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Journal of Fluorine Chemistry 112 (2001) 117–121

JOURNAL OF FLUORINE CHEMISTRY

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New synthesis of hydrofluoroethers

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Abstract

Polyfluorinated ethers $R_fCH_2OR_f$ react with fluoroethylenes in the presence of SbF_5 catalyst under mild conditions. The reaction of $CF_3CH_2OCF_2CF_2H$ (**1a**) with terafluoroethylene rapidly proceeds at ambient temperature and results in high yield formation of $CF_3CH_2OCF(C_2F_5)CF_2H$, along with small amount of $CF_3CH_2OC(C_2F_5)_2CF_2H$. On the other hand, the condensation of **1a** with trifluoroethylene proceeds with formation of $CF_3CH_2OC(CFHCF_3)_2CF_2H$ as a major product. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrofluoroethers; Electrophilic condensation; Fluoroolefins; Antimony pentafluoride

1. Introduction

Hydrofluoroethers became of significant importance in last few years. Potential commercial applications of these materials include use as refrigerants, heat transfer fluids and polymerization media [1–3]. Several materials of this type have been commercialized recently. In general, the synthetic methods of preparation of hydrofluoroethers either are based on either fluorination of ethers or utilization of "building blocks" approach. The former includes nucleophilic addition of alcohols to fluoroolefins [4], electrophilic alkylation of polyfluorinated alkoxy anions by reagents such as $(CH_3)_2SO_4$ [3,5], radical addition of ethers to fluoroolefins [6], Lewis acid catalyzed trifluoromethylation of polyfluorinated alcohols using CCl_4 in anhydrous HF [7] and electrophilic alkylation of perfluorinated carbonyl compounds by alkyl fluorides [8].

This paper report a new method of preparation of hydrofluoroethers, based on the condensation polyfluorinated ethers and fluoroethylenes catalyzed by antimony pentafluoride.

2. Results and discussion

The stability of polyfluorinated ethers towards the action of strong Lewis acids varies significantly and in general depends on the degree of fluorination and the structure of ether. For example, perfluorinated ethers are quite stable to the action of acids at ambient temperature and react with Lewis acids ($AlCl_3$ or SbF_5) only at high temperature [9]. On the other hand, partially fluorinated compounds R_fCF_2OR interact with SbF_5 under mild conditions. The reaction of $CF_3CFHCF_2OCH_3$ with antimony pentafluoride, results in rapid decomposition of ether with formation of $CF_3CFHC(O)F$ and methyl fluoride [10].

In this study, it is found that ethers $R_fCH_2OR_f$ have much higher stability towards SbF_5 compare to R_fCF_2OR. For example, the addition of SbF_5 to $CF_3CH_2OCF_2CF_2H$ (**1a**) at ambient temperature does not result in cleavage of ether, but leads to the formation of clear homogeneous solution. The reaction of solution SbF_5 in ethers **1a–d** and olefin **2** proceeds under mild conditions resulting in insertion of fluoroolefin in C–F bond of difluoromethyl group of ether and formation of compounds **3a–d** [11]:

$$\underset{\textbf{1a-d}}{CF_3CH_2OCF_2X} + \underset{\textbf{2}}{CF_2{=}CF_2} \xrightarrow[SbF_5]{25^\circ C,\ 12h} \underset{\textbf{3a-d}}{CF_3CH_2OCFX(C_2F_5)} \tag{1}$$

	X	
1a	$-CF_2H$	**3a**, 76%
1b	$-CFHCF_3$	**3b**, 57.5%
1c	$-CFHOC_3F_7$	**3c**, 22%
1d	$-CFHCl$	**3d**, 62%

Detailed analysis of the crude product of the reaction ether **1a** and olefin **2** revealed the presence of a few percent of compound **4**. The formation of **4** is result of insertion of 2 mol of olefin into molecule of ether **1a**:

$$\underset{\textbf{1a}}{CF_3CH_2OCF_2CF_2H} + 2\,CF_2{=}CF_2 \xrightarrow[SbF_5]{25^\circ C,\ 12h} \textbf{3a} + \underset{\textbf{4},\ 7.4\%}{CF_3CH_2OC(C_2F_5)_2CF_2H} \tag{2}$$

ratio **3a** : **4** = 9 : 1

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PII: S0022-1139(01)00476-6

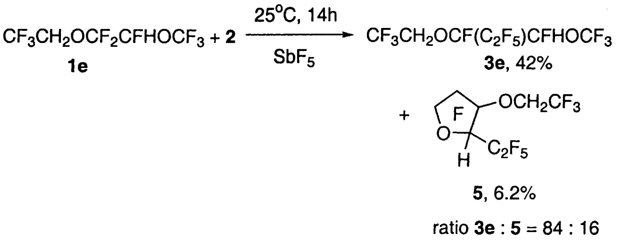
Table 1
Condensation of polyfluorinated ethers with fluoroethylenes catalyzed by antimony pentafluoride

