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Defluorination of homologous chlorofluoroethers to chlorofluoroacetates

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Abstract

The research was focused on the defluorination of chlorofluoroethers to corresponding esters using porous aluminum fluoride (PAF) or MF_n/PAF. In the work up process, the product was easily separated from the reagent. Thus, the reaction would be a practical preparation method for polyfluorinated esters. Trifluoromethyl chlorodifluoroacetate was obtained by the reaction of 1,2-dichlorotrifluoroethyltrifluoromethyl ether with fuming sulfuric acid in 49% yield.

Keywords: Porous aluminum fluoride; Defluorination; Chlorofluoroether

1. Introduction

The polyfluorinated esters have been considered to be possible substitutes of SF_6 or CF_4 in semiconductor manufacture [1]. Also fluorinated esters are candidates for electrolyte of lithium rechargeable battery [2].

To date, a few literatures have reported on their preparations. Mainly there are two ways. One is the preparation of the esters of chlorofluoroacetic acid by treatment of corresponding ethers, $CHClFCF_2OR$, with concentrated sulfuric acid or fuming nitric acid [3,4]. On this way, fluorine atoms attached to carbon which also bears an alkoxy group are known to be labile to electrophilic reagents. This kinds of ethers are readily hydrolyzed in concentrated sulfuric acid, thus would give a route to esters of fluorinated carboxylic acids [5]. However, the separation of product is difficult to handle in the process. The other is the reaction of fluorinated carbonyl compounds with ethanol. The fluorinated carbonyl compounds were obtained by treating polyfluoroalkyl ethers with Lewis acid, such as $ZnCl_2$, BF_3–Et_2O and $AlCl_3$ [6,7].

In our research, we devised and prepared new reagents based on their insolubility in water and in organic solvents for exploiting the defluorination process of chlorofluoroethers. Though the reagents contains OH group on their surface, they are inert for HF and HCl media, thus can be easily separated from the reaction medium. The OH group would be the source of oxygen in the defluorination. Previously we reported that porous aluminum fluoride (PAF) was used successfully in preparing methyl chlorodifluoroacetate (**3**) from 1,2-dichloro-1,1,2-trifluoro-2-methoxyethane (**1**) [8,9].

Here, we will report the detail investigation of the defluorination using various types of ethers and reagents and show the application scope of this method.

2. Results and discussion

2.1. Defluorination of $CH_3OCFClCF_2Cl$ (1) to $CF_2ClCOOCH_3$ (3)

Based on our previous report about the defluorination of **1** to **3** on CrF_3/PAF and CoF_2/PAF [8], further we attempted to use various metal fluorides supported on PAF to investigate the defluorination of **1** to **3**. The reaction scheme and results of the reaction of **1** with different kinds of metal fluorides were summarized in Scheme 1 and Table 1, respectively. Although metal fluoride had an effect on this reaction, the yield of **3** was less than 50%.

In order to investigate the effect of Lewis acid strength on the surface of PAF to the reaction, PAF was treated by gaseous fluorine in advance and used in the reaction to replace PAF, the yield of **3** increased from 33 to 54% (Table 1). This might be attributed to that fluorination increases acid strength of residual hydroxyl groups on PAF surface [10–12]. The possible mechanism is shown in Scheme 2.

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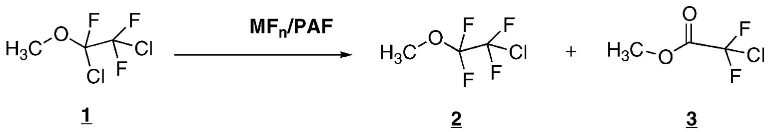


Scheme 1.

Table 1
Reaction of $CH_3OCFClCF_2Cl$[a]

Entry	Reagent	Reaction temperature (°C)	Products yield (%)[b]		Recovery of **1** (%)
			2	**3**	
1	NiF_2/PAF	200	15	2	0
2	NiF_2/PAF	150	24	10	0
3	FeF_2/PAF	200	30	40	0
4	FeF_2/PAF	150	30	41	24
5	ZnF_2/PAF	150	38	30	11
6	MgF_2/PAF	150	2	18	63
7	SbF_3/PAF	200	46	36	1
8	SbF_3/PAF	150	58	29	10
9[c]	PAF	200	12	33	0
10[d]	PAF treated by F_2	200	5	54	2
11[e]	$AlF_m(OH)_{3-m}$	180	3	84	2

[a] From entries 1–8, reaction time 1 h, starting material (**1**) about 2 mmol, and reagent 2 g for each reaction, Ni, Sb, Fe, Zn and Mg in catalyst 5 wt.%.

