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Synthesis of trifluoroethyl ethers from 2,2,2-trifluoroethyl chloride (HCFC-133a) in high temperature aqueous medium

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Abstract

Treatment of 2,2,2-trifluoroethyl chloride (HCFC-133a) with alcohols (phenols) and aqueous KOH in autoclave at 240–280 °C gives the corresponding 2,2,2-trifluoroethyl (2-chloro-1,1-difluoroethyl) ethers in good yields.

Keywords: 2,2,2-Trifluoroethyl chloride (HCFC-133a); Trifluoroethyl ethers; High temperature water

1. Introduction

Fluorine-containing ethers are one of the most important classes of fluorine organic compounds [1]. High molecular-weight ethers, e.g. poly(perfluoro)ethers poly(perfluoroformaldehyde), $-(CF_2O)_x-$, poly(perfluoropropylene oxide, $-[CF(CF_3)CF_2O]_x-$ are viscous liquids with exceptional chemical and physical properties which are used extensively in industry as lubricants, dielectric fluids, diffusion pump oils and blood substitutes due to their high O_2 solubility [2]. Several low molecular-weight fluorinated ethers are good anaesthetics, such as isoflurane ($CF_3CHClOCHF_2$), desflurane ($CF_3CHFOCHF_2$), enflurane ($CHClFCF_2OCHF_2$) and sevoflurane [$(CF_3)_3CHOCH_2F$] [3]. Recently, a quite variety of fluorinated ethers has been synthesized and evaluated as candidates for chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs). Some of them can be used as refrigerants, blowing agents and cleaning solvents [4].

Generally, simple fluorinated ethers are prepared by nucleophilic addition of alcohols and phenols to fluorinated olefins in the presence of base [1,5]. Direct fluorination of chlorinated ethers with fluorine gas [6] or cobalt trifluoride [7] or by electrochemical means [8] is another choice. The most simple and convenient methods for preparing fluoroethers are alkylation (arylation) of alkyl halides (Williamson reaction) [1] and alkoxylation of tosylate (perfluoroalkanesulfonate) esters [9] with alkoxide(phenoxide) anions, respectively.

$$RX + OR'^{-} \rightarrow ROR' \text{(Williamson reaction)}$$

$$R''SO_3R + OR'^{-} \rightarrow ROR' \quad (R = p\text{-}CH_3H_6H_4,\ R_F)$$

Many fluoroethers have been prepared using Williamson reaction from CFCs and Halons, e.g. difluoromethyl alkyl and aryl ethers [$HCF_2OR(Ar)$] from base catalyzed reactions of $CHClF_2$ or CF_2Br_2 with alcohols and phenols, respectively [1]. However, CFCs and halons could be used no further and stopped to produce because they causes the depletion of ozone layer. Thus, we have to seek for other way for synthesizing fluorinated ethers. Naturally, HFC-134a (CF_3CH_2F) and its precursor HCFC-133a (CF_3CH_2Cl) would be considered as good starting materials for this purpose because HFC-134a is now produced in large scale from HCFC-133a by gas-phase HF-fluorination [10]. The problem, one might meet when using HCFC-133a as a reactant, is its inertness because its analogues, 2,2,2-trifluoroethyl bromide and iodide are shown to be difficult to react with nucleophiles due to the presence of a strongly deactiviated trifluoromethyl group [11–13]. However, the conversion of HCFC-133a into HFC-134a could be achieved, indeed, even with aqeous KF at 300 °C [14] or 270 °C [15]. One of these methods [15] is expected to be the first commercial process of making HCFC-134a by liquid-phase KF-fluorination [16]. Similarly, preparation of 1,1,1-trifluoroethanol with KOH/NaOH at 250 °C [17,18] from HCFC-133a or from its acetate, $RCO_2CH_2CF_3$ at 180–200 °C [19–21] was also described. All the results may be ascribed

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to the promotion by the near-critical water (NCW) which probably were not recognized by the authors. Therefore, it would be of significance to convert HCFC and HFC to useful fluorine-containing material at forced conditions, i.e. in NCW in spite of that a few reports on the chemical transfermation of HCFC-133a with organometallic reagents under normal conditions have appeared [22,23]. We, herein, present the results of synthesis of 2,2,2-trifluoroethyl (2-chloro-1,1-difluoroethyl) ethers at high temperature aqueous medium.