Entry no.	Ratio of reactants (mol)	SbF_5 (mol%)	Temperature (°C) (time, h)	Products (yield, %)[a]	Boiling point (°C) (mmHg)
1	**1a**, **2** (3:2)	17	25 (12)	**3a** (76), **4** (trace)	**3a** 65.2–65.8
2	**1a**, **2** (1:2)	17	25 (12)	**3a** (70)[b], **4** (7.4)	4,112–115
3	**1b**, **2** (1:1)	13	25 (14)	**3b** (57.5)	90.3–91
4	**1c**, **2** (1:1)	7	25 (14)	**3c** (22)	122–126
5	**1d**, **2** (1:1)	16	25 (14)	**3d** (62)	106–109
6	**1e**, **2** (1:1)	6	25 (14)	**3e** (42)[c], **5** (6.2)	98–99, 112
7	**6a**, **2** (3:2)	5	25 (12)	**6b** (5), **6c** (**9**)	
8	**7a**, **2** (1:2)	13	25 (12)	**7b** (41), **7c** (57)	77.5–77.9, 113.5–114.5
9	**8a**, **2** (3:2)	17	25 (12)	**8b** (52), **8c** (33)	74.8, 99.2
10	**1a**, **9** (1:2)	20	25–30 (4)	**10a** (61)	114–120
11	**1b**, **9** (1:2)	22	25–30 (5)	**10b** (51)	136–143
12	**1a**, **11** (2:1)	10	10–35 (4)	**12a** (53)	50–51 (20)
13	**1b**, **11** (2:1)	10	10–25 (4)	**12b** (42)	55–56.5 (25)
14	**8a**, **11** (3:2)	10	10–25 (4)	**12c** (43)	56–58 (25)
10	**12b**, Zn, C_2H_5OH	–	Reflux (2)	**13** (83)	108–110

[a] Isolated yields.
[b] Ratio of **3a**:**4** in crude product 9:1.
[c] Ratio of **3e**:**5** in crude product 84:16.

All attempts to increase the yield of this material by increasing the amount of **2** in the reaction mixture failed. The amount of **4** in all reaction mixtures never exceeded 10% (see Table 1).

The condensation of ether **1e** and **2** leading to the formation of compound **3e** as a major product, is accompanied by formation of noticeable amount of another material, identified as cyclic ether **5** (NMR and GC–MS):



$$CF_3CH_2OCF_2CFHOCF_3 + \mathbf{2} \xrightarrow[SbF_5]{25^\circ C,\ 14h} CF_3CH_2OCF(C_2F_5)CFHOCF_3$$

1e

3e, 42%

5, 6.2%

ratio **3e** : **5** = 84 : 16

(3)

In general, ethers containing $-OCF_3$ fragment have lower reactivity towards **2**. The reaction proceeds with formation of products **6b**, **c** and **7a**, **c**, respectively, although formation of significant amount polytetrafluoroethylene is observed in both reactions:[1]

$$R_fCH_2OCF_2X + \mathbf{2} \xrightarrow[SbF_5]{25^\circ C,\ 14h} R_fCH_2OCFXC_2F_5 + R_fCH_2OCX(C_2F_5)_2 \quad (4)$$

	R_f	X		
6a	CF_3-	F	**6b**	**6c**
7a	HCF_2CF_2-	F	**7b**	**7c**
8a	CF_3-	H	**8b**	**8c**

On the other hand, $CF_3CH_2OCF_2H$ (**8a**) is more active in the reaction with **2** giving a mixture of **8b**, **c** in high yield (Table 1).

The condensation of ethers **1a** and **b** and trifluoroethylene (**9**) proceeds regioselective, with exclusive attack on CFH–group of olefin. The orientation of addition is in a good agreement with the electrophilic mechanism of the reaction [12]. However, in both cases the major products are 1:2 adduct of ether and olefin **9**:

$$\underset{\mathbf{1a,b}}{CF_3CH_2OCF_2X} + \underset{\mathbf{9}}{CFH{=}CF_2} \xrightarrow[SbF_5]{25\text{-}30^\circ C,\ 4\text{-}5\ h} CF_3CH_2OCX(CFHCF_3)_2 \quad (5)$$