[b] From entries 1–11, the by-products are CH_3Cl and $FCOCF_2Cl$.

[c] Reaction time 1 h, (**1**) about 2.0 mmol, reagent 1.2 g.

[d] PAF (1.2 g) was treated by 2 mmol gaseous fluorine in advance.

[e] Reagent $AlF_3{\cdot}3H_2O$ was treated under 300 °C for 10 h, and about 1 g was used in each reaction.

As described in the previous paper [8], $AlF_m(OH)_{3-m}$ gave **3** in much better yield than PAF (Table 3). Probably, the amount of OH in $AlF_m(OH)_{3-m}$ is larger than in PAF, so defluorination proceeded predominately to give **3** in good yield.

2.2. Defluorination of $CH_3OCF_2CF_2Cl$ (2) to $CF_2ClCOOCH_3$ (3)

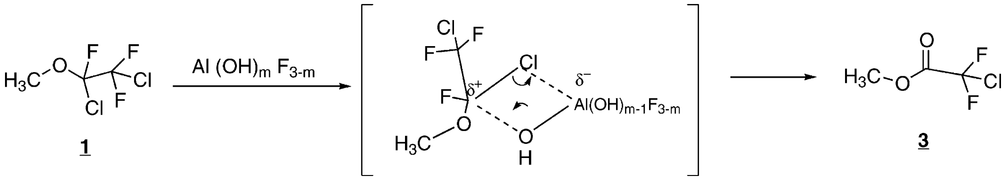
The defluorination of **2** to **3** was examined with various reagents (Scheme 3) and the results were shown in Table 2. When α-chlorine of **1** was replaced by fluorine to form **2**, the defluorination of **2** did not occur by using PAF, PAF treated by gaseous fluorine, porous calcium fluoride (PCF), $AlF_m(OH)_{3-m}$ and CoF_2 + CrF_3/PAF (Table 2). In order to prompt coordination of reagent with fluorine in α-position, strong Lewis acid, SbF_5, was impregnated on PAF to enhanced acid center strength. The reaction of **2** with SbF_5/PAF gave the ester **3** successfully although SbF_5 itself caused decomposition of **2**. Compound **3** was obtained in 67% yield by the reaction at 200 °C. The process can be explained that SbF_5 impregnated on PAF increased the strength of Lewis acid and is advantageous to abstracting fluorine from a C–F bond to give intermediate hemiacetal. Therefore, PAF absorbing SbF_5 makes the transformation from **2** to **3** possible. With above reagent, the defluorination of chlorofluoroethers is now accomplished in one clean step. However when reaction is carried out about 300 °C, most of starting material decomposed to CH_3Cl and $FCOCF_2Cl$.

Scheme 3.

2.3. Defluorination of $CF_3OCFClCF_2Cl$ (5) to CF_3OCOCF_2Cl (6)

To our knowledge, the defluorination of $R_fOCFClCF_2Cl$ to CF_3OCOCF_2Cl is not reported yet. In fact, the defluorination of 1,2-dichlorotrifluoroethyltrifluoromethyl ether (**5**), where $-CH_3$ of **1** was replaced by $-CF_3$, can not be carried out using above reagents (Table 3). In our research, **6**, as a new compound, was obtained by reaction of **5** with fuming sulfuric acid at 200 °C (Scheme 4). The results under different temperature were shown in Table 4, which indicated the substrate decomposed and the yield of **6** decreased when reaction temperature is over 200 °C.

For promoting the yield of **6**, the nitrogen was filled into vessel with substrate to increase the reaction pressure. The results were shown in Table 5 which indicated the yield of **6** increased from 38 to 49% with the pressure increasing from 0.1 to 3.9 MPa, but too high pressure is not advantageous to the formation of product (entry **5** in Table 5). It is assumed



Scheme 2.

