2OCH_2CH_2COOH$

6

An alternate synthesis of 1 began with the known[4,5] reaction of vinylidene fluoride with paraformaldehyde and methanol in hydrogen fluoride which gave methyl 3,3,3-trifluoropropyl ether (7) in 60% yield based on vinylidene fluoride. Efforts to thermally crack 7 directly to 1 over a variety of catalysts failed. However, treatment of 7 with hydrogen bromide in sulfolane at 120° cleanly converted it to the bromide 8. Reaction of 8 with aqueous sodium hydroxide under phase transfer conditions gave very pure 1 in essentially quantitative yield.

$$CF_2{=}CH_2 + CH_3OH + CH_2O + HF \longrightarrow CF_3CH_2CH_2OCH_3$$

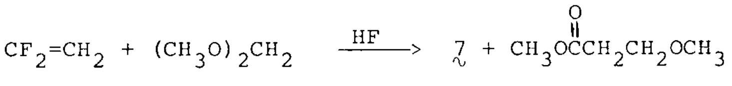
7

$$7 + HBr \xrightarrow[\text{sulfolane}]{} CF_3CH_2CH_2Br$$

8

$$8 \xrightarrow[H_2O]{NaOH} 1$$

Reaction of vinylidene fluoride with dimethoxymethane in hydrogen fluoride gave 7 in 50% yield together with about 15% of methyl 3-methoxypropionate (9).



$$CF_2{=}CH_2 + (CH_3O)_2CH_2 \xrightarrow{HF} 7 + CH_3O\overset{O}{\overset{\|}{C}}CH_2CH_2OCH_3$$

9

DISCUSSION

The three step sequence (vinylidene fluoride → 7 → 8 → 1) provides a convenient synthesis of trifluoropropene. Each reaction proceeds in good to excellent yield under mild conditions of temperature and pressure. The sequence can be run without purification of intermediates to give pure final product.

The by-products **4**, **5**, and **6** are analogous to those previously reported[4] from a similar reaction using vinylidene chloride. The overall mechanism of the conjugate addition process has been discussed.[4]

NMR data for **2**, **3**, **7**, **8**, and some related compounds prepared as part of this work are collected in Table 1.

Table 1

NMR Spectra of $CF_3CH_2CH_2X$ Derivatives[a]

X	$\delta(CH_2X)$	δX	δCF_3
OAc	4.25	2.07	-65.79
$O(CH_2)_2CF_3$	3.68	----	-65.63
OCH_3	3.58	3.33	-65.56
Br	3.45	----	-66.80
Cl[b]	3.66	----	-66.37
NH_2[c]	2.97	1.67	-65.50

a. In $CDCl_3$, ppm from TMS (proton) or $CFCl_3$ (fluorine). The protons adjacent to CF_3 appear as a tripled ($J \approx 6.5$ Hz) quartet ($J \approx 11$ Hz) centered at ca. δ 2.3.

b. Prepared according to Reference 1.

c. Prepared according to Reference 7.

EXPERIMENTAL

Anhydrous hydrogen fluoride was used as received from Air Products. All other reagents were commercial samples, used as received. Proton NMR spectra were obtained on a Varian A-60 instrument in $CDCl_3$ with TMS as internal standard. Fluorine

NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz using $CFCl_3$ as internal standard. Glpc data were obtained on a Hewlett-Packard 5700A instrument using the indicated columns and conditions.