10a, X= CF_2H, 61%
10b, X= $CFHCF_3$, 51%

The reaction of ethers **1a** and **b** and **8a** with 1,2-dichlorodifluoroethylene (**11**) rapidly proceeds at ambient temperature and atmospheric pressure producing corresponding 1:1 adducts (**12a–c**) in moderate to high yield:

$$\underset{\mathbf{1a,b,\ 8a}}{CF_3CH_2OCF_2R_f} + \underset{\mathbf{11}}{CFCl{=}CFCl} \xrightarrow[SbF_5]{10\text{-}25^\circ C,\ 4\text{-}5\ h} CF_3CH_2OCF(CFClCF_2Cl)R_f \quad (6)$$

12a, R_f= CF_2H, 53%
12b, R_f= $CFHCF_3$,42%
12c, R_f= H,43%

Dehalogenation of compound **12b** by Zn in ethanol affords allylic ether **13**:

$$\mathbf{12b} + Zn \xrightarrow[\text{reflux, 2 h}]{C_2H_5OH} \underset{\mathbf{13},\ 83\%}{CF_3CH_2OCF(CF{=}CF_2)CFHCF_3} \quad (7)$$

It should be pointed out, the reaction of hydrofluoroethers is limited to fluoroethylenes and hexafluoropropylene does not interact with either **1a** or **1b** even at elevated temperature (50°C, 12 h). On the other hand, only ethers containing –

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[1] The formation of polytetrafluoroethylene often observed in electrophilic reactions of tetrafluoroethylene catalyzed by SbF_5 proceeds probably, as a radical process, initiated by oxidative fluorination of olefin by SbF_5.

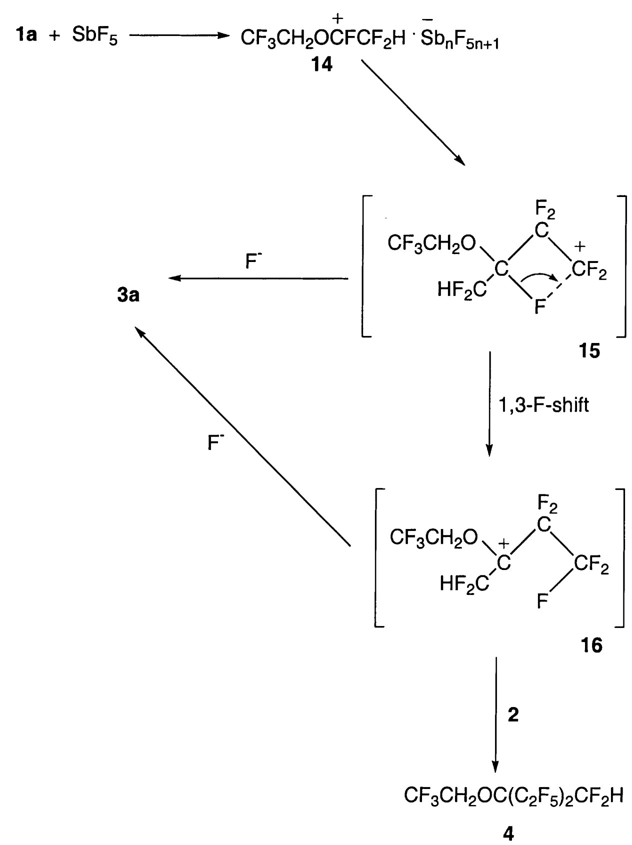
CH_2O– spacer are active in condensation reaction and no evidence for the formation of condensation product was found in reaction of $C_3F_7OCFHCF_3$ and **2** at ambient temperature in the presence of SbF_5.