Table 2
Reaction of $CH_3OCF_2CF_2Cl$[a]

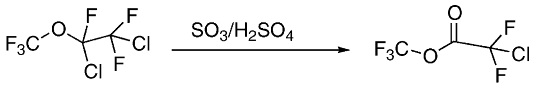
Entry	Reagent	**2** (mmol)	Reaction condition		Product yield of **3** (%)	Recovery of **2** (%)
			Temperature (°C)	Time (h)		
1	PAF[b]	2.0	200	2	0	100
2	PAF treated by F_2	2.9	200	2	0	100
3	PCF[c]	2.0	200	2	0	100
4	$AlF_m(OH)_{3-m}$	2.0	200	1	0	100
5[d]	$CoF_2 + CrF_3/PAF$	2.1	100	2	0	100
6[d]	$CoF_2 + CrF_3/PAF$	2.1	200	2	0	97
7[d]	$CoF_2 + CrF_3/PAF$	2.1	300	1	0	48
8	$CoF_2 + CrF_3/PAF$	2.1	300	3	0	20
9	SbF_5	2.0	200	2	0	0
10[d]	SbF_5/PAF	2.6	200	2	67	3
11[d]	SbF_5/PAF	2.0	300	2	1	5

[a] Reaction reagent about 1 g for each reaction; by-products from entries 9–12: CH_3Cl and $FCOCF_2Cl$.
[b] Porous aluminum fluoride.
[c] Porous calcium fluoride.
[d] Co, Cr and Sb 5 wt.% in reagent, respectively.

Table 3
Reaction of $CF_3OCFClCF_2Cl$ with different reagents[a]

Entry	Substrate	Reagent	Reaction condition		Recovery of substrate (%)
			Temperature (°C)	Time (h)	
1	$CF_3OCFClCF_2Cl$	PAF (treated by F_2)	200	1	100
2	$CF_3OCFClCF_2Cl$	SbF_5/PAF	200	1	95
3	$CF_3OCFClCF_2Cl$	SbF_5/PAF	300	2	82
4[b]	$CF_3OCFClCF_2Cl$	SbF_5/PAF	300	10	0

[a] Substrate (2 mmol) and reagent (1.5 g) for each reaction; Sb in reagent 5 wt.%.
[b] Main products: CF_2ClCOF, CF_3H.



5 **6**

Scheme 4.

that the high pressure liquefies the substrate to enhance the reaction, whereas the reaction occurs at the interface between liquid fuming sulfuric acid and gaseous **5** under low pressure.

Table 4
Yield of **6** under different reaction temperatures

Entry	Reaction temperature (°C)	Yield of **6** (%)	Recovery of **5** (%)	By-product (%)
1	100	Trace	94	0
2	150	9	83	Trace
3	180	23	67	4
4	200	38	45	9
5	220	18	17	3
6	250	6	3	0

Reaction conditions: 1.3 mmol $CF_3OCFClCF_2Cl$; reaction time 5 h; amount of fuming sulfuric acid: 3.2 g.

3. Experimental

3.1. Chemicals

Compounds **1** and **2** are prepared according to literature [8]. Anhydrous hydrogen fluoride (AHF) was obtained from Morita Chem. Ind. Co Ltd., Japan. $SbCl_5$ was from Wako Pure Chemical Industries Ltd., Japan. Trifluoromethyl trifluorovinyl ether (**4**) purchased from SynQuest Lab. Inc. Surface area and pore volume (V_s) of PAF were 75 m^2/g and 0.3 cm^3/g, respectively [8].

Table 5
Yield of **6** under different reaction pressures

Entry	Reaction pressure (MPa)	Yield of **6** (%)	Recovery of **5** (%)	By-product (%)
1	0.1	38	45	9
2	1.1	43	37	9
3	2.1	47	30	9
4	3.9	49	24	8
5	7.9	43	20	7

Reaction conditions: 1.3 mmol $CF_3OCFClCF_2Cl$; reaction time 5 h; amount of fuming sulfuric acid: 3.2 g.

3.2. Instrument

^{1}H NMR and ^{19}F NMR were recorded on JNM-EX270 (JEOL, 270 MHz) at 25 °C with $(CH_3)_4Si$ and $CFCl_3$, respectively, as internal reference in $CDCl_3$ as a solvent.