2. Results and discussion

In order to check up the S_N2 reactivity of β,β,β-trifluoroethyl chloride (HCFC-133a) (**1**), some experiments were carried out. It was found that treatment of **1** with EtOH, KOH in DMF, dimethylacetamide, or DG at 110, 155, 165 °C for 9 h gave 0, 15, 17% conversion of **1**, respectively. The conversion of **1** and yield of $CF_3CH_2OC_2H_5$ (**3b**) were only 18 and 11%, respectively, when **1** was treated with C_2H_5ONa in DG at 165 °C for 4 h. The results indicated the inertness of **1**, indeed, and promoted us to employ forced condition, i.e. at high temperature aqueous medium.

First, we tried to find a proper reaction temperature, and a reaction with ethanol (**2b**) was chosen to react with HCFC-133a (**1**), KOH and H_2O (**1:2b**:KOH:H_2O = 1:2.1:1.5:11.5) in an autoclave (Table 1). It was found that no reaction occurred at 150 °C for 11 h. When raising temperature to 180 °C, the reaction did take place, however, the conversion of **1** was only 8%. At temperature >210 °C, besides, a liquid product, a gaseous mixture was accompanied whose ingredients were identified to be HFC-134a (**5**) and CF_2=CHCl (**4**) by GC–MS and comparison with authentic samples. The desired product 1,1,1-trifluoroehtyl ethyl ether (**3b**) was obtained in 67% yield with 87% conversion of **1** at 240 °C for 11 h in addition to a small amount of **4** (∼3%) and **5** (∼3%). When the temperature was raised to 280 °C, the conversion of **1** decreased significantly (see entry 6, Table 1).

Table 1
Reaction of **1** with C_2H_5OH (**2b**), KOH and H_2O[a]

Entry	Temperature (°C)	Pressure (atm)	Time (h)	Conversion (%) of **1**[b,c]
1	150	1.4	11	0[d]
2	180	4.6	11	8[d]
3[e]	200	55	11	66
4	210	57	11	71
5	240	60	11	87
6	280	100	8	58
7[f]	250	65	9	0

[a] **1**:**2a**:KOH:H_2O = 1:2.1:1.5:11.5.
[b] Determined by ^{19}F NMR analysis.
[c] A gaseous mixture is also produced unless otherwise noted.
[d] No gas was produced.
[e] **1**:**2a**:KOH:H_2O = 1:2.1:1.5:23.
[f] In the absence of KOH.

Table 2
Reaction of **1** with ROH, KOH and H_2O[a]

Entry	ROH (**2**)	Temperature (°C)	Pressure (atm)	Time (h)	Conversion (%)[b]	**3**, Yield (%)[c]
1	**2a**	260	76	10	74	55
2	**2b**	240	60	11	87	67
3	**2c**	280	110	13	61	42
4	**2d**	285	115	10	63	45
5	**2e**	280	115	11	70	64
6	**2f**	285	110	14	7	–[d]
7	**2g**	250	102	13	77	70

[a] **1**:**2**:KOH:H_2O = 1:2.1:1.5:11.5.
[b] The conversion was determined by ^{19}F NMR analysis.
[c] Isolated yield; a small amount of **4** (∼3%)and **5** (∼3%) were also obtained.
[d] The yield was too low and only detected by GC.

Notably, the reaction did not occur in the absence of base (KOH) (entry 7, Table 1), indicating that the formation of alkoxide with KOH is necessary in the NCW-induced reaction [24,25].

Various alcohols reacted with **1** to give the corresponding 1,1,1-trifluoroethyl ethers (**3**) at different temperatures. With increasing the molecular-weight and steric hindrance of alkyl group in **2**, the reaction temperatures needed were higher. For example, the reaction with *n*-butanol-1 (**2c**), 2-methylpropanol (**2d**), 1-methylpropanol-1 (**2e**) could occur with 60–70% conversion of **1** at 280 °C for 12 h, while with *t*-BuOH (**2f**) with very low conversion (∼7%) even at 285 °C for 14 h. Symmetric bis(1,1,1-trifluoroethyl) ether (**3g**), a good CFCs displacement candidate [26], could be synthesized at somewhat lower temperature. The results are listed in Table 2.

$$\underset{\mathbf{1}}{CF_3CH_2Cl} + \underset{\mathbf{2}}{ROH} + KOH \xrightarrow{H_2O} \underset{\mathbf{3}}{ROCH_2CF_3} + \underset{\mathbf{4}}{CF_2{=}CHCl} + \underset{\mathbf{5}}{CF_3CH_2F} + KCl \quad (1)$$

R=CH_3(a), C_2H_5(b), *n*-C_4H_9(c),$(CH_3)_2CHCH_2$(d), C_2H_5-$(CH_3)CH$(e), $(CH_3)_3C$(f), CF_3CH_2(g).