Caution! Hydrogen fluoride is extremely corrosive to human tissue, contact resulting in painful, slow-healing burns. Laboratory work with HF should be conducted only in an efficient hood with operator wearing full face shield and protective clothing

Preparation of 3,3,3-Trifluoropropylacetate (2)

A 1 l stirred Hastelloy autoclave was swept with N_2 and charged with 60 g (2 mole) of paraformaldehyde and 150 g (2.5 moles) of acetic acid. The clave was closed, cooled with dry ice/acetone, evacuated and charged with 160 g of HF. The resulting mixture was warmed to 30° and stirred vigorously. Vinylidene fluoride was admitted to the autoclave at 15 psi until 115 g (1.8 moles) were absorbed. Addition of the vinylidene fluoride required 3/4 hr. After standing overnight the contents of the autoclave were blown onto 300 g of ice. With strong cooling the mixture was neutralized by the slow addition of 50% aq KOH. An upper organic layer was separated, dried over $MgSO_4$ and filtered, giving 148 g of colorless liquid. Distillation of the liquid through a 6" Vigreaux column gave 120 g of distillate bp 100-108° and 25 g of pot residue. The distillate was analyzed by proton and fluorine NMR (cf. Table 1) as a mixture of 66% of 3,3,3-trifluoropropyl acetate and 34% 3,3,3-trifluoropropyl ether.

The combined pot residues from two runs (48.8 g) were distilled through a short path distillation head giving 30.2 g of colorless liquid, bp 85-95° at 4 mm. Glpc analysis of the liquid using a 10 ft x 1/4 in 10% SE-30 column at 200° showed two peaks with retention times of 3.9 min (32%) and 5.9 min (68%) Samples of each were obtained by prep glpc. The minor component was identified as $CF_3CH_2CH_2OOCCH_2CH_2OCH_2CH_2CF_3$, proton NMR ($\delta$) 4.33 (2H, t), 3.73 (2H, t), 3.68 (2H, t), 2.60 (2H, t), 2.0-2.9 (4H, m); fluorine NMR -65.52 (3F), -65.72 (3F). The major component was identified as $CF_3CH_2CH_2OOCCH_2CH_2OOCCH_3$; proton nmr ($\delta$) 4.32 (4H, t), 2.62 (2H, t), 2.1-2.9 (2H, m), 2.05 (3H, S); fluorine nmr -65.58.

Continued distillation of the pot residue gave 9 g of colorless liquid bp 90-95° at 1.4 mm. Glpc analysis showed in addition to the above compounds a third component of longer retention time. A pure sample of this material was obtained by diluting a 5 g sample of the distillate with 50 ml ether. The ether solution was extracted with 2 x 30 ml 5% aq KOH. The combined KOH extracts were acidified with conc HCl and extracted with 2 x 30 ml ether. The combined ether extracts were dried ($MgSO_4$), filtered and concentrated in vacuo to 2.3 g of colorless liquid identified as $CF_3CH_2CH_2OCH_2CH_2COOH$; proton NMR ($\delta$) 10.40 (1H, S), 3.73 (2H, t), 3.68 (2H, t), 2.62 (2H, t), 2.0-2.8 (2H, m); fluorine NMR -65.35.

Pyrolysis of 3,3,3-Trifluoropropylacetate (**2**)

An 8" quartz tube packed with silicon carbide chips was mounted in a vertical electric furnace. The base of the tube was attached to two traps, the first cooled in ice water, the second cooled in dry ice/acetone. A constant pressure addition funnel was placed on top of the pyrolysis column. The system was swept with N_2 and the quartz tube was heated to 500°. A mixture (15 g) consisting of about 89% of **2** and 11% of **3** was added dropwise to the column from the addition funnel over 2 hr. After the addition was complete the column was swept with a slow flow of N_2 for 2 hr. The traps were disconnected. The dry ice trap contained 6.5 g of pure **1** identified by glpc comparison with an authentic sample on a 4 ft x 1/8 in Poropak Q column at 60°. The ice water trap contained 6.3 g of liquid identified by proton NMR as a mixture of acetic acid and **3**.