3. Mechanistic considerations

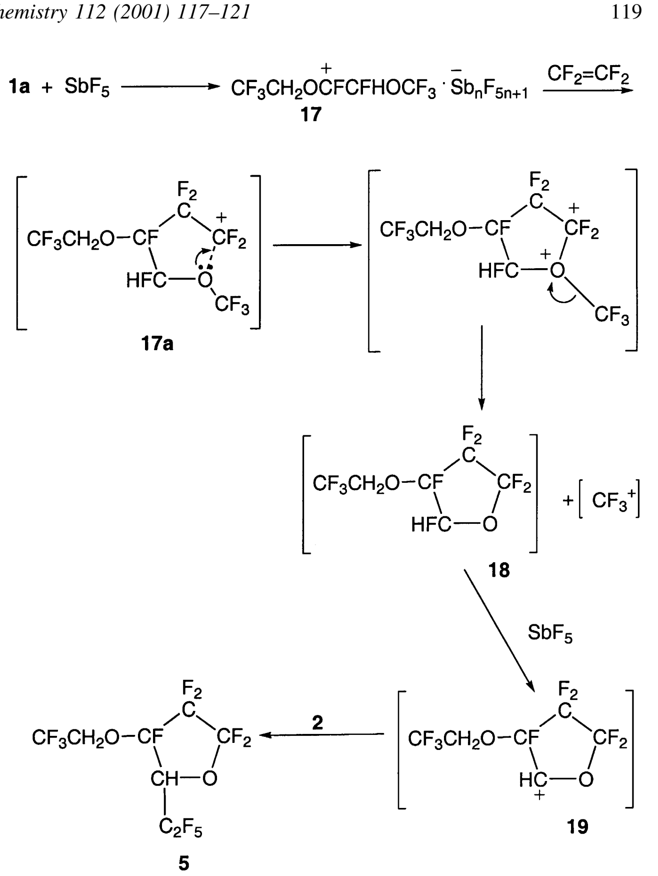
The regiochemistry of addition polyfluorinated ethers to trifluoroethylene and chlorotrifluoroethylene [11] is indicative of carbocationic mechanism of the process. The formation of corresponding oxonium cations under action of SbF_5 on corresponding ethers has been reported earlier [13]. However, it should be pointed out that the formation of product **4** was observed only in the reaction of **1a** and **2**, but not in the reaction between **3a** and **2**. It may be an indication that compounds **3a** and **4** are formed as a result of consecutive rather then independent processes. The first step probably, involves the formation of cation **14** [13]. This step is followed by electrophilic attack on olefin to give intermediate **15** (Scheme 1).

Cation **15** can be stabilized by addition of fluoride anion producing **3a** or it may rearrange into **16** through 1,3-migration of fluorine [14]. The compound **16** may either produce **3a** through the addition of F^- or it may react with second mole of olefin to give **4** as a final product.

The formation of compound **5** in the reaction of **1e** and **2** is a result of another process. Intermediate **17a** (formed as a result of attack of cation **17** [13] on **2**) may undergo cyclization through the electrophilic attack of cationic center on oxygen of trifluoromethoxy group with formation of cyclic ether **18** and CF_3^+. Further reaction of **18** with a second mole of **2** (through the formation of intermediate cation **19**) leads to cyclic ether **5** (Scheme 2).



Scheme 1.



Scheme 2.

4. Experimental

4.1. Starting materials

Fluorinated alcohols (used for preparation of **1a–e**, **6a**, **7a**) trifluoroethylene, 1,2-dichlorodifluoroethylene ether **8a**, (PCR), tetrafluoroethylene, hexafluoropropene (DuPont) were commercially available and used without further purification. Polyfluorinated ethers **1a–e**, were prepared using procedures described in [4,7,13]. SbF_5 (Ozark-Mahoning, 99%) was handled inside of dry-box and used without further purification.

Caution: *Both trifluoroethylene and tetrafluoroethylene are hazardous materials and should be handled by properly trained personnel. All reactions with these materials should be carried out inside of barricade*!

^{19}F and ^{1}H NMR spectra were recorded on QE-300 (General Electric, 200 MHz) using $CFCl_3$ or $(CH_3)_4Si$ as internal standard and $CDCl_3$ as lock solvent. All new materials were characterized by ^{19}F and ^{1}H NMR. Satisfactory HRMS