Unlike alcohols, the reaction of phenols with **1** did not give the expected trifluoroethyl aryl ethers, $ArOCH_2CF_3$, which was previously prepared by the reaction with CF_3CH_2I/K_2CO_3 in DMF at 130 °C [27]. Instead, 1-chloro-2,2-difluoroethyl phenyl ether (**7a**) and a small amount of 1,1-difluoroethylglycol diaryl ether (**8a**) were obtained from the reaction of phenol (**6a**) with **1**. When phenol (**6a**) reacted with **1** in ratio **1**:**6a**:KOH:H_2O = 1:2.5:2.5:16.3 at 250 °C for 11 h, **8a** became the main product. However, for other phenols, e.g. *p*-$CH_3C_6H_4OH$ (**6b**) and *o*-$CH_3C_6H_4OH$ (**6c**), **7** was the sole product, no **8b–c** were obtained even in the presence of higher concentration of ArO^- (entry 6,7, Table 3). Treatment of hydroquinone or catecol with **1** under the similar conditions only gave a complicated fluorine-containing mixture, which was difficult to purify. The results

Table 3
Reaction of **1** with phenols (**6**), KOH and H_2O for 11 h[a] at 250 °C

Entry	6	Product	Pressure (atm)	Conversion (%)[b]	Yield (%)[c]
1	**6a**	**7a**	47	83	76
2	**6b**	**7b**	38	78	73
3	**6c**	**7c**	42	61	52
4	**6d**	**7d**	48	78	67
5[d]	**6a**	**8a**	45	77	72
6[d]	**6b**	**7b**	44	74	68
7[d]	**6c**	**7c**	46	74	71

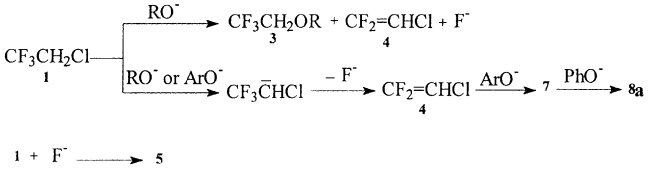
[a] **1**:**6**:KOH:H_2O = 1:0.5:0.5:8.3. The pressure is 38–47 atm.
[b] The conversion was determined by ^{19}F NMR.
[c] Isolated yields; besides **7** and **8**, a small of amount of **4** (~3%) and **5** (~3%) were obtained.
[d] **1**:**6**:KOH:H_2O = 1:2.5:2.5:16.3.

are listed in Table 3.

$$\underset{\mathbf{1}}{CF_3CH_2Cl} + \underset{\mathbf{6}}{ArOH} + KOH \xrightarrow{H_2O} \underset{\mathbf{7}}{ArOCF_2CH_2Cl} + \underset{\mathbf{8a}}{ArOCH_2CF_2OAr} + \underset{\mathbf{4}}{CF_2{=}CHCl} + \underset{\mathbf{5}}{CF_3CH_2F} \quad (2)$$

Ar=C_6H_5(a), *p*-$CH_3C_6H_4$(b), *o*-$CH_3C_6H_4$(c), *t*-BuC_6H_4(d).

The alkoxide ion generated from the base and alcohol undergoes either mainly nucleophilic attack on **1** to give the ether **3** or deprotonation and elimination to yield the by-product **4** and fluoride ion. As for phenoxides, the generation of **4** becomes a major step and another equivalent ArO^- adds to **4**, giving the final product **7**. In fact, a nucleophilic addition of phenoxide to **4** in acetone at room tempareture to afford **7a** was first reported in [28]. Nucleophilic substitution of **7a** by another PhO^- results in the formation of by-product **8a**. The fluoride ion produced in both cases reacts with HCFC-133a (**1**), as reported in the patents [14,15], to afford HFC-134a (**5**).



As mentioned above, all these processes can be hardly occurred at ambient temperature [11–13], however, the reactions did take place in high temperature water, i.e. in NCW. The key role of NCW is the changes of chemical and physical properties of water. These changes make the solvent properties of water (density, dielectric constants) at high temperature similar to those of polar organic solvent at room temperature, thus facilitate the organic reactions which have never been occurred under normal conditions [29–31].