Preparation of Methyl 3,3,3-Trifluoropropyl Ether

A 1 l stirred Hastelloy autoclave was swept with N_2 and charged with 96 g (3 moles) of methanol and 90 g (3 moles) of paraformaldehyde. The vessel was closed, cooled with dry ice/acetone, evacuated and charged with 280 g of HF. The mixture was warmed to 20° and stirred vigorously. Vinylidene fluoride was admitted at 10 psi until 160 g (2.5 mole) had been absorbed. After standing overnight the solution was discharged onto 300 g of ice. With strong cooling the solution was neutralized by bubbling in ammonia gas. A lower organic layer was separated, dried over $MgSO_4$, and filtered to give 205 g of crude methyl 3,3,3-trifluoropropyl ether. Distillation through a 6-inch Vigroux column gave 179 g (56%) of ether bp 60-62°.

Preparation of 1-Bromo-3,3,3-trifluoropropane

A 200 ml Hastelloy bomb was charged with 38.4 g (0.3 mole) of **7** and 60 ml of sulfolane. The bomb was closed, cooled in dry ice/acetone and charged with 48.6 g (0.6 mole) of hydrogen bromide The resulting mixture was agitated at 120° overnight, then cooled to room temperature and vented. The contents of the autoclave were poured over 100 g of ice. A lower organic layer was separated washed twice with 50 ml H_2O, dried over $MgSO_4$, and filtered to gid 49 g of liquid. Distillation of the liquid gave 44 g (83%) of 1-bromo-3,3,3-trifluoropropane bp 60-62°.

Preparation of 3,3,3-Trifluoropropene from 1-Bromo-3,3,3-trifluoropropane

A 250 ml round bottom flask was equipped with a heating mantle, magnetic stirrer, a constant pressure addition funnel, a thermometer, and a condenser with a tube leading to two traps. The first trap was cooled in ice water, the second in dry ice/acetone. The system was flushed with N_2. The round bottomed flask was charged with 16 g (0.4 mole) of sodium hydroxide pellets, 2 g of benzyltrimethylammonium chloride and 130 ml of water. The stirred solution was heated to 55° and 1-bromo-3,3,3-trifluoropropane (53.1 g, 0.3 mole) was added dropwise over 1 hr. After the addition was complete, the mixture was stirred for an additional 2 hr. From the dry ice trap was isolated 26 g (90%) of 3,3,3-trifluoropropene which was 99% pure by glpc (4 ft x 1/8 ft) Poropak column at 60°). An aliquot of the product dissolved in $CDCl_3$ showed complex absorption in the proton NMR at δ 5.4-6.2 and a peak at -67.37 in the fluorine NMR.

REFERENCES

1 R. N. Haszeldine, J. Chem. Soc. 3371 (1953); A. L. Henne and M. Nager, J. Amer. Chem. Soc. 73, 1042 (1951).

2 J. A. Valicenti, R. L. Halm, F. O. Stark, U.S. Patent 3,739,036 (June 12, 1973) (CA 79, 52775g); H. Wada, Y. Hiramatsu, I. Morioka, Japan 74,133,308 (December 21, 1974) (CA 82, 139,283f); French 1,343,392 (November 15, 1963) (CA 60, 9148f); A. N. Nesmeyanov, V. N. Kost, L. I. Zakharkin, and R. K. Freidlina, Izvest. Akad. Nauk S.S.S.R., Otdel Khim Nauk, 447 (1960) (CA 54, 22343); R. P. Ruh, R. A. Stowe and R. A. Davis, U.S. Patent 2,889,379 (June 2, 1959) (CA 54, 1295a).

3 W. R. Hasek, W. C. Smith, and V. A. Engelhardt, J. Amer. Chem. Soc. 82, 543 (1960).

4 L. S. German and I. L. Knunyantz, Angew. Chem. Inter. Ed. 8, 349 (1969).

5 L. S. German and I. L. Knunyantz, Zh. Vses, Khim. Obshchestva. von D. I. Mendeleeva 11, 356 (1966) (CA 65, 15215h).

6 P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, J. Amer. Chem. Soc. 77, 2783 (1953).

7 A. V. Podol'skii, L. S. German, and I. L. Knunyantz, Izv Akad. Nauk SSSR, Ser. Khim. 1575 (1966) (CA 66:95004d)