Table 2
Analytical data for selected products

Compound	^{19}F NMR δ (ppm) (J, Hz)	^{1}H NMR δ (ppm) (J, Hz)	Analysis or MS found (calculated)
3a	−75.40 (3F, t, 7); −80.53 (3F, d, 8); −125.51 (1F, dt, 296); −126.23 (1F, dd, 296); −132.31 (1F, dd, 312, 55); −133.54 (1F, dd, 312, 55); −144.00 (1F, br. s)	4.50 (2H, q, 8); 6.38 (1H, t, 55)	C, 23.81 (24.02); H, 0.99 (1.01); F, 69.97 (69.64)
4	−75.90 (3F, t, 8); −80.07 (6F, m); −116.30 (A:B pattern, 4F, ddm, 290); −125.60 (2F, dm, 51)	4.37 (2H, q, 8); 6.38 (1H, t, 51)	C, 23.49 (24.02); H, 0.75 (0.76); F, 70.75 (71.23)
3e[a]	−60.75 (2 signals, 3F); −76.12 (3F, t, 8); −81.10 (3F, m); −124.90 to 127.20 (4 signals, 2F); −141 to 143.5 (4 signals, 2F)	4.33 (2H, m); 6.21 (1H, dm, 55)	C, 21.71 (22.97); H, 0.90 (0.83); F, 67.67 (67.47)
5[a]	Major isomer: −74.98 (3F); −79.40 (1F, dm, 130); −83.80 (3F, s); −90.80 (1F, dm, 130); −126.90 (1F, dm, 245); −127.80 (2F, m); −131.85 (1F, dm, 245); −141.35 (1F, m). Minor isomer: −75.10 (3F); −82.00 (1F, dm, 146); −82.80 (3F, s); −86.75 (1F, dm, 146); −127.80 (1F, dm); −128.80 (2F, m); −131.85 (1F, dm, 245); −141.85 (1F, m)	4.32 (2H, m); 4.78 (1H, m)	*m/e* (mixture of isomers): 377.9883 (377.9925)
7b	−81.92 (3F, t, 10); −88.09 (2F, s); −124.60 (2F, pent, 8); −129.80 (2F, s); −138.31 (2F, d, 52)	4.39 (2H, t, 11); 5.88 (1H, tt, 52, 4)	C, 23.13 (24.02); H, 0.99 (1.01); F, 69.85 (69.64)
7c	−80.55 (6F, br. s); −122.30 (2F, dd, 290); −123.48 (2F, dd, 290); −125.20 (2F, s); −138.50 (2F, d, 52); −138.78 (1F, s)	4.35 (2H, t, 12); 5.86 (1H, tt, 52, 4)	*m/e*: 380.9926 [380.9960, (M–F)$^{+}$]
8b	−74.86 (3F, s); −82.28 (3F, s); −129.5 (2F, d, 259); −145.71 (1F, dm, 60)	4.18 (2H, m); 5.65 (1H, dm, 59, 5)	C, 23.34 (24.02); H, 1.19 (1.21); F, 69.78 (68.38)
8c	−75.11 (3F, t); −82.40 (6F, br. s); −119.10 (2F, dm, 300); −123.15 (2F, dm, 300)	4.14 (2H, q, 10); 4.39 (1H, m, 7)	*m/e*: 330.9978 [330.9992, (M–F)$^{+}$]
10b[a]	−71 to −73.5 (4 signals, 9F); −75.50 (3F); −204 to −210.50 (4 signals, 3F)	4.20 (2H, m); 5.0–5.6 (3H, m)	*m/e*: 395.0114 [395.0117, (M–F)$^{+}$]
12b[a]	−55 to −66 (2F, m); −72.70 to –73.90 (4 signals, 6F); −125 to 138 (8 signals, 2F); −125.30; −198.10 (2 signals, 1F)	4.15 (2H, m); 5.1 (1H, m)	C, 21.15 (21.95); H, 0.82 (0.79); F, 54.34 (54.57)
12c[a]	−64.60 to −65.28 (2F, dm, 173); −74.78; −74.83 (3F); −131.52; −132.71 (1F, m); −135.03; −139.08 (1F dm)	4.15 (2H, m); 5.63 (1H, dm)	C, 20.98 (21.22); H, 0.90 (1.07); F, 47.11 (47.00)
13[a]	−73.54; −74.10; −74.85 (6F, m); −88.53 (1F, m); −106.12 (1F, m); −126.15; −137.18 (1F, m); −128.50 (1F dm, 156); −208.56; −210.12 (1F, m)	4.20 (2H, m); 4.92 (1H, dm, 45)	C, 26.72 (26.94); H, 1.09 (0.97); F, 66.63 (66.96)

[a] Mixture of diastereomers.

or elemental analysis were obtained for all new materials. The ratio of reactants and reaction conditions are given in Table 1. NMR spectra and analytical data for selected products are given in Table 2.

5. General procedure for reaction of ethers with fluoroolefins

5.1. Method A (tetrafluoroethylene)

A 400 ml Hastelloy shaker tube was charged with 0.2–0.7 mol of ether **1a–e**, **6a**, or **7a**, 5–17 mol% of SbF_5 and 0.1–0.5 mol of **2** and reaction mixture was maintained at ambient temperature 12–14 h. The reactor was vented. To remove SbF_5 the crude reaction mixture was washed with cold water. It was dried over $MgSO_4$ and distilled using a spinning-band column.

5.2. Method B (trifluoroethylene and CFCl=CFCl)

Ethylene is slowly added (either through a gas phase **9** or as a liquid **11**) to a solution of SbF_5 in the corresponding ether to maintain the temperature inside of reactor at 10–35°C. In the end, the reaction mixture is diluted with a cold 20% solution of HCl; organic layer is separated, dried over $MgSO_4$ and distilled using a spinning-band column.

Acknowledgements

The author thanks Dr. F. Davidson for recording and help in the interpretation of NMR spectra of compound **5** and Dr. D.D. Khasnis for technical assistance.

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