In conclusion, we have developed a novel practical method for synthesizing 1,1,1-trifluoroethyl and 2-chloro-1, 1-difluoroethyl ethers from commercially available HCFC-133a in high temperature aqueous medium.

3. Experimental section

Boiling points were uncorrected. The ^1H NMR spectra were carried out on Bruck AM-300 (300 MHz) NMR spectrometer. The ^{19}F NMR spectra were obtained on a Varian EM-360 (56.4 MHz) spectrometer. Chemical shifts were reported in parts per million relative to TMS as an internal standard for ^1H NMR and to CF_3COOH as an external standard for ^{19}F NMR (downfield shift being designated as negative). The solvent for NMR measurement was $CDCl_3$ or CD_3COCD_3. The MS and HRMS spectra were recorded on Hewlett-Packard HP-5989A spectrometer and Finnigan MAT-8483 mass spectrometer. GC and GC–MS data were obtained on Hewlett-Packard HP-6890 and Finnigan MD-800 spectrometer.

3.1. General procedure for the reaction of *1*

The compound CF_3CH_2Cl (20.17 g, 0.17 mol) was gathered in a gas receptacle, which had been cooled in an acetone/solid CO_2 bath. The compound KOH (14.30 g, 0.26 mol) was solved in 25 ml de-ionized water. Then the aqueous KOH solution and 25 ml ethanol (19.52 g, 0.424 mol) and CF_3CH_2Cl was added quickly to the stainless autoclave (volume, 0.1 l), which had been also cooled in an acetone/solid CO_2 bath. After the autoclave was warmed to room temperature, it was placed in a heatable device and heated at 240 °C. After 11 h, 800–1000 ml gas was collected in a gasbag. The organic layer of the liquid mixture was dried (Na_2SO_4) and distilled to provide a crude product, bp 45–55 °C. It was redistilled in the presence of a small amount of sodium to give pure **3b** [32] (14.47 g, 67%), bp 48–50 °C (lit. 49.8 °C). ^1H NMR: δ 1.23 (t, 7.0 Hz, 3H), 3.66 (q, 7.0 Hz, 2H), 3.80 (q, 8.8 Hz, 2H). ^{19}F NMR: δ −3.50 (t, 8.8 Hz, 3F). MS: 128 (M^+), 43 (CH_3CH_2), 59 ($M - CF_3$), 101 ($M - CH_2{=}CH_2$).

The gas product was subjected to GC–MS on GC8000-MD800 using a GS-GRASPRO column (30 m × 0.32 mm) at constant temperature 120 °C, a pressure of 10^{-6} Torr, a source temperature of 250 °C and an acceleration voltage of 70 eV. The GC–MS chromatograms were obtained with and analyzed by data library (NIST). For the compound **4**, $m/z = 98$ and for **5**, $m/z = 102$. The gas product was confirmed by authentic samples on HP6890 using GSC-Gas separator column (30 m × 0.32 mm) at constant temperature 130 °C.

3.2. ***3a***: *$CF_3CH_2OCH_3$ [32]*

Bp: 31–33 °C (lit. 31.2 °C). ^1H NMR: δ 3.50 (s, 3H), 3.93 (q, 8.7 Hz, 2H). ^{19}F NMR: δ −3.53 (t, 8.7 Hz, 3F). MS: 114 (M^+), 83 ($M - OCH_3$), 69 ($M - CH_3OCH_2$), 45 ($M - CF_3$).

3.3. ***3c***: *$CF_3CH_2OCH_2CH_2CH_2CH_3$ [33,34]*

Bp: 82–85 °C. ^1H NMR: δ 0.93 (q, 7.31 Hz, 3H), 1.39 (m, 2H), 1.60 (m, 2H), 3.61 (t, 6.5 Hz, 2H), 3.81 (q, 8.7 Hz, 2H).

^{19}F NMR: δ −3.60 (t, 8.7 Hz, 3F). MS: 156 (M^+), 83 ($M - HOCH_2CH_2CH_2CH_3$), 113 ($M - CH_2CH_2CH_3$).

3.4. **3d**: $CF_3CH_2OCH_2CH(CH_3)_2$ [33,34]

Bp: 80–82 °C. ^{1}H NMR: δ 0.91 (d, 6.7 Hz, 6H), 1.88 (m, 1H), 3.36 (d, 6.7 Hz, 2H), 3.80 (q, 8.8 Hz, 2H). ^{19}F NMR: δ −3.14 (t, 8.8 Hz, 3F). MS: 156 (M^+), 141($M - CH_3$), 113 ($M - CH(CH_3)_2$).