FT-IR spectrometer (FT/IR-620, Japan Spectroscopic Co Ltd.) was used for measuring product in vacuum line.

GC–MS was a Hewlett-Packard 5790 series system equipped with a Jet Separator for the 5890A GC. The capillary column was Pora plot *Q* with 0.32 mm i.d. and 25 m length from J&W Scientific Inc. The operation condition of GC is as follows; column temperature 80 °C for 2 min and heated for 20 min at a rate of 10 °C/min; detector temperature 200 °C; carrier gas, ~1 cm^3 He/min; split ratio 45:1; sample size 1.2 μl; pressure 50 kPa.

Products were handled in glass and metal vacuum line system. Amounts and molecular weight of products were determined by measuring the sample pressure under a certain volume in the vacuum line.

3.3. Reaction procedure

3.3.1. Preparation of MF$_n$/PAF

MF$_n$/PAF with different metal fluorides supported on PAF was prepared by following procedure: The PAF was dehydrated by heating at 300 °C for 10 h and then impregnated to a sufficient amount of salt solution overnight. The amount of metal chloride in the solution was adjusted to give final metal loading to 5 wt.%. The saturated support was dried at 120 °C for 2 h and 200 °C for 2 h. The dried pellets were packed on Inconel alloy reactor and fluorinated by $N_2/AHF = 1 : 1$ (100 ml:100 ml) at 200 °C for 2 h, then pure AHF at 200 °C for 2 h and 300 °C for 2 h. Finally remaining AHF on the MF$_n$/PAF was washed by nitrogen. The prepared MF$_n$/PAF is used to fluorination procedure.

3.3.2. PAF treated by gaseous fluorine

About 1 g of PAF was placed in a stainless steel vessel with 80 cm^3 volume, then reactor was cooled to −196 °C and 2 mmol of gaseous fluorine was introduce to the reactor. The reactor was allowed to warm up slowly to 20 °C overnight. Unreacted gaseous fluorine was pumped out.

3.3.3. Typical reaction procedure of PAF, MF$_n$/PAF, with **1** or **2**

One gram of solid reagent prepared by previous method was placed in a stainless steel reactor with 80 cm^3 volume, the reactor was cooled to −196 °C. Then 2 mmol of **1** or **2** was transferred to reactor and heated to 200 °C and keep for 2 h at the temperature. Products were transferred to a trap (−196 °C), and their amount and molecular weight were measured using vacuum line after separation (−90 and −196 °C). Finally the products were analyzed by FT-IR, ^{1}H NMR and ^{19}F NMR. The amount of each product was calculated from NMR results.

3.3.4. Preparation of **5**

Compound **5** was prepared by the reaction of **4** with equimolar amount of gaseous chlorine. Twenty millimoles of **4** and same amount of gaseous chlorine were introduced to 500 ml glass reactor cooled to −196 °C. The reactor was allowed to warm up from −196 °C to room temperature during 5 h. The product (99% in yield) was determined by GC–MS, ^{1}H NMR and ^{19}F NMR. The data of MS and NMR chemical shifts of **1** are listed as follows; MS: *m/z*: 69, $(+)CF_3$; 85, $(+)CClF_2$; 115, $(+)CF_3OCFCl$; 201, $(+)CF_3OCFClCF_2$. ^{19}F NMR: δ (ppm), –55.05 (d, 3F); δ (ppm), −71.00 (dd, 2F); δ (ppm), −77.89 (m, F).

3.3.5. Synthesis of **6**

Fuming sulfuric acid (3.2 g) was placed in a stainless steel vessel with 85 cm^3 volume, the reactor was cooled to −196 °C. Then 1.3 mmol of **5** was transferred to reactor and heated to 200 °C and keep for 5 h at the temperature. Products were transferred to a trap (−196 °C), and their amount was measured using vacuum line after separation (−90 and −196 °C). Finally the products were analyzed by FT-IR and NMR, and the yield was determined by ^{19}NMR. For **6**, a new compound, spectroscopic data were listed as follows; ^{19}F NMR: δ (ppm), −58.73 (s, 3F); δ (ppm), −65.55 (s, 2F). FT-IR data shows C=O peak at 1847 cm^{-1}.

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