3.5. **3e**: $CF_3CH_2OCH(CH_3)CH_2CH_3$ [33,34]

Bp: 81–83 °C. ^{1}H NMR: δ 0.91 (t, 6.4 Hz, 3H), 1.16 (d, 6.2 Hz, 3H), 1.44 (m, 2H), 3.48 (m, 1H), 3.82 (q, 8.7 Hz, 2H). ^{19}F NMR: δ −2.93 (t, 8.7 Hz, 3F). MS:156 (M^+), 140 ($M - CH_3O$), 127 ($M - CH_3CH_2O$), 56 ($M - CF_3CH_2O$).

3.6. **3g**: $CF_3CH_2OCH_2CF_3$ [33,34]

Bp: 60–62 °C (lit. 62–63 °C). ^{1}H NMR: δ 3.97 (q, 8.8 Hz, 4H). ^{19}F NMR: δ −2.98 (t, 8.8 Hz, 6F). MS:182 (M^+), 113 ($M - CF_3$), 83 ($M - OCH_2CF_3$).

3.7. **7a**: $C_6H_5OCF_2CH_2Cl$ [35]

^{1}H NMR: δ 4.24 (t, 8.8 Hz, 2H),7.20 − 7.42 (m, 5H). ^{19}F NMR: δ −2.4 (t, 8.8 Hz, 2F) MS: 192 (M^+), 194 ($M + 2$), 99 ($^+CF_2CH_2Cl$), 77 ($C_6H_5^+$), 92 (C_6H_5OH).

3.8. **7b**: p-$CH_3C_6H_4OCF_2CH_2Cl$ [35]

^{1}H NMR: δ 2.35 (s, 3H), 4.21 (t, 9.0 Hz, 2H), 7.13 (d, 8.4 Hz, 2H), 7.24 (d, 8.4 Hz 2H). ^{19}F NMR: δ −4.8 (t, 9.0 Hz, 2F). MS: 206 (M^+), 157 ($M - CH_2Cl$), 108 ($M - CF_2CH_2Cl$), 77 (C_6H_5), 94 (C_6H_5O). Analysis: calculated for $C_9H_9ClF_2O$: C, 52.32; H, 4.39; F, 18.39%; found: C, 52.39; H, 4.38; F, 18.56%.

3.9. **7c**: o-$CH_3C_6H_4OCF_2CH_2Cl$ [35]

^{1}H NMR: δ 2.31 (s, 3H), 4.17 (t, 8.8 Hz, 2H), 7.18−7.24 (m, 4H). ^{19}F NMR: δ −3.0 (t, 8.8 Hz, 2F) MS: 206 (M^+), 157 ($M - CH_2Cl$), 108 ($M - CF_2CH_2Cl$), 77 (C_6H_5), 93 (C_6H_5O). Analysis: calculated for $C_9H_9ClF_2O$: C, 52.32; H, 4.39; F, 18.3%; found: C, 52.20; H, 4.46; F, 18.49%.

3.10. **7d**: p-$(CH_3)_3CC_6H_4OCF_2CH_2Cl$

^{1}H NMR: δ 1.31 (s, 9H), 4.20 (t, 8.9 Hz, 2H), 7.16 (d, 8.5 Hz, 2H), 7.46 (d, 8.5 Hz, 2H) ^{19}F NMR: δ −2.3 (t, 8.9 Hz, 2F). MS: 248 (M^+), 233 ($M - CH_3$), 133 ($M - OCF_2CH_2Cl$), 77 (C_6H_5). Analysis: calculated for $C_{12}H_{15}F_2ClO$: C, 57.96; H, 6.08; F, 15.28%; found: C, 58.19; H, 6.12; F, 15.42%.

3.11. **8a**: $C_6H_5OCF_2CH_2OC_6H_5$

IR(film): 690,752,1237,1493,1582,1600. ^{1}H NMR: δ 4.46 (t, 8.5 Hz, 2H), 7.08 − 7.15 (m, 4H), 7.25 − 7.45 (m, 6H). ^{19}F NMR: δ −0.28 (t, 8.5 Hz, 2F). MS: 250 (M^+), 156 ($M - C_6H_5OH$), 77 (C_6H_5), 94 (C_6H_5OH). HRMS: calculated for $C_{14}H_{12}F_2O_2$: 250.08054; found: 250.08062